Chemical Process Industry Safety

About the Author

K S N Raju is a retired professor of chemical engineering with involvement in chemical engineering education and research covering graduate and undergraduate students for *50 years*. He received BSc (Honors) degree in chemical engineering from Andhra University in 1958, M.Tech from IIT Kharagpur in 1959 and PhD from Panjab University in 1971.

Dr Raju has been involved in active interaction with the industry, taking up projects and executing them with the induction of graduate students onsite in selected industries. He has also been responsible for developing chemical engineering departments at Panjab University, Chandigarh, India; Padmasri Dr B V Raju Institute of Technology, Andhra Pradesh, India; and BS University of Technology, Libya; besides being involved in curriculum development for several institutions as member of their boards of studies.

Dr Raju has published over 90 papers and articles in international magazines and journals. He has supervised graduate research at doctoral and postdoctoral levels, and reviewed publications in international journals and magazines in engineering, including the prestigious assignment by Applied Mechanics Reviews of American Institute of Mechanical Engineers.

He has delivered invited lectures on plate heat exchangers at the NATO Advanced Research Institute along with highly distinguished speakers at the international level. He has given onsite courses in industry, covering refineries, gas processing, petrochemical, and fertilizer plants with practice-oriented approach, including lectures on several areas of chemical engineering to trainees and practicing engineers in petroleum and petrochemical industry and at international forums.

His authorships include the book *Fluid Mechanics, Heat Transfer, and Mass Transfer*: *Chemical Engineering Practice* as a joint publication of the American Institute of Chemical Engineers and an American publisher. His other publications include *Low Reynolds Number Heat Exchanger Design* along with several distinguished authors by and an earlier book on *Applied Chemistry*.

He can be contacted at *k_snraju@hotmail.com*

Chemical Process Industry Safety

K S N Raju
Retired Professor of Chemical Engineering
University Institute of Chemical Engineering and Technology
Panjab University, Chandigarh

Mc
Graw
Hill
Education

McGraw Hill Education (India) Private Limited
NEW DELHI

McGraw Hill Education Offices

New Delhi New York St Louis San Francisco Auckland Bogotá Caracas
Kuala Lumpur Lisbon London Madrid Mexico City Milan Montreal
San Juan Santiago Singapore Sydney Tokyo Toronto

McGraw Hill Education (India) Private Limited

Published by McGraw Hill Education (India) Private Limited
P-24, Green Park Extension, New Delhi 110 016

Chemical Process Industry Safety

Copyright © 2014 by McGraw Hill Education (India) Private Limited.

No part of this publication may be reproduced or distributed in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise or stored in a database or retrieval system without the prior written permission of the publishers. The program listings (if any) may be entered, stored and executed in a computer system, but they may not be reproduced for publication.

This edition can be exported from India only by the publishers,
McGraw Hill Education (India) Private Limited.

ISBN (13): 978-9-33-290278-7
ISBN (10): 9-33-290278-X

Managing Director: *Kaushik Bellani*

Head—Higher Education (Publishing and Marketing): *Vibha Mahajan*
Senior Publishing Manager (SEM & Tech. Ed.): *Shalini Jha*
Editorial Executive: *Harsha Singh*
Manager—Production Systems: *Satinder S Baveja*
Assistant Manager—Editorial Services: *Sohini Mukherjee*
Assistant Manager—Production: *Anjali Razdan*

Assistant General Manager—Higher Education: *Vijay Sarathi*
Senior Product Specialist: *Sachin Tripathi*
Senior Graphic Designer—Cover: *Meenu Raghav*

General Manager—Production: *Rajender P Ghansela*
Manager—Production: *Reji Kumar*

Information contained in this work has been obtained by McGraw Hill Education (India), from sources believed to be reliable. However, neither McGraw Hill Education (India) nor its authors guarantee the accuracy or completeness of any information published herein, and neither McGraw Hill Education (India) nor its authors shall be responsible for any errors, omissions, or damages arising out of use of this information. This work is published with the understanding that McGraw Hill Education (India) and its authors are supplying information but are not attempting to render engineering or other professional services. If such services are required, the assistance of an appropriate professional should be sought.

Typeset at Mukesh Technologies Pvt. Ltd., Puducherry, India 605 008 and
printed at Rashtriya Printers, M-135, Panchsheel Garden, Naveen Shahdara, Delhi 110 032

Cover Printer:

A life without adventure is likely to be unsatisfying, but a life in which adventure is allowed to take whatever form it will is likely to be short.

Bertrand Russell

Contents

CHAPTER 1
Introduction 1

CHAPTER 2
Basic Principles 18

Foreword

Process safety in chemical process industry gained serious attention internationally after the Flixborough disaster that witnessed a catastrophic explosion causing major loss to life and property in the United Kingdom in 1974. In 1984, the Bhopal toxic gas release incident caused by a runaway reaction was unprecedented in the history of chemical industry. This was followed, in the late 1980s, by an explosion in an offshore platform (Piper Alpha) in the United Kingdom. Devastating incidents continue to happen even today, and the Indian chemical process industry contributes to its own share of such incidents. On account of such events, the importance of *safety* has made deep inroads into the Indian chemical process industry. Today, understanding the intricacies and importance of *process safety* is a must for every engineer, particularly chemical engineers.

Although in the past, people thought of safety superficially, only in terms of workplace injuries, the serious realization has dawned now that avoiding major catastrophes in the chemical industry is a serious business concern, requiring deep knowledge of technical nature as well as of management systems. Chemical engineers, therefore, must be deeply concerned about understanding the nature of chemicals and their hazards, fundamentals of the hazardous processes, and their potential for uncontrolled behavior and methods for control of such processes to prevent hazardous consequences. Safety in "chemical process industry" has, in fact, become a subject of paramount importance for all chemical engineers before they graduate.

Chemical Process Industry Safety sets the tone for understanding safety in the chemical process industry by commencing with explanation of the basic properties of chemicals, basic chemical engineering principles involved in chemical processes, and then dealing with methods to identify, analyze, control, and contain the hazards.

The author of this book has used his knowledge and experience of theory and best practices in chemical engineering to introduce the subjects to the readers. The book, comprising six chapters, adopts a step-by-step approach to first introduce the reader to safety on process plant operations, starting with a discussion on major process safety incidents and importance of process safety. The book covers case studies of significant incidents that have occurred, involving chemical plants, oil spills, nuclear power industry, inclusive of the devastating Fukushima nuclear power incident, and others. The author then goes on to discuss the physical, chemical, and thermodynamic properties of chemicals in Chapter 1 and continues with detailed explanation of various unit operations in chemical engineering and various reactions in chemical process, which are relevant to process safety such as heat transfer, diffusion, combustion phenomena, explosion basics, etc. This is followed by detailed explanation on chemical hazards, hazard identification, hazard evaluation, and methods to control and mitigate hazards in the chemical process industry. Important aspects of process safety, dealing with topics, such as inherently safe design, effect of human factors on process operations, etc., have also been explicitly covered in the chapters that follow.

I am more than convinced that the comprehensive coverage by the book will help even engineers of other disciplines, viz. mechanical, electrical, and instrumentation, to pick up sufficient concepts of chemical processes and to appreciate the safety aspects of the chemical process industry.

During the many years of my experience in refining and petrochemical process technology, process operations and management, I have found that there are not many books in the field of process safety, providing such detailed information on chemical engineering principles coupled with process safety requirements. I strongly believe that this book provides an excellent tool to enhance the knowledge of persons who aspire to learn chemical process safety. I am sure that this book can be used both as a textbook and as a reference manual by students in technical colleges and universities, and also by engineers in refining, chemical, engineering, construction, and other industries.

I have known the author for several years, and I really commend him on his pioneering effort in collating and developing the information on process safety and presenting the same in such a systematic and lucid manner. It is my firm conviction that this book will travel a long way in helping the cause of process safety in the industry.

P K Kapil
Executive Director
Reliance Industries Limited
28 December, 2013

Preface

The book is written with a balanced and comprehensive approach toward process industry safety, involving hazards, both of materials and process, analysis of hazards in a plant or unit of a plant, in order to try to quantify them, and lastly preventive and protective measures, intended for use by undergraduate and graduate students, faculty in chemical, mechanical, electrical, mining and metallurgical engineering, chemical sciences, and environmental disciplines in educational institutions, industry professionals, consulting organizations, marketing personnel, and others involved in safety aspects in the process industry. In order to cater to the understanding of the contents by all professionals mentioned above, underlying basic principles are discussed in the form of Chapter 1, broadening its scope.

During the courses given to industry professionals—managers having considerable experience—it was noted that overconfidence and complacency among the management and the so-called experienced personnel led to overlook of the realities involved in safety, which, in turn, led to many accidents. Many a time, safety was left to safety departments who confined themselves to display of signboards and use of safety gadgets such as helmets, goggles, clothing, earplugs, and the like.

During maintenance of relief systems, confined space entry norms get neglected. Examples include vehicle entry into plant areas without inspection and maintenance of exhaust systems, lack of appreciation of codes of practice, and use of hazardous practices leading to several accidents. In one case involving an ammonia plant, a high-pressure multilayer separator, which was leaking, was repaired through welding rather than replacing as per norms. This led to an explosion, destroying the plant. It took over two years to reconstruct the plant. Frequent shut-downs and start-ups can lead to development of stresses in the materials of construction, which ultimately can lead to leaks.

In a smaller case, welding work was carried out on a fuel oil tank containing sludge at its bottom, leading to a fire. Complacency and overconfidence in a person, who was using a heater in an oil field, led him to mention that he was practicing this for many years, instead of correcting this practice, which could provide an ignition source to a passing gas. These examples are from the knowledge of the author while conducting onsite courses to industry personnel.

Smaller-level industries, which have limited resources and availability of the expertise, involve frequent accidents due to lack of all the considerations mentioned in the book.

Available literature in the form of magazine articles, NFPA, OSHA, NIOSH, manufacturer literature, and other sources has been used in the preparation of the book to make it practice-oriented.

Salient Features

- The text comprehensively covers hazards such as toxicity, radiation, flammability, fires, explosions, and reaction hazards. It also describes different methods involved in analyzing the hazards in order to quantify them and help devise means for plant safety.
- The book highlights the preventing measures such as inherent safety, plant layout, industrial hygiene, electrical systems, maintenance, and lastly the protective measures, including relief systems, plant modifications, human factors, management involvement, and safety audit.
- Chapter 2 is included with the objective of a quick recap of the basic underlying principles of chemical plant processes.
- Glossary, definitions, abbreviations, and acronyms are provided as an appendix.
- Important keywords are given at the end of each chapter that can be searched on the Web for further literary assistance.
- Rich pedagogy includes the following:
  - 133 figures
  - 121 tables
  - 347 exercise questions

Chapter Organization

The book is divided into 6 Chapters.

Chapter 1 highlights the important accidents that took place, covering chemical plants, oil spills, nuclear power industry, inclusive of the devastating Fukushima nuclear power accident, Bhopal tragedy involving pesticide manufacture, and others. Incidents are taking place almost regularly, due to lack of appreciation toward safety, with the drive on profits through productivity.

Chapter 2 covers basic principles with the objective to make the scope of the book enlarged for use by mechanical and electrical engineers, and others.

Chapter 3 comprehensively covers hazards such as toxicity, radiation, flammability, fires, explosions, and reaction hazards.

Chapter 4 covers physical and plant operational hazards, such as high or low pressure, leakages, high or low temperature, level, and the like.

Chapter 5 describes different methods involved in analyzing the hazards, indicating the systematic steps, in order to quantify the hazards and to help devise means for plant safety.

Chapter 6 highlights the preventing measures such as inherent safety, plant layout, electrical systems, maintenance, and lastly the protective measures, including relief systems, plant modifications, human factors, and management involvement. Changes in managements and the criticality involved in such changes are highlighted. Terrorism and security aspects are also covered.

Online Learning Center

The Online Learning Center (OLC) can be accessed at http://www.mhhe.com/raju/cpis1 and contains comprehensive PowerPoint lecture slides for instructors.

Acknowledgements

No author of any book, other than books written as research or biographical publications, can claim the contents are his or her own as original contributions by them

The author admits that the book is a compilation of the material available in literature, in an organized manner. The author acknowledges those whose contributions in evolving the subject matter over long periods of time. The author wishes to dedicate the book to all such pioneering individuals or groups of them.

The author wishes to acknowledge the help, encouragement, suggestions, and other involvement by several persons at different stages of development of the book.

In particular Ms. Vibha Mahajan, Ms. Shalini Jha, Sri Mitadru Basu, Ms. Harsha Singh, Ms. Anjali Razdan, and other members of McGraw Hill Education India team who accepted the book proposal and involved in its publication work.

The author acknowledges the pains taken by the reviewers.

Sanjay Verma	*Ujjain Engineering College,* *Ujjain, Madhya Pradesh*
H. K. Mohanta	*Birla Institute of Technology and Science (BITS) Pilani, Rajasthan*
Suantak Kamsonlian	*Motilal Nehru National Institute of Technology (MNNIT), Allahabad, Uttar Pradesh*
Prakash Kotecha	*Indian Institute of Technology (IIT) Gawhati, Assam*
C. M. Narayan	*National Institute of Technology (NIT)* *Durgapur, West Bengal*
Mangalya Kar	*Mahatma Gandhi Mission's College of Engineering and Technology, Mumbai, Maharashtra*
V. K. Rathod	*Institute of Chemical Technology, Mumbai, Maharashtra*
P. Shiva Shanmugam	*National Institute of Technology (NIT) Trichy, Tiruchirapalli, Tamil Nadu*
Goli Venkat Reddy	*National Institute of Technology (NIT) Warangal, Andhra Pradesh*

The author is particularly indebted to Sri P.K.Kapil, Executive Director, Reliance Industries Ltd., being an extremely busy person with involvement in managing one of the largest petroleum complexes in the world, having readily agreeing to write **foreword** for the book. It is extremionalely nice of him to do so.

A number of the author's old students and retired and present teaching staff who served and serving as teaching staff connected to different institutions in India

and abroad have urged and encouraged the author to write such a book. It is difficult for me to single out such personals. Sri Pushpinder Singh Puri, a senior professional with illustrious career in U.S. and Canada, Paul Mathias of Flour Corporation (U.S), who was the co-author of 8th edition of Perry's Chemical Engineers Handbook of McGraw Hill, Sardul Singh Minhas ge (U.S.), Michael Leventhal and Ms. Kate McKay, well wishers from John Wiley, Sanchari Sil of Thompson press, Sri Eswar Kiran, Sri Pradeep Jain, old students, and many others deserve special mention.

The unlimited encouragement and help from Sri K.V. Vishnu Raju, Chairman of Sri Vishnu Educational Society, is unforgettable.

Valuable contributions by my son, K.R. Prasad, who is a professional engineer in consultancy, added to the value of the book.

Cooperation and inputs by other family members, Bangarramma, Anuradha, Suhasa, Amulya, and Arjun cannot be ignored.

K. S. N. Raju

Chapter 1

Introduction

Learning Objectives

1.0 Introduction

In the chemical process industry, accidents of varying degrees of severity continue to occur at a surprisingly high rate, despite the almost universal acceptance of excellent codes of practice in the design and operation of chemical plants. As the chemical and petrochemical industries began to grow in complexity, size, and use of new technologies, there has been a concomitant increase in the consequences of accidents and environmental concerns, and major accidents have increased political pressure for legislation to enact controls on the industry.

Currently, many hazardous materials are being processed/used, for example, cryogenic liquids in space applications and elsewhere, chemicals of extreme toxicity in pesticide applications, highly flammable and explosive materials as propellants for missiles and space flights, and materials such as beryllium, zirconium, and radioactive substances for different applications.

The important hazardous conditions characteristic of chemical industry are toxic release, fire and explosion, physical hazards, hazards associated with radiation, biological hazards, ergonomical hazards, and so on. Often, the damage and attending losses resulting from an accident involving any or all of these hazards can cripple the industrial organization. The cost of accidents in the chemical process industry is usually high, generally involving heavy damage to equipment and facilities, loss of life, release of hazardous materials, long or permanent shut-down of the process, and bad public image.

Problems in fluid processing have become central as heavy investments, with attending focus, have been on petroleum, petrochemical, pharmaceutical, and other chemical industries, in view of high degree of toxicity and flammability hazards involved in these industries.

1.1 Factors Contributing to the Costs of Accidents

Following a major industrial accident, cost statements generally comprise allowances for

(i) Lost production
(ii) Legal costs
(iii) Fines
(iv) Reconstruction costs

Reconstruction costs of a plant are primarily based on the physical cost of equipment parts and thus do not include the costs of onsite personnel, contractors and plant redesign, civil and health authorities, public information, safety reviews and safety planning, etc.

Table 1.1 summarizes some of the direct and indirect losses that could result from an industrial accident.

Table 1.1 Losses resulting from an accident

Production and capital losses
Costs of lost production, business interruption, and markets
Recovery, salvage, repair/replacement of damaged/destroyed equipment, structures, and buildings
Collateral costs, for example, sale of crude oil due to lack of refining capacity
Repair of offsite damage, for example, shattered windows/windscreens, burnt-out houses, cars, and so on
Investigations by statutory bodies, inspection, and public inquiry
Decontamination and environmental clean-up of the affected area
Independent studies and research
Penalties/fines imposed by regulatory bodies for failure to take action to prevent hazards
Reconstruction costs
Reallocation of production to other sites, storage, and/or rerouting of base process materials
Cost of obsolescence of process, technology, equipment, controls, etc.
Cost of corrective actions to prevent recurrences
Cost to neighboring plants that may be affected by temporary road closures, or even the need to shut-down and evacuate their own premises
Increased insurance premiums
Legal and administrative costs
Drop in market share and loss of share value
Transportation costs
Personnel
Costs of emergency assistance, equipment, and supplies, including fire fighting, ambulance services, police, patrolling, etc.
Death claims
Medical treatment, health support, and long-term health monitoring
Sick pay, disability benefits, etc.
Evacuation, support, and temporary accommodation of local population
Compensation awards (out of legal actions or otherwise)
Loss of experienced personnel and training costs for replacements
Short-term contractor staff, lost time of nonproductive staff due to plant shut-down, transfers of staff to other production areas, etc.
Public relations

Press briefings, setting up visitors centres and upgrading communications facilities
Policing of the incident, special patrols to inform and reassure the public, direct traffic, support the other emergency services, and deter looters
Review
Review of safety and general emergency procedures (employment of outside contractors)
Other
National implications involving loss of exports, increased imports, and lost tax
Revenue (through loss of sales by the company)
Morale, prestige, and public confidence

Safety is strongly related to energy and environmental pollution. The greater the concentration of energy, the greater the hazards. Release of undesirable materials into the environment increases pollution levels that in turn threaten the health and safety of the community that is exposed to such pollution. Chemical process industry is normally associated with high energy densities with great potential for fires and explosions. Storage facilities represent largest quantities of materials with high energy content concentrated in relatively small land area at both plant sites and storage terminals, inclusive of those located close to markets.

The ever-increasing rate and concentration of industrial complexes in clusters has meant that large quantities of potentially hazardous materials are collected together in greater concentrations than in the past, with great potential for damage to industry and exposure of the workers within the industry as well as the surrounding community to greater hazards.

Losses that arise from fires in storage areas could be enormous, representing major losses sustained by industry, but these are generally economic when compared with loss of life. Large petroleum storage terminals involve capacities of the order of 400–500 m^3 or higher. In many tank fires, usually more than one tank is involved. Thus, losses from a single fire could be colossal. Loss of containment from storage of toxic materials such as ammonia and chlorine represents one of the worst kinds of disasters, as it threatens human life besides material losses.

Petroleum storage terminals continue to greatly impact the surrounding communities. Not only do leaking tanks and past spills still present hazards, but poor environmental practices can lead to new oil spills and thus to widespread contamination of soil, water, and air. Spills can also devastate the local environment. Ground water contamination is becoming quite common, often contaminating drinking water. Losses resulting from fires in oil terminals could be colossus.

Oil spills from supertankers have become common phenomena, creating havoc to marine environment. Oil well fires, besides their intense heat radiation hazards, release carbon dioxide, smoke, and unburnt hydrocarbons in huge quantities, affecting visibility, weather, and health.

Pressure on land use with growth of populations has increased tremendously, particularly in developing countries. Consequently, constraints on land availability for the location of new plants and addition of associated plants and other facilities to the existing industrial complexes, increasing plant capacities and development of other industrial activities have become critical. Moreover, build-up of human settlements around industrial complexes has also increased greatly, limiting availability of *no-activity* zones around the plants to a large extent. There are numerous examples of cities expanding toward and ultimately surrounding industrial complexes, which when initially located, might have been far away from populated areas. This has increased exposure hazards to large populations. The catastrophic effects from loss of containment of extremely toxic methyl isocyanate (MIC) at the Union Carbide India Limited (UCIL) pesticide plant in Bhopal, Madhya Pradesh, India, on the night of December 2–3, 1984, is an example of one of the greatest human catastrophes in industrial accident history.

The potential for both short-term and long-term environmental damage could be great, not only due to accidental releases but also hitherto considered normal releases. The cumulative effect of *normal* releases from a number of plants in a cluster of industries could be very high, making intolerable living conditions for the community in the area.

The awareness of the community about hazards and environmental damage by the industry has increased significantly in the recent past. Environmental protection has become a major concern. Activities in which industrial hazards and environmental damage play a major part have attracted the attention of law makers in an effort to reduce exposure hazards to a reasonable minimum. Incidents such as Bhopal disaster involving release of extremely toxic MIC and radioactive materials to the environment at Chernobyl and elsewhere have increased public awareness. Many plants had to be shut-down/altered due to problems of pollution.

The rights of the community to know about the hazards and environmental damage that could result from an industrial activity as well as the role of the community in emergency planning and response is one of the subjects in such laws. Many plants had to be shut-down or had to undergo change/modification processes due to their hazardous nature or environmental problems posed by them. The combination of increased levels of potential hazards with the increased awareness of them has caused the issue of hazards from the process industries, in particular, to be one of the major concerns. The variety of materials processed/produced/handled and transported is innumerable and poses additional hazards due to their toxicity, reactivity, explosibility, carcinogenic nature, radioactivity, and other hazardous properties.

The modern process industries are highly complex, making safety a trying exercise. Improvements in process development, design of *inherently safer* plants, *process intensification* techniques resulting in significant reduction of inventories of hazardous materials, engineering of facilities, equipment, components, instrumentation, and control systems have tended to reduce the probability of releases of hazardous materials. Despite all such developments, accidents do take place, making safety a highly integrated exercise involving not only technological improvements but also human and other factors that include complacencies and practices from a wide spectrum of *misses* at different levels.

System safety: System safety uses systems engineering approaches to prevent foreseeable accidents and minimizes the occurrence of unforeseeable accidents. Losses, in general, may include destruction of property, loss of mission, and environmental damage. The primary concern of system safety is the management of hazards, the stages for which are based on their identification, evaluation, elimination, and control through analysis, design, and management procedures. System safety activities start in the earliest concept development stages of a project and continue through design, production, testing, operational use, and disposal. One aspect that distinguishes system safety from other approaches to safety is its primary emphasis on the early identification and classification of hazards so that corrective action can be taken to eliminate or minimize such hazards before final design decisions are made.

1.2 List of Some Notable Accidents in the Process Industry/Selected Case Histories

The following are some of the notable accidents that are briefly highlighted:

Union Carbide, Bhopal, India, Midnight of December 2–3, 1984

Bhopal disaster is claimed by many as the worst industrial disaster in history. It was caused by the accidental release of 40 tonnes of highly toxic and heavier than air MIC gas from a Union Carbide pesticide plant located in the heart of the city of Bhopal. In addition to MIC, hydrogen cyanide and phosgene gases were believed to have been released. The gas scrubber was placed on standby and therefore did not attempt to clean escaping gases with sodium hydroxide, which could have brought the concentration down to a safe level. The water curtain was not designed to contain a leak of such magnitude. The flare tower used to burn off gases before they are allowed to escape into the air was inoperational, pending repairs. At least 16,000 people died and 150,000 to 600,000 suffered multisystemic injuries due to the exposure to the heavy gas, which rolled along ground level. Many of the survivors are still suffering from genetic and other disorders. The damage caused to the people is beyond quantification. Compensations were paltry ($0.5–1 billion in losses).

Nypro Chemical Plant, Flixborough, UK, 4.53 pm, Saturday, June 1, 1974

At about 16:53 hours on Saturday, June 1, 1974, the Nypro (UK) site at Flixborough was severely damaged by a large explosion. The explosion was by far the most serious and thoroughly researched accident that occurred in UK chemical industry: 28 workers were killed and a further 36 suffered injuries. It is recognized that the number of casualties would have been more if the incident had occurred on a weekday, as the main office block was not occupied. Off-site consequences resulted in 53 reported injuries. Property damage extended over a wide area, and a preliminary survey showed that 1,821 houses and 167 shops and factories had suffered to a greater or lesser degree. Losses included $232 million in property damages.

Before the explosion, on March 27, 1974, it was discovered that a vertical crack in reactor 5 was leaking cyclohexane. (There were six reactors in series in the train in which cyclohexane was oxidized to cyclohexanone and cyclohexanol by air injection in the presence of a catalyst. The product from the reactors still contained approximately 94 percent of cyclohexane. The liquid reactants flowed from one reactor to the next by gravity. In subsequent stages, the reaction product was distilled to separate the unreacted cyclohexane, which was recycled to the reactors. Insubsequent stages the reaction product was distilled to separate the unreacted cyclohexane which was recycled to the reactors. Reactor No.5 was leaking cyclohexane. The plant was subsequently shut-down for an investigation. The investigation that followed identified a serious problem with the reactor and decision was taken to remove it and install a bypass assembly to connect reactors 4 and 6 so that the plant could continue production. During the late afternoon of June 1, 1974, a 0.5-m (20 inch) bypass system ruptured, which may have been caused by a fire on a nearby 0.2-m (8 inch) pipe. This resulted in the escape of a large quantity of cyclohexane. The cyclohexane formed a flammable mixture and subsequently found a source of ignition. At about 16:53 hours, there was a massive vapor cloud explosion, which caused extensive damage and started numerous fires on the site. Eighteen fatalities occurred in the control room as a result of the windows shattering and the collapse of the roof. No one escaped from the control room. The fires burned for several days, and after 10 days those that still raged were hampering the rescue work.

Temporary plant modification (illustrated in Figure 1.1), failure, and release of 23 tonnes (some sources mention 50 tonnes) of boiling cyclohexane led to Unconfined Vapor Cloud Explosion (UVCE). The flammable cloud was ignited about 1 min or so after the release. A very violent explosion occurred. The blast was equivalent to an explosion of about 16 tonnes of trinitrotoluene (TNT). From the Flixborough disaster, one can learn that a reduction of inventory in the process could have resulted in a smaller flammable gas cloud; control of plant and process modification was an important issue and use of blast-resistant control rooms and buildings would have saved many lives. The traditional cyclohexane oxidation process to produce a mixture of cyclohexanone and cyclohexanol (ketone/alcohol oil K/A oil) was operated at low conversion rates (typically 3–5 percent) to avoid formation of unwanted by-products. The K/A oil was subsequently converted into adipic acid and caprolactam for the production of nylon. Oxidation of cyclohexane with air instead of oxygen is common practice to reduce risks of transition from a partial oxidation reaction to an uncontrolled deflagration in bubbles or in the vapour space in the reactor.

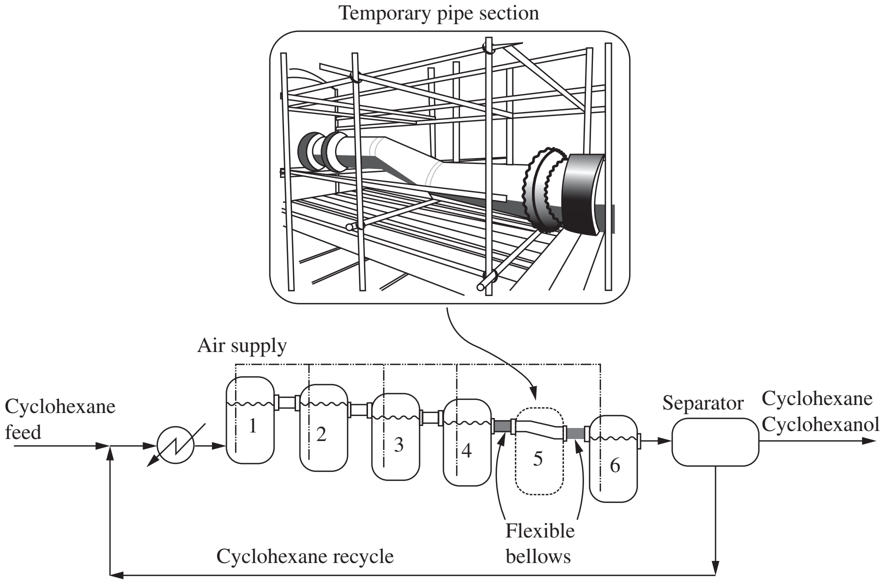


Figure 1.1 Temporary modification as a result of removal of reactor 5

Low conversions and reaction rates led to large inventories of liquid cyclohexane. Plant modification occurred without a full assessment of the potential consequences. Only limited calculations were undertaken on the integrity of the bypass line. No calculations were undertaken for the dog-legged line or for the bellows. No drawing of the proposed modification was produced.

PEMEX LPG Terminal in San Juande Ixhuatepec, Mexico City, Mexico, November 19, 1984

On the morning of November 19, a drop in pressure was noticed by the control room and a pipe line pumping station, but the operators were unable to determine that the cause was the rupturing of a 20-cm (8 inch) pipe connecting one of the spheres to a series of cylinders. The release of LPG continued for between 5 and 10 min, resulting in a 2-m-high cloud covering an area of 200 m by 150 m. When the cloud reached the flare tower, the first explosion occurred and emergency shutdown procedures were too late to halt the catastrophe. A total of 15 of the 48 vessels were under (boiling liquid expanding vapor explosion BLEVEs), which continued for approximately an hour and a half, in domino fashion, as vessels exploded, further spreading burning LPG. The resulting fires and explosions were powerful enough to be registered on a seismograph at the University of Mexico, 20 km away from the destroyed terminal. Nine explosions were recorded, the largest being 0.5 on the Richter scale. About 550 people were killed, 2,000 received severe burns, and 7,231 were injured. A total of 200,000 people were evacuated. The plant was 25 years old, built to 1950 API standards and too congested with poor maintenance and poor operator training.

Chernobyl Nuclear Disaster, Ukraine, April 26, 1986

This was considered to be the costliest accidents and biggest socio-economic catastrophes in history. A chemical explosion at the station's fourth reactor and an uncontrolled graphite fire that followed led to the release of more than 450 radio-nuclides, comprising about 3.5 percent of the fuel stored in the reactor core. The accident was officially attributed to power plant operators who violated the procedures and were ignorant of safety measures. The death toll attributed to Chernobyl disaster, including people who died of cancer years later, is estimated to be 125,000. Over 200,000 people were to be evacuated and resettled while 1.7 million people were affected directly. Total civilian casualties are not known and may never be known. Areas up to 65 km from the reactor were affected. Fifty per cent area of Ukraine was contaminated. The total costs, including clean-up, resettlement, and compensation to people was estimated to be roughly $200 billion. The cost of a new steel shelter for the plant alone was $2 billion. The measures that could have averted the catastrophe are as follows:

(i) Use of less combustible material on the roof of the reactor
(ii) Immediate dispensation of potassium iodide tablets among population within a radius of at least 160 km
(iii) Provision of protective equipment at the reactor site and establishment of dispensaries in nearby settlements

Many of Chernobyl's ramifications (e.g. tumors and leukemias) still lie ahead.

Fukushima Nuclear Disaster, Japan, 05:46 GMT, Friday, March 11, 2011

On March 11, 2011, an earthquake occurred under the sea about 70 km east of Oshika peninsula, Japan, at a depth of about 32 km. It was the most powerful earthquake that had ever hit Japan, and fifth strongest in the world since 1900. This earthquake triggered big tsunami with waves reaching up to 40 m. The wave height was smaller, being about 8 m in Fukushima area. Japanese authorities reported 15,854 deaths and 3,155 missing people. In addition, about 27,000 were injured. Fukushima Daiichi plant comprised six separate nuclear reactors. All reactors were boiling water type, maintained by Tokyo Electric Power Company (TEPCO).

The plant was protected by a seawall protection designed to withstand 5.7 m tsunami waves. Obviously, this was not high enough to protect against the tsunami on March 11, 2011.

At the time of the quake, reactor 4 had been defuelled, whereas 5 and 6 were in cold shutdown for a planned regular maintenance (refuelling). Reactors 1, 2, and 3 were operating. At the time of the quake, the reactors were automatically shut down. Emergency generators started to run to pump the water needed to cool the reactors.

The 8- to 14-m tsunami wave arrived 15 min after the earthquake. The entire plant was flooded, including low-lying generators and electrical devices in the reactor basements. Connection to the electrical grid was broken.

Although the reactors were cooled down, there were large amounts of fission products in the reactor core. About 6 percent of the total energy of fission was released through beta and gamma decay of fission products. This energy was ultimately transformed into heat. Although the chain reaction was stopped, it was necessary to cool down the reactor core, until the radioactivity of fission products decreased significantly below a certain level.

There were three independent cooling systems, but all of these failed; some of these because connection to the electricity was interrupted. Independent cooling, based on generators was also broken, because they were flooded by the tsunami. Without any cooling, reactors and spent fuel pool started to heat up due to the radioactive decay of fission products. Soon after the tsunami, evidence arose of partial core meltdown in reactors 1, 2, and 3.

Hydrogen formed in chemical reactions exploded and destroyed the upper cladding of the buildings housing reactors 1, 3, and 4. Explosion on reactor 3 severely damaged the reactor building number 4. There were explosions and fire on reactor 2. Spent fuel rods stored in spent fuel pools of units 1–4 began to overheat as water levels in the pools dropped. Heat evolution continued due to gamma and beta radioactive decay of fission products. The accident was much more complex than Chernobyl disaster, where only one reactor was destroyed.

The main problem was to enable cooling of all damaged reactors and spent fuel pools. All work on damaged reactors was seriously hindered by high level of radiation within reactor buildings and around them. Radioactive contamination from the Fukushima plant forced evacuation of communities up to 37 km away and affected up to 100,000 residents, although it did not cause any immediate deaths.

Radioactive material released into the atmosphere produced extremely high-radiation dose rates near the plant and left large areas of land uninhabitable, especially to the northwest of the plant. Contaminated water from the storage tanks of the plant spilled into the sea. This forced the government to step in to enforce measures such as freezing of the soil by pumping refrigerants into the soil. Many countries had to review and revise their ambitious plans for nuclear power generation as an alternative to fossil fuel power, so as to reduce the generation of waste gases that could cause environmental pollution and global warming.

Exxon Valdez Oil Tanker Spill, Alaska, March 24, 1989

The spilled oil affected 1,900 km of Alaskan coastline. Although Exxon's initial report of 10.8 million gallons (40,900 m^3) of oil spilled was widely accepted, other sources estimated the spill at 30 million gallons (110,000 m^3). Large quantities of fresh oil was pushed by a storm onto the rocky shores of many of the beaches in the Knights Island chain. A total of $287 million for actual damage and $5 billion for punitive damages was awarded by an Anchorage jury in 1994. The punitive damages amount was based on a single year's profit by Exxon at that time.

Exxon spent an estimated $2 billion cleaning up the spill and a further $1 billion to settle civil and criminal charges related to the case.

Thousands of animals died immediately: the best estimates include 250,000 sea birds, 2,800 sea otters, 300 harbour seals, 250 bald eagles, up to 22 orcas, and billions of salmon and herring eggs.

In addition to the environmental effects of the spill, the disruption to the lives of the people affected is noteworthy. Native American groups in the area were impacted and the fishing industry also experienced serious changes as a result.

Piper Alpha Disaster, Occidental Petroleum, Scotland, July 6, 1988

This is considered to be the world's worst off-shore oil disaster. On July 6, 1988, as part of routine maintenance, technicians removed and checked safety valves. There were 100 identical such valves that were checked. Unfortunately, the technicians made a mistake by forgetting to replace one of the valves. At 10 PM that night, a technician pressed the start button for the liquid gas pumps and the world's most expensive oil rig accident was set in motion. Within 2 h, the 200 ft platform was engulfed in flames. It eventually collapsed killing 167 workers and resulting in $3.4 billion in damages.

Prestige Oil Spill, November 13, 2002

The prestige oil tanker was carrying 77,000 tons of heavy fuel oil when one of its 12 tanks burst during a storm off Galicia, Spain. Fearing that the ship would sink, the captain called for help from Spanish rescue workers, expecting them to take it into harbour. Pressure from local authorities forced the captain to steer away from the coast. The captain tried for help from French and Portuguese authorities, but they too ordered the ship away from their shores. The storm eventually took its toll on the ship, resulting in the tanker splitting into half, spilling 20 million gallons of oil into sea. According to a report, the total clean-up cost was about $12 billion.

Caribbean Petroleum Facility Fire and Explosion, Catano, Puerto Rico, 12.23 am, October 23, 2009

A tank farm was engulfed in flames behind the entrance to the facility. An explosion and huge fire ripped through an oil storage and refinery site outside Puerto Rico's capital San Juan on Friday October 23, 2009, forcing the evacuation of around 350 people from a nearby neighborhood. At the time of the incident, a tank was being filled with gasoline from a ship docked in San Juan harbor. Investigations revealed that a likely scenario leading to the release was an accidental overfilling of the tank. Gasoline spilled from the tank without detection, vapourised, and spread across the facility.

It was estimated that the vapor cloud spread to over 600 m diameter until it reached an ignition source in the northwest section of the facility. At least 11 tanks at the oil distribution center were set ablaze.

BP's Texas City Refinery Explosion, March 23, 2005

A fire and explosion occurred in the isomerization plant at BP's Texas City Refinery in Texas City, Texas, killing 15 workers and injuring more than 170 others. BP was charged with criminal violations of federal environmental laws and was subjected to lawsuits from the victim's families. The Occupational Safety and Health Administration slapped BP with a then-record fine for hundreds of safety violations, and subsequently imposed an even larger fine after claiming that BP had failed to implement safety improvements following the disaster. The incident was an explosion caused by heavier-than-air hydrocarbon vapors burning after coming into contact with an ignition source, probably a running vehicle engine. The hydrocarbons originated from liquid overflow from a blow-down stack, following the operation of an overpressure protection system caused by overfilling and overheating of the contents. The failure to start liquid rundown from the column, and the failure to take effective emergency action, resulted in the loss of containment that preceded the explosion. Supervisors assigned to the unit were not present to ensure conformance with established procedures, which had become custom and practice on what was viewed as a routine operation. The severity of the accident was increased by the presence of many people congregated in and around temporary trailers, which were inappropriately sited too close to the source of relief. Many of those injured could have been warned and left the area safely had warning been provided by those who were aware of events. It is unclear why those aware of the process upset failed to sound a warning. The likelihood of this incident could have been reduced by discontinuing the use of the blow-down stack for light end hydrocarbon service and installing inherently safer options when they were available. The investigative team found no evidence of anyone consciously or intentionally taking actions or decisions that put others at risk.

The explosion occurred in an isomerization unit at the site resulting in deaths and injuries. According to a report issued after the accident, actions taken or not taken led to overfilling the raffinate splitter with liquid, overheating of the liquid and the subsequent over pressurization and pressure relief. Hydrocarbon flow to the blow-down drum and stack overflowed, resulting in liquids carrying over out of the top of the stack, flowing down the stack, accumulating on the ground, causing a vapour cloud, which was ignited by a contractor's pickup truck when he repeatedly attempted to start the engine. The report identified numerous failings in equipment, risk management, staff management, working culture at the site, maintenance and inspection, and general health and safety assessments.

Oil Storage Facility, Indian Oil Corporation, Jaipur, 7.30 PM (IST), October 29, 2009

The Jaipur oil depot fire broke out at the giant tank holding 8,000 kl of oil, in Sitapura industrial area on the outskirts of Jaipur, Rajasthan, killing 12 persons and injuring 300. The blaze continued to rage out of control for over a week after it started and during the period, half a million people were evacuated from the area. The facility is about 16 km south of the city of Jaipur, India.

The incident occurred when gasoline was being transferred from the IOC's oil depot to a pipeline. There were at least 40 IOC employees at the terminal, situated close to the Jaipur Airport, when the pipeline caught fire with an explosion.

The Meteorological Department recorded a tremor measuring 2.3 on the Richter scale at the time of the first explosion at 7.36 PM, which resulted in shattering of glass windows nearly 3 km from the accident site.

The fire was a major disaster in terms of deaths, injury, loss of business, property and man-days, displacement of people, and environmental impact in Jaipur, the capital city of the Indian state of Rajasthan and a popular tourist destination.

At 7.35 PM, a huge ball of fire with loud explosion broke out engulfing the leaking gasoline tank and other nearby gasoline tanks with continuous fire with flames rising 30–35 m and visible from a 30 km radius.

Petrobras, Brazil, March 2001

This was an off-shore oil platform explosion. A total of 10 people were killed and resulted in $5 billion in losses. Platform sank into the Atlantic Ocean.

Ammonium Nitrate Explosion, Toulouse, France, September 21, 2001

Massive detonation of ammonium nitrate pile took place. A total of 31 people were killed and 2,442 injured. The estimated loss was US$ 700 million.

Venezuela's Biggest Refinery Fire and Explosion, 1.10 AM, August 25, 2012

A total of 41 people were killed and hundreds injured. The victims included 18 National Guard troops and 17 civilians; 6 remain unidentified. The accident, which also wounded dozens of people, was the worst to hit Venezuela's oil industry. It ranks as one of the deadliest refinery accidents in the recent history of the global oil industry. A gas leak that formed a cloud at the refinery exploded at 1.10 AM on August 25, sending a ball of flame into the air and destroying a National Guard post and damaging about 500 homes.

*Note: Accident cases are too numerous to record in a book and are occurring every day, with repetitive causes, often within the same facilities world over, despite lessons learned and precautions implemented, emphasizing the complexities involved in safety measures. Terrorism is an added threat in recent times, with emphasis on intelligence inputs and security measures.

1.3 Some Common Features of High-Cost Accidents

Some of the most common features of high-cost accidents are described below:

***Isolation valves*:** Problems with isolating leaks of ignited flammable substances were major factors in some of the accidents. In these cases, isolating valves could not be closed because they were not remotely operable and could not be accessed because of their proximity to the fire or they were damaged by the fire.

Fire water: In several of the accidents, water supplies for fire fighting were found to be inadequate.

Storage: A lack of understanding and poor management of storage/process/chemical segregation was a common factor in some of the accidents.

Perceived low risk: At least few of the accidents involved activities that were not considered to be the main high-risk activity on site.

Escalation potential: In some of the accidents, the intense heat generated by fire posed a real threat of escalation to involve adjacent storage tanks. In these cases, the fire service set-up portable water monitors to provide cooling.

Routine inspection and maintenance of critical equipment: Some of the accidents revealed deficiencies in the inspection and maintenance procedures for what turned out to be critical items of plant equipment.

Unreliable and inadequate control systems: Some of the accidents revealed a combination of inadequate and unreliable process control equipment. In one case, a process motor/pump had failed for several hours; in another level indicators were known to give false readings; and in yet another case, the process system failed to identify the correct position of valve equipment, and vital pressure information was not displayed on the VDU used by the operators.

Location of key buildings: Some of the accidents resulted in the total destruction of, or severe damage to, control room buildings.

Loss of process control: Runaway reactions were involved in some of the accidents.

1.4 Reasons for High Priority Toward Safety

There may be hundreds of reasons why safety in chemical plant is vitally important. Table 1.2 summarizes some of the reasons why safety has assumed greater importance in recent years.

Table 1.2 Why high priority is given to safety in chemical process industry?

Safety It is imperative that industrial plants operate safely so as to promote the well-being of people (who include workers, employers, and other people in and out of plant premises) and property and equipment within the plant and in the nearby communities.
To reduce turn over of employees and increase productivity
Environmental regulations Industrial plants must comply with environmental regulations concerning the discharge of gases, liquids, and solids beyond the plant boundaries.
To avoid law suits and penalties.
Protection of personnel both inside the organization and general public at large. Concern of a facility has to go beyond its premises to include neighboring as well as global environment, risks of loss of containment during transport and handling outside the plant premises, safe waste disposal issues, etc.
Product specifications and production rate To be profitable, a plant must make products that meet specifications concerning product quality and production rate.
Wide variety of chemicals processed/produced with a wide range of hazards

Hazards associated with storage and transport of large quantities of materials
Oil spills and oil well fires with their potential for enormous damage to the environment
Large inventories of hazardous materials in process and storage involving high energy density
Increased plant and equipment sizes
High degree of interlinking of plants
Increased depth of technology with more rigorous operating conditions than in the past
More critical conditions in process control and selection of materials of construction
Increased pressure on land around industries, reducing availability of "no-activity" areas outside the plant boundaries
Increased public awareness of potential risks, stricter legal requirements, and increased complexity of modern industrial plants
To ensure survival of business, achieve targets of manufacture, and enhancement of reputation of the company

Past practices placed great emphasis on corrective actions largely based on accident history. Learning from mistakes is, and always has been, an important safety consideration. Analysis of accidents largely resulted in devising safety regulations and codes of practice. The approach involving anticipation of hazardous incidents before they arose started receiving greater attention at relatively recent times. Even today, many managements tend to give low priority to safety and surprisingly many experienced technical personnel contribute to this state of affairs, largely out of complacence. Many a time, there is lack of openness in the approach, particularly in reporting or paying attention to incidents either dismissing them as inconsequential or out of fear of action by the management by fixing responsibility on the operator. Many a time, the so-called *inconsequential incidents* provide early warning for an impending major accident.

Knowledge on the hazardous properties of materials is improving continuously with greater attention and effort being devoted in that direction with the objective of improving safety standards. Materials once considered to be nonhazardous have subsequently been found to be hazardous, for example, vinyl chloride monomer. Stringent measures are being adopted in plants engaged in its manufacture and handling on finding that exposure to vinyl chloride could lead to cancer. The list of hazardous materials is growing at a fast rate.

Developments in engineering and technology tended to reduce the probability of release of hazardous materials to the environment.

The growing awareness of the risks of industrial installations by the community and managements largely contributed to the improvements in safety standards with an integrated approach. The following are the essential components of integrated safety:

(i) The hazardous properties of all the materials, whether raw materials, possible intermediate or final products, should be determined at the initial stages of process development. "Green Chemistry" is the catch word used in developing alternative materials.

(ii) The identification of hazards and development of safety measures should form an integral part of the planning process.

(iii) Hazard assessment should cover the life cycle of the product(s) involving the stages of research, manufacture, use, and disposal.
(iv) Controls are an essential feature and must be ensured by means of organizational measures. A clear-cut and effective organizational structure with well-defined responsibilities goes a long way in improving safety standards.
(v) All the personnel involved, whether in planning, design, operation, maintenance or emergency response, should be treated as essential elements of safety.

Prevention of an accident should be the primary objective of any safety program. Providing the necessary *controls* through sound instrumentation should be the next objective. *Protective measures* are important for reassuring safety when deviations could be part of the operations, as in start-up and shutdown or unexpected upsets. Under emergency situations, *mitigation* becomes the necessity. Approaches toward safety is summarized in Table 1.3.

Table 1.3 Approaches toward safety

Prevention	*Control*	*Protection*	*Mitigation*
Mechanical integrity	Automatic control	Alarms	Emergency response systems
Operator intervention	Sprinkler, deluge		
Preventive maintenance	Manual controls	Interlocks, trips	Dike/trench
Inspection, testing	Online spares	Emergency shutdown	Barricade
Operator training	Back-up systems	Emergency relief	Blast wall
Human errors	Last resort controls		Water curtain
Impact barriers	Ignition source control		
	Personnel protection equipment		

Figure 1.2 summarizes the approaches of steps involved toward safety.

Research and development stage provides the most effective means of eliminating hazards at their sources rather than attempting to compensate them at a later stage. Thorough knowledge of the properties of materials handled, reaction kinetics, and heat effects should be gathered at this stage. Alternative processes affording better safety conditions should be considered.

Plants should be designed, wherever possible, so that they can tolerate departures from ideal operation/maintenance—whether due to human error or equipment failure—without serious effects on safety, output, or efficiency. The objectives toward inherently safer plants include features such as simplicity, the use of safer materials in place of hazardous materials, smaller inventories of hazardous materials, and the use of hazardous materials in the least hazardous form, under less severe conditions. Application of *process intensification* concepts will go a long way in miniaturization of the plants with reduced inventories of materials. Training and continuing education of staff, provision of information on possible hazards and safety measures,

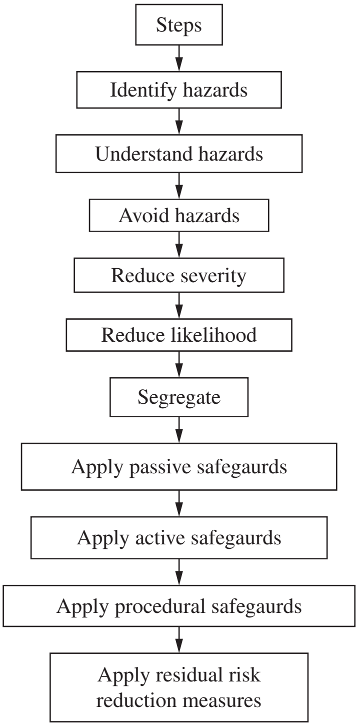


Figure 1.2 Summary of steps involved toward safety

clear instructions, and the motivation to perform their tasks in an attentive and safe manner are important elements of any safety activity. Table 1.4 gives a checklist of different areas of concern involved in safety and health in a chemical process industry. Contract labour without adequate training and supervision contributed to several accidents involving deaths and material damage.

Table 1.4 Safety and health-related areas of concern in a chemical process industry

Hazardous materials	Handling, storage, and processing of flammable and toxic gases, liquids and solids, oxidizers, corrosives, radioactive substances, and explosives
High or low pressure	Leakage or failure of pressure vessels, collapse of storage operations, tanks, fired heaters, boilers, fluid moving and heat transfer equipment, malfunction or failure of relief systems, instrumentation and control systems, corrosion and selection of materials of construction, inspection and testing inadequacies, human errors, etc.
Hazardous chemical reactions	Reactions involving unstable compounds, polymerizations, heat release, heat addition or removal problems, runaways, etc.

Design and layout	Explosion protection, maintaining distances as per codes, accessibility considerations and fire fighting facilities
Control rooms	Design and siting issues
Plant modifications	Screening and control of all modifications and designs through hazard analysis techniques and follow-up measures, proper documentation and training on such modifications
Confined space entry issues involved	1. oxygen deficiency 2. toxic contamination 3. flammable environment 4. cleaning and purging before entry 5. possibility of electrocutions through electrical equipments 6. possibility of toxic gas generation during work 7. providing proper lighting and ventilation 8. providing self-contained breathing equipment 9. welfare monitoring of personnel working in confined spaces through use of life line 10. safe escape on emergency 11. enforcement of permit to work system
Ignition source control	Electrical equipment and area/zone classifications, inerting, purging and pressurization, static electricity problems, welding practices, etc.
Sampling and gauging	Avoidance of spillages and exposures, dip gauging and proper precautionary measures, and earthing practices
Security	Security concerns and entry restrictions and patrolling practices

Review Questions

1. What are the factors that contribute to the costs of accidents?
2. (a) What are the present-day capacities of oil refineries in the world?
   (b) Which is the largest oil refining facility in the world?
3. What is systems safety? How does it help in safety?
4. What are the causes of Bhopal tragedy?
5. (a) Which of the major accidents contributed toward important changes to siting, layout and design concepts to process industry safety?
   (b) What are factors that contributed to the scale of the disaster in this accident?
6. Explain how Fukushima nuclear plant accident contributed to nuclear power generation issues world over?
7. Name the largest oil spill that contributed to catastrophic damage to environment. Explain.
8. How Jaipur IOC terminal triggered a major fire and damage? What are the lessons learned from this accident?
9. What are the hazardous characteristics of ammonium nitrate? Where did an explosion take place involving ammonium nitrate?
10. List down some common features of high-cost accidents.

11. Give reasons as to why safety should receive attention and remedial steps to be taken on a continued basis giving the importance that these should be attended by the managements of industry with equal priority as manufacture/production.
12. What are the desirable approaches toward safety enhancement?
13. What are the safety and health-related areas of concern in chemical industry?

Keywords for Internet searches: Case histories of major accidents in process industry.

Note: *Vast number of sites are given in Appendix A of the book for the purpose of use in Internet searches for key words by enterprising teachers, students, industry professionals, and managements*.

Chapter
2
Basic Principles

Learning Objectives

2.1 Specific Gravity
2.2 Liquid Density
2.3 Density Differences of Liquids
2.4 Vapor Density
2.5 Newtonian Fluids
2.6 Viscosity of Liquids
2.7 Rheology
2.8 Viscosity of Gases
2.9 Yield Stress
2.10 Turbulence
2.11 Drag Coefficient
2.12 Water Hammer
2.13 Cavitation
2.14 NPSH
2.15 Two-Phase Flow
2.16 Compressible Fluids
2.17 Dielectric Properties
2.18 Surface Tension
2.19 Vapor Pressure
2.20 Partial Pressure
2.21 PVT Relationships
2.22 Raoult's Law
2.23 K-Values
2.24 Henry's Law
2.25 Heat and Thermodynamics
2.26 Heat-Transfer Basics
2.27 Diffusion and Mass Transfer
2.28 Stoichiometry
2.29 Combustion
2.30 Chemical Reactions

2.1 Specific Gravity

Specific gravity is the weight of the material compared to that of an equal amount of water. Substances that have a specific gravity of 1.0 will sink in water, whereas those with specific gravity less than 1.0 will float. Most flammable liquids have a specific gravity less than 1.0; and if not soluble, it will float on water. This is important for fire suppression and for handling emergency spill situations where something might enter a body of water. It also has bearing on how the substance is handled in conjunction with other substances with which it might be mixed.

2.2 Liquid Density

Liquid density is an important parameter from safety point of view. Liquid density influences spills in the sense that spills create pools that influence vaporization process and formation of vapor clouds, which on ignition, can lead to unconfined vapor cloud explosions (UVCEs) and disasters.

It is important to obtain density data, either through experimentation or using different methods of estimation. Many a time, Antoine equation is used for this purpose, which requires experimentally determined constants that are available in literature. Many correlations are developed, which only require critical constants as input.

Prominent among them are Lydersen, Greenkorn, and Hougen correlation. On depressurization of pressure vessels with liquids at their boiling points, vaporization/flashing is promoted. For example, is rapid vaporization of LPG spills may lead to vapor cloud formation.

2.3 Density Differences of Liquids

The specific gravities of liquid chemicals vary widely, for example, the majority of hydrocarbons have specific gravity is < 1.0; but for some natural oils and fats and chlorinated hydrocarbons, it is > 1.0. Density decreases generally by an increase in temperature. As a result, on heating, thermal expansion of a liquid in sealed piping, equipment, or a container may exert sufficient pressure to cause rupture or failure. Therefore, specific filling ratios are followed with containers such as road tankers.

A lighter liquid can spread over, and if immiscible, it remains on top of a denser liquid. Thus, liquid hydrocarbon spills and many organic liquids will spread on water, resulting in a hazard in sumps, pits, or sewerage systems and often precludes the use of water in fire fighting.

Stratification of immiscible liquids may occur in unagitated process or storage vessels. In one incident that involves a railway tank car that was parked in a yard for two months, stratification resulted in a chemical reaction, with heat release at the interface, causing an explosion.

The boiling point of a mixture of immiscible liquids can be significantly lower than that of either material, therefore violent boiling may occur on mixing them while hot.

2.4 Vapor Density

Vapor density is the weight of a gas compared to an equal amount of air, which is 1.0. If the density is > 1.0, such as kerosene (4.7), its vapors will sink. If it is < 1.0, such as ammonia (0.596), it will rise. This factor can be a problem, depending on whether one is working in a low or high position, particularly in confined spaces, and the vapor rises or falls easily.

It is also of interest in emergency spill situations where large quantities might escape and either rise quickly above ground level, presenting little danger to people, or remaining close to ground level and presenting a health threat. On release, vapors heavier than air tend to spread at low level and get accumulated in pits, sumps, depressions in ground, etc. This may promote a fire/explosion hazard, or a toxic hazard, or may lead to an oxygen-deficient atmosphere, depending on the chemical.

Heavy vapor can remain in empty vessels after draining out liquid and venting via the top with similar associated hazards. On release, vapors that are denser than air at ambient temperature may tend to spread at low level when cold (e.g. vapor from liquid ammonia or liquefied natural gas spillages). Gases less dense than air may rise upward through equipment, or buildings; and if not vented, it will tend to accumulate at high level. This is an important consideration with piped natural gas that tends to diffuse upward from fractured pipes, open valves, or faulty appliances. Hydrogen from leakages, or from electrolytic processes, rapidly diffuses upward. Electrical fixtures in the ceiling of buildings pose ignition hazards, unless made flame-proof.

Fire and explosion hazards can be possible from heavy gases such as propane, butane, and gasoline; other flammable vapors may ignite at ground-level ignition sources. Toxic hazards are presented by vapors such as chlorine and chlorinated hydrocarbons.

Hot gases rise by thermal draft. In the open air, they will disperse. Within buildings, this is a serious cause of fire escalation and toxic/asphyxiation hazards if smoke and hot gases are able to spread without restriction (or venting) to upper levels.

Methane, hydrogen, and ammonia are lighter than air and rise in air atmospheres. Leaked ammonia, however, containing about 14 percent or higher droplets becomes heavier than air and creep over surfaces. Toxic and flammable gases can be a potential hazards. Table 2.1 gives densities of some toxic gases relative to air at 20°C.

Table 2.1 Densities of some toxic gases relative to air at 20°C

Gas	σ_v/σ_{air}	*Mol (wt)*
Chlorine	2.46	71
Ammonia	0.59	17
SO_2	2.22	64
Phosgene	3.43	99
HF vapor	0.69	20
HCN vapor	0.94	27
Bromine vapor	5.54	160
Acrylonitrile vapor	84	53

2.5 Newtonian Fluids

In Newtonian fluids, viscosity is constant, regardless of the shear forces applied to the layers of fluid. At constant temperature, the viscosity is constant with changes in shear rate or agitation. Fluids for which a plot of shear stress versus shear rate at a given temperature is a straight line with a constant slope, independent of the shear rate, are called Newtonian fluids. This slope is called absolute viscosity of the fluid, represented by the equation $\mu = \tau/\gamma$. Absolute viscosity is sometimes called shear viscosity. When written as $\tau = \mu$ du/dy, the equation represents Newton's law and the fluids that follow Newton's law are Newtonian fluids. All fluids for which viscosity varies with shear rate are called non-Newtonian fluids. For such fluids, viscosity, defined as the ratio of shear stress to shear rate, is called apparent viscosity to emphasize the distinction from Newtonian behavior. For such fluids, apparent viscosity is given by $\tau = \eta\gamma$, where τ is the shear stress, η is the *apparent* viscosity. Any fluid that does not obey the Newtonian relationship between the shear stress and shear rate is called non-Newtonian. The subject of rheology is devoted to the study of the behavior of such fluids. High-molecular-weight liquids that include polymer melts and solutions of polymers, as well as liquids in which fine particles are suspended (slurries and pastes), are usually non-Newtinian. Fluids such as water, ethanol, and benzene and air and all gases are Newtonian. Also, low-molecular-weight liquids and solutions of low-molecular-weight substances in liquids are usually Newtonian. Non-Newtonian fluids can be divided into two broad categories on the basis of their shear stress/shear rate behavior: those whose shear stress is independent of time or duration of shear (time-independent) and those whose shear stress depends on time or duration of shear (time-dependent).

The slope of the shear stress versus shear rate curve will not be constant as one can change the shear rate. When the viscosity decreases with increasing shear rate, the fluid is called shear thinning. However, the rate of increase is less than linear as shown in Figure 2.1.

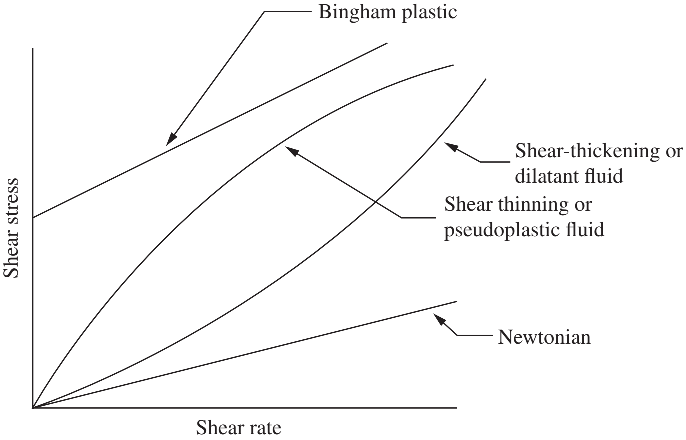


Figure 2.1 Shear rate versus shear stress diagrams for Newtonian and non-Newtonian fluids

Where the viscosity increases as the fluid is subjected to a higher shear rate, the fluid, is called shear thickening. For a shear thickening fluid, τ increases faster than linearly with increasing g. Shear-thinning behavior is more common than shear thickening behavior.

Most shear-thinning fluids behave in a Newtonian manner (i.e. their viscosity is independent of g) at very high and very low shear rates. examples of shear-thinning fluids are polymer melts such as molten polystyrene; polymer solutions such as polyethylene oxide in water, emulsions, molten sulfur, molasses, greases, starch suspensions, paper pulp, biological fluids, soaps, detergent slurries, toothpastes, cosmetics, and some pharmaceuticals and inks and paints as paints and printing inks of high concentrations, gum arabic in water, and solutions of certain surfactants.

Most shear-thickening fluids tend to show shear-thinning behavior at very low shear rates. However, at high shear rates, the suspension expands (dilates), such that the amount of liquid present cannot overcome the frictional forces between the particles and the consequent increase in apparent viscosity, μ_a.

2.6 Viscosity of Liquids

Viscosity of a liquid is a measure of the resistance to flow for the liquid by an external force such as a pressure differential or gravity. Viscosity is the measure of the internal friction of a fluid. This friction becomes apparent when a layer of fluid is made to move in relation to another layer. The greater the friction, the greater the amount of force required to cause this movement, which is called *shear*. Shearing occurs whenever the fluid is physically moved or distributed, as in pouring, spreading, spraying, mixing, etc. Highly viscous fluids, therefore, require more force to move than less-viscous materials.

High-viscosity liquids will create flow problems and cause blockages in piping. They tend to stick on surfaces, causing film/deposit formations in tanks and vessels and retard cleaning and maintenance operations. Similarly, tank bottoms are difficult to drain and sludges accumulate. To cite an example, welding operations were carried out after permit-to-work form was signed to clear for such welding, although cleaning was said to have been carried out. The fuel oil sludges from the bottom of the tank were not thoroughly subjected to ensure complete cleanliness; and when welding was carried out on the top section of the tank, a fire resulted, causing damage to the vessel. The welders escaped in time to save their lives. Another factor that gives rise to ignition hazards is the residues sticking to the inner walls of heavy oil tanks contain pyrophoric iron sulfides that, when dry, act as sources of ignition for any leftover fuels and ignitable vapors. Low-viscosity liquids get vaporized, exerting their vapor pressure and increasing the tank pressure when exposed to the sun, leading to tank leaks/rupture hazards.

2.7 Rheology

Rheology is defined as the study of the change in form and the flow of matter, embracing elasticity, viscosity, and plasticity are involved in rheological properties. The equation for viscosity is called Newton's equation, which is:

$$\tau = -\mu\ (\mathrm{du/dy}) \tag{2.1}$$

where τ is *shear stress*, μ viscosity and (du/dy) is *shear rate*, γ.

Equation for viscosity becomes:

$$\mu = \tau\gamma \tag{2.2}$$

which is the ratio of shear stress to shear rate. μ is absolute viscosity which is sometimes called shear viscosity. τ is shear stress and γ is shear rate. The commonly used unit of absolute viscosity is Poise (*P*).

Viscosity affects the magnitude of energy loss in a flowing fluid. High viscosity fluids require greater shearing forces than low viscosity fluids at a given shear rate.

Viscosity is a general property of all fluids, which includes both liquids and gases. While the basic concept of viscosity is the same for liquids and gases, changes in temperature affect the viscosity of liquids and gases differently.

It is a quantitative property of a fluid. Viscosity arises from the directed motion of molecules past each other and the transfer of momentum. Temperature changes viscosity, rather dramatically. Arrhenius expressed this dependence as follows:

$$\eta = A \exp\ (E_\eta/RT) \tag{2.3}$$

With A, a constant for a given liquid and E_η, the activation energy for viscous flow. This is the energy barrier that must be surmounted in order for a molecule to *squeeze* by its neighbors. Low viscosity liquid spills and leaks readily spread over larger areas and also vaporises more easily than high viscosity liquids. In most cases, lower viscosity is beneficial to applications such as air pollution. The following phenomena, commonly encountered in air pollution control, are directly affected by liquid viscosity:

- (i) Pump performance
- (ii) Size distribution of liquid droplets
- (iii) Settling rate of droplets
- (iv) Absorption of gaseous and particulate pollutants by liquids
- (v) Gravitational settling of solids in liquid

Viscosity relates directly to pump performance, and therefore to the system connected to the pump. Before designing a pump, it is important to determine the viscosity of the fluid at the expected operating conditions. An increase in liquid viscosity generally increases the required net inlet pressure and the required pump input power. Further, an increase in the viscosity generally corresponds to a *decrease* in the maximum allowable pump speed.

Viscosity affects the size of liquid droplets. Size of droplets influence surface areas that can create mists and fogs that influence hazards such as toxicity and flammability. Liquid droplets can be formed by vapor condensation or by spraying liquid into the gas stream. Increasing the viscosity tends to increase the size of the droplets, which in turn increases their gravitational settling rates.

For a given mass of liquid, smaller-sized droplets (lower viscosity) yield greater total surface area than do larger droplets. Greater surface area provides increased contact between the gas stream and the liquid and is generally beneficial for cooling a gas stream and collecting pollutants.

Absorption is an important technique used by many types of air pollution control equipment to collect pollutants. The rate of absorption is partly dependent on both the size distribution and settling rate of droplets entering the gas stream, both of which are affected by viscosity.

Suspended solids in a liquid of a relatively quiescent state will settle by gravity if the solids have a greater density than the surrounding liquid. Suspended solids settle more quickly in liquids with lower viscosities than with higher viscosities.

There are two basic methods for expressing viscosity: *absolute* (dynamic) viscosity (μ), and *kinematic* viscosity (ν). In an industrial context, pumps must apply more force, or torque, to a high viscosity liquid than to a low viscosity liquid to attain the same liquid flow rate. As the torque required to move a liquid increases, the power requirement of the pump increases and the life of the pump decreases. Energy requirements increase rapidly in mixing of liquids with increased viscosity. Unloading high viscosity liquids from reactors and vessels is more difficult and residues left over can pose flammability or toxicity hazards.

The temperature dependence of liquid viscosity is the opposite of the temperature dependence of gases. In the case of gases, the viscosity *increases* with temperature.

Kinematic viscosity: The kinematic viscosity is simply absolute viscosity divided by the density of the liquid as shown in Eqn. 2.4

$$\upsilon = \mu/\rho \tag{2.4}$$

υ = kinematic viscosity
μ = absolute viscosity

ρ = density

The units of kinematic viscosity are as follows:

$$(\text{length})^2/\text{time} \tag{2.5}$$

Since the density of a liquid is not altered significantly by temperature, the effect of temperature on kinematic viscosity is the same as on absolute viscosity. Highly viscous liquids retard flow and heat transfer in reactors, giving rise to temperatures increases and reaction rates. Flow of viscous liquids through relief valves, reducing their capability to relieve pressure in equipment and can lead to failure and explosions. Blockages of relief valves and flow lines can lead to stoppages for flow and failure of piping and pumping systems. Low viscosities can affect lubrication of rotating equipment and increases in friction and seizure.

2.8 Viscosity of Gases

Viscosity of gases increases as temperature increases and is approximately proportional to the square root of temperature. This is due to the increase in the frequency of intermolecular collisions at higher temperatures. Since most of the time the molecules in a gas are flying freely through the voids, anything that increases the number of times one molecule is in contact with another will decrease the ability of the molecules as a whole to engage in the coordinated movement. The more these molecules collide with one another, the more disorganized their motion becomes.

2.9 Yield Stress

For many CPI applications, yield stress is an important parameter to measure. Yield stress is the force required to cause a material to begin flowing. For example, yield stress represents the force that must be overcome when a pump is switched on. The start-up torque required for a pump must be calculated to ensure proper sizing. Controlled stress rheometers are the tools of choice in measuring yield stress. The method involves applying increasing torque to a spindle until rotation of the instrument is observed. Such a test can yield a numerical value that can be used by process engineers to determine yield stress of the material. This information can, in turn, be used in pump sizing calculations for start-up torque and full-flow conditions.

2.10 Turbulence

Turbulence is irregular and seemingly random (chaotic) movement of fluid elements in all directions, the net flow being unidirectional. Turbulence manifests itself at high flow velocities at Reynolds numbers above 10,000. The origin of turbulence is rooted in the instability of shear flows. It is also derived from buoyancy-driven flows. Turbulence is rotational and three-dimensional motion. Large-scale turbulent motion is roughly independent of viscosity. In other words, at high Reynolds numbers, viscous forces, which contribute to flow stability, are insignificant compared to inertial forces that contribute to flow instability. Turbulence is associated with high levels of vorticity fluctuations. Smaller scales are generated by the vortex stretching mechanism. Turbulence is highly dissipative and requires a source of energy to maintain it. Rapid mixing involved in turbulence increases momentum, heat, and mass transfer processes. Turbulence can be generated by contact between two layers of fluid moving at different velocities or by a flowing stream in contact with a solid boundary. Turbulence can arise when a jet of fluid from an orifice flows into a mass of fluid.

2.11 Drag Coefficient

Drag coefficient, C_{d}, is a dimensionless number given by the following relation:

$$C_{\mathrm{d}} = F_{\mathrm{D/}}0.5\ \rho AV^2 \tag{2.6}$$

(drag force)/(projected area)/(velocity head) where F_{D} is the drag force, ρ is the fluid density, V is the fluid velocity, and A is the projected area of the solid object.

2.12 Water Hammer

Water hammer is generally defined as pressure wave or surge or momentary increase in pressure or hydraulic shock, caused by the kinetic energy of a non-viscous fluid in motion when it is forced to stop or change direction suddenly. Kinetic energy of the moving mass of liquid upon sudden stoppage or abrupt change of direction is transformed into pressure energy. Slow or abrupt start-up or shut-down of a pump system, pipe breakage, turbine failure, or electric power interruption to the motor of a pump are some examples. Surge is a slow motion mass oscillation of water caused by internal pressure fluctuations in the system. Water hammer occurs during the start-up or energizing of a steam system. If the steam line is energized too quickly without proper warm up time and the condensate created during the start-up is not properly removed, water hammer will be the result.

When a rapidly closed valve suddenly stops water flowing in a pipeline, pressure energy is transferred to the valve and pipe wall. Shock waves are set up within the system. Pressure waves travel backward until encountering the next solid obstacle, then forward, and then back again. The velocity of the pressure wave is equal to the speed of sound. It generates damaging noise as it travels back and forth, until dissipated by frictional losses.

Successive reflections of the pressure wave between pipe inlet and closed valve resulting in alternating pressure increases and decreases often result in severe mechanical damage. A valve closing in 1.5 s or less depending on valve size and system conditions causes an abrupt stoppage of flow.

The pressure spike (acoustic wave) created at rapid valve closure can be as high as five times the system working pressure. Incorrect flow direction through valves can induce pressure waves, particularly as the valve functions. The pressure wave or spike can travel at velocities exceeding 1,400 m/s for steel tubes. Rapid changes in flow, operation of positive displacement pumps, entrained or separated gases, and increased temperatures induce damaging pressure changes.

When a vapor bubble collapses as in the case of cavitation, water rushes into this space from all directions causing hammer. Lack of proper drainage ahead of a steam control valve can result in water hammer. When the valve is opened, a slug of condensate enters the equipment at high velocity impinging on the interior walls, causing hammer. Improper operation or incorporation of surge protection devices can do more harm than good. An example is over sizing the surge relief valve or improperly selecting the vacuum breaker—air release valve.

Mixing of steam with relatively cool water in a pipe or confined space also results in water hammer. If not controlled, the transients in pressures cause damage to pipes, fittings, valves, and steam traps, causing leaks and shortening the life of the system. Liquid for all practical purposes is not compressible and any energy that is applied to it is instantly transmitted. Neither the pipe walls nor the liquid will absorb the created shocks. Such transients can also lead to blown diaphragms, destruction of seals, gaskets, meters, gauges, and steam trap bodies, heat exchanger tube failures, and injuries to personnel.

2.13 Cavitation

Cavitation occurs in liquid when bubbles form and implode in pump or flow systems or around impeller of a pump. Pumps put liquid under pressure; but if the pressure of the liquid drops or its temperature increases, it begins to vaporize, just as boiling water. The bubbles that form inside the liquid are vapor bubbles, gas bubbles, or a mixture of both. Vapor bubbles are formed due to the vaporization of the liquid being pumped, at a point inside the pump where the local static pressure is less than the vapor pressure of the liquid. A cavitation condition induced by formation and collapse of vapor bubbles is commonly referred to as vapor cavitation. Gas bubbles, by contrast, are formed due to the presence of dissolved gases in the liquid that is being pumped. In many situations, the gas dissolved is air.

Vapor cavitation bubbles get carried in the liquid as it flows from the impeller eye to the impeller tip, along the trailing edge of the blade. Due to the rotation of the impeller, the bubbles first attain very high velocity, then reach the regions of higher pressure. The pressure around the bubbles begins to increase until they collapse.

This process is an implosion (inward bursting). Hundreds of bubbles implode at approximately the same point on each impeller blade. The bubbles collapse in such a way that the surrounding liquid rushes to fill the void, forming a liquid microjet. The microjet subsequently ruptures the bubbles with such a force that a hammering action occurs.

After bubbles collapse, a choke wave emanates outward from the point of collapse. This choke wave is what is actually heard and called cavitation. The collapse of the bubbles also ejects destructive microjets of extremely high velocity, up to 100 m/s, causing abnormal sounds, vibrations, and extreme erosion of a pump parts, pitting, and denting in the metal of the casing and the impeller blades. It has been estimated that during collapse of bubbles pressures of the order of 10^4 bar develops. Apart from erosion of pump parts, cavitation can also result in imbalance of radial and axial thrusts on the impeller, due to lack of symmetry in the bubble formation and collapse.

In many cases, cavitation also leads to corrosion. The implosion of bubbles destroys protective layers on the metal surface, making the metal permanently activated for the chemical attack. Gas bubble cavitation that amounts to two phase pumping occurs when any gas (most commonly air) enters a centrifugal pump along with liquid. Unlike vapor cavitation, gas bubbles seldom cause damage to the impeller or casing. Instead, their main effects are surge and choke phenomena that cause deterioration of pump head and capacity. Separation of the gas phase from the liquid phase, accompanied by a tendency of the gas to coalesce in large pockets at the impeller blade entry, results in a sonic choke effect. The pump performance decreases continuously as the gas volume increases, until at a certain critical gas content the pump stops delivering liquid. Cavitation occurs not only in centrifugal pumps but also in orifices, valves, and similar equipment involving flow restrictions.

2.14 NPSH

When the absolute suction pressure is low, then it may result in cavitation. In order to avoid this, it is necessary to maintain a net positive suction head, NPSH, which is the total head of the liquid at the pump center line minus vapor pressure of the liquid at the prevailing temperature, expressed in equivalent of head units. Sometimes, NPSH is written as NPIP, which means net positive inlet pressure. This terminology is used for positive displacement pumps for which the inlet conditions are traditionally defined in pressure terms rather than the head terms. NPIP is inlet pressure minus fluid vapor pressure.

2.15 Two-Phase Flow

Bubble flow, slug flow, churn flow, annular flow, and mist flow. The flow regime depends on the interaction of two forces, namely, gravity and vapor shear, acting in different directions. At low vapor flow rates, gravity dominates, giving rise to stratified, slug-plug, or bubble flow, depending on the relative amounts of liquid present. At high vapor velocities, vapor shear dominates, giving rise to wavy, annular, or annular mist flow.

Bubble flow: When vapor/gas bubbles, distributed in the liquid, move along at about the same velocity as the liquid, the flow is described as bubble flow. Bubble flow describes the flow of distinct, roughly spherical vapor regions surrounded by continuous liquid. Generally, the diameter of the bubbles is considerably smaller than that of the container through which they flow.

Slug flow: Slugs of gas bubbles flow through the liquid. If the vapor and liquid are flowing through a pipe, bubbles may coalesce into long vapor regions that have almost the same diameter as the pipe. This is called slug flow. Slug flow develops when high waves of liquid develop with progressive increase of gas or vapor content in wavy flow.

Churn flow: At moderate to high flow velocities and roughly equal proportions of vapor and liquid, the flow pattern is often very irregular and chaotic. If the flow contains no distinct entities with spherical or, in a pipe, cylindrical symmetry, it is called churn flow. Churn flows, sometimes called froth flows, are characterized by strong intermittency and intense mixing, with neither phase easily described as continuous or dispersed.

Annular and droplet flow: When liquid forms a film or ring around the inside wall of the pipe and gas flows at higher velocity as a central core, the flow is called annular flow.

Droplet flow: In annular droplet flow, liquid, besides forming annular film along the walls of the conduit, may get entrained as small roughly spherical droplets in the vapor or gas stream. In droplet flow, only entrained droplets flow with the absence of liquid film. If the droplet sizes are very small, they can be treated as mists. These flows are possible at high velocity vapor or gas flows. In annular droplet flow, liquid, besides forming annular film along the walls of the conduit, may get entrained as small roughly spherical droplets in the vapor or gas stream. In droplet flow, only entrained droplets flow with the absence of liquid film. If the droplet sizes are very small, they can be treated as mists. These flows are possible at high velocity vapor or gas flows.

Spray/dispersed/mist flow: Gas and liquid flow in dispersed form. All the liquid is carried as fine droplets in the gas phase. In such flows, gas velocities involved are high, of the order of 20–30 m/s. Figure 2.2 illustrates patterns of two phase flow in vertical pipes.

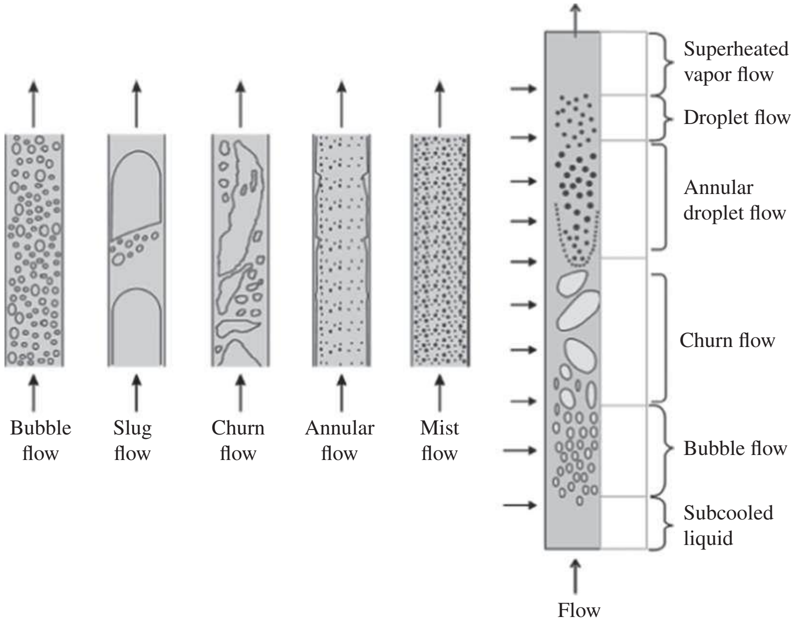


Figure 2.2 Two-phase flows in vertical pipes

2.16 Compressible Fluids

Maximum velocity attainable for a fluid in a pipe is critical/sonic velocity in the fluid. Maximum velocity in a pipe is limited by the velocity of propagation of a pressure wave that travels at the speed of sound in the fluid. Shock waves travel at supersonic velocities and exhibit a near discontinuity in pressure, density, and temperature. Normally, velocities are limited to 30 percent of sonic velocity.

Sonic velocity in an ideal gas is $c = (kRT/M_W)$ (2.7)

where c is the sonic velocity or speed of sound or acoustic velocity, k is the ratio of specific heats (Cp/Cv), Mw is the molecular weight, and T is the absolute temperature.

Mach number: Mach number is defined as the speed of an object relative to a fluid medium, divided by the speed of sound in that medium. It is the number of times the speed of sound an object or a duct, or the fluid medium itself, moves relative to the other.

Mach number is commonly used both with objects traveling at high speed in a fluid and with high-speed fluid flows inside channels such as nozzles, diffusers, or wind tunnels. At a temperature of 15°C and at sea level, Mach 1 is 340.3 m/s (1,225 km/h or 761.2 mph) in the earth's atmosphere. The speed represented by Mach 1 is not a constant but temperature dependent. Since the speed of sound increases as the temperature increases, the actual speed of an object traveling at Mach 1 will depend on the fluid temperature around it.

Mach number is useful because the fluid behaves in a similar way at the same Mach number. For example, an aircraft traveling at Mach 1 at sea level (340.3 m/s and 1225.08 km/h) will experience shock waves in much the same manner as when it is traveling at Mach 1 at 11,000 m (36,000 ft), even though it is traveling at 295 m/s (654.632 mph, 1062 km/h, and 86 percent of its speed at sea level). It can be shown that Mach number is also the ratio of inertial forces (also referred to as aerodynamic forces) to elastic forces.

High-speed flows can be classified as follows:

(i) Subsonic: $M < 1$
(ii) Sonic: $M = 1$, transonic, $0.8 < M < 1.2$, and supersonic: $1.2 < M < 5$
(iii) Hypersonic: $M > 5$

At transonic speeds, the flow field around the object includes both subsonic and supersonic components. The transonic regime begins when first zones of $M > 1$ flow appear around the object. In case of an airfoil (such as the wing of an aircraft), this is typically above the wing. Supersonic flow can decelerate back to subsonic only in a normal shock, which typically happens before the trailing edge. As the velocity increases, the zone of $M > 1$ flow increases toward both leading and trailing edges. As $M = 1$ is reached and passed, the normal shock reaches the trailing edge and becomes a weak oblique shock, the flow decelerating over the shock but remaining supersonic. A normal shock is created ahead of the object and only subsonic zone in the flow field is a small area around the leading edge of the object. Compressibility factor quantifies the departure from ideal conditions for a gas. An ideal gas obeys the following equation

$$PV = nRT \tag{2.8}$$

For a nonideal gas,

$$PV = ZnRT \text{ or } Z = PV/nRT \tag{2.9}$$

For example, a gas for which $Z = 0.90$ will occupy only 90 percent of the volume occupied by an ideal gas at the same temperature and pressure. The values of Z range from about 0.2 to a little over 1.0 for pressures and temperatures of up to 10 times the critical values. Z is a complex function of reduced temperature (T_r) and reduced pressure(P_r).

2.17 Dielectric Properties

The study of dielectric properties concerns the storage and dissipation of electric and magnetic energy in materials. It is important to explain various phenomena in electronics, optics, and solid-state physics.

Dielectric constant is the property of an electrical insulating material (a dielectric) equal to filled with the given material to the capacitance of an identical capacitor in a vacuum without the dielectric material. The insertion of a dielectric between the plates of, say, a parallel-plate capacitor always increases its capacitance, or ability to store opposite charges on each plate, compared with this ability when the plates are separated by a vacuum. If C is the value of the capacitance of a capacitor filled with a given dielectric and C_0 is the capacitance of an identical capacitor in a vacuum, the *dielectric constant* is simply expressed as kappa = C/C_0. Dielectric constant is a number without dimensions. It denotes a large-scale property of dielectrics without specifying the electrical behavior on the atomic scale.

The dielectric constant is an essential piece of information when designing capacitors, and in other circumstances where a material might be expected to introduce capacitance into a circuit. If a material with a high dielectric constant is placed in an electric field, the magnitude of that field will be measurably reduced within the volume of the dielectric. This fact is commonly used to increase the capacitance of a particular capacitor design. The layers beneath etched conductors in printed circuit boards (PCBs) also act as dielectrics.

The relative static permittivity of a solvent is a relative measure of its polarity. For example, water (very polar) has a dielectric constant of 80.10 at 20°C while n-hexane (very nonpolar) has a dielectric constant of 1.89 at 20°C. This information is of great value when designing separation, sample preparation, and chromatography techniques in analytical chemistry.

Before getting into understanding about dielectric constant, it is a must to understand about what is a dielectric. An insulating material that does not have the ability to conduct electricity is termed as dielectric. Such a material is transparent to an electromagnetic field. In short, a dielectric is a material that does not conduct electricity properly. A typical example of a dielectric material is dry air. If one places a dielectric material in an electric field, no current flows through it. As a result, there is electric polarization.

Dielectric constant compares permittivity of a substance to that of vacuum. Permittivity is basically a measure of how much a material is polarized by electric field. In dielectric constant measure, this permittivity is expressed in ratio form. The constant shows the extents to which a material can concentrate electric flux. In short, the dielectric constant, k, of a material is basically a ratio of the materials permittivity versus the permittivity of vacuum. It is thus, an indication of the relative permittivity of a material. The dielectric constant of vacuum is 1.0 and that of other materials will always be more than 1.0. For air, the dielectric constant value at room temperature is 1.00059. In case of water, it is 78.2 for water; and for barium titanate, it is 2,000.

Not every material has the same level of dielectric constant. Different materials have different dielectric constant levels and their usage is defined accordingly. If a material has a high dielectric constant, it indicates that it can hold an electric charge for a long time. A high dielectric constant in a material shows that material has a high electric flux density. Such materials are recommended for use in high-value capacitors. They are also used in memory cells wherein data is stored in the form of an electric charge.

Materials that have low dielectric constants have low permittivity, and hence they cannot hold electric charge for long. This makes them good insulators, and they are used in the manufacture of multi-layered integrated circuits. Examples of materials with low dielectric constants are dry air and dry gases such a helium and nitrogen. Materials with medium dielectric constants are distilled water, glass, paper, mica, and ceramics.

Dielectric constant, measures the extent that a material concentrates electrostatic flux. It is also known as the relative static permittivity, static dielectric constant, and relative dielectric constant of a material, and is essential when determining if a substance is suitable to use in a capacitor as well as in various chemistry and physics applications.

The generation of static charge is influenced by the dielectric properties of the material, that is, the insulating properties, which will accumulate the more charge. Good conductors such as metals tend to dissipate the charge immediately. Poor conductors or good insulators (paper, plastics, and synthetic fabrics) will hold the charge for long periods.

2.18 Surface Tension

Surface tension is a property of the surface of a liquid that allows it to resist an external force. It is revealed, for example, in floating of some objects on the surface of water, even though they are denser than water. This property is caused by cohesion of like molecules, and is responsible for many of the behaviors of liquids.

The same intermolecular forces that determine viscosity create surface tension. Surface tension is a measure of the internal forces generated by molecules due to their position in the surface of a liquid or the interface between two liquids. Surface tension forms what appears to be a membrane on the free surface of a liquid that allows insects to rest.

Surface tension has the dimension of force per unit length, or of energy per unit area. The two are equivalent—but when referring to energy per unit of area, people use the term surface energy, which is a more general term in the sense that it applies also to solids and not just liquids. Liquid droplets tend to form a spherical shape since this shape produces the least amount of surface area for a given volume.

Since viscosity and surface tension are closely related, surface tension determines the size of liquid droplets in the same manner as viscosity. As surface tension increases, so does droplet size. For example, mercury at room temperature tends to form larger droplets than water and oil do because mercury has a higher surface tension. Surface tension corresponds to the efficiency of inertial impaction for particulate matter. Particles can more easily penetrate liquid droplets with lower surface tensions than ones with higher surface tensions.

Therefore, impaction is inversely proportional to surface tension. As surface tension influences droplet formation, efficiency of fogging of liquids such as spraying of pesticides, deodorants, and disinfectants is related to surface tension. Fogging should not be applied to flammable liquids due to the risks of fire and explosion. It should be noted that small droplets travel longer distances affecting larger areas and living beings like animals and people in these areas. Proper protective equipment such as safety goggles, gloves, protective clothing, and other appropriate measures should be adopted.

2.19 Vapor Pressure

Vapor pressure is an important property, and when high it can make liquids evaporate causing vapor build up in the open quickly. Vapor pressure of a chemical provides an indication of its volatility at any specific temperature. *Vapor pressure* is important for people concerned with shipping, storing, and disposal. Liquids that evaporate easily are worrisome because vapor can build up around quickly. It is a particularly major problem in confined spaces. It increases steeply with increased temperatures, as illustrated in Figure 2.3.

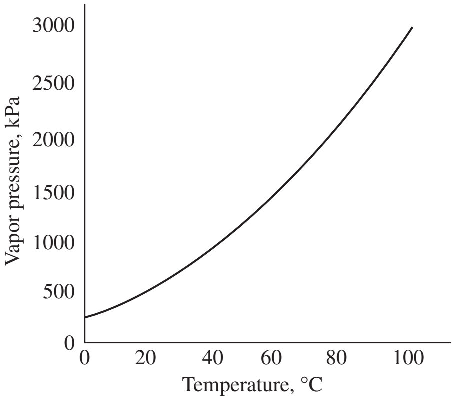


Figure 2.3 Vapor pressure as a function of temperature

Reliable methods for estimating the vapor pressures of organic materials are of increasing importance as a tool in predicting the behavior and fate of chemicals that are introduced into the environment. When a chemical such as a CFC or HFC has been spilled, for example, one must know its approximate vapor pressure in order to estimate its rate of evaporation. This is also important in situations involving leaks, oil spills from tankers, evaporation losses from storage tanks, formation and spread of vapor clouds, and the like.

Vapor pressure or equilibrium vapor pressure is the pressure of a vapor in thermodynamic equilibrium with its condensed phases in a closed system. All liquids have a tendency to evaporate, and some solids can sublime into a gaseous form. Vice versa, all gases have a tendency to condense back to their liquid form, or deposit back to solid form. The equilibrium vapor pressure is an indication of the evaporation rate of a liquid. It relates to the tendency of particles to escape from the liquid (or a solid). A substance with a high vapor pressure at normal temperatures is often referred to as *volatile*.

Numerous equations and correlations for estimation of vapor pressure are presented in the literature. In general, they require information on at least three of the following properties, namely the critical temperature, T_c, the critical pressure, P_c, the heat of vaporization, ΔH_v and/or (4) the vapor pressure (P°) at some reference temperature.

The vapor pressure of any substance increases non-linearly with temperature. The normal boiling point of a liquid is the temperature at which the vapor pressure equals the ambient atmospheric pressure. With any incremental increase in that temperature, the vapor pressure becomes sufficient to overcome atmospheric pressure and lift the liquid to form vapor bubbles inside the bulk of the substance. Bubble formation deeper in the liquid requires a higher pressure, and therefore higher temperature, because the fluid pressure increases above the atmospheric pressure as the depth increases.

The vapor pressure that a single component in a mixture contributes to the total pressure in the system is called partial vapor pressure. For example, air at sea level, saturated with water vapor at 20°C has a partial pressures of 24 mbar of water, and about 780 mbar of nitrogen, 210 mbar of oxygen, and 9 mbar of argon.

The major estimating methods for vapor pressures are Riedel, Riedel–Planck–Miller, Gomez–Thodos, and Lee–Kessler.

2.20 Partial Pressure

In a mixture of ideal gases, each gas has a *partial pressure* that is the pressure which the gas would have if it alone occupied the volume. The total pressure of a gas mixture is the sum of the partial pressures of each individual gas in the mixture. The partial pressure of a gas dissolved in a liquid is the partial pressure of that gas which would be generated in a gas phase in equilibrium with the liquid at the same temperature. The partial pressure of a gas is a measure of thermodynamic activity of molecules of the gas. Gases will always flow from a region of higher partial pressure to one of lower pressure; the larger this difference, the faster the flow. Gases dissolve, diffuse, and react according to their partial pressures, and not necessarily according to their concentrations in a gas mixture.

2.21 PVT Relationships

Ideal gas law: $$PV = nRT \tag{2.10}$$

Real gas law: $$PV = znRT \tag{2.11}$$

where P is pressure, V is volume, n is number of moles, R is gas constant, and z is non ideality factor. Antoine equation. What for it is used?

$$\text{Ln } P^\circ = A - B/(T + C) \tag{2.12}$$

$$\text{Log}_{10} P^\circ = A - B/(T + C) \tag{2.13}$$

P = vapor pressure, bar
T = absolute temperature, K
A, B, and C are Antoine constants

Antoine equation is an empirical equation used for representing vapor pressure data generated from experimentation. While using Antoine equation, one should keep in mind that the equation is dimensional, not dimensionless. The constants A, B, and C apply when a specific set of units is used for temperature and vapor pressure and when a specific logarithm function, common log, or natural log, is used. Therefore, care should be exercised in using tabulated values from different sources, temperature range for which the values of the constants are applicable. Most references include this information with the tabulated constants and warn against extrapolation beyond the specified range.

The applicable temperature range is not large and in most cases corresponds to a pressure interval of about 0.01–2 bar. This typically represents an upper temperature limit slightly above the normal boiling point and a lower limit approximately 50–150°C below the upper limit.

Antoine equation should never be used outside the stated limits. There are several methods for prediction of vapor pressures using critical properties and a review and recommendations are given in the book, *Poling, Reid, and Sherwood, Properties of Gases and Liquids*. Lee–Kessler, Redlich–Kwong, and Peng–Robinson equations are examples.

2.22 Raoult's Law

Raoult's law states that system pressure multiplied by vapor composition is equal to vapor pressure of the species multiplied by liquid composition and is represented by the equation,

$$Py_i = P_i x_i, \tag{2.14}$$

where P is the system pressure, P_i is the vapor pressure of the species and y_i and x_i are the equilibrium compositions in mole fractions of the species in liquid and vapor phases respectively. Py_i is the partial pressure of the species. Assumptions involved are that the vapor phase behaves as an ideal gas (low pressures) and liquid phase is an ideal solution (components are chemically similar).

Raoult's law gives an approximation to the vapor pressure of mixtures of liquids. It states that the activity (pressure or fugacity) of a single-phase mixture is equal to the mole fraction-weighted sum of the vapor pressures of the components:

$$P_{\text{total}} = \Sigma P^\circ_i x_i \tag{2.15}$$

where P° is vapor pressure, i is a component index, and x is mole fraction of that component in liquid mixture. The term $P_i x_i$ is the *partial pressure* of component I in the mixture. Raoult's law is applicable only to nonelectrolytes (uncharged species); it is most appropriate for nonpolar molecules with only weak intermolecular attractions (such as London forces). Systems that have vapor pressures higher than indicated by the above formula are said to have positive deviations. Such a deviation suggests weaker intermolecular attraction than in the pure components, so that the molecules can be thought of as *being held* in the liquid phase less strongly than in the pure liquid. An example is the azeotrope of approximately 95 percent ethanol and water. Because the azeotrope's vapor pressure is higher than predicted by Raoult's law, it boils at a temperature below that of either pure component.

There are also systems with negative deviations that have vapor pressures that are lower than expected. Such a deviation is evidence for stronger intermolecular attraction between the constituents of the mixture than exists in the pure components. Thus, the molecules are *held in* the liquid more strongly when a second molecule is present. An example is a mixture of trichloromethane (chloroform) and 2-propanone (acetone), which boils above the boiling point of either pure component.

When vapor phase is considered ideal but liquid phase cannot be considered ideal, nonideality of the liquid phase is described by the activity coefficient for the species and Raoult's law is modified as below:

$$Py_i = P^\circ_i \, \gamma_i x_i \tag{2.16}$$

Activity coefficients, $\gamma_{i,}$ are obtained from experimental data, available for a large number of binary systems, or by activity coefficient correlations like those of Wilson, NRTL, UNIQUAC, and UNIFAC equations.

2.23 *K*-Values

K is defined as the ratio of vapor phase composition to the liquid phase composition. $K_i = y_i/x_i$ and shows the volatility of an individual component, that is, the composition in the vapor phase relative to the composition in the liquid phase. It indicates the ease with which a component in a mixture undergoes phase change from liquid to vapor phase.

For the more volatile components in a mixture the *K*-values are greater than 1.0, whereas for the less volatile components they are less than 1.0. In general *K*-values for all components in a mixture are function of the pressure, temperature and composition of the vapor and liquid phases present. For light hydrocarbons, the equilibrium ratio for any one component increases at higher temperatures and decreases at higher pressures. In addition, the value of *K* is altered by the other components present in the system, as well as the concentration of the specified component in the liquid phase.

The value of the equilibrium ratio usually decreases as the molecular weight increases for a homologous series of compounds. This is because the vapor pressure at any fixed temperature decreases as molecular weight increases. However, the variation of α with temperature is less than the variation of *K* with temperature, which adds to the convenience of calculative methods using the relative volatility. The components making up the system plus temperature, pressure, composition, and degree of polarity affect the accuracy and applicability, and hence the selection of method for estimating *K*-values. For many systems, for example, light hydrocarbons, *K* is a function of temperature and pressure and independent of composition. *K*-values for such systems, can be determined from De Priester charts. In these charts, *K*-values for individual components are plotted on the ordinate as a function of temperature on the abscissa with pressure as a parameter. In each chart the pressure range is from 70 to 7,000 kPa and the temperature range is from 4 to 250ºC.

It has been observed that if a hydrocarbon system of fixed overall composition was held at constant temperature and the pressure is increased, the *K*-values of all components converged toward a common value of unity (1.0) at some high pressure.

This pressure is termed c*onvergence pressure* of the system and is used to correlate the effect of composition on *K*-values. Plotting this way permits generalized *K*-values to be presented in a moderate number of charts.

In some publications, *K*-values are plotted as a function of pressure on the abscissa with *convergence pressure* and temperature as parameters. In order to use these charts, convergence pressure should be determined first which involves a trial and error procedure. Equations of state such as BWR, Soave–Redlich–Kwong and Peng–Robinson are used for estimating fugacity coefficients, Φ.

Several nomographs are available in literature for finding *K*-values. Notable examples are those developed by De Priester, Hayden–Grayson, and Lenoir and their extensions.

These methods involve trial and error calculations. If vapor phase is assumed to be ideal (as is the case for low pressures), the above equation reduces to

$$K_i = P_i^{sat}\gamma_i/P \tag{2.17}$$

γ_i is liquid phase activity coefficient which takes into consideration liquid phase non-ideality. If both phases are ideal, this equation reduces to Raoult's law.

For a two component system, relative volatility compares the volatility of one component to the other. It is defined as follows:

$$\alpha = K_1/K_2 = y/x/(1-y)/(1-x) = y(1-x)/x(1-y) \tag{2.18}$$

A relative volatility of 1.0 indicates that both components are equally volatile and no separation takes place.

"Relative volatility, α, is defined as $\alpha = K_i/K_j$".

For ideal systems, that is, systems obeying Raoult's law,

$$\alpha_{ij} = P^\circ_i/P^\circ_j \tag{2.19}$$

For systems with liquid phase being nonideal,

$$K_i = \mathrm{P}^\circ_i\gamma_i/\mathrm{P} \tag{2.20}$$

For near-ideal systems, α can be estimated from a knowledge of boiling points and enthalpies of vaporization using the following empirical equation:

$$\alpha = \exp[0.25164(1/T_{b1} - 1/T_{b2})(\lambda_1 - \lambda_2)] \quad \text{(Wagle)} \tag{2.21}$$

where T_{b1} and T_{b2}, λ_1 and λ_2 are boiling points and enthalpies of vaporization of the components 1 and 2, respectively.

Negative and positive deviations from Raoult's law: If the volatilities of all components are increased, the deviation from idealism is considered positive. If the volatilities of all components are reduced, the deviation from idealism is considered negative:

$$\text{Positive deviations: } \log\gamma > 0\ (\gamma > 1) \tag{2.22a}$$

$$\text{Negative deviations: } \log\gamma < 0\ (\gamma < 1) \tag{2.22b}$$

2.24 Henry's Law

For species present as a very dilute solute in the liquid phase, Henry' law states that the partial pressure of the species in the vapor phase is directly proportional to its liquid-phase mole fraction and is given by the following equation:

$$y_i P = x_i H \tag{2.23}$$

where y_i is mole fraction of component i in vapor phase, x_i is mole fraction in the liquid phase, P is total pressure, H_i is Henry's law constant

At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid. An equivalent way of stating the law is that the solubility of a gas in a liquid at a particular temperature is proportional to the pressure of that gas above the liquid. Henry's law has since been shown to apply for a wide range of dilute solutions, not merely those of gases.

2.25 Heat and Thermodynamics

Enthalpy

Energy cannot be created or destroyed but is converted from one form to another. Thermodynamics involves study of energy transfer during reactions and on the work done by chemical systems. It defines the energy required to start a reaction or the energy given out during the process. During chemical reactions energy may be absorbed or liberated.

Heat Capacity

When heat is transferred to an object, the temperature of the object increases. When heat is removed from an object, the temperature of the object decreases. The relationship between the heat (q) that is transferred and the change in temperature (ΔT) is

$$q = C\Delta T = C\,(T_f - T_i) \tag{2.24}$$

The proportionality constant in this equation is called the heat capacity (C). The heat capacity is the amount of heat required to raise the temperature of an object or substance by one degree. The temperature change is the difference between the final temperature (T_f) and the initial temperature (T_i). In the International System of Units (SI), heat capacity is expressed in units of Joules per Kelvin. Derived quantities that specify heat capacity as an intensive property, independent of the size of a sample, are the molar heat capacity, which is the heat capacity per mole of a pure substance, and the specific heat capacity, often simply called specific heat, which is the heat capacity per unit mass of a material.

Enthalpy of Formation

The *standard enthalpy of formation or standard heat of formation* of a compound is the change of enthalpy that accompanies the formation of one mole of a substance in its standard state from its constituent elements in *their* standard states (the most stable form of the element at one bar of pressure and the specified temperature, usually 298.15 K or 25°C). Its symbol is

$$\Delta H_\mathrm{f} \text{ or } \Delta_\mathrm{f} H \tag{2.25}$$

For example, the standard enthalpy of formation of carbon dioxide would be the enthalpy of the following reaction under the conditions above:

$$\mathrm{C\ (s,\ graphite)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \tag{2.26}$$

The standard enthalpy of formation is measured in units of energy per unit amount of substance. Most are defined in kilojoules per mole (kJ mol^{-1}), but can also be measured in calories per mole, joules per mole or kilocalories per gram (any combination of these units conforming to the energy per mass or amount guideline). In physics, the energy per particle is often expressed in electron volts that corresponds to about 100 kJ mol^{-1}.

All elements in their standard states (oxygen gas, solid carbon in the form of graphite, etc.) have a standard enthalpy of formation of zero, as there is no change involved in their formation.

Enthalpy Change of Solution

The enthalpy of solution, enthalpy of dissolution, or heat of solution is the enthalpy change associated with the dissolution of a substance in a solvent at constant pressure, resulting in infinite dilution. The enthalpy of solution is one of the three dimensions of solubility analysis. It is most often expressed in kJ/mol at constant temperature. Just as the energy of forming a chemical bond is the difference between electron affinity and ionization energy, the heat of solution of a substance is defined as the sum of the energy absorbed, or endothermic energy, expressed in positive values and unit kJ/mol, and energy released, or exothermic energy (negative value).

Because heating decreases the solubility of a gas, dissolution of gases is exothermic. Consequently, as a gas continues to dissolve in a liquid solvent, temperature will decrease, while the solution continues to release energy. This is an effect of the increase in heat or of the energy required to attract solute and solvent molecules. In other words, this energy outweighs the energy required to separate solvent molecules. When the gas is completely dissolved (this is purely theoretical as no substance can infinitely dissolve), the heat of solution will be at its maximum. Dissolution can be viewed as occurring in three steps: Breaking solute–solute attractions (endothermic), see for instance lattice energy in salts. Breaking solvent–solvent attractions (endothermic), for instance that of hydrogen bonding. Forming solvent–solute attractions (exothermic), in solvation.

The value of the overall enthalpy change is the sum of the individual enthalpy changes of each of these steps. For example, dissolving ammonium nitrate in water decreases the temperature of the solution. Solvation does not compensate energy spent in breaking down the crystal lattice, while adding potassium hydroxide will increase it.

Solutions with negative enthalpy changes of solution form stronger bonds and have lower vapor pressure. The enthalpy of solution of an ideal solution is zero since the attractive and repulsive properties of ideal fluids are equal, irrespective of the compounds, thus mixing them does not change the interactions.

Enthalpy Change on Mixing

Mixing of different chemicals with different molecular structures can result in temperature changes, that is, increase when the process is exothermic and decrease when the process is endothermic in nature. Such changes can result in increase or decrease in volume. Leakages and spillages from equipment and, sometimes, explosions can result. A well known example is mixing of water and sulfuric acid. The sequence of adding water to concentrated acid results in spurting and spilling, giving rise to safety hazards. It is safer to add acid to water in any batch operation. The heat of mixing involved in acids and water are considerably large, with consequent hazards involved in such operations.

Joule–Thomson Effect

Joule–Thomson effect or Joule–Kelvin effect or Kelvin–Joule effect describes the temperature change of a gas or liquid when it is forced through a valve or porous plug while kept insulated so that no heat is exchanged with the environment.

The rate of change of temperature T, with respect to pressure P, in a Joule–Thomson process (i.e. at constant enthalpy H) is the Joule–Thomson (Kelvin) coefficient. This coefficient can be expressed in terms of the volume V of the gas, its heat capacity at constant pressure, C_p, and its coefficient of thermal expansion, α.

All real gases have an *inversion point* at which the value of Joule–Thomson coefficient changes sign. The temperature of this point, the *Joule–Thomson inversion temperature*, depends on the pressure of the gas before expansion. In a gas expansion the pressure decreases.

Helium and hydrogen are two gases whose Joule–Thomson inversion temperatures at a pressure of one atmosphere are very low (e.g. about 51 K (−222°C) for helium). Thus, *helium and hydrogen warm up when expanded at constant enthalpy* at typical room temperatures. On the other hand nitrogen and oxygen, the two most abundant gases in air, have inversion temperatures of 621 K (348°C) and 764 K (491°C), respectively: these gases can be cooled from room temperature by the Joule–Thomson effect. For an ideal gas, Joule–Thomson coefficient is always equal to zero. Ideal gases neither warm nor cool upon being expanded at constant enthalpy.

In practice, the Joule–Thomson effect is achieved by allowing the gas to expand through a throttling device, usually a valve, which must be very well insulated to prevent any heat transfer to or from the gas. No external work is extracted from the gas during the expansion. The effect is applied in the Linde technique as a standard process in the petrochemical industry, where the cooling effect is used to liquefy gases, and also in many cryogenic applications (e.g. for the production of liquid oxygen, nitrogen, and argon). Only when the Joule–Thomson coefficient for the given gas at the given temperature is greater than zero can the gas be liquefied at that temperature by the Linde cycle. In other words, a gas must be below its inversion temperature to be liquefied by the Linde cycle. For this reason, simple Linde cycle liquefiers cannot normally be used to liquefy helium, hydrogen, or neon. With respect to safety, it must be recognized that gases such as hydrogen warm up on liquefaction, and can involve in fire hazards, especially with the added effect of minimum ignition energy requirements for hydrogen, unless steps are taken to cool it externally to compensate this warming effect.

Phase Change

Heat of vaporization: Heat of vaporization is an important property, while considering safety involving change of phase from liquid to vapor and vice versa. Vaporization leads to cooling and, for example, subsequent dousing of fires with water sprays cools and finally puts off fires. Spills and leakages of hot liquids involve taking heat of vaporization from the environment and slowing down vapor cloud formation. Such cooling can also lead to brittle fracture of materials of construction.

High pressure and refrigerated liquids such as LPG, LNG, or low boiling liquids such as ammonia, on leakage/spillage, can give rise to sizable vapor clouds. Flammable and toxic atmospheres form when vaporization of liquids, particularly in confined spaces, is involved. Vaporization in confined spaces can lead to pressure build-up and explosions.

Sudden cooling of storage tanks containing vapors can result in condensation, followed by generation of vacuum inside the tanks, leading to collapse of the tanks when vents are blocked or inadequate. Cooling of vapor in vented vessels can be a cause for air ingress and formation of explosive mixtures with the vessel contents. Contact of water or volatile liquids with molten metals, molten salts or hot oils can result in physical explosions. Estimation of heat of vaporization as a function of temperature is of importance in vaporization/condensation processes. Clapeyron equation relates vapor pressure to heat of vaporization.

Flashing of vapors: If a liquid near its boiling point at one pressure is *let down* to a reduced pressure, flashing to a vapor will occur. This will cease when the liquid temperature is reduced, due to removal of the latent heat of vaporization, to a temperature below the saturation temperature at the new pressure. As a result, flashing

As a result: Flashing of vapor containing entrained mist may occur on venting equipment or vessels containing volatile liquids. This may create a toxic or flammable hazard depending on the nature of the material. Rupture of equipment can produce a similar effect.

Escapes or spillages of liquefied petroleum gas, or chlorine or ammonia, rapidly generate a vapor cloud. Loss of containment, for example, due to a crack or open valve, from beneath the liquid level in a liquefied gas vessel is potentially more serious than if it occurs from the gas space because the mass flow rate is greater.

Absorption of heat and consequent temperature reduction on flashing may have a serious effect on associated heat transfer media, upon the strength of materials of construction, and result in frosting at the point of leakage. Exposure of personnel carries a risk of frostbite.

Freezing, Expansion/Contraction, Blockages, and Melting

Freezing of water in pipelines exposed to winter months with temperatures going down to sub zero values can lead to bursting of the pipelines.

Hazardous situations can develop from thermal expansion and contraction of solids. For a given material the extent of linear expansion or contraction in one direction is directly related to temperature and its original size, that is length, diameter, and circumference.

$$\text{Change in length} = \alpha \, L \, \Delta T \qquad (2.27)$$

where α is coefficient of linear expansion, ΔT is temperature difference, and L is length.

Unacceptable stress conditions may develop in rigid constructions in piping and equipment due to large fluctuations in temperatures to which these are subjected. These stress conditions can lead to leakages, weakening of structures, and failures. An example is the thermal shock and breakage of ordinary glass.

Liquids can also expand or contract due to temperature changes. Serious accidents can result from such expansions and contractions unless design takes care of such situations involving solids or liquids. Application of measures to prevent failures include use of expansion joints, expansion bellows, expansion loops, decrease in pipe wall thickness, supports, guides, anchors, relief valves, and the like.

Melting of solids in sealed containers can exert significantly high internal pressures. Exposure of viscous liquid pipelines to low temperatures can lead to increased viscosities, blockages, and subsequent failure and leakages. Viscosity of lubricants can increase, increasing friction and seizure of moving parts of machinery.

2.26 Heat-Transfer Basics

Conduction

Thermal energy is transported within a solid by lattice vibrations inside the material. The transport of energy is hindered by the presence of imperfections or by any kind of scattering sites. If there is macroscopic transport of matter (e.g. fluid flow) inside the body, the mass flow makes an additional contribution to the transport of energy (convective heat transfer). This contribution is disregarded when studying conduction heat transfer. In gases and liquids, conduction is due to collisions and diffusion of the molecules during their random motion. In solids, conduction is due to a combination of vibrations of molecules in a lattice and energy transport is by free electrons. Rate equation for conduction is described by Fourier law:

$$q = -kA\Delta T \tag{2.28}$$

where q = heat transfer rate, W
k = thermal conductivity, a thermodynamic property of the material, (W/mK)
A = cross-sectional area in the direction of heat flow, m^2
ΔT = gradient of temperature gradient, k/m

k is proportionality constant, designated as thermal conductivity, which is a measure of ability of the material to conduct heat. It is one of the transport properties, such as viscosity. According to Fourier's law, k is independent of temperature gradient, ΔT. It is dependent on temperature, but not strongly. For small temperature ranges, k might be considered independent of T. For large temperature ranges, k may be approximated as a function of temperature by the equation of the form

$$k = a + bT \tag{2.29}$$

where a and b are constants.

The negative sign on the right-hand side signifies that conduction is in the direction of decreasing temperature. It indicates that thermal energy flows from hot regions to cold regions.

***Thermal conductivity*:** Thermal conductivity is a thermodynamic property of a material. Thermodynamic properties of pure substances are functions of two independent thermodynamic intensive properties: temperature and pressure. Thermal conductivity of real gases is largely independent of pressure and may be considered a function of temperature alone. For solids and liquids, properties are largely independent of pressure and depend on temperature alone.

$$k = k(T) \tag{2.30}$$

Molecules/atoms of various materials gain energy through different mechanisms. Gases, in which molecules are free to move with a mean free path sufficiently large compared to their diameters, possess energy in the form of kinetic energy of the molecules. Energy is gained or lost through collisions/interactions of gas molecules.

Solids, on the other hand, have atoms/molecules which are more closely packed which cannot move as freely as in gases. Hence, they cannot effectively transfer energy through these same mechanisms. Instead, solids may exhibit energy through vibration or rotation of the nucleus. Hence, the energy transfer is typically through lattice vibrations.

Another important mechanism in which materials maintain energy is by shifting electrons into higher orbital rings. In the case of electrical conductors the electrons are weakly bonded to the molecule and can drift from one molecule to another, transporting their energy in the process. Hence, flow of electrons, which is commonly observed in metals, is an effective transport mechanism, resulting in a correlation that materials which are excellent electrical conductors are usually excellent thermal conductors.

Convection

Energy transfer across a system boundary due to a temperature difference by the combined mechanisms of intermolecular interactions and bulk transport. Convection requires a fluid.

Newton's law of cooling:

$$q = h\,A_s\,\Delta T \tag{2.31}$$

where q = Heat flow from surface, W

h = Heat transfer coefficient, which is not a thermodynamic property of the material, but may depend on geometry of the surface, flow characteristics, thermodynamic properties of the fluid, and the like, W/m^{2}k

A_s = surface area from which convection is taking place, m^2

ΔT = temperature difference between surface and coolant, K

Thermal diffusivity: Thermal diffusivity, α, is defined as heat conducted/heat stored = $k/\rho c_p$, m^2/s, Values of thermal diffusivity, α, range from 0.1 0 x 10^{-6} mostly absorbed by material and small amount conducted further. Large value of α denotes that heat is propagated fast into the medium. Small value of α means heat is mostly absorbed by material and small amount conducted further Thermal diffusivity is a measure of the ability of a material to transfer thermal energy by conduction compared to the ability of the material to store thermal energy. Heat flux: Q/A. Units are kJ/(s)(m^2 c.s. area).

Convection heat transfer: It can be defined as transport of heat from one point to another in a fluid as a result of macroscopic motions of the fluid, the heat being carried as internal energy and convection between a solid surface and adjacent fluid that is in motion involves combined effects of conduction and fluid motion. Density differences between adjacent layers of fluids induce relative motion between fluid layers. The density differences may be due to temperature differences between two layers of the same fluid or two different fluids with different densities at the same temperature. External means of energy input could also induce relative motion. Convection can be free or natural, induced by buoyancy forces, forced, induced by external means, and may occur with phase change involving boiling or condensation.

Natural or free convection: If fluid motion is caused by buoyancy forces that are induced by density differences due to variation in fluid temperature or due to variation in densities of two different fluids adjacent to each other or solid–fluid interfaces are at different temperatures. Convection currents are induced by temperature differences only without any external energy inputs such as pump energy. Local velocities are generally low, giving rise to near laminar flow conditions.

Forced convection: Fluid is forced over the surface by external means such as a fan, pump, mixer, or wind, in addition to natural temperature difference induced convection currents, to increase localized velocities to increase turbulence and hence heat transfer coefficients.

Boiling

Linde boiling surface consists of a thin layer of porous metal bonded to the heat transfer substrate. Bubble nucleation and growth are promoted within a porous layer that provides a large number of stable nucleation sites of a predesigned shape and size. Linde boiling surface is illustrated in Figure 2.4.

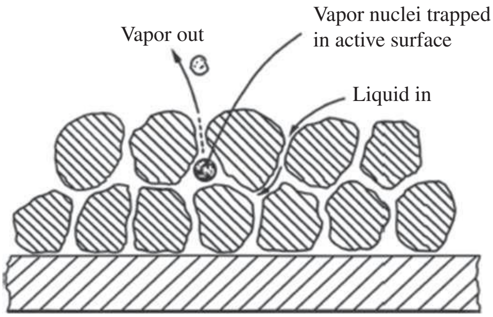


Figure 2.4 Linde boiling surface

Microscopic vapor nuclei in the form of bubbles entrapped on the heat transfer surface must exist in order for nucleate boiling to occur. Surface tension at the vapor–liquid interface of the bubbles exerts a pressure above that of the liquid. This excess pressure requires that the liquid be superheated in order for the bubble to exist and grow. The porous surface substantially reduces the superheat required to generate vapor. Boiling regimes are illustrated in Figure 2.5 by means of the boiling curve, ΔT versus heat flux. Figure 2.5 illustrates pool boiling curve and stages involved in pool boiling curve.

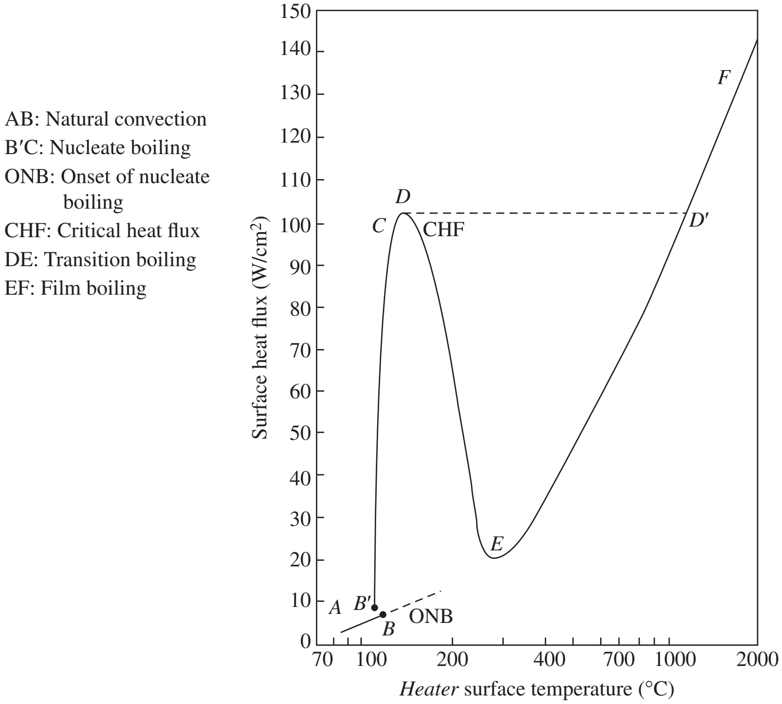


Figure 2.5 Pool boiling curve for water at atmospheric pressure

Natural convection boiling (AB): As the temperature of the heater is increased from the initial bulk value, the liquid close to the heated surface rises and is replaced by cooler fluid. Since no vapor is formed in the heating process, the heat transfer is governed by natural convection. Transport by natural convection occurs until the heater temperature is slightly greater than the boiling/saturation temperature (2–6°C for water). Liquid is slightly superheated and vaporizes when it reaches the surface.

Between *B′* and *C*, the nucleate boiling, that is, hot surface temperature further increases, increasing rate of bubble formation. Bubbles rise as numerous continuous columns of vapor in liquid, reach free surface and break up, releasing vapor from liquid. The curve has a very steep slope, ranging from 2 to 4 and heat transfer coefficient can be represented by Eqn. (2.32):

$$h = a\Delta T^{\mathrm{m}} \tag{2.32}$$

where $\Delta T = T_{\mathrm{w}} - T_{\mathrm{sat}}$

Boiling can be nucleate boiling, film boiling, pool boiling or flow boiling. The position of the *B*0*C* part of the curve is affected by the solid surface characteristics, surface tension, pressure, dissolved gases or solids, or presence of high boiling components in the liquid mixture. and at large temperature difference, large part of heater surface is covered by bubbles and the curve reaches *C*, which represents maximum heat flux at *C*. This is called critical heat flux (*CHF*). At the critical point, the vapor forms patches and columns near the heater surface. Because of the differences in thermal properties of the two phases, the heat transfer rate to the vapor is considerably less than that to the liquid. Therefore, the vapor effectively insulates the surface. With increasing the surface temperature, the vapor covers more of the surface.

In *nucleate boiling*, (*B′C*) vapor bubbles form at the heat transfer surface, break away, and are carried into the mainstream of the fluid. Once in the fluid mainstream, the bubbles collapse because the bulk fluid temperature is not as high as the heat transfer surface where the bubbles are created. When the pressure of a system drops or the flow decreases, the bubbles cannot escape as quickly as they are formed at the heat transfer surface. Similarly, if the temperature of the heat transfer surface increases, more bubbles are formed than can be efficiently carried away. The bubbles then grow and coalesce with the neighboring bubbles covering small areas of the surface with vapor film. This is known as *partial film boiling*. Since vapor has lower heat transfer coefficient than liquid, the vapor patches on the heat transfer surface act as insulation, making heat transfer more difficult. As the area of the heat transfer surface covered with vapor increases, temperature of the surface rapidly increases, while heat flux from the surface decreases. This unstable situation continues until the surface is covered by a stable blanket of vapor, preventing contact between the surface and the liquid. This condition after the stable vapor blanket has formed is called *film boiling*.

Pool boiling will occur when liquids form pools, once liquids leak out onto surface, floors forms puddles or pools. If heat levels reach boiling stages, boiling takes place, leading to vaporization and pool fires.

Flow boiling results when hot leaked liquids start flowing in boiling condition in pipes, tubes and surfaces, spreading fires over distances. In flow boiling, fluid is forced to move in a heated pipe or surface by external means, for example, by a pump. Flow boiling is, simply stated, boiling taking place while the liquid is flowing. In flow boiling, nucleation processes are suppressed and liquid gets superheated and transported from the tube wall by turbulent eddies to the vapor–liquid interface, where vaporization takes place.

Leidenfrost Phenomena: Leidenfrost noted that when liquids were spilled/placed on very hot surfaces, drops were formed that did not contact the surface but floated above it and slowly vaporized. When surface temperature was reduced below a certain value, the drops contacted the surface and rapidly vaporized. This phenomenon is called Leidenfrost phenomenon and point *E* on the boiling curve is called Leidenfrost point. Temperature at point *E* is known by different terms that include Leidenfrost temperature, minimum film boiling temperature (TMFB), rewetting temperature, quench temperature, and film boiling collapse temperature.

Condensation

Film condensation: In film condensation, the initially formed drops quickly coalesce and spread as a film on the solid surface. The film acts as a barrier for heat transfer to condense more liquid. Thus, it offers more resistance for heat transfer than

dropwise condensation. Consequently, heat transfer coefficients are far less for film condensation than for *dropwise condensation*. Film condensation is the normal mode in practice and therefore assumed in heat transfer estimations for design purposes.
Direct contact condensation: In direct contact condensation, the coolant liquid is sprayed into the vapor, which directly condenses on the sprayed coolant droplets. Solid surface for condensation is eliminated making heat transfer highly efficient, but results in mixing of the condensate and coolant. It is used where the coolant and condensate are of the same material or they become immiscible layers that are separated by settling processes.

Homogeneous condensation: In homogeneous condensation, the liquid phase forms directly from supersaturated vapors. For condensation to occur this way, microscopic contaminants should be present in the vapors to act as nuclei for initiating condensation process as in the case of rain. In industrial equipment, this process is important in fog formation in condensers.

Condensation of vapors in confined spaces can lead to vacuum inside storage tanks, leading to collapse of the tanks, under certain circumstances such as insufficient venting conditions or blockages. Condensation of water vapor or corrosive fluids can weaken and premature failure of vessels can occur.

Radiation-Definitions

Energy is emitted by matter in the form of electromagnetic waves (or photons) as a result of changes in electronic configurations of atoms or molecules. Unlike conduction and convection, energy transfer by radiation does not require presence of an intervening medium. It is the fastest mechanism for heat transfer, traveling at the speed of light. Thermal radiation is due to temperature of the emitting body, unlike X-rays, g-rays, radio waves, microwaves, TV waves, and so on, which are not related to temperature. Radiation heat transfer is predominant above 300°C. Radiation has much higher sensitivity to temperature than conduction and convection.

Emissive power, or flux density, is defined as (energy)/(time)(surface area), due to emission from it through a hemisphere. Emissive power of a surface is given by Eqn. 2.80

$$E = \sigma\varepsilon T_s^4,\ \mathrm{W/m^2} \tag{2.33}$$

where

ε = emissivity, which is a surface property (for a black body, $\varepsilon = 1$)
σ = Steffan Boltzman constant = 5.67 x 10^{-8}, $\mathrm{W/m^2K^4}$
T_s = absolute temperature of the surface, K

The above equation is derived from Stefan–Boltzman law, which describes a gross heat emission rather than heat transfer. The expression for the actual radiation heat transfer rate between surfaces having arbitrary orientations can be quite complex. The rate of radiation heat exchange between a small surface and a large surrounding is given by the expression:

$$q = \varepsilon\cdot\sigma\cdot A\cdot(T_s^4 - T_{\mathrm{surface}}^4) \tag{2.34}$$

where ε = surface emissivity
A = surface area
T_s = absolute temperature of surface, K
T_{surface} = absolute temperature of surroundings, K

A black body absorbs all radiation incident on its surface and the quantity and intensity of the radiation it emits are completely determined by its temperature. A blackbody emits the maximum amount of heat at its absolute temperature.

The emissivity (ε) of a medium is the fraction of energy a body emits at a given temperature compared to the amount it could emit (E_b) if it were a black body. Real objects do not radiate as much heat as a perfect black body. They radiate less heat than a black body and are called gray bodies. Emissivity is simply a factor by which the black body heat transfer is multiplied to take into account that the black body is the ideal case.

Absorptivity is fraction of radiation incident on a surface that is absorbed. Kirchhoff's law states that emissivity ε and absorptivity α are equal at the same temperature and wavelength.

Reasons for Fires and Explosions in Furnaces: Delayed ignition during lighting, fuel leakage into the firebox, or insufficient firebox purging, failure to establish reliable pilot flames before opening main fuel supply, rapid readmission of air to correct insufficient air supply. Flashback into waste gas supply manifold to incinerator, tube rupture due to thermal shock, over-firing, corrosion/erosion, or high temperature due to flame impingement or internal tube fouling, and closure of flue gas damper or trip of induced draft fan.

2.27 Diffusion and Mass Transfer

Diffusion

Diffusion describes the spread of molecules/particles through random motion from regions of higher concentration to regions of lower concentration. The time dependence of the statistical distribution in space is given by the diffusion equation. The concept of diffusion is tied to that of mass transfer driven by a concentration gradient, but diffusion can still occur when there is no concentration gradient (but there will be no net flux). Figure 2.6 illustrates the concepts of diffusion and mass transfer.

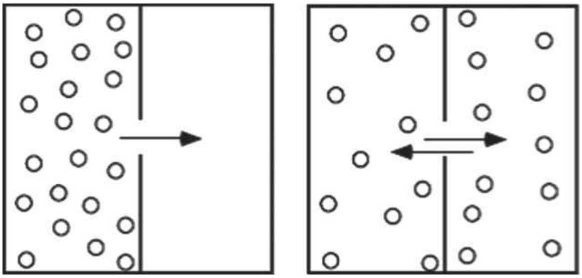


Figure 2.6 Diffusion and mass transfer as a result of concentration differences

Diffusion processes are important in propagation of fires and explosions and toxic substances in the environment. Diffusion processes may be divided into two types: (1) steady state and (2) unsteady state. Steady-state diffusion takes place at a constant rate—that is, once the process starts the number of atoms (or moles) crossing a given interface (the flux) is constant with time. This means that throughout the system dc/dx = constant and dc/dt = 0. Unsteady-state diffusion is a time dependent process in which the rate of diffusion is a function of time. Thus dc/dx varies with time and dc/dt ≠ 0. Both types of diffusion are described quantitatively by Fick's laws of diffusion. The first law concerns both steady state and unsteady state diffusion, while the second law deals only with unsteady state diffusion.

Diffusion Flux

Just as momentum and energy (heat) transfer have two mechanisms for transport, molecular and convective, so does mass transfer. However, there are convective fluxes in mass transfer, even on a molecular level. The reason for this is that in mass transfer, Fick's law proportionality, D_{AB}, is known as mass diffusivity (simply as diffusivity) or as the diffusion coefficient. Diffusivity is normally reported in cm^2/sec; the SI unit being m^2/sec. Diffusivity depends on pressure, temperature, and composition of the system.

Diffusivities of gases at low density are almost composition independent, increase with the temperature and vary inversely with pressure. Liquid and solid diffusivities are strongly concentration dependent and increase with temperature. Whenever there is a driving force, there is always a net movement of the mass of a particular species which results in a bulk motion of molecules. Of course, there can also be convective mass transport due to macroscopic fluid motion. The mass (or molar) flux of a given species is a vector quantity denoting the amount of the particular species, in either mass or molar units, that passes per given increment of time through a unit area normal to the vector.

Fick's First Law

Fick's First Law states that the diffusive flux is proportional to the concentration gradient.

$$J = -D(dc/dx) \tag{2.35}$$

The negative sign in this relationship indicates that particle flow occurs from regions of higher to regions of lower concentration. General range of diffusivity values:

Gases:	5×10^{-6}	to	1×10^{-5} m²/sec
Liquids:	10^{-6}	to	10^{-9} m²/sec
Solids:	5×10^{-14}	to	1×10^{-10} m²/sec

Like chemical reactions, diffusion is a thermally activated process and the temperature dependence of diffusion appears in the diffusivity as an *Arrhenius-type* equation:

$$D = D_0 e^{-Ea/RT} \tag{2.36}$$

Eddy/Turbulent Diffusion

Eddy/Turbulent diffusion is any diffusion process by which substances are mixed in the atmosphere or in any fluid system due to eddy motion. In another definition, it is mixing that is caused by eddies that can vary in size. Because the microscopic processes responsible for atmospheric mixing are too complex to model in detail, atmospheric modelers generally treat atmospheric mixing as a macroscopic eddy diffusion process. In this approach, the diffusion rate at each pressure level is parameterized by a quantity known as the *eddy diffusion coefficient* (sometimes also called *eddy diffusivity*).

Mass Transfer

Design and operation of chemical process equipment involves preparation of reactants, carrying out chemical reactions and separation of the resultant products. Ability to carry out the above operations largely rests on the proficiency of principles of mass transfer, which is largely the domain of chemical engineers. Mass transfer is meant to be the tendency of a component in a mixture to travel from a region of higher concentration to one of lower concentration.

Mass transfer occurs in many processes, such as absorption, evaporation, adsorption and drying. Mass transport occurs when a particle or component of a mixture moves to another location because of a difference in concentration. Mass transfer is used by different scientific disciplines for different processes and mechanisms. The phrase is commonly used in engineering for physical processes that involve molecular and convective transport of atoms and molecules within physical systems.

Mass transfer by convection involves the transport of material between a boundary surface (such as solid or liquid surface) and a moving fluid or between two relatively immiscible, moving fluids.

Mass transfer involves movement of a component from one phase to another due to concentration difference between the phases, for example, concentration gradient. Mass transfer encompasses diffusion and convection currents set up due to flows, laminar or turbulent, temperature differences and concentration differences, which are complementary to one another, across phase boundaries.

Mass transfer coefficients generally represent rates that are much greater than those that occur by diffusion alone, as a result of convection or turbulence at the *interface* where mass transfer occurs.

There are two different cases of convective mass transfer: Mass transfer takes place only in a single phase either to or from a phase boundary, as in sublimation of naphthalene (solid form) into the moving air. Mass transfer takes place in the two contacting phases as in extraction and absorption. Some common examples of mass transfer processes are the evaporation of water from a pond to the atmosphere;

Absorption is used for separation of acidic impurities from mixed gas streams, for example, CO_2, H_2S, and SO_2, other organics such as carbonyl sulfide (COS) and mercaptans, NH_3, HCN, NO_x, and VOC control in environmental clean up, odor control, waste water stripping, the diffusion of chemical impurities in lakes, rivers, and oceans from natural or artificial point sources. In industrial processes, mass transfer operations include separation of chemical components in distillation columns, adsorption and absorption such as in carbon filtration and in cooling towers where hot water flows down over the fill material as air flows up in contact with water, evaporating some of the water. The transfer of mass within a fluid mixture or across a phase boundary is a process that plays a major role in many industrial etc.

Applications such as liquid–liquid and solid–liquid extraction, pharmaceuticals and foods, extraction and refining of fats and oils, de-waxing and aromatic extraction from lube oils, leaching of ores, etc.

Humidification, dehumidification, and water cooling, drying, adsorption, chromatography, parametric pumping, ion exchange membrane separation processes is based on molecular-size differences, gas–gas, gas–liquid, and liquid–liquid.

Liquid membranes, for example, for H_2S removal, reverse osmosis, ultra and micro filtration, pervaporation, bubble and foam fractionation, etc.

Dispersion of gases from stacks, removal of pollutants from plant discharge streams by absorption, stripping of gases from waste water, neutron diffusion within nuclear reactors, air conditioning are further examples.

Many day-to-day experiences also involve mass transfer, for example, a lump of sugar added to a cup of coffee eventually dissolves and then diffuses to make the concentration uniform, evaporation of water from ponds increases the humidity of passing air stream, pleasant fragrance of perfumes, etc. When a system contains two or more components whose concentrations vary from point to point, there is a natural tendency for mass to be transferred, minimizing the concentration differences within a system. The transport of one constituent from a region of higher concentration to that of a lower concentration is called mass transfer. The transfer of mass within a fluid mixture or across a phase boundary is a process that plays a major role in many industrial processes. Examples of such processes are as follows:

separation processes such as gas absorption, distillation, extraction, adsorption, crystallization, air–water contact processes such as evaporative cooling, drying, reverse osmosis, micro filtration, and the like are prominent examples.

Absorption: Absorption is defined as the process of transfer of molecules of one substance directly to another substance. It may be either a physical or a chemical process. Physical absorption depends on the solubility of the substance absorbed and chemical absorption involves chemical reactions between the absorbed substance and the absorbing medium. It is a gas–liquid transfer process. It is used in the selective removal of a gaseous contaminant or product from a gas mixture. Removal is often effected by absorption in a liquid in which only the gas concerned is soluble.

It is sometimes also necessary to free a liquid from dissolved gases. This can be achieved by contact with an insoluble gas, in which case the process is known as *stripping* or *scrubbing*.

Mist carryover in exit gases should be avoided. If absorber is to remove toxic gases from a gas stream, prior to discharge to atmosphere failure of liquid flow should initiate emergency action.

Reactive Absorption: Reactive absorption involves absorption with chemical reactions. Chemical reactions enhance absorption rates considerably, making reactive absorption an attractive process. Environmental considerations dictate use of reversible reactions for recovery and recycle of the solvent. The mass transfer enhancement due to chemical reactions is often accounted through the use of the so called *enhancement factors*, which are obtained from experimental data or from theoretical considerations with simplified model assumptions. Examples include sulfuric and nitric acid manufacture and H_2S removal from natural gas streams.

Reactive absorption can handle gases with low concentrations of solutes with low solvent requirements.

Reactive absorption involves liberation of heat of reaction (most reactions in reactive absorptions are exothermic in nature), which is a limitation, requiring use of inter coolers for heat removal.

Most reactive absorptions involve steady-state operations involving liquid phase reactions, although some applications involve both liquid and gas phase reactions.

Reactive absorption is a complex rate controlled process that occurs far from thermodynamic equilibrium. Therefore the equilibrium concept is insufficient to describe the process, requiring rate controlled kinetic models.

Modeling and design of reactive absorption processes are usually based on the equilibrium stage model which assumes that each gas stream leaving a tray or equivalent packed section (HETP) is in thermodynamic equilibrium with the corresponding liquid stream leaving. For reactive absorption, chemical reaction must also be taken into account. With very fast reactions, the reaction–separation process can be satisfactorily described assuming reaction equilibrium.

A proper modeling approach is based on the non reactive equilibrium stage model, which is extended by simultaneously considering the reaction equilibrium relationship and the tray/stage efficiency. If the reaction rate is slower than the mass transfer rate, the influence of reaction kinetics increases and becomes a dominant factor. This tendency is taken into account by integrating the reaction kinetics into the material and energy balances. This approach is widely used.

In real reactive absorption processes, thermodynamic equilibrium is rarely reached. Therefore parameters such as tray efficiencies or height equivalent to a theoretical plate (HETP) values are introduced to adjust the equilibrium-based theoretical description to real column conditions. However, reactive absorption normally takes place in multi component systems, for which this simplified concept often fails.

Among major industrial applications are the absorption of SO_3 in oleum in the production of H_2SO_4 and of HCl and NO_2 in water in hydrochloric and nitric acid manufacturing, scrubbing of corrosive, obnoxious, or hazardous gases, vapors and particulates from a gas stream, purification of various process streams to prevent pollution, corrosion, catalyst poisoning or condensation in subsequent treatment, etc.

Other examples of the applications include large scale removal of CO_2 from air or natural gas prior to liquefaction, absorption of sulfur compounds from sour natural gas, removal of acidic components from olefin plants, CO_2 removal from ammonia synthesis gas, absorption of formaldehyde in water to produce aqueous solutions and drying of gases, *particulate removal,* NO_x *removal, VOC control, odor control, waste water stripping, and the like*.

Distillation: Distillation is a method of separating mixtures based on differences in volatilities of components in a boiling liquid mixture. Distillation is a physical separation process.

Commercially, distillation has a number of applications. It is used to separate crude oil into more fractions for specific uses such as transport, power generation and heating. Water is distilled to remove impurities, such as salt from seawater. Air is distilled to separate its components, notably oxygen, nitrogen, and argon for industrial use.

Distillation of fermented solutions has been used since ancient times to produce distilled beverages with a higher alcohol content. The application of distillation can roughly be divided into four groups: laboratory scale, industrial distillation, distillation of herbs for perfumery and medicinals (herbal distillate), and food processing.

Different practices in distillation processes:

(i) Equilibrium flash vaporization

(ii) Carrier distillation: steam distillation for water-immiscible liquids, such as high boiling petroleum fractions, purification of high boiling chemical products which form immiscible phases with water, oils of vegetable origin, essential oils and the like. Use of carriers, other than steam, such as low boiling petroleum fractions such as propane for distillation of high boiling fractions

(iii) Differential distillation

(iv) TBP distillation, azeotropic, and extractive distillation

(v) Batch and continuous fractionation of binary or multi component mixtures

(vi) Steam stripping

(vii) Fractionations using open steam

(viii) High-pressure distillation

Retrograde phenomena: In normal distillation processes, as pressure is increased condensation is favored and vice versa. In *super-critical distillations,* there are operating regions on the phase envelopes where increased pressure promotes vaporization instead of condensation. Similarly as pressure is decreased, instead of vaporization, condensation takes place. This phenomena is called *retrograde condensation* and *retrograde vaporization*, respectively. In gas separations near critical regions, retrograde phenomena must be recognized and column pressures fixed accordingly as otherwise premature column flooding or blowing can occur.

(ix) Azeotropic and extractive distillation, reactive distillation, and reactive extractive distillation

(x) Reactive separation processes such as reactive distillation, sorption-enhanced reaction absorption, reactive extraction, and reaction crystallization combine the essential tasks of reaction and separation in a single vessel. The most important example of reactive separation processes is reactive distillation (RD), which is the combination of chemical reaction and distillation in a single column. Reactive distillation is used with reversible liquid phase reactions.

(xi) **Vacuum distillation:** The relative volatility between components generally increases as the boiling temperature drops. This higher relative volatility improves the ease of separation, which lowers the number of theoretical stages needed for a given separation. If the number of theoretical trays is held constant, the reflux ratio required for the same separation can be reduced. In addition, if the number of theoretical plates and the reflux ratio are maintained constant, product purity will be increased.

Lower distillation temperatures are desirable when processing heat sensitive products. Lower bottoms temperatures retard undesirable reactions such as product decomposition, polymerization, or discoloration. Separations can be achieved for components with very low vapor pressures or compounds that degrade at temperatures near their atmospheric boiling point. Lower reboiler temperatures permit the use of less costly energy sources such as low pressure steam or hot water. Usually, the top column pressure is set by the selection of the vacuum-producing equipment.

(xii) **Molecular distillation:** Distillation process that is carried out at such low pressures that the distance between the hot and condensing surfaces is less than the mean free path of the molecules. Each unit is a single stage, but several units in series are commonly employed. Molecular distillation is applied to thermally sensitive high-molecular-weight materials with molecular weights in the range of 250–1,200. Contact times in commercial units may be as low as 0.001 s. In the centrifugal type still, the material that is charged to the bottom creeps up the heated, rotating conical surface as a thin film, vaporized, condensed, and discharged. The film thickness is of the order of 0.05–0.1 mm. Typical distillation unit involves a column, either involving plates or packing. A plate column is illustrated in Figure 2.7.

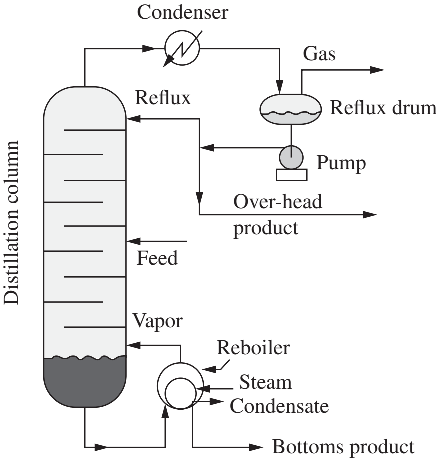


Figure 2.7 Typical distillation unit

In vacuum operations, air ingress is possible, whereas in pressure operations, vapor emissions are likely. With flammables, distillation is always inherently hazardous. Large amounts of flammables in reboilers, in column internals and associated piping pose flammable and explosion hazards in distillation units. Thermosiphon reboilers are a better choice in this respect, due to less inventories compared to kettle reboilers. Provision of emergency isolation of heat input to reboilers in case of coolant failure or low flows is necessary. Columns may require pressure relief as well as vacuum may be necessary. Accidental entry of water into hot oil systems led to explosions. Care should be exercised while purging when residues are present. There have been cases of fire with residues present on packings. Concentration gradient between top and bottom of the column has a bearing on safety. Concentration of impurities in the column can lead to hazards.

Extraction: Extraction is a process whereby a mixture of several substances in the liquid phase is at least partially separated upon addition of a liquid solvent in which the original substances have different solubilities. When some of the original substances are solids, the process is called leaching. In a sense, the role of solvent in extraction is analogous to the role of enthalpy in distillation. Differences in solubility, and hence of separability by extraction, are associated with differences in chemical structure, whereas differences in vapor pressure are the basis of separation by distillation.

Examples include extraction of lubricating oils for removal of aromatics from petroleum fractions, separation of paraffins and aromatics. recovery of BTX (benzene–toluene–xylenes) by using sulfolane, ethylene glycol, etc., as solvents, separation of p-xylene from mixed xylenes using HF, boron trifluoride, or other solvents. Distillation requires very large number of trays to achieve separation because of close-boiling nature of these mixtures. Removal CO_2, H_2S, and other acidic contaminants from liquefied petroleum gases (LPGs) generated during operation of fluid catalytic crackers and cokers in petroleum refineries and from LNG. The acid gases are extracted from the liquefied hydrocarbons (primarily C_1 to C_3) by reversible reaction with amine solvents. Production of glacial acetic acid by separation from aqueous mixtures using ethyl or isopropyl acetate or Methyl isobutyl ketone (MIBK) as solvents, separation of fatty acids from oil using propane as solvent, purification of caprolactum, extraction of pharmaceuticals, purification of penicillin, extraction of tranquilizers, recovery of antibiotics and other complex organics from fermentation broth by using a variety of oxygenated organic solvents such as acetates and ketones, recovery of citric acid from fermentation broth with tertiary amines, vitamin manufacture, waste water treatment involving removal of high boiling contaminants, removal of dissolved salts from crude organic stream using water as solvent as an alternative to crystallization and filtration, are some of the examples.

In the treatment of water to remove trace amounts of organics, when the concentration of impurities in the feed is greater than about 20–50 ppm, liquid–liquid extraction may be more economical than adsorption of the impurities by using carbon beds, because the latter may require frequent and costly replacement of the adsorbent. At lower concentrations of impurities, adsorption may be the more economical option because the usable lifetime of the carbon bed is longer.

Recovery of phenolic compounds from water by using methyl isobutyl ketone is a prominent example.

Inventories of flammables in mixer-settler units are large compared to columns and centrifugal extractors. Ignition due to static electricity problems is possible due to mixing/agitation

Supercritical processes: Supercritical fluids are those fluids whose temperature is greater than its T_c and pressure is greater than its P_c is a supercritical fluid.

Figure 2.8 illustrates supercritical region on the phase diagram for a solvent. It is a plot of temperature versus pressure, showing the equilibrium coexistence of two phases along the phase boundaries separating different regions. As one can see, the solid–liquid phase boundary is a plot of the freezing point at various pressures, the liquid-vapor boundary is a plot of vapor pressure of the liquid against temperature and the solid–vapor boundary is a plot of the sublimation vapor pressure against temperature.

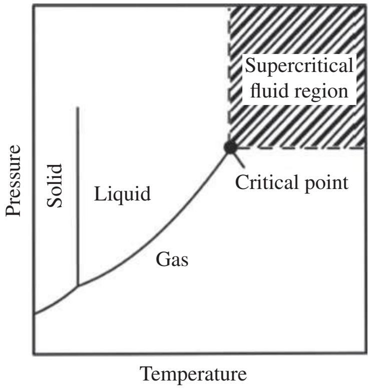


Figure 2.8 Pressure–temperature diagram for a pure compound

Solid, liquid, and gas phases are in equilibrium at the intersection of these three boundaries, known as the triple point. Supercritical region is shown Figure 2.8. A fluid in this region is neither a liquid nor gas, but possesses some of the properties of each. At this stage, no matter how much pressure is applied, a fluid in this region will not condense and no matter how much the temperature is increased, it will not boil. At critical temperature, interface between the fluids disappear, at which condition the densities of liquid and vapor are equal. Above its critical values, liquid–vapor phase boundary of a compound does not exist and its fluid properties can be tailored by adjusting the pressure or temperature. Although supercritical fluid has liquid-like density, it exhibits gas-like diffusivity, surface tension and viscosity. Its gas-like viscosity results in high mass transfer. Its low surface tension and viscosity lead to greater penetration into porous solids.

Because of its liquid-like density, the solvent strength of a supercritical fluid is comparable to that of a liquid. At critical conditions, the molecular attraction in a supercritical fluid is counterbalanced by the kinetic energy. In this region, the fluid density and density-dependent properties are very sensitive to pressure and temperature changes. The solvent power of a supercritical fluid is approximately proportional to its density. Thus, solvent power can be modified by varying its temperature and pressure.

Extraction of uranium and plutonium, extraction of zirconium, hofnium and niobium, using MIBK as solvent, extraction of rare earths, hydrometallurgy of copper, extraction of cobalt, nickel, beryllium, etc., are other examples.

Each of the three corners of the triangular diagram represents pure components *A*, *B*, and *C*. The triangular diagrams can be equilateral (Figure 2.9) or right angled. Representation of equilibria on rectangular coordinates is also common.

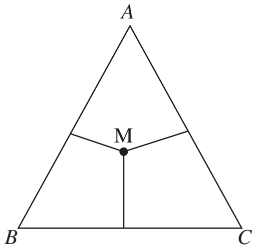


Figure 2.9 Triangular diagram

Examples of leaching processes: Leaching of minerals from ores, for example, copper minerals from ore using sulfuric acid or ammonical solutions, uranium ore slurries using acidic solutions, bauxite leaching, nickel, and cobalt recovery, gold, vegetable oils from oil seeds, sugar from sugar beets, tannins from tree barks, pharmaceutical products from plant roots, extraction of tea/coffee from tea leaves/coffee seeds, washing of solids to free mother liquors, etc.

Crystallization: A crystal may be defined as a solid composed of atoms arranged in an orderly, repetitive array. The inter atomic distances in a crystal of any definite material are constant and characteristic of that material. Crystals are, in short, high purity products with consistent shape and size, good appearance, high bulk density, and good handling characteristics. Because the pattern or arrangement of the atoms is repeated in all directions, there are definite limitations on the shapes that crystals may assume. For each chemical compound, there are unique physical properties differentiating that material from others, therefore the formation of a crystalline material from its solution or mother liquor is accompanied by unique growth and nucleation characteristics. Crystals possess a well defined three-dimensional order. Crystallization is the process by which a chemical is separated from solution as a high purity, definitively shaped solid.

Supersaturation: Supersaturation is defined as the excess dissolved solute in the mother liquor with reference to the solubility curve. In order to drive the process of crystallization, the solution must be supersaturated with solute. Supersaturation can be quantified by the ratio of the mass solute concentration in the bulk solution to the concentration in the solution at the point of saturation.

Crystal properties: Crystal properties include purity, appearance, agglomeration, caking tendency, specific surface area, surface characteristics, crystal size distribution, morphology/shape, polymorphic form, bulk density, bioavailability, flow properties, crystal strength, dissolution rate, and mother liquor and other impurities.
Polymorphic system: is one that includes a chemical compound that can exist as two or more crystal structures with different internal unit cells, as measured by an X-ray diffraction pattern. This can result in different chemical and physical properties, which influence parameters like ease of formulation and bioavailability (e.g. solubility). Polymorphism is displayed by both organic and inorganic compounds. For example, calcium carbonate has three forms of polymorphism, namely, aragonite, vaterite, and calcite. Calcite is the most stable of the three.

Mechanisms involved in crystallization processes: Crystallization from solution can be considered to be a two-step process. The first step is the phase separation or birth of new crystals. The second is the growth of these crystals to larger size. These two processes are known as nucleation and crystal growth, respectively.

Analysis of industrial crystallization processes requires knowledge of both nucleation and crystal growth. These two processes together govern the crystal size distribution (CSD).

Mixing processes in crystallization: *Mesomixing* refers to turbulent dispersion of an incoming fresh feedstock plume by mixing it with the bulk liquid. *Macro-mixing* refers to overall mixing performance during large-scale mixing and bulk fluid movement and blending. Macromixing reduces local differences in temperature, concentration, supersaturation, and suspended solids density. *Micromixing or turbulent mixing* at the molecular level occurs locally in a small volume of the process, the materials coming in contact with each other as result of molecular diffusion.

Crystal habit and polymorphic state: A crystalline particle is characterized by definite external and internal structures. Habit describes the external shape of a crystal, whereas polymorphic state refers to the definite arrangement of molecules inside the crystal lattice.

The use of different solvents and processing conditions may alter the habit of recrystallized particles, besides modifying the polymorphic state of the solid. Subtle changes in crystal habit at this stage can lead to significant variation in raw material characteristics.

Various indices such as particle orientation, flowability, packing, compaction, suspension stability, and dissolution can be altered even in the absence of significantly altered polymorphic state. These effects are a result of the physical effect of different crystal habits.

Crystal properties include purity, appearance, agglomeration, caking tendency, specific surface area, surface characteristics, crystal size distribution, morphology/shape, polymorphic form, bulk density, bioavailability, flow properties, crystal strength, dissolution rate, and mother liquor and other impurities.

Factors that restrict productivity and purity of crystals:

Agglomeration: Product size can be affected by agglomeration and fracture mechanisms. When growing crystals collide, they may stick together and form new particles and when the collisions are inelastic, agglomerates form. The strength of the physical bonds thus form determines the stability of the agglomerates upon further collisions. For limiting crystal size, use of a surfactant can be effective to reduce stickiness. Agglomeration will be more extensive if there are more particles, which increase the probability of collisions or if the colliding particles are sticky. In general, agglomeration is associated with higher degree of supersaturation and even operation in the unstable zone, conditions under which large number of smaller size crystals are formed. To minimize agglomeration, supersaturation should be limited.

Liquid inclusion in individual crystals and agglomerates: Liquid can get trapped inside growing crystals through several mechanisms. Higher growth rates are responsible for increased amounts of liquid entrapment. Thus, higher supersaturation could be problematic, particularly when large amounts of liquid impurities are present. Liquid can also get entrapped between colliding particles during agglomeration process. Again, the probability of this happening increases with increased supersaturation. In this regard, it is necessary to reduce the time for interaction and/or rapidly relieve the supersaturated condition.

Liquid Impurities Outside the Crystals

When product collection is through filter cake, the amount of liquid outside the crystals, in the voids, is much larger than the amount within them. Since this quantity is, in general, inversely proportional to the square root of the mean crystal size, cakes containing small particles require larger quantities of wash liquid to achieve the same washing efficiency than cakes containing larger crystals.

Cavitation: Although cavitation has been successfully used for homogenization, it has a destructive effect on the materials of construction and thus disrupting the process. Therefore more durable and expensive materials, such as polycrystalline diamond and stainless steel must be used. It is also necessary to determine whether thermal or sonochemical reactions occur and if their importance to the system is under consideration.

Sonocrystallization: The principle involved in sonocrystallization is that high intensity sound initiates nucleation and helps to control crystal size and habit to yield products that meet better required specifications. Application of ultrasound to crystallization improves quality of the product. The most important mechanism by which ultrasonic irradiation can influence crystallization is ultrasonic cavitation. Sonocrystallization eliminates the need to add seed crystals, which can be advantageous in contained, sterile operations involved in the manufacture of pharmaceuticals and fine chemicals. Controlled ultrasound at different stages of crystallization may be used to modify and tailor product properties to meet different requirements. Effect of ultrasound on a fluid is to impose an oscillatory pressure on it. At low intensity, this pressure wave will induce motion and mixing within the fluid. This process is known as acoustic streaming. At higher intensities, the local pressure in the expansion phase of the cycle falls below the vapor pressure of the fluid, causing minute bubbles or cavities to grow. A further increase generates negative transient pressures within the fluid, enhancing bubble growth and producing new cavities on the fluid. These latter processes comprise the phenomenon of cavitation, which is the most important effect of ultrasound in chemical and crystallization systems.

Humidification and Water Cooling:

Definitions:

Absolute humidity → mass of water vapor/mass of dry air

Molar humidity → moles of water vapor/moles of dry air

Percent humidity → 100 (humidity of air)/(humidity of saturated air)

Percent relative humidity → 100(partial pressure of water vapor in air)/(vapor pressure of water at the same temperature)

Humid volume → volume of unit volume of dry gas + its associated vapor at the prevailing temperature and pressure

Saturated volume → volume of unit mass of dry air + its associated vapor

Humid heat → heat required to raise temperature of unit mass of dry air + its associated vapor through 1°C at constant pressure

Dew point: It is the temperature at which vapor–air mixture is saturated when cooled at constant pressure out of contact with liquid; temperature at which first signs of fog formation on cooling occurs. Below dew point condensation continues when air is further cooled.

Adiabatic saturation temperature is the steady-state temperature of water/liquid being re-circulated in a confined space through which air/gas is passed in intimate contact with the water/liquid. If contact between water/liquid droplets and air/gas is kept long enough, the leaving air/gas is saturated at the adiabatic saturation temperature. Adiabatic saturation temperature is the *steady-state equilibrium temperature* attained when a *large amount of water/liquid* is contacted with the entering air/gas.

Wet bulb temperature is the *steady* state non equilibrium temperature reached when small amount of water/liquid is contacted. Since liquid is in small amount, temperature and enthalpy of air/gas remain unchanged. For adiabatic saturation case, T and H change.

*Hygrometer*s are devices that indirectly measure humidity by sensing changes in physical or electrical properties in materials due to their moisture content. Materials such as hair, skin, membranes, and thin strips of wood change their length as they absorb water. The change in length is directly related to the humidity.

Humidity chart. Figure 2.10 represents a typical humidity chart.

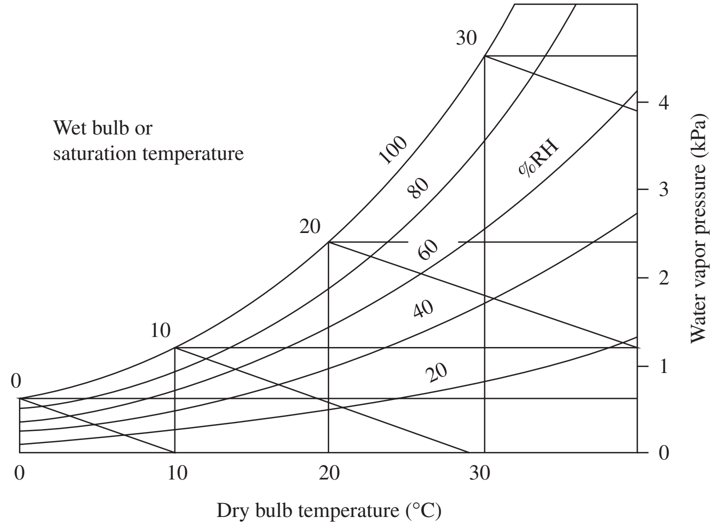


Figure 2.10 Humidity chart

Dehumidification: When a warm gas–vapor mixture is contacted with a cold liquid so that humidity of the bulk gas is more than that at the interface, dehumidification takes place.

Methods by which dehumidification processes are carried out:

Cooling by the use of refrigeration coils: Air to be dried passes through a cooling coil, which lowers the temperature of the air stream below its dew point. Water vapor condenses on the cooling coil surface and falls to the drain pan as liquid. In absolute terms air is drier, but it also has a relative humidity close to 100 percent. If low relative humidity is needed in addition to a lower absolute amount of moisture, the air can be heated after it leaves the cooling coil.

Cooling by the use of desiccants: In a desiccant system, for example, adsorption using silica gel, alumina, etc., as adsorbents. The process air stream passes through a desiccant medium, which adsorbs moisture from the air stream. Desiccant dehumidifiers can produce dew points below–18°C. The equipment uses differences in vapor pressure to remove moisture from air by chemical attraction. The driving force for the process is the difference in vapor pressures between the surface of the desiccant, which has a very low vapor pressure and the humid air. Eventually, the desiccant surface finally gets saturated with water vapor, requiring reactivation for reuse by drying.

Evaporative cooling and cooling towers: Heat transfer processes involved in evaporative cooling; transfer of heat as latent heat of vaporization, which accounts for about 80 percent of total heat transferred; sensible heat transfer due to temperature difference between air and hot liquid, which accounts to about 20 percent of the total heat transferred. Different types of equipment used in industry for water cooling are as follows:

Atmospheric cooling towers: These involve cross-flow of air, depends on wind blowing horizontally across the tower, are not capable of cooling water to temperatures much closer than 2°C of wet bulb temperature of entering air, require no fan, consume power only to pump water to top of the tower, and require large ground area and open areas around to permit un-obstructed air flow.

Natural draft cooling towers: These involve positive movement of air through a tall tower that makes use of density differences, that is, natural draft. Natural draft cooling towers operate most efficiently in climates with high humidity. In climates with lower humidity, buoyancy effect may be enhanced in natural draft towers with the assistance of a fan.

Other types include mechanical draft cooling towers, forced draft (fan is at lower end), induced draft (fan is at the top), induced draft (cross-flow), spray chambers (used for adiabatic humidification–cooling operations with water recirculation), refrigeration coils for dehumidification, spray ponds (used where close approach to wet bulb temperature is not required and high drift losses can be tolerated).

Hazards: Unless properly routed/provided automatic shut-off blower and exhaust ducts can be fire hazard. Ducts may assist in spread of fires. Possible air contamination due to contact with water in the system, respiratory infections from air borne microorganisms, is possible. Cooling towers and humidifiers are treated with chlorine at 5 ppm twice a year. Organic contamination is reduced by bleed off and filtration of particulates. Addition of treatment chemicals may give rise to toxic hazards.

In plants with fire hazards location of fin-fan coolers needs consideration because, if left running in a fire, they can assist fire spread through forced draft. Water coolers and condensers may require pressure relief on water side for protection against tube failure. Cooling water systems should be highly reliable to avoid reaction runways on water failure to reactor cooling systems.

Drying: Drying or dehydration of foods is used as a preservation technique. Micro organisms that cause food spoilage and decay cannot grow and multiply in the absence of water. Also, many enzymes that cause chemical changes in food and other biological materials cannot function without water. When the water content is reduced below about 10 wt percent, the micro-organisms are not active. However, it is usually necessary to lower the moisture content below 5 wt percent to preserve flavor and nutrition.

Drying is one of the most energy intensive processes due to phase change and high latent heat of vaporization and the inherent inefficiency of using hot air as the (most common) drying medium. Energy consumption for drying ranges from about 5 percent of chemical products to as high as 35 percent for cellulosic materials.

Definitions:
Free moisture It is the content of a solid in excess of equilibrium moisture content (*unbound moisture*), and it exerts vapor pressure of pure water at the prevailing temperature.

Bound moisture: It is the moisture retained by a solid in such a way that it exerts a vapor pressure *less than* vapor pressure of pure water at the same temperature. Moisture contained inside cell walls of plant matter/structure or in loose chemical combination with cellulosic material. It may be retained in capillaries and crevices throughout the solid or adsorbed on surfaces.

Equilibrium moisture content: When a *hygroscopic* material is exposed to air at constant temperature and humidity for prolonged periods of time, the material attains a definite moisture content which remains constant if temperature and humidity of air remains the same. Further exposure to air under the same conditions of humidity and temperature will not result in any change in moisture content. In other words, it is the moisture content in a solid, which is in equilibrium with the gas phase at a given partial pressure of vapor. It depends on temperature. With the increase in temperature, equilibrium moisture content somewhat decreases; but for moderate changes in temperature, there is no much effect. It is equal to *zero* when there are no dissolved solids and no bound moisture (non hygroscopic materials). Examples include inorganic salts such as zinc oxide and other materials such as glass wool and kaolin. Spongy or cellular materials such as wood, leather, and tobacco have high equilibrium moisture content. At high relative humidities (60–80 percent), equilibrium moisture content increases rapidly with increase in relative humidity. At low relative humidities, equilibrium moisture content is *very high* for foods high in protein, starch and high molecular weight polymers and *low* for foods with high percent solubles, crystalline salts, sugars, etc. It depends on the direction from which equilibrium is approached, that is, whether a wet material is dried or a dry material adsorbs moisture. This is due to adsorption hysterisis.

Mechanisms involved in the transport of moisture during drying process:

Liquid Diffusion: Diffusion of moisture occurs when there is a concentration difference between the depths of the solid and the surface and it takes place if the wet solid is at a temperature below the boiling point of the liquid and solids are close to homogeneity, from within to surface of solid due to concentration gradients setup during drying from the surface. Transport of moisture usually occurs in relatively homogeneous nonporous solids where single-phase solutions are formed with the moisture, such as wood, leather, paper, starch, textiles, paste, clay, soap, gelatin, and glue. In drying many food materials, the movement of moisture toward the surface (falling rate period) is mainly governed by molecular diffusion and therefore follows Fick's law.

Vapor Diffusion: It takes place if the liquid vaporizes within the material. For example, if heat is supplied to one surface of the solid while drying proceeds from another, moisture may vaporize beneath the surface and diffuse out as vapor.

Knudsen Diffusion: It takes place if drying takes place at very low temperatures and pressures, for example, in freeze drying.

Surface Diffusion: Diffusion of vapor from the surface into the bulk of air.

Capillary Diffusion: In substances with a large open-pore structure and in beds of granular and porous solids, the unbound moisture flows from regions of low concentration to those of high concentration by capillary action. When granular and porous solids such as clays, sand, soil, plant pigments, and minerals are being dried, unbound or free moisture moves through the capillaries and voids of the solids by capillary action, not by diffusion. This mechanism, involving surface tension, is similar to the movement of oil in a lamp wick. A porous solid contains interconnecting pores and channels of varying pore sizes. As water is evaporated, a meniscus of liquid water is formed across each pore in the depths of the solid. This sets up capillary forces by the interfacial tension between the water and solid. These capillary forces provide the driving force for moving water through the pores to the surface. Small pores develop greater forces than those developed by large pores.

In a drying operation, the driving forces for (i) heat transfer and (ii) mass transfer are as follows:

For heat transfer → (dry bulb temperature) – (wet bulb temperature) – $dW/d\theta = hA(T_D - T_W)/\lambda$ (2.37)

For mass transfer → (pressure at wet bulb temperature) –

(pressure at dew point – $dW/d\theta = k'_g A_m(H_W - H_D)$ (2.38)

Constant rate period: When a solid surface is completely covered with water, rate of drying is fairly constant. This period is called constant rate period.

Falling rate period: Begins when dry patches start appearing on the solid surface (i.e. the solid surface is no more *completely* covered with water). Area for mass transfer progressively gets reduced (certain areas on the solid have moisture and certain areas are dry).

Critical moisture content: Moisture content at the end of constant rate period is called *critical moisture content*. A plot of rate of drying versus free moisture content is known as drying rate curve? (Figure 2.11).

At zero time, the initial free moisture content is shown at point *A*.

In the beginning, the solid is usually at a colder temperature than its ultimate temperature, and the evaporation rate will increase. Eventually at point *B*, the surface temperature rises to its equilibrium value.

Alternatively, if the solid is quite hot to start with, the rate may start at point *A′*. This initial unsteady-state adjustment period is usually quite short and it is often ignored in the analysis of times of drying.

From point *B* to *C* in Figure 2.11, the line is straight. Hence, the slope and rate are constant during this period. This constant rate of drying period is shown as line *BC*.

During the constant rate period, external heat/mass transfer rate is controlling. Water evaporates as if there is no solid present, and its rate of evaporation is not dependent on the solid. This continues until water from the interior is no longer freely available at the surface of the solid. Point *C* in Figure 2.11 is critical moisture content, X_C, which represents the point of transition from constant rate to falling rates. From point *C*, the drying rate starts to decrease. *CE* represents falling rate

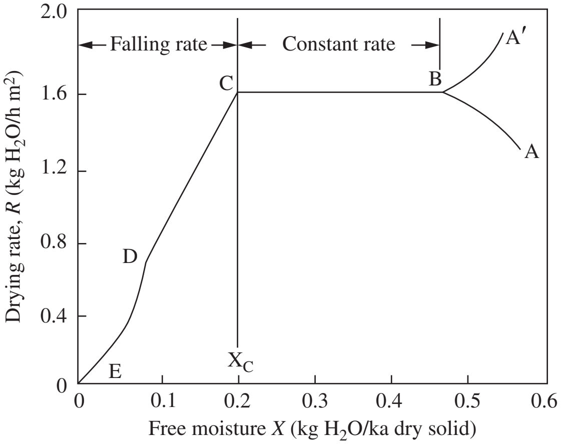


Figure 2.11 Illustrates typical drying rate curve

period during which internal heat/mass transfer rates control. The plane of evaporation slowly recedes from the surface. Heat for the evaporation is transferred through the solid to the zone of vaporization. Vaporized water moves through the solid into the air stream. Although the amount of water removed in the falling rate period is relatively small, it can take considerably longer than in the constant rate period. The falling rate period has two sections as can be noted in Figure 2.12. *CD* represents first falling rate period. From *C* to *D*, the wet areas on the surface decrease progressively, increasing dry patches. There is insufficient water on the surface to maintain a continuous film of water. The surface becomes completely dry as point *D* is reached. Moisture is present in the interior of the solid pores. In this first falling rate period, the rate shown as line *CD* in Figure 2.1 is often linear. Point *D* is the point at which all exposed surface becomes completely unsaturated and represents starting point where internal moisture movement controls drying rate. From point *D*, the rate of drying falls even more rapidly, until it reaches point *E*, where the equilibrium moisture content is *X*. When the surface is completely dry (point *D*), the evaporation process continues moving toward the center of the solid as shown by the curve *DE*, which represents the second falling rate period (internal moisture movement).

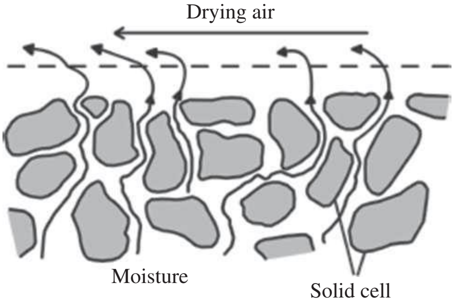


Figure 2.12 Movement of moisture during drying of porous materials

In some materials being dried, no sharp discontinuity occurs at point *D*, and the change from partially wetted to completely dry conditions at the surface is so gradual that no sharp change is detectable. *CD* may constitute all of the falling rate period.

Non hygroscopic materials have a single falling rate period, whereas hygroscopic materials have two or more periods. In the first period, the plane of evaporation moves from the surface to inside the solid, and water vapor diffuses through the dry solids to the drying air. The second period occurs when the partial pressure of water vapor is below the saturated vapor pressure and drying is by desorption. Figure 2.12 illustrates movement of moisture during drying of porous solids.

Dryers *Dryers for high capacities* → These include and indirect rotary dryers, spray dryers, drum dryers, tunnel dryers, fluid bed dryers, pneumatic/flash dryers. Figure 2.13 illustrates a typical spray dryer:

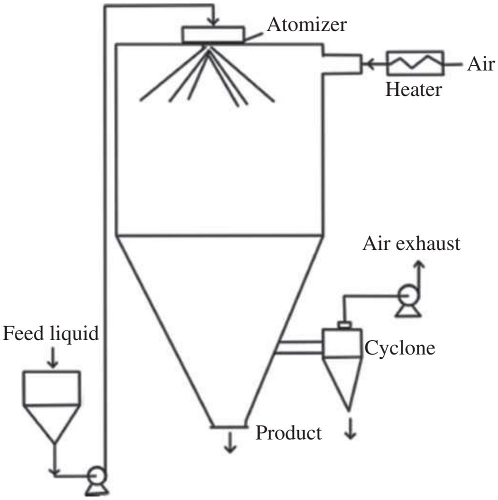


Figure 2.13 Schematic of a spray dryer

Dryers for small capacities: These include vacuum tray dryers, agitated batch dryers, through circulation dryers, fluid bed dryers, vacuum shelf dryers, spouted bed dryers, and freeze dryers. Principle of operation of a freeze dryer: Removal of moisture from the solid is through sublimation, which takes place below triple point of water. Figure 2.14 illustrates phase diagram of water, showing its triple point.

Causes of explosions in dryers: Some dryers, including ductwork and associated equipment such as cyclones and dust collectors, are prone to accumulation of deposits on dryer walls and duct work. Solids often accumulate on atomizers at the top of spray dryers where the temperatures can be highest. The main cause of explosions in dryers is attributed to build-up of deposits on the heated surfaces of the dryer. When a layer of organic solids builds up, the material layer may undergo self-heating due to non dissipation of heat inside the solid deposit. When its temperature reaches self-ignition temperature (SIT) of the material, explosion can occur. The characteristics of materials deposited on walls or other surfaces may change during drying

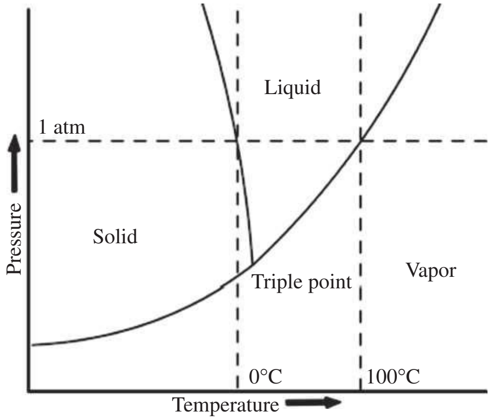


Figure 2.14 Phase diagram of water

resulting change in SIT when the materials are exposed to high temperatures or other operating conditions. There have been several instances of explosions in dryers.

Smooth surfaces, elimination of potential points of solids accumulation can reduce solids deposits. Entrainment of fine solids inside the dryers can also lead to dust explosions inside dryers. To prevent such explosions, frequent monitoring and cleaning of the dryers is necessary. Many drying operations involve the vaporization of a flammable solvent from a combustible powder. This combination of a flammable vapor and combustible dust is called a *hybrid mixture*. Hybrid mixtures represent a greater explosion hazard than that presented by the combustible dust alone due to the following reasons:

(i) Minimum energy is required for a hybrid mixture to explode and minimum explosible concentration are usually lower than dust–air mixtures alone.
(ii) A hybrid mixture may cause more severe explosion than dust–air mixtures alone.
(iii) Dryers and drying systems that can generate electrostatic charges must be properly bonded and grounded to drain off electrostatic charges and minimize the possibility of fires and explosions. Inerting is often needed to prevent such occurrences.
(iv) Many dusts are heat-sensitive and may decompose at high temperatures, resulting in an overpressure or fire. It is very important to determine if organic powders are thermally unstable and, if so, that they be tested for thermal stability to establish a safe operating temperature for the drying operation.
(v) Drying operations may give rise to toxic or flammable dusts, vapors and gases. Ignition of dust clouds/dust layers, deposits generated may be possible. Bulk powders may self-heat and ignite.
(vi) Large quantities of hazardous gases or vapors may be evolved due to decomposition of dried solids.

Adsorption

Definitions:

Adsorbent: It is the surface of the solid material.
Adsorbate: It is the gas or vapor contacting the adsorbent.
Adsorptive: It is the gas or vapor in the bulk phase.
Adsorption: It is the process describing the accumulation of material on the adsorbent surface.

Desorption: The adsorbate in the condensed phase passes from the surface (of the adsorbent) to the fluid phase.

Physical adsorption: In physical adsorption, solute is held by the solid surface by weak (van der waals) physical forces. Multilayer adsorption possible. Heat liberated is of the order of heat of condensation. Significant at relatively low temperatures.

Chemisorption: In chemisorption (also called activated adsorption), forces are stronger and of the order of forces existing in chemical reactions.

Monolayer Adsorption: Heat liberated is of the order of heat of reaction (> 2–3 times latent heat of adsorption), may involve dissociation of adsorbed species; and is possible over a wide temperature range. Electron transfer leading to bond formation between adsorbate and adsorbent. Adsorbed molecules loose their identity and can be irreversible.

Heat of adsorption: It is small and is of the same order as heat of vaporization (condensation).

Rate of adsorption: It is controlled by resistance to mass transfer; rapid rate at low temperatures; large, many times greater than the heat of vaporization (condensation); controlled by resistance to surface reaction; low rate at low temperatures; specificity is low for physical adsorption; entire surface availability for physical adsorption; high for chemical adsorption limited to active sites on the surface; surface coverage complete and extendable to multiple molecular layers for physical adsorption; incomplete and limited to a layer, one molecule thick for chemisorption; activation energy is low for physical adsorption; high for chemisorption, corresponding to a chemical reaction; quantity adsorbed per unit mass in physical adsorption is high; low for chemisorption. Figure 2.15 illustrates typical pores on adsorbents.

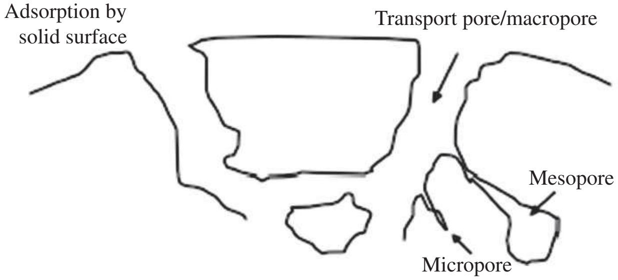


Figure 2.15 Types of pores on adsorbents

Molecular sieves: A molecular sieve is a material that can separate molecules based on size and shape. A sub-group of molecular sieves is zeolites. Molecular sieves are adsorbents composed of aluminosilicate crystalline microporous polymers (zeolites).

They efficiently remove low concentrations of polar or polarizable contaminants such as H_2O, methanol, H_2S, CO_2, COS, mercaptans, sulfides, ammonia, aromatics, and mercury down to trace concentrations. These are available in the form of beads, granules and extrudates, including standard pellets. Surface areas of molecular sieves range from 600,000 to 700,000 m^2/kg. Zeolite films have large potential in many application areas such as sensors, catalysts, and membranes. (zeolite is a crystalline aluminosilicate).

Applications of adsorption: Drying of gases, refrigerants, solvents, transformer oils, and so on. Silica gel is the common adsorbent used in these applications and as desiccant in packaging.

Removal of organics, acetone, $C_2H_{4,}$ and SO_2 from process off gases, removal of CO_2 and sulfur compounds from natural gas and other gas streams, separation of N_2 and O_2 from air, H_2 from synthesis gas/hydrogenation processes, normal paraffins from isoparaffins and aromatics, p-xylene from C_8 aromatics, fructose–dextrose mixtures, ethanol from ethanol–water azeotrope and dehydration of aqueous azeotropes, and so on. Carbons for odor control, recovery of solvent vapors, decolorizing syrups, sugars, and water purification (removal of phenols, halocarbons, pesticides, chlorine, etc.). Active clays for treatment of vegetable oils, lube oils, removal of organic pigments, and so on. Pollution control (removal of Hg, NO_X, and SO_X from gases). Polymers (usually copolymers) and resins are used for water purification, separation of aliphatics from aromatics.

Pressure swing adsorption: Adsorption is carried out at high pressures and desorption at low pressures by using two beds, one operating at pressures of several atmospheres and the other operating at atmospheric pressure as regenerator (by depressurization). Pressure swing gas adsorption process is primarily used for the dehydration of air and for the separation of air into nitrogen and oxygen. It is also used for hydrogen purification and separation of normal and isoparaffins.

Ion Exchange: Ion exchange is a chemical process that can be represented by a stoichiometric equation, for example, when ion A in solution replaces ion B in the solid phase: A (solution) + B (solid) + A (solid) + B (solution) Ion exchange processes function by replacing undesirable ions of a liquid with ions such as H^+ or OH^- from a solid material in which the ions are sufficiently mobile, usually some synthetic resin. The resin becomes exhausted on use and may be regenerated by contact with a small amount of solution with a high content of the desired ion.

Applications of ion exchange processes: Water demineralization, decolorization of sugar solutions, recovery of uranium from acid leach solutions, recovery of gold, silver, and platinum, recovery of antibiotics and vitamins from fermentation broth, pharmaceutical processing and formulations, artificial organs, solvent, and reagent purification, and so on.

Membrane Separations: Reverse osmosis, dialysis, electrodialysis, microfiltration, ultra filtration, and pervaporation are examples of membrane processes.

2.28 Stoichiometry

Stoichiometry deals with the relative quantities of reactants and products in chemical reactions. In a balanced chemical reaction, the relations among quantities of reactants and products typically form a ratio of whole numbers. For example, in a reaction that forms ammonia (NH_3), exactly one molecule of nitrogen (N_2) reacts with three molecules of hydrogen (H_2) to produce two molecules of NH_3:

$$N_2 + 3H_2 \rightarrow 2NH_3 \tag{2.39}$$

Stoichiometry can be used to calculate quantities such as the amount of products that can be produced with given reactants and percent yield (the percentage of the given reactant that is made into the product). Stoichiometry calculations can predict how elements and components diluted in a standard solution react in experimental conditions. Stoichiometry is founded on the law of conservation of mass: the mass of the reactants equals the mass of the products.

Reaction stoichiometry describes the quantitative relationships among substances as they participate in chemical reactions. In the example above, reaction stoichiometry describes the 1:3:2 ratio of molecules of nitrogen, hydrogen, and ammonia.

Composition stoichiometry describes the quantitative (mass) relationships among elements in compounds. For example, composition stoichiometry describes the nitrogen to hydrogen (mass) relationship in the compound ammonia: That is, one mole of nitrogen and three moles of hydrogen are in every mole of ammonia.

2.29 Combustion

Combustion is a fast chemical reaction involving a fuel and oxygen, with the liberation of heat. A flame is produced when the heat liberated is considerable. As the temperature of the reactants rises, ignition temperature, specific to the fuel, is reached and the combustion process begins, and spreads to the surrounding fuel–air mixture. When the heat loss is less than the heat liberated, an explosion can result. As combustion increases progressively, the flame front attains supersonic velocities, compression from the shock wave causes an increase in temperature and results in detonation. Most organic materials will burn, and carbon in the presence of excess oxygen, will produce carbon dioxide:

$$C + O_2 = CO_2 \tag{2.40}$$

As most fuels are hydrocarbons, products of combustion can be complex and depend upon nature of fuel, amount of oxygen present, and the temperature. A great deal of energy is required to break the carbon–carbon and carbon–hydrogen bonds Once the energy barrier is overcome, subsequent chain of events proceeds readily with the evolution of energy, often sufficient to maintain the combustion process. Simple hydrocarbons in excess oxygen will produce carbon dioxide and water vapor:

$$2C_2H_6 + 7\ O_2 = 4CO_2 + 6H_2O \tag{2.41}$$

If nitrogen and sulfur compounds are present, the products of combustion contain their oxides. In the absence of excess oxygen, incomplete combustion results in formation of carbon monoxide, aldehydes, ketones, phenols, and oxides of nitrogen. High temperature combustion will give rise to formation of oxides of nitrogen, NO_x. Since air comprises 21 percent O_2 and 79 percent N_2 with traces of other gases, complete combustion of methane in air can be represented by the equation:

$$CH_4 + 2O_2 + 8N_2 = CO_2 + 2H_2O + 8N_2 \tag{2.42}$$

Some materials, such as oily cotton rags, are prone to spontaneous combustion. Some metals like magnesium in powder or ribbon form, when subjected to heating to its melting point in the presence of oxygen burns, producing magnesium oxide. Pyrophoric iron sulfide, on exposure to air, glows red hot and act as a source of ignition and fires.

Flame Temperature

Flame temperature is an important consideration involving safety in boilers, fired heaters, incinerators and other fuel/waste burning equipments, as these can result tube/equipment failures, leading to leakages and fire and explosion propagation.

Adiabatic flame temperature is the (maximum) temperature obtained when a fuel is burning at a constant pressure with no heat loss (to walls, equipment, etc.) and no radiation losses from the flame. The maximum adiabatic flame temperature occurs close to the stoichiometric composition. Because this cannot be achieved in practice (given the inefficiencies of combustion) and is never achieved in a fire situation, adiabatic flame temperatures are calculated values. If all of the energy released by combustion reaction were used to raise the temperature of the products (CO_2, H_2O, and N_2) with no heat losses, the resultant temperature would be the adiabatic flame temperature, which represents the maximum possible theoretical temperature for a particular fuel/oxidant combustion. Table 2.2 gives adiabatic flame temperatures for selected fuels.

Table 2.2 Adiabatic flame temperatures of selected fuels, *K*

H_2	2525
CO	2660
CH_4	1446
C_2H_6	1502
C_2H_4	2562
C_2H_2	2910
C_3H_8	1554
C_3H_6	2505
n-Butane	1612
n-Octane	1632
n-Heptane	1692
n-Pentane	1564

2.30 Chemical Reactions

Enthalpy of Reaction

The standard enthalpy of reaction is the enthalpy change that occurs in a system when one mole of matter is transformed by a chemical reaction under standard conditions. The enthalpy change of any reaction under any conditions can be computed, given the standard enthalpy of formation of the reactants and products. The standard enthalpy of formation is used in thermo chemistry to find the standard enthalpy change of a reaction.

Limiting Reactant

Chemical reactions in which one of the reactants is used up before the others—the reaction stops as soon as one of the reactants is consumed. The reactant that is completely consumed in a chemical reaction is called the *limiting reactant (or limiting reagent)* because it determines (or limits) the amount of product formed.

Rate of Reaction

Although thermodynamics describes the energy requirements of a reaction, the speed at which it progresses is termed kinetics. It is important to be able to control the rate of chemical reactions for commercial and safety reasons. If a reaction takes too long to progress the rate at which a product is manufactured would not be viable. Alternatively, if reactions progress too fast and *runaway* out of control there could be dangers such as explosions. The rate at which reactions take place can be affected by the concentration of reactants, pressure, temperature, wavelength and intensity of light, size of particles of solid reactants, or the presence of catalysts (i.e. substances which alter the speed of reactions without being consumed during the reaction) or impurities. Catalysts tend to be specific to a particular reaction or family of reactions. Thus, nickel is used to facilitate hydrogenation reactions (e.g. add hydrogen to C == C, double bonds), whereas platinum is used to catalyze certain oxidation reactions. Sometimes, care is needed with the purity of reactants since impurities can act as unwanted catalysts; alternatively, catalysts can be inactivated by *poisoning*. The effect of temperature on different types of reactions is shown in Figure 2.16.

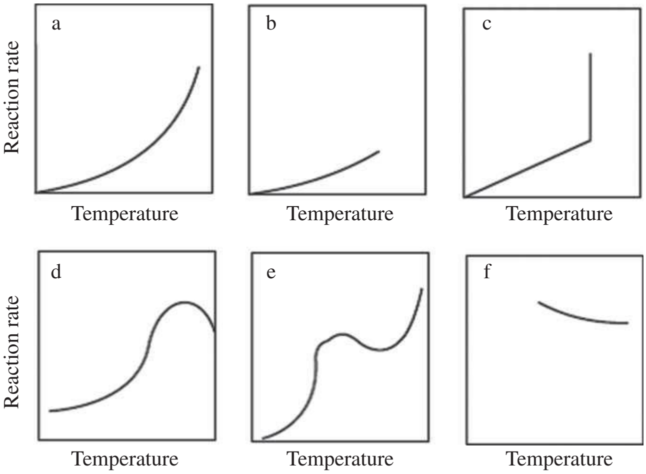


Figure 2.16 Types of reaction rate/temperature curve

Rapid increase with temperature—normal characteristic. Slow increase in rate with temperature—characteristic of some heterogeneous reactions. Very rapid increase at one point—the ignition point in an explosion. Decrease in rate at higher temperature—characteristic of catalytic reactions.

Decrease in rate at intermediate temperatures, followed by an increase. Slow decrease in rate with temperature. For reactions which progress slowly at room temperature it may be necessary to heat the mixture or add a catalyst for the reaction to occur at an economically viable rate. For very fast reactions the mixture may need to be cooled or solvent added to dilute the reactants and hence reduce the speed of reaction to manageable proportions. In general the speed of reaction doubles for every 10°C rise in temperature; is proportional to the concentration of reactants in solution; increases with decreased particle size for reactions involving a solid; increases with pressure for gas phase reactions.

Reaction rates can be affected by the concentration of the reactants, pressure, temperature, wave length and intensity of light, particle size of reacting solids, catalysts, or impurities present. It is important to be able to control speed of a reaction for safety and commercial reasons. If reactions become fast, control is lost and reaction *runaways* can result. For many exothermic homogeneous reactions,

$$\text{Rate of heat generation} \propto e^{RT_r} \qquad (2.43a)$$

where R is gas constant and T_r is absolute temperature.

If heat is removed through convective cooling,

$$\text{Rate of heat removal} \propto T_r - T_a \qquad (2.43b)$$

where T_a is coolant temperature. Since heat generation rate is exponential and removal rate is linear, for any exothermic reaction in a specific reactor configuration, a critical temperature condition may be reached, beyond which reaction *runaway* may occur. A slow reaction at ambient temperature may become fast as temperature is raised.

With some reactions such as polymerization, severe hazards may arise at elevated temperatures, as polymerization increases viscosity, which further reduces convective heat removal processes. Exothermic reactions may require provisions for control such as temperature control, dilution of reactants, evaporation cooling, controlled addition of one of the reactants, containment, venting, and provision for emergencies.

Many liquid phase or heterogeneous solid–liquid or gas–liquid reactions, may give rise to gaseous products, which may be toxic or flammable or result overpressurization of the containment vessel. Causes for pressurization may include reactions with water, contaminants, materials of construction, electrolytic corrosion, self-initiated reactions, decomposition, and the like. Provisions, such as pressure relief, may be required in such cases.

Activation Energy

Activation energy is defined as the energy that must be overcome in order for a chemical reaction to occur. Activation energy may also be defined as the minimum energy required to start a chemical reaction. For a chemical reaction to proceed at a reasonable rate, there should exist an appreciable number of molecules with energy equal to or greater than the activation energy. Understanding and control of runaway reactions is related to considerations involving activation energy. Activation energy is the energy barrier that the reactants must surmount in order to react. Therefore activation energy is viewed as an energetic threshold for a fruitful reaction.

Arrhenius Equation

The theory of the temperature effect on the reaction rate originated from the temperature effect on the equilibrium constant. It is known that

$$\mathrm{dln}K/d(1/T) = -\,H/R \qquad (2.44)$$

where K is an equilibrium constant, R is the gas constant, and H is the heat of reaction. The equilibrium constant is $K = k_1/k_2$, where k_1 and k_2 are the rate constants for the forward and reverse reactions respectively. Substituting the relationship into Eqn. (2.43), one obtains:

$$d \ln k_1/d(1/T) = -\, d \ln k_2/d(1/T) = -\, H/R \tag{2.45}$$

Arrhenius recognized that Eqn. (2.45) could be conveniently divided into two parts, each having the form of:

$$\mathrm{d} \ln k/d(1/T) = -\, E/R \tag{2.46}$$

where E is referred by Arrhenius as representing the energy difference between the reactants and an activated species. The term E is therefore called the activation energy. Taking E as a constant, Eqn (2.46) can be integrated to yield the following relation:

$$\ln k = \ln A - E/RT \tag{2.47}$$

where ln A is the constant of integration. Eqn. (2.47) can be converted to

$$k = Ae^{-E/RT} \tag{2.48}$$

which is the most widely adopted form of the Arrhenius equation. The term A is the *pre-exponential factor*. This is related to the frequency of molecular collisions in the collision theory and to the entropy term in the transition state theory.

Arrhenius equation is of use in stability testing involving pharmaceutical manufacture and other chemical reaction systems. In the isothermal method, the system to be investigated is stored under several high temperatures with all other conditions fixed. Excess thermal exposure accelerates the degradation and thus allows the rate constants to be determined in a shorter time period.

Dissociation

Dissociation in chemistry and biochemistry is a general process in which ionic compounds (complexes or salts) separate or split into smaller particles, ions, or radicals, usually in a reversible manner. For instance, when a Bronsted–Lowry acid is put in water, a covalent bond between an electronegative atom and a hydrogen atom is broken by heterolytic fission, which gives a proton and a negative ion. Dissociation is the opposite of association and recombination. The process is frequently confused with ionization.

Dissociation Constant: For reversible dissociations in a chemical equilibrium

$$AB \rightleftharpoons A + B \tag{2.49}$$

The dissociation constant, K_d, is the ratio of dissociated to undissociated compound:

$$K_d = [A][B]/[AB] \tag{2.50}$$

where the brackets denote the equilibrium concentrations of the species.

Polymerization

Any process in which relatively small molecules, called *monomers*, combine chemically to produce a very large chain-like or three-dimensional network molecule, is called a polymer. The monomer molecules may be all alike, or they may represent two, three, or more different compounds. Usually at least 100 monomer molecules must be combined to make a product that has certain unique physical properties—such as elasticity, high *tensile strength*, or the ability to form fibres—that differentiate polymers from substances composed of smaller and simpler molecules; often, many thousands of monomer units are incorporated in a single molecule of a polymer. There are many forms of polymerization and different systems exist to categorize them.

Nitration

Nitration is a general chemical process for the introduction of a nitro group into a chemical compound. The dominant application of nitration is for the production of nitrobenzene, the precursor to methylene diphenyl diisocyanate. Nitrations are famously used for the production of explosives, for example the conversion of glycerin to nitroglycerin and the conversion of toluene to trinitro toluene (TNT).

Alkylation

Alkylation is the transfer of an alkyl group from one molecule to another. The alkyl group may be transferred as an alkylcarbocation, a free radical, a carbonium or a carbene (or their equivalents). Alkylating agents are widely used in chemistry because the alkyl group is probably the most common group encountered in organic molecules. Many biological target molecules or their synthetic precursors are composed of an alkyl chain with specific functional groups in a specific order. Selective alkylation, or adding parts to the chain with the desired functional groups, is used, especially if there is no commonly available biological precursor. Alkylation with only one carbon is termed methylation. In oil refining contexts, *alkylation* refers to a particular alkylation of isobutane with olefins. It is a major aspect of the upgrading of petroleum.

Review Questions

1. (a) How does specific gravity of a liquid have a bearing on safety? Explain.
   (b) What happens if a flammable liquid spills over water? What could be the consequences of such spills?
2. (a) Give the limitations of Antoine equation for the estimation of vapor pressures.
   (b) Name some correlations based on corresponding state principle for the estimation of vapor pressures of pure components. What is their advantage over Antoine equation?
3. What are the consequences of stratification of liquids in the absence of agitation? Give an example of an accident that caused such an event.
4. What are the hazards that can arise in plant operations involving high or low vapor densities? Explain how emergency spills contribute to such hazards.
5. Ammonia vapor is lighter than air and rises upward on escape from a vessel. Under what circumstances does it become heavy and reaches ground level?
6. (a) What are the differences between Newtonian and non-Newtonian fluids?
   (b) What are the types of non-Newtonian fluids?
7. What safety issues are involved in handling high viscosity liquids? Give examples.
8. (a) What is pyrophoric iron sulfide? In what type of situations can these be found, and in what way are these troublesome?
   (b) What are the precautions in removing deposits of this material from cleaning operations?

9. (a) What is rheology? How it is related to viscosity?
   (b) Name the air pollution phenomena associated with viscosity.
10. What are the hazards that pose operational problems in industrial processes?
11. How does viscosity of a gas change with temperature? Why?
12. What is turbulence? Does it influence viscosity?
13. (a) What is water hammer? Give examples illustrating origins of water hammer.
    (b) What are the damaging effects of water hammer?
14. (a) What is cavitation? How does it influence pump performance?
    (b) What are the different types of cavitation?
15. Name different types of two phase flow. Describe their phenomena.
16. What is the maximum velocity attainable for a fluid in a pipe? What is Mach number?
17. What are dielectric properties? How are electrostatic problems related to dielectric properties?
18. How does surface tension influence droplet formation? How is fogging of liquids influenced by surface tension? What undesirable activity such as spraying of pesticides is related to surface tension? Is such spraying desirable with flammable liquids?
19. How do evaporation rates of liquids influenced by vaporization? Name some equations for the estimation of vapor pressures.
20. What is Reid vapor pressure? In what way is it different from absolute vapor pressure?
21. (a) What is the utility of *K*-values?
    (b) State Raoult's and Henry's laws? On what types of systems are these applicable?
22. How does enthalpy change on mixing influence safety? Give an example.
23. (a) What is Joule–Thomson effect? How is it useful in liquefaction processes?
    (b) What hazards are posed from expansion of hydrogen from hydrogen leaks from high pressure equipment? How such hazards are related to Joul–Thomson effect? Explain.
24. How does heat of vaporization influence safety in dousing fires? Explain both positive and negative aspects.
25. How can vaporization in confined spaces be hazardous?
26. What can happen on sudden cooling of atmospheric storage tanks?
27. What are the hazards involved in handling molten metals?
28. What are the hazards involved in depressurization processes?
29. How does freezing of water in piping exposed to cold weather conditions, particularly in cold countries?
30. What is the necessity for providing expansion joints in piping? Is it necessary to provide such joints in plastic piping?
31. What are the ill-effects of exposing piping carrying viscous liquids through pipelines exposed to cold weather conditions?
32. What are the laws governing heat conduction, momentum transfer, mass transfer, and electrical energy transfer?
33. What is the difference between natural and forced convection? Give examples.
34. What is Linde boiling surface? How does it influence the boiling phenomena?
35. Explain the phenomena of nucleate boiling, film boiling, pool boiling, and flow boiling.
36. What is Leidenfrost phenomena?
37. What are the hazards that are possible from condensation of water vapors?

38. Name different mass transfer operations involved in industrial operations?
39. What are the applications of absorption processes in pollution control and emergency situations? Why Bhopal tragedy took place despite provision of an emergency absorber?
40. What is reactive absorption? What are its advantages and applications?
41. What are the hazards involved in pressure and vacuum distillation processes? What safety measures are incorporated in these distillation processes?
42. With respect to inventories of hazardous liquids in distillation units, what are the relative advantages of kettle or thermosiphon-type reboilers?
43. (a) What are the inherent hazards involved in the process of distillation?
    (b) Are there any alternative processes for separation of liquid mixtures?
44. Give examples involving separation processes.
45. How are lower operating temperatures are achieved in a distillation process?
46. What are the consequences of water entry in the bottom section of a distillation column involving high boiling liquids?
47. (a) Give examples of liquid–liquid extraction processes.
    (b) What is leaching?
48. (a) What are the factors that restrict productivity and purity of crystals in a crystallization process?
    (b) What is sonocrystallization?
49. (a) What are hygrometers?
    (b) What are the different types of water cooling equipment used in industrial water cooling systems?
    (c) What are the hazards involved in cooling tower operation?
50. What are the causes of explosions in industrial dryers?
51. (a) What are molecular sieves?
    (b) What are the applications of adsorption processes?
52. What is reverse osmosis? Illustrate.
53. What is pervaporation? Explain.
54. Briefly describe microfiltration, ultrafiltration, dialysis, and electrodialysis. State their applications.
55. What is adiabatic flame temperature?
56. (a) What is limiting reactant?
    (b) What are the likely hazards involved in liquid phase or solid-liquid reactions?
    (c) What are the causes of over-pressurization in chemical reactors?
57. What is activation energy? Give Arrhenius equation and state its significance and usefulness.
58. What are the hazards involved in carrying out nitration processes?

Key words for Internet searches

Activation energy; adiabatic flame temperature; membrane separation processes; sonocrystallization; pervaporation; reboilers; hazards of distillation operations; Linde boiling surface; Joule–Thomson effect; pyrophoricity.

Note: *Vast number of sites are given in Appendix A of the book for the purpose of use in Internet searches for keywords by enterprising teachers, students, industry professionals, and managements.*

Chapter 3

Material Hazards

Learning Objectives

3.1 Introduction

Hazard is a potential condition or set of conditions, either internal and/or external to a system, product, facility, or operation, which when activated transforms the hazard into a series of events that culminate in loss (an accident). A simpler and more fundamental definition of hazard is a condition that can cause injury or death, damage to or loss of equipment or property, or environmental harm.

Several types of hazards exist in the processing, handling, transportation and storage of a variety of chemicals, their mixtures, and other materials. Chemical industry, being one of the highly energy-intensive industries, most of the hazards might be related to one form of energy or other.

Hazards may arise out of inherent characteristics of the materials and their mixtures under different conditions of their existence, which will be discussed as *material hazards*, or during process operations involving high or low pressures and temperatures or deviations from intent, or characteristic of the process itself, which will be discussed as *process hazards*.

Some of the general hazards associated with different forms of energy in chemical processing are summarized in Table 3.1.

Table 3.1 Hazards associated with different forms of energy

Form of energy	***Associated hazard(s)***	***Typical accidental event(s)***
Chemical	Flammability	Vessel failure on ignition of vapors.
Energy	–	Unconfined vapor cloud explosion (UVCE)
	–	Boiling liquid expanding vapor explosion (BLEVE)

(*Continued*)

Table 3.1 (Continued)

	–	Flash fire/pool fire
Combustibility	–	Bulk material fire; dust explosion; flash fire of vapors from heated combustible solid or liquid
–	Pyrophoricity	Fire on contact with air
–	Ability to self-polymerize	Uncontrolled polymerization and heat release
–	Shock-sensitivity	Detonation of explosive mixture
–	Thermal instability	Thermal explosion due to self-heating
–	Peroxidizing ability	Contact with oxygen over time; energetic peroxide decomposition
–	Oxidizing or reducing ability	Contact with oxidizer; bulk material fire
–	Increased reactivity	Contact with incompatible material, heat, pressure, or toxic gas generation
–	Reduced reactivity	Personnel entry into confined space with reduced oxygen (inerting) level; uncontrolled redox reaction
–	Water reactivity	Reaction on contact with water or humidity
–	Acidity or causticity	Acid gas release (e.g. anhydrous HCl); corrosive liquid or solid spill; uncontrolled acid/base reaction
–	Toxicity	Toxic material release.
Thermal energy	High temperature –	Hot Material release; hot surface contact. Steam explosion vessel rupture from thermal expansion of blocked-in fluid
–	Low temperature	Cryogenic release; failure of embrittled material
Pressure	Gas/vapor at	Tank rupture
Volume	High pressure	High velocity leak
Energy	Liquefied gas/vapor under pressure	Rapid phase transition; BLEVE.
–	Gas/vapor at low pressure	Tank collapse.
Potential energy	Process material at elevated position	Toppling over of stacked drums. Falling material from spill/over-flow. Fluid surge from failed container.
Kinetic energy	Moving process material Impingement by process material. Water hammer	Over-pressure/temperature

(*Continued*)

Table 3.1 (Continued)

Form of energy	*Associated hazard(s)*	*Typical accidental event(s)*
Electrical energy	High voltage	Electric shock
Radiation	High electromagnetic radiation levels	Unshielded laser/microwave radiation associated with process

Source: DOE handbook 1100–2004, Chemical Process Hazards Analysis, August 2004.

Table 3.2 Some potentially hazardous processes and operations

Involving intrinsically unstable compounds/potentially unstable reactions/undesirable side reactions, e.g. spontaneous heating/combustion/polymerization/decomposition
Which are highly exothermic with reaction runaway hazards
Subject to explosive reaction or detonation
Subject to dust/mist/vapor explosion hazards
Involving highly toxic materials, dangerous bacteria or radio-active materials
Operating in or near explosive range of materials
With large inventories of stored pressure energy
Side reactions capable of producing toxic/explosive/corrosive materials or other hazardous wastes or causing dangerous fouling
Involving violent reactions with water or common contaminants
React energetically with water
Incompatibility with common materials of construction
Containing flammables and operated at high temperature/low temperature/high pressure
Processes subject to spontaneous polymerization/heating
Examples of potentially hazardous processes include *hydrogenation* (addition of hydrogen atoms to both sides of a double or triple bond)
Hydrolysis (reaction of a chemical with water)
Isomerization (re-arrangement of atoms within a molecule)
Sulphonation (introduction of an SO_3H radial into an organic molecule, e.g. by reaction with H_2SO_4)
Neutralization (reaction between acid and base)
Alkylation (addition of alkyl group to a compound)
Esterification (reaction between alcohols and acids)
Oxidation (combination of oxygen with substances)
Polymerizations (linking small molecules to produce large ones)
Condensations (joining together two or more molecules with elimination of water)
Halogenations (substitution of, for example, H atoms in organic molecules by halogen)
Operations

(*Continued*)

Table 3.2 (Continued)

Involving high or low temperatures/pressures of unstable liquids. Higher temperatures increase reaction rates with increase in heat release rates in exothermic processes and volume and pressure rises. Low temperatures cause brittle fracture of materials of construction, freezing of liquids in exposed piping and loss of confinement
Involving flammable liquids above their boiling points
Involving vaporization/diffusion of flammable/toxic liquids/gases. Start-ups and shut-downs giving rise to hazards such as rapid flashing of water to steam. Unplanned introduction of water into hot oil systems is an example of rapid flashing, as water has great potential than hydrocarbons in generating large volumes of vapors
Involving mixing of flammable/combustible materials with strong oxidizing agents. This hazard arises especially during start-up and shut-downs. Involving poor mixing/mal-distribution of reactants or difficult heat removal conditions, e.g. due to high viscosity of the liquids
Involving sprays/mists/fogs of flammable or strong oxidizing agents
Involving formation of combustible/toxic dust clouds
Involving separation of hazardous materials from diluents/inerts
Loss of power, steam, cooling water, boiler feed water or instrument air or mal-function of level controls

Partial source: Batch reactor hazards and their control by Phillip Carson and Clive Mumford, IChemE, 2003.

3.2 Hazardous Substances—Categories

United Nations Classification for Transport

1 *Explosives*
  1.1 Substances and articles that have a mass explosion hazard
  1.2 Substances and articles that have a projection hazard but not a mass explosion hazard
  1.3 Substances and articles that have a fire hazard and either a minor blast hazard or a minor projection hazard but not a mass explosion hazard
  1.4 Substances and articles which present no significant hazard
  1.5 Very insensitive substances that have a mass explosion hazard
  1.6 Extremely insensitive articles that do not have a mass explosion hazard
2 *Gases*
  2.1 Flammable gases
  2.2 Nonflammable, nontoxic gases
  2.3 Toxic gases
3 *Flammable liquids*
4 *Flammable solids*
  4.1 Flammable solids
  4.2 Substances liable to spontaneous combustion
  4.3 Substances which in contact with water emit flammable gases

5 *Oxidizing substances, organic peroxides*
  5.1 Oxidizing substances
  5.2 Organic peroxides
6 *Poisonous/toxic substances*
  6.1 Toxic substances
  6.2 Infectious substances
7 *Radioactive material*
8 *Corrosive substances*
9 *Miscellaneous hazardous substances*

3.3 Toxicity

Toxic hazards directly affect human health, whereas fire hazards affect, to a greater extent, property damage. Accidental release of toxic materials into the environment is one of the worst accidents of the chemical industry. Release of methyl isocyanate (MIC) at the Union Carbide pesticides plant at Bhopal, India killed thousands of people, which additionally caused/causing permanent damage to human life, is a well known example involving toxicity. Chernobyl accident which involved release of radioactive materials is another incident of radioactive toxic material. Release of mercury into river waters in Japan, is another example of toxic hazard which forced caustic soda industry to ban mercury process which was replaced by membrane processes. Enforcing tighter controls by PVC industry on fugitive emissions of vinyl chloride monomer, a carcinogenic substance, banning DDT and asbestos are other examples involving toxic materials. There are thousands of toxic materials processed and used by the society, in addition to the naturally occurring ones.

Toxic materials can be of chemical or physical nature. Toxics of chemical nature are classed according to the types of their toxic effects, for example, mutagenic, teratogenic, carcinogenic, corrosive, irritant, sensitizers, and so on. Those which can be considered to be causing physical effects include dusts, fibers, noise, and so on. Some common toxic substances in the environment are briefly discussed below.

PCBs: Polychlorinated biphenyls (PCBs) cause a wide variety of health effects, often at very low exposure levels. Some have properties such as dioxin (one of the most toxic man-made compounds in the world. Dioxins are a group of chlorinated organic chemicals with similar chemical structures). Some PCBs act like hormones and others are nerve poisons. PCBs alter major systems in the body immune, and therefore, affect a wide variety of body organs and functions. Human exposure to dioxins can cause slow development (both, physical and mental, especially motivation), as well as reproductive and immune dysfunction. It is also strongly indicated that dioxins promote cancer, by making its proliferation easier (in other words, they do not create cancer cells, but do create favorable conditions for their expansion).

Lead: Over-exposure to lead is one of the most common overexposures found in industry and is a leading cause of work place illness. Lead accumulates in blood, bones, kidneys, liver, brain, and other parts of human body, and inorganic lead compounds are well known to cause significant health effects following long term (chronic) exposure. If a significant amount of lead has accumulated in the body, symptoms of long-term toxicity may develop after what may seem to be a short-term acute exposure.

Mercury: When elemental mercury is released into the environment, either from the atmosphere or from industrial or other human sources, bacteria in rivers and lakes may convert the metal into the organic form, called methyl mercury. This form of the metal is assimilated by larger organisms when they consume the bacteria and mercury begins its journey up the food chain. Symptoms of acute mercury poisoning include numbness or tingling in the fingers, toes, and mouth, headache; memory or hearing loss; visual or speech disorders; and lack of coordination. In the most severe cases, it can lead to coma and death.

Pesticides: Hazard of using pesticides is the potential for injury, or the degree of danger involved in using a pesticide under a given set of conditions. Hazard depends on the toxicity of the pesticide and the amount of exposure to it. By understanding the difference in toxicity levels of pesticides, a user can minimize the potential hazard by selecting the pesticide with the lowest toxicity that will control the pest. For example, organophosphates may cause acute or chronic poisoning. Suspected chronic effects from exposure to certain pesticides include birth defects, toxicity to a foetus, production of benign or malignant tumors, genetic changes, blood disorders, nerve disorders, endocrine disruption, and reproduction effects. The symptoms of pesticide poisoning can range from a mild skin irritation to coma or even death. Different classes or families of chemicals cause different types of symptoms. Individuals also vary in their sensitivity to different levels of these chemicals. The effects, or symptoms, of pesticide poisoning can be broadly defined as either topical or systemic. Dermatitis, or inflammation of the skin, is accepted as the most commonly reported topical effect associated with pesticide exposure. Systemic effects often include nausea, vomiting, fatigue, headache, and intestinal disorders. In advanced poisoning cases, the individual may experience changes in heart rate, difficulty in breathing, convulsions, and coma, which could lead to death.

Solvents and petroleum products: These substances are serious toxins and usually cause symptoms after the fumes have been accidentally inhaled. The symptoms are drowsiness, dizziness, nausea, and occasionally vomiting. If severe exposure occurs, the patient may become unconscious. If they are swallowed, they usually produce the same symptoms, but nausea, and vomiting are worse. They may also enter human body through skin contact. Many are carcinogens and central nervous system poisons. They should be avoided.

Chlorine: Both acute and chronic exposures to chlorine vapors can be unhealthy.

Nickel carbonyl, $Ni(CO)_4$: is one of the most poisonous inorganic compounds. Both nickel and CO, both being themselves poisonous, add to the poisonous effects of nickel carbonyl. Nickel in catalysts is the source of nickel carbonyl formation in reactors and other process equipment. Many hazardous incidents took place in refineries, ammonia plants, hydrogenation units for oils and fats plant shut-down conditions are most favorable for nickel carbonyl formation.

Vanadium poisoning: Residual fuel oils may contain 10–600 ppm by weight of vanadium. V_2O_5 give rise to acute poisoning. TLV is 0.5 mg/m^3 air in dust form and 0.1 mg/m^3 as fumes. Furnace cleaning operations and cleaning chambers containing spent catalyst involve the risk of exposure to vanadium dusts.

Introduction to Toxicology

Toxicology refers to the study of adverse effects of chemicals on human health, whereas *toxicity* is a measure of degree of harmful nature of a substance.

Poisons and toxins: A chemical is said to be a poison if it causes some degree of metabolic disfunction in organisms. Strictly speaking, a toxin is a poisonous chemical of biological origin, being produced by a microorganism, plant, or animal. In common usage, however, the words *poison* and *toxin* are often used interchangeably. It is important to understand that potentially, all chemicals are toxic. All that is required for a chemical to cause toxicity, is a dose (or exposure) that is large enough to affect the physiology of an organism. *Neurotoxins* are chemicals that attack nerve cells, examples being chlorinated hydrocarbons, organophosphate pesticides, formaldehyde, heavy metals and industrial solvents.

Biological hazards which cause *transmissible diseases* like acute respiratory infections, diarrhea, tuberculosis, malaria, AIDS, Hepatitis B, and measles. These are caused by living organisms such as pathogens, for example, bacteria, viruses, parasites, and protozoa.

Biological hazards which cause also *nontransmissible diseases* such as cardiovascular disorders, cancer, diabetes, malnutrition, bronchitis, etc. If an exposure to a chemical is to cause poisoning, it must result in a dose that exceeds a threshold of physiological tolerance. Smaller exposures to the same chemical do not cause poisoning, at least not on the short term.

Species of plants, animals, microorganisms, and humans differ enormously in their tolerance of exposures to potentially toxic chemicals. Even within populations of the same species, there can be substantial differences in sensitivity to chemical exposures. Some individuals, for example, may be extremely sensitive to poisoning by particular chemicals, a phenomenon known as *hypersensitivity*.

Because chemicals are present everywhere, all organisms are continuously exposed to potentially toxic substances. In particular, the environments of modern humans involve especially complex mixtures of chemicals, many of which are synthesized through manufacturing and are then deliberately or accidentally released into the environment. People are routinely exposed to potentially toxic chemicals through their food, medicine, water, and the atmosphere.

Toxicity can be expressed in many ways. Some measures of toxicity examine biochemical responses to exposures to chemicals. These responses may be detectable at doses that do not result in more directly observed effects, such as tissue damage, or death of the organism.

Many poisonous chemicals are present naturally in the environment. For example, metals and other elements are widespread in the environment, but under some circumstances they may occur naturally in concentrations that are large enough to be poisonous to at least some organisms. Examples are exposures of minerals containing large concentrations in natural environment. In the modern world, humans are responsible for many of the toxic chemicals that are now being dispersed into the environment. In some cases, humans are causing toxic damages to organisms and eco-systems by emitting large quantities of chemicals that also occur naturally, such as sulfur dioxide, hydrocarbons, and metals.

***Mode of entry of toxic substances into human body*:** Major *routes* of exposure are through the skin (topical), through the lung (inhalation) or through the gastrointestinal tract (ingestion). In general, inhalation is likely to cause more damage than ingestion, which, in turn, is more harmful than skin exposure.

Skin absorption: This is the least likely route of penetration since the natural thickness of the skin plus its natural coating of grease and sweat provide some protection against chemicals. However, some materials are capable of penetrating intact, healthy skin, for example, aniline, hydrogen cyanide, some steroid hormones, organic mercury compounds, nitrobenzene, organophosphate compounds, and phenol. Phenol itself can be lethal if absorbed for a sufficient time through a few square centimeters of skin and inappropriate protective clothing, for example, incorrect gloves may cause absorption rate to increase. The natural protection of the skin may also be bypassed through cuts, abrasion or puncture wounds for example, needle-stick injury.

Inhalation: Gases and vapors, aerosols and fumes are readily inhaled and may cause harm (including asphyxiation) anywhere in the respiratory system and may also be absorbed into the blood stream, but inhalation of particles depends on their size and shape, the smaller the particle, the further into the respiratory tract they can go. Large particles are filtered off in the nose. Smaller particles, or those breathed in by mouth, settle on the walls of the upper respiratory tract or throat and are coughed up and either ejected or swallowed. If swallowed, they may enter the digestive system and cause damage as if they had been ingested. The smallest particles of dust and fibers can be inhaled down into the lungs where they can cause local damage, sometimes by interaction with the cells in the lungs which normally remove bacteria. These particles may also be absorbed into the blood stream. Particles $< 5\ \mu$ m are readily inhaled.

Ingestion: Airborne particles that are eventually swallowed are the most likely source of ingested chemical. Otherwise, ingestion of potentially toxic substances is likely to be accidental on contaminated food, drink, or make-up. Once absorbed through the stomach or intestine, the route to excretion may be complex and damaging.

Measures of Toxicity

Toxicity of chemicals is determined in the laboratory. The normal procedure is to expose test animals by *ingestion*, application to the *skin or eye absorption, inhalation*, or some other method which introduces the material into the body, or by placing the test material in the water or air of the environment of the test animals.Toxicity is measured in terms of mortality (death), teratogenicity (ability to cause birth defects), carcinogenicity (ability to cause cancer), and mutagenicity (ability to cause heritable change in the DNA). Teratogens are chemicals, radiation, viruses that cause birth defects during development of human embryo. Examples include PCBs, phthalido amide, steroid hormones, and heavy metals. Carcinogens are chemicals, radiation, and viruses that cause/promote growth of malignant tumors. Mutagens are chemicals that cause mutations. Example is radioactive substances.

Dose and response: *Dose* is the amount of a potentially harmful substance a person has ingested, inhaled, or absorbed, whereas *response* is the amount of damage to health for a given dose. Dose–response is a relationship between exposure and health effect. Some such measures are given in Table 3.3.

Table 3.3 Measures of toxicity

Parameter	*Description*
Median lethal dose, LD_{50}	The amount (dose) of a chemical that produces death in 50 percent of a population of test animals to which it is administered by any of a variety of methods and expressed as mg of substance per kg of the body weight of the test animal. The period of exposure is 4 hr and observation period is 14 days.
Median lethal concentration, LC_{50}	The concentration of a chemical in an environment (generally air or water) which produces death in 50 percent of an exposed population of test animals in a specified time frame, expressed as milligrams of substance per liter of air or water (or as ppm).
Lethal dose low, LD_{LO}	Lowest dose reported to have caused death in animals/humans.
Toxic concentration low, TC_{LO}	Lowest concentration reported to have produced any toxic effect.
Threshold limit value, TLV	TLV is a level to which it is believed a worker can be exposed of a chemical substance day after day for a working life time without adverse health effects. TLV for chemical substances is defined as a concentration in air, typically for inhalation or skin exposure. Its units are in ppm of air for gases and in milligrams per cubic meter (mg/m^3) for particulates such as dust, smoke, and mist. TLVs are recommended values by American Conference of Governmental Industrial Hygienists (ACGIH)
Types of TLVs:	–
Time weighted average TLV_{TWA},	Average exposure on the basis of a 8 hr/day, 40 hr/week work schedule
Short term exposure limit, TLV_{STEL}	Spot exposure for a duration of 15 min, that cannot be repeated more than 4 times per day

(*Continued*)

Table 3.3 (Continued)

Ceiling limit, TLV_C	Absolute exposure limit that should not be exceeded at any time
Excursion limits	There is a general excursion limit recommendation that applies to those TLV_{TWA}s that do not have TLV_{STEL}s. Excursions in worker exposure levels may exceed 3 times the TLV_{TWA} for not more than a total of 30 min during a work day and under no circumstances should they exceed five times the TLV_{TWA}, provided that the TLV_{TWA} is not exceeded.
Permissible exposure limits, PELs	These are regulatory limits on the amount or concentration of a substance in air and are enforceable.
Biological limit values, BLVs	BLV is a reference value presented as the concentration in the appropriate biological medium of the relevant agent, its metabolite, or indicator of effect.
	BLVs refer to limiting values of substances to which a worker may be exposed without any health hazard. BLVs are reference values for the evaluation of potential health risks in the practice of industrial hygiene. BLVs are representative of the levels of determinants which are observed in workers exposed to the respective chemical, exclusively by inhalation. BLVs do not indicate a sharp distinction between hazardous and nonhazardous exposures. Due to biological variability, it is possible for an individual's measurement to exceed the BLV without there being an increased health risk.
Immediately dangerous exposed to a life or health IDLH	The maximum level to which a healthy individual can be exposed to chemical for 30 min and escape without suffering irreversible health effects or impairing symptoms. The term IDLH is defined by Occupational Safety and Health Administration of U.S. (OSHA) as an atmosphere that poses an immediate threat to life, would cause irreversible adverse health effects, or would impair ability of an individual to escape from a dangerous atmosphere. The OSHA definition is part of a legal standard, which is the minimum legal requirement. National institute for occupational safety and health (NIOSH) definition: IDLH condition is one that poses a threat of exposure to airborne contaminants when that exposure is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment. IDLH values are often used to guide the selection of breathing apparatus that are made available to workers or fire fighters in specific situations.

Notes: LD_{50} < 1 mg/kg → Extremely toxic> 15 mg/kg → Relatively harmless. TLVs are only guidelines framed based on available information and are often changed based on new/upto date information/evidence. For example, for ethylene dichloride TLV is reduced from 20 to 10 ppm and for vinyl chloride monomer from 200 ppm (1973), 10 ppm (1975), and present 1.0 ppm. TLVs do not provide a relative index of hazard.

For example, TLV for SO_2 is 2.0 ppm based on its irritation and for vinyl chloride monomer it is 1.0 ppm based on its potential for cancer. These values do not indicate that vinyl chloride monomer is considered to be twice as toxic as SO_2.

BLVs are determined based on two types of medical tests:

(i) Quantities of chemical in tissues and body fluids such as blood, urine and exhaled breath.
(ii) Physiological responses in terms both biochemical constituents of body and effects on body functions.

BLVs may be used to compliment or in some cases, replace TLVs.

There are TLVs for physical agents as well as chemical substances. TLVs for physical agents include those for noise exposure, vibration, ionizing and nonionizing radiation exposure, and heat and cold stress.

ACGIH TLVs do not have a legal force in the USA. They are only recommendations. Occupational Safety and Health Administration (OSHA) of the U.S. Department of Labour (USDOL) publishes permissible exposure limits (PEL). ACGIH exposure limits are in many cases more protective than those of OSHA. The National Institute for Occupational Safety and Health (NIOSH) has the statutory responsibility for recommending exposure levels that are protective to workers. Other exposure limits published by US organizations include the following:

The American Industrial Hygiene Association (AIHA); The Mine Safety and Health administration (MSHA); The American National Standards Institute (ANSI); The U.S. Navy.

Toxic effects are expressed in terms of duration of doses, namely, *acute, chronic*, or *subchronic* categories. *Acute effects* are due to accidental exposures—high concentrations over short periods. *Chronic effects* are due to exposure in normal work environments, that is, after repeated/regular exposure to low concentrations over long periods of time (for a time greater than half of its life expectancy). *Sub-chronic effects* are due to repeated applications for a time frame less than half the life expectancy of the organism—but more often than a single dose or multiple doses are applied for only a short time.

Table 3.4 gives values of LD_{50} for some substances.

Table 3.4 LD_{50} values for selected substances

Substance	***LD_{50} value (mg/kg) body weight***
Dioxin	20 ppb
Nerve gas	60 ppb
HCN	1
Parathion	2
Potassium cyanide	5
Nicotine	15
Mercury	26
Chromium	30
Sodium oxalate	155

(*Continued*)

Table 3.4 (Continued)

Caffeine	192
Phenol	414
Chloral hydrate	479
Acetyl salicylic acid	1,000
Aspirin	1,750
Table salt	3,750
Dimethyl formamide	2,800
Trichloroacetic acid	5,000
Methanol	13,012

Notes: The lower the LD_{50} dose, the more toxic the substance. For example, a pesticide with an LD_{50} value of 10 mg/kg is 10 times more toxic than a pesticide with an LD_{50} of 100 mg/kg.

Table 3.5 gives TLV and IDLH values for selected chemicals.

Table 3.5 TLVs and IDLH values for selected chemicals, ppm

Material	TLV_{TWA}	TLV_{STEL}	***IDLH***
Acetic acid	10	15	50
Ammonia	25	35	300
Arsine	0.05	–	3
Benzene	0.5	2.5	500
Bromine	0.1	0.2	3
Carbon dioxide	5,000	30,000	40,000
Carbon monoxide	25	–	1,200
Chlorine	0.5	1	10
Ethanolamine	3	6	30
Fluorine	1	2	25
Hydrogen cyanide	10	4.7	–
(OSHA TWA skin contact)			
Hydrogen sulfide	10	15	100
LPG	1,000	–	–
Mercury	0.025 mg/m³	1 mg/m³	10 mg/m³
ACGIH (TWA)	Ceiling (vapor) (OSHA)	(vapor)	
Methyl alcohol	200	250	6,000
Methyl ethyl ketone	200	300	3,000

(*Continued*)

Table 3.5 (Continued)

Methyl isocyanate (MIC)	0.02	–	–
Naphthalene	10	15	250
Nickel carbonyl	0.05 (ACGIH$_{TWA}$)	–	–
(One of the most poisonous 0.001 (OSHA TWA) inorganic compounds. Both Ni and CO are involved)			
Nitric acid	2	4	25
Phosgene	0.1	–	2
Phosphine	0.3	1	50
Potassium cyanide	–	5 mg/m^3	–
NaOH	2 mg/m^3	–	–
Sulfur dioxide	2	5	100
Toluene	200	100	150
Toluene diisocyanate	0.005	0.02	2.5
Trichloroethylene	50	100	1,000
VCM	1	–	–

Types of Toxic Effects

Toxic effects depend on nature of material, its physical state, frequency and duration of exposure, and concentration of the material. Most toxic substances can be classified as asphyxiants, irritants, narcotics, systemic poisons, neurotics, hypnotics, anesthetics, carcinogens, sensitizers, mutagens, and/or teratogenic substances. Systemic poisons may be further segregated into the categories of hepatotoxic agents, nephrotoxic agents, neurotoxic agents, agents that act on the blood or hematopoietic system, and agents that damage the lung.

Table 3.6 summarizes some of the types of toxic hazards.

Table 3.6 Types of toxic effects

Nature of effect	*Examples of materials*	*Remarks*
Asphyxia (physical)	N_2, He, argon, CO_2, NO, H_2 hydrocarbon gases	Displace O_2 in the atmosphere and starve the body of oxygen
Asphyxia (chemical)	CO, H_2S, HCN have specific blocking action and prevent sufficient oxygen supply reaching the tissues. Forms stable compounds with hemoglobin in the blood. E.g. $CO + Hb \rightarrow CO.Hb$ and $CO + O_2 \rightarrow CO.O_2$	

(*Continued*)

Table 3.6 (Continued)

Irritation	NH_3, Cl_2, H_2S, NO_x, phosgene HCl, dusts, fumes, O_3	NH_3: 400 ppm severe irritation of throat, (respiratory, skin, nasal passages and upper nasal tract and eye) 700 ppm severe eye irritation, Cl_2:15 ppm throat irritation
Narcotic	Alcohols, esters, hydrocarbons, aromatics, halocarbons	Some narcotics, e.g. toluene diisocyanate, produced from urethane fires, make the person euphoric and oblivious of danger
Systemics	Methanol, benzene, phenols, poisons, halocarbons, metals	Permanent damage at points other than point of contact. Benzene and phenol affects bone marrow, spleen. Methanol affects nervous system, atrophy of optic nerve and blindness. Cause injury to kidneys or liver. Some toxic metals such as mercury, lead, cadmium, antimony, and manganese interfere functions of body organs, blood, and bones
Hypnotics	Barbiturates, paraldehydes, and chloral hydrate	Sleep inducing drugs
Anesthetics	Halocarbons such as trichloroethylene, ethylene, nitrous oxide, ethyl ether, ethylene, nitrous oxide, chloroform	Cause loss of sensation by depressing nervous system
Hepatotoxins	CCl_4, tetrachloroetane, and nitrosoamines	Damage the normal functioning of lever
Nephrotoxins	Some halogenated hydrocarbons, uranium	Damage the functioning kidneys
Neurotics	Ethanol (depressant), caffeine, organometallic compounds such as methyl mercury, tetraethyl lead, CS_2	Depress or stimulate nervous system, brain or spinal chord
Carcinogenic	Vinyl chloride monomer, asbestos, benzene, aromatic amines, amino-nitro phenyls, cigarette smoke, metals like beryllium, cadmium, nickel and their compounds	Cancer producing. Coal tar pitch, benzene affects bone marrow. Cigarette smoke causes lung cancer
Genetic disorders (mutagenic)	Radioactive materials, some drugs like phthalidoamide	Effects are transmitted to future generations. Phthalido amide causes congenital abnormalities in new born babies
Reproductive toxicants	Lead, aniline, benzene, toluene, formaldehyde, inorganic mercury	Affect human reproductive activity such as infertility, spontaneous abortions and still births in women

(*Continued*)

Table 3.6 (Continued)

Sensitizers or allergens	Pollens, odors, insect bites, smog, dusts and a variety of materials	People who are exposed to one of these materials may not be abnormally affected the first time but may experience significant and possibly dangerous effects even in the presence of very low levels of the contaminant if exposed again. Victims become extremely allergic to the material and possibly others of a similar nature
Corrosives	Strong acids and alkalis, iodine, chlorine, fluorine	Damage by chemical reaction with skin, mouth, throat, stomach
Skin absorbents	Tetra ethyl lead, aniline, boranes, hydrazine, nitroglycerine	Some times more dangerous since absorbed directly into bloodstream than entry through respiratory or digestive system which may provide defensive mechanisms

Notes: Some relatively harmless materials may get converted to extremely poisonous substances (gases/vapors) under fire exposure. For example CCl_4 gives off phosgene gas at above 250°C. Some foams, plastics used for furniture, etc., give rise to toxic gases and fumes on fire exposure. Toxic effects for selected chemicals at different concentrations are given in Table 3.7.

Table 3.7 Toxic effects for selected chemicals at different concentrations (concentrations are expressed in ppm)

NH_3	Lighter than air, rises and disperses in the atmosphere, but can be heavier when droplets of liquid NH_3 are present at percentages above 16–20 percent. Expanding gas cools, (e.g. from a leak at high pressure, leading to droplet formation). NH_3 release is potentially one of the worst hazards of chemical industry like Cl2 release
TLV	25
An average person detects ammonia by odor at around	17
The least amount of ammonia that is found to be irritating to the eyes, nose, and throat of the most sensitive individuals	50
Concentrations causing severe irritation of throat, nasal passages and upper nasal tract	400
Concentrations believed to be not life threatening health effects	500

(*Continued*)

Table 3.7 (Continued)

Concentrations causing severe eye irritation	700
Concentrations causing coughing, bronchial spasms and chest pain, possibly fatal for exposure of less than 30 min	1,700
Concentrations causing oedema, strangulation, asphyxia, fatal almost immediately	5,000
Concentrations promptly fatal	10,000
CO	
TLV	50
Concentrations causing frontal headaches within 1–2 hr, life threatening after 3 hr	400
Concentrations inhalable for 1 hr without appreciable effect	400–500
Concentrations causing a just appreciable effect for exposure of 1hr	600–700
Concentrations causing nausea and convulsions within 20 min, death within 2 hr	800
Concentrations causing unpleasant symptoms but not dangerous for exposure of 1 hr about	1,200
Concentrations causing nausea within 20 min, death within 1 hr	1,600
Concentrations dangerous for exposure of 1 hr	1,500–2,000
Concentrations fatal for exposure of less than 1 hr	4,000
Concentrations causing death within 1–3 min	12,800
Cl_2	
TLV	1
Threshold concentrations of odor perception with considerable variation among people	0.2–0.4
Concentrations causing mild, mucous membrane irritation, tolerated for up to 1 hr	1–3
Minimum concentration detectable by odor	3.5
Maximum concentration inhalable for 1 hr without damage	4
Concentrations causing moderate irritation of the respiratory tract	5–15
Minimum concentration causing coughing, immediate chest pain, vomiting, dyspnea, and cough	30
Concentrations dangerous for exposure for half an hour	40–60

(*Continued*)

Table 3.7 (Continued)

Concentrations lethal over 30 min	430
Concentration probably fatal after a few deep breaths	1,000
H_2S (ppm)	–
TLV	10
Concentrations threshold for eye irritation	10–20
Concentrations causing slight symptoms after exposure of several hours	70–150
Concentrations causing paralyzing effect on the olfactory perception, so that the odor can no longer be recognized as a warning signal above	150
Maximum concentration inhalable for 1 hr without serious effects	170–300
Concentrations causing pulmonary oedema with risk of death	320–530
Concentrations dangerous for exposure of half an hour	400–700
Concentrations causing immediate collapse with paralysis of respiration	1,000–2,000
Phosgene	
TLV	0.1
Minimum concentration detectable by odor	0.5–2
Maximum concentration for exposure of 15 min	1
Minimum concentration affecting throat, nose and eyes	3.1
Concentration probably fatal for exposure of half an hour	5
Concentration dangerous for exposure of half an hour	25
Concentration rapidly fatal for short exposure	50
Concentration capable of causing injury in 2 min	167
Methyl isocyanate (MIC)	–
TLV	0.02
Concentration likely to cause coughing, chest pain, breathing pain (dyspnea), asthma, eye irritation and nose, throat, and skin damage	0.4
Concentration likely to cause lung oedema, emphysema (damage of lung tissue), hemorrhaging, bronchial pneumonia, and death	21

Figures 3.1 and 3.2 illustrate the effects of exposure to chlorine in terms of exposure time and chlorine concentration in the environment.

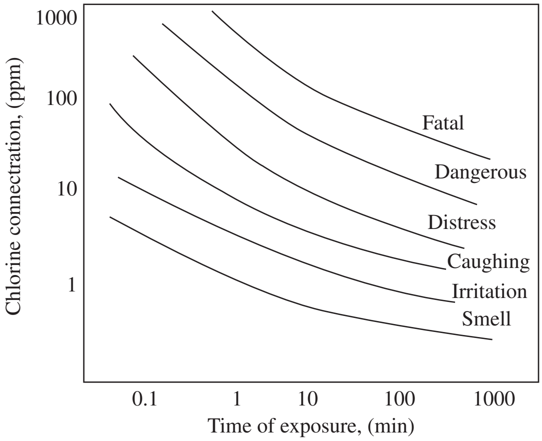


Figure 3.1 Effects of exposure to chlorine (not to scale)

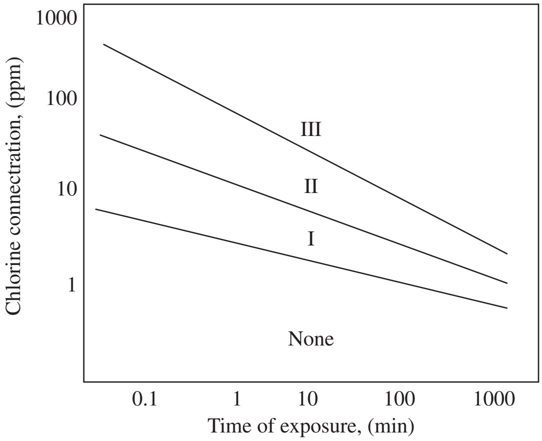


Figure 3.2 Hazard categories (not to scale)

Table 3.8 gives effects of exposure to reduced oxygen levels.

Table 3.8 Effects of exposure to reduced oxygen levels

Volume percent O_2 in air	*Effect(s)*
17	Reduced night vision and increased levels of breathing and heart beat
16	Impaired attention, judgment, and coordination; intermittent breathing; rapid fatigue; loss of muscle control; very faulty judgment; very poor muscular coordination; loss of consciousness; and permanent brain damage

(*Continued*)

Table 3.8 (Continued)

Volume percent O_2 in air	*Effect(s)*
10	Inability to move; nausea; and vomiting
6	Spasmatic breathing; convulsive movements; and death in 5–8 min

Source: Physics division cryogenic safety manual, Argonne National Laboratory, U.S.

U.S. Environmental Protection Agency (EPA) classifies toxicity for pesticides as given in Table 3.9.

Table 3.9 U.S. EPA toxicity classification for pesticides (systemic toxicity, eye irritation, and skin irritation)

Class	*Description*	*Comments*
I	Danger	Fatal if ingested; corneal opacity; and corrosive to skin
II	Warning	May be fatal if ingested; reversible corneal opacity; and severe skin irritation
III	Caution	Harmful if ingested; no corneal opacity; and moderate skin irritation
IV	Caution	May be harmful if ingested; no eye irritation; and mild/no skin irritation

Systemic toxicity, eye irritation, and skin irritation test results are used to categorize pesticides in one of the four toxicity classes. The toxicity category appears on the pesticide label, along with an associated signal word and precautionary statements. The signal word "danger" indicates highly toxic pesticides and "caution" indicates pesticides of low toxicity.

Different indices for the evaluation of toxicity hazards: Evaluation of toxicity hazards is based mainly on two factors, namely, vapor pressures and published exposure limits. Several indices, other than the ones discussed so far, have been proposed by several researchers. These are briefly presented in the subsequent paragraphs.

Vapor pressure hazard index, VHI given by the following expression,

$$\text{VHI} = \text{Log}\ (1{,}000{,}000 \times \text{P}^\circ/\text{TLV}) \tag{3.1}$$

where P° = vapor pressure, atms, at 21.1°C (70°F) and TLV is in ppm.

*(Ref. William Popendorf, AIHA J., 45 (10), 1984).

Substance Hazard Index, SHI, given by the following equation:

$$\text{SHI} = 1{,}000{,}000 \times \text{P}^0/\text{ATC} \tag{3.2}$$

ATC = acutely toxic concentration, ppm, which is one of three referenced, namely, (i) emergency response planning guideline (ERPG-3), published by AIHA, (ii) level of concern, published by EPA, or (iii) ATC developed by the State of New Jersey.

*(Ref. Organizational Resources Counsellore, Inc., Washington D.C., 1988)

SHI developed by OSHA, as given by the following relation:

$$\text{SHI}_{\text{OSHA}} = \text{EVC/ERPG-3} \tag{3.3}$$

EVC = equilibrium vapor concentration at 20ºC, given by the following equation:

$$\text{EVC} = 1{,}000{,}000 \times P°/760 \tag{3.4}$$

$P°$ is in mm Hg.

Toxic chemicals with SHI more than 5,000 are considered to be extremely catastrophic hazard potential.

Equation 3.5 gives an adjusted SHI to allow use of additional measures of chemical toxicity:

$$\text{ASHI} = \text{Log}\ [\text{EVC}/(\text{OEL} \times X \times Y)] \tag{3.5}$$

OEL is occupational exposure limit, ppm.

EVC is at 20 or 25ºC.

X = correlation factor to account for increased risk of exposure associated with skin absorptive chemicals. X is equal to 0.5, whenever is listed to have skin absorption potential.

Y = correlation factor to adjust for inherent differences between types of occupational limits.

Y is 1.0 for TLV_{TWA}, 0.3 for ceilimg limit and 0.2 for EPA's level of concern.

Whenever possible, OEL used in Eqn. 3.5 should be TLV. published by ACGIH or permissible exposure limits (PEL) published by OSHA.

NFPA health hazard ratings are given in Table 3.10.

Table 3.10 NFPA health hazard ratings, N_h

Rating number	*Rating*	*Description*
4	Danger	May be fatal on short exposure, even though prompt medical treatment is given. Specialized protective equipment required should include: materials that can penetrate ordinary rubber protective clothing; materials that under normal conditions or under fire conditions give off gases which are extremely hazardous (i.e. toxic or corrosive) through inhalation or through contact with or absorption through the skin.
3	Warning	Corrosive or toxic. Materials that upon short-term exposure could cause serious temporary or residual injury even though prompt medical treatment is given, including those requiring protection from all bodily contact. This degree should include materials giving off highly toxic combustion products; materials corrosive to living tissue or toxic by skin absorption. Inhalation should be avoided.
2	Warning	May be harmful if inhaled or absorbed. Materials which on intense or continued exposure could cause temporary incapacitation or possible residual injury unless prompt medical treatment is given, including those requiring use of respiratory protective equipment

(*Continued*)

Table 3.10 (Continued)

Rating number	*Rating*	*Description*
		with independent air supply. This degree should include materials giving off toxic combustion products; materials giving off highly irritating combustion products; materials that either under normal conditions or under fire conditions give off toxic vapors lacking warning properties.
1	Caution	Materials that on exposure would cause irritation but only minor residual injury even if no treatment is given, including those which require use of an approved canister type gas mask. This degree should include: materials which under fire conditions would give off irritating combustion products materials that on the skin could cause irritation without destruction of tissue.
0		No unusual materials that on exposure under fire conditions would offer no hazard beyond that of ordinary combustible material.

Note 1: TLV → 0–100 ppm (for categories 3 and 4)
Note 2: SAX lists the ratings as *toxic hazard ratings* (THRs) in which 3 and 4 are merged under category 3. Another category is listed as U, *UNKNOWN*, stating *effect unknown*.
Table 3.11 gives toxicity classification of EPA.

Table 3.11 Toxicity classification of U.S. Environmental Protection Agency (systemic toxicity, eye irritation, and skin irritation)

Class	*Classification*	*Remarks*
Class I	Danger	Fatal if ingested; cornea opacity; and corrosivity to skin
Class II	Warning	May be fatal if ingested; reversible corneal opacity; and severe skin irritation
Class III	Caution	May be fatal if ingested; no corneal opacity; and moderate skin irritation
Class IV	Caution	May be harmful if ingested; no eye irritation; and mild/no skin irritation

$$\text{Toxicity index } (Th + Ts\ (1+GPH+SPH))/100 \qquad (3.6)$$

where SPH = special process hazard
GPH = general process hazard
Th = toxicity factor based on the NFPA hazard index (0–4)
Ts = correction factor (additional penalty) for toxicity based on maximum allowable concentration (MAC) value in ppm.

Toxicity factors and correction factor for MAC values are given in Tables 3.12 and 3.13.

Table 3.12 Toxicity factors

NFPA hazard rating number	*Toxicity factor (Th)*
0	0
1	50
2	125
3	250
4	325

Table 3.13 Correction factors for MAC

MAC (ppm)	*Toxicity factor (Th)*
≥ 5	125
5–50	75
> 50	50

Threshold quantities are determined for inventory of maximum amounts of hazardous materials in a facility. Threshold quantity means that quantity of material, prescribed which, if exceeded, identifies a facility on which it is present or is likely to be present as a *major hazard facility*. These quantities must be the maximum present, or likely to be present, at the facility, taking into account possible daily, seasonal or other variations. Table 3.14 gives threshold quantities (TQs) for toxic chemicals determined on the basis of calculated ASHI values.

Table 3.14 Threshold quantities for toxic chemicals

Toxicity class	*ASHI range*	*TQ (kg)*
T1	8 ≥ ASHI	23
T2	7.5 ≥ ASHI ≥ 7.99	45
T3	7 ≥ ASHI ≥ 7.49	113
T4	6.5 ≥ ASHI ≥ 6.99	227
T5	6 ≥ ASHI ≥ 6.49	453
T6	5.5 ≥ ASHI ≥ 5.99	1,134
T7	5 ≥ ASHI ≥ 5.49	2,267
T8	4.5 ≥ ASHI ≥ 4.99	4,536
T9	4 ≥ ASHI ≥ 4.49	11,340
T10	3.5 ≥ ASHI ≥ 3.99	22,680

Source: Encyclopedia of chemical process design

The following paragraphs provide, briefly, information on toxic hazards of important operations and materials involved in process industry.

Toxic Hazards of Cryogenic Fluids

There are three groups of health hazards associated with cryogenic liquids, namely, extreme cold, asphyxiation, and toxicity.

Extreme cold hazard: Cryogenic liquids and their associated cold vapors and gases can produce effects on the skin similar to a thermal burn. Brief exposures that would not affect skin on the face or hands can damage delicate tissues such as the eyes. Prolonged exposure of the skin or contact with cold surfaces can freeze tissue and cause frostbite. The skin appears waxy yellow. There is no initial pain, but there is intense pain when frozen tissue thaws. Unprotected skin can stick to metal that is cooled by cryogenic liquids. The skin can then tear when pulled away. Even nonmetallic materials are dangerous to touch at low temperatures. Prolonged breathing of extremely cold air may damage the lungs. Intense hypothermia (abnormal accumulation of blood) usually takes place. In addition, a blood clot may form along with the accumulation of body fluids, which decreases the local circulation of blood. Eye and hand protection is required at all times when working with cryogenic fluids.

Asphyxiation hazard: When cryogenic liquids form a gas, the gas is very cold and usually heavier than air. This cold, heavy gas does not disperse very well and can accumulate near the floor. Even if the gas is nontoxic, it displaces air. When there is not enough air or oxygen, asphyxiation and death can occur. Oxygen deficiency is a serious hazard in enclosed or confined spaces. Small amounts of liquid can evaporate into very large volumes of gas, of the order of 700–800 times their liquid volume. one L of liquid nitrogen vaporizes to 695 L of nitrogen gas when warmed to room temperature (21°C). Even small amounts of liquid can displace large amounts of oxygen gas and decrease the oxygen content of the atmosphere below a safe level with a possibility of asphyxiation.

Toxic hazards: Each gas can cause specific health effects. For example, liquid carbon monoxide can release large quantities of carbon monoxide gas, which can cause death almost immediately. Material safety data sheets are normally the source for information about the toxic hazards of a particular cryogenic.

Toxic Hazards of Welding Operations

Welding is very common in fabrication and maintenance in every industry. Therefore, this hazard is included under toxic exposure effects. The following listing of welding-related hazards highlights this common activity:

Exposure to metal fumes (such as zinc, magnesium, copper, and copper oxide) can cause metal fume fever. Symptoms of metal fume fever may occur 4–12 hr after exposure, and include chills, thirst, fever, muscle ache, chest soreness, coughing, wheezing, fatigue, nausea, and a metallic taste in the mouth. Welding smoke can also irritate the eyes, nose, chest, and respiratory tract and cause coughing, wheezing, shortness of breath, bronchitis, pulmonary edema (fluid in the lungs), and pneumonitis. Gastrointestinal effects, such as nausea, loss of appetite, vomiting, cramps, and slow digestion, have also been associated with welding.

Some components of welding fumes, for example cadmium, can be fatal in a short time. Secondary gases given off by the welding process can also be extremely dangerous. For example, ultraviolet radiation given off by welding reacts with oxygen and nitrogen in the air to form ozone and nitrogen oxides. These gases are deadly at high doses and can also cause irritation of the nose, throat, and serious lung disease. Ultraviolet rays given off by welding can also react with chlorinated hydrocarbon solvents, to form phosgene gas, which is highly toxic. Arc welding should never be performed within 70 m of degreasing equipment or solvents.

Long-term (chronic) health effects include risk of cancer of lungs, voice box, and urinary track, primarily due to presence of cancer-causing metals such as cadmium, nickel, beryllium, chromium, and arsenic. Welders may also experience a variety of chronic respiratory problems, including bronchitis, asthma, pneumonia, emphysema, pneumoconiosis, decreased lung capacity, silicosis, and siderosis (a dust-related disease caused by iron oxide dust in the lungs). Other health problems that appear to be related to welding include heart disease, skin diseases, hearing loss, inflammation, and ulcers of the stomach and small intestine. Welders exposed to heavy metals such as chromium and nickel have also experienced kidney damage reproductive risks. Welders who perform welding or cutting on surfaces covered with asbestos insulation are at risk of asbestosis, lung cancer, mesothelioma, and other asbestos-related diseases. Heat and noise associated with welding are other hazards associated with welding.

Toxic Hazards from Mixtures

Toxic gases may be evolved following mixing of some chemicals. Examples are given in Table 3.15.

Table 3.15 Toxic hazards from mixtures

Chemical A	*Chemical B*	*Product*
Arsenical materials	Any reducing agent	Arsine
Azides	Acids	Hydrogen azide
Cyanides	Acids	Hydrogen cyanide
Hypochlorites	Acids	Chlorine or hypochlorous acid
Nitrates	H_2SO_4	Nitrogen dioxide
Nitric acid	Copper, brass or any heavy metals	Nitrogen dioxide
Nitrites	Acids	Nitrous fumes
Phosphorus	Caustic alkalis or reducing agents	Phosphine
Selenides	Reducing agents	Hydrogen selenide
Sulfides	Acids	H_2S
Tellurides	Reducing agents	Hydrogen telluride

Biohazards

Biohazards are infectious agents or dangerous biological materials that present a risk or potential risk to human or animal health or the environment. The risk can be direct through infection or indirect through damage to the environment. Pathogens are germs that can cause disease. Simply stated, microbes, biohazards, and pathogens are germs. Common types of germs are bacteria, viruses, and fungi. There are a variety of germs in buildings that can pose a potential health risk. They include viruses like *HIV-1, Hepatitis A, B, C, Herpes Simplex, and Influenza*; bacteria such as *Staphylococcus, Pseudomonas, Salmonella, E-coli*, stubborn antibiotic strains such as vancomycin-resistant enterococcus (VRE) and methicillin resistant staphylococcus aureus (MRSA); and toxic mold strains such as stachyboctrys.

Chemicals used to control germs range from the familiar detergents and disinfectants people use in their homes to highly toxic agents used to sterilize inanimate objects in hospitals. General disinfectants are used for institutional and industrial care of buildings.

Vibration and Noise

Effects include loss of hearing sensitivity, rupture of ear drums annoyance distraction, contributions to other disorders, and interference with other sounds.

Impulsive noises include sudden noises, for example, due to an explosion, rifle shot, impact of heave hammer, and the like. At these conditions most of the mechanisms of the ear are incapable of providing self-protection. Under shock wave of an explosion, pressures developed may be so great that ear drums may rupture. Loud impulsive noises can cause tightening of blood vessels that reduces blood flow. In addition, it will cause release of adrenalin into blood by the body mechanisms as a defensive measure. The result will be headaches, and fatigue.

Annoyance: Annoyance can lead to errors in work and to accidents. Types and levels for annoyance vary from person to person.

Distraction: Some types of annoying noises can also distract persons from their normal activities. Other types include noises produced from public address systems, telephone ringing, etc.,

Other noise effects: Nervousness, psychosomatic illnesses, and inability to relax.

Measures to reduce noise levels: Selection of equipment with low vibration and noise levels, for example, use of presses instead of drop hammers. Rotating and reciprocating equipment like pumps, fans, motors, presses, etc., should be selected to work at low speeds. The use of large, slow machines should be preferred compared to slow, and fast moving ones with the same capacity will reduce noise levels. Use of dynamic dampers, rubber/plastic bumpers, flexible mountings/couplings, resilient flooring, low fluid velocities in ducts, avoidance sudden direction and velocity changes in piping and ducts, avoidance quick opening valves in liquid systems to avoid water hammer, etc., are other examples.

3.4 Radiation

In the broadest sense, radiation is energy that is transmitted in the form of waves or particles. There are many types of radiation. Visible light is the most obvious. Microwaves, radio waves, and television signals are other forms of radiation that are common. The various types of radiation associated with the use of nuclear energy are categorized as *ionizing* radiation. That means, the radiation has sufficient energy to produce ions when it interacts with matter, that is, it can eject an electron from an atom. Industrial sources of radiation include nuclear reactors, X-ray radiography, electron microscopy, food, and medical sterilization, mining, smoke detectors, electron beam welding, thickness gauges, and the like. Natural sources of ionizing radiation include cosmic rays and nucleides such as potassium-40, carbon-14, and isotopes of thorium and uranium which are present in rocks, earth, and building materials.

Radioactivity: A radioactive substance is one whose atomic nucleous is unstable. Nuclei continuously disintegrate spontaneously into nuclei of lower atomic weight elements with emission of nulear particles and energy. This process is known as radioactivity. X-rays are produced in a vacuum tube, and γ-rays are produced by radioactive materials, natural, or manufactured. X-rays can be turned off by shattering off the equipment, whereas radioactive materials cannot.

Electromagnetic radiation: Energy emitted or absorbed as small discrete pulses are called quanta or photons. X-rays, γ-rays, and cosmic rays are much shorter and have higher frequencies than radio waves and move with higher energies.

Thermal radiation: It is the electromagnetic radiation emitted from all matter due to its possessing thermal energy that is measured by the temperature of the matter. Thermal radiation is generated when thermal energy is converted to electromagnetic radiation by the movement of the charges of electrons and protons in the material. The characteristics of thermal radiation depends on various properties of the surface it is emanating from, including its temperature, its spectral absorptivity and spectral emissive power, as expressed by Kirchhoff's law. The radiation is not monochromatic, that is, it does not consist of just a single frequency, but comprises a continuous dispersion of photon energies, its characteristic spectrum. If the radiating body and its surface are in thermodynamic equilibrium and the surface has perfect absorptivity at all wavelengths, it is characterized as a black body. A black body is also a perfect emitter. The radiation of such perfect emitters is called black body radiation. The ratio of emission of any body relative to that of a black body is the emissivity of the body, so that a black body has an emissivity of unity. Thermal radiation impact to humans from a fire should be based on the dosage—that is, the intensity of exposure and the duration of exposure. Further, such an impact from thermal radiation on population should consider the protection offered by clothing/buildings and the ability of a person to find a shelter from radiation. Usually, the surface emissive power for a hydrocarbon flame is 180–250 kW/m2 and the radiation intensity drops as the square of the distance. Table 3.16 provides a rough guidance on typical impacts from heat exposure.

Table 3.16 Critical thermal radiation values

Radiation intensity	***Level of damage*** (kW/m^2)
37.5	Sufficient to cause damage to process equipment
25	Minimum energy required to ignite wood at indefinitely long exposure

(*Continued*)

Table 3.16 (Continued)

Radiation intensity	***Level of damage*** (kW/m^2)
12.5	Minimum energy required for piloted ignition of wood, and melting of plastic tubing. The value is typically used as a fatality number
9.5	Sufficient to cause pain in 8 s and second degree burns in 20 s
5	Sufficient to cause pain in 20 s. Second-degree burns are possible. No fatality. This value is often used as an injury threshold
1.6	Discomfort for long exposures

Thermal radiation hazards can manifest in terms of burns of different degrees: First-degree burns are superficial injuries that involve only the epidermis or outer layer of skin. Second-degree burns occur when the first layer of skin is burned through and the second layer, the dermal layer, is damaged, but the burn does not pass through to underlying tissues. Usually, second-degree burns heal within three weeks. Third degree burns involve all the layers of the skin. While a third-degree burn may be very painful a burnt person feels little or no pain because the nerve endings have been destroyed. As the burns heal, dense scars form.

Ionization radiation: Ionizing radiation is radiation, which interacts with matter to form ions; high energy electromagnetic radiation and particle radiation are capable of producing ions in their passage through matter. Atoms are ionized. X-rays, γ-rays, and cosmic rays produce ionization by the high kinetic energies of the quanta they emit. α-, β-, and neutron particles and X-rays and γ-rays are ionizing radiations. Each of these may cause injury by producing ionization of cellular components leading to functional changes in the body tissues. α-, β-particles, and neutrons and other nuclear particles can produce ionizing injury. α- and β-particles are produced from substances used in industry.

β-particles: Alpha particles are produced from the radioactive decay of heavy elements such as uranium. These are emitted from radio nuclei at high speed and with high energy. However, they have short ranges in dense materials. Even those with maximum energy will just penetrate the epidermis composed of mostly dead cells, with little effect on living tissue. α-particles from external sources constitute no danger. If α-source is inhaled/ingested into the body, it can damage living tissue.

χ-particles: Beta particles are electrons that come from transformation of a neutron in the nucleus of an atom to a proton. They can travel up to about five metres in air and one centimetre in tissue.These are far smaller than α-particles β-source may be an external hazard, if energy of it is great enough since the particles may penetrate the dead cells of the skin. A thin metal sheet like aluminum can act as a shield but the metal must be selected with care to ensure that it is not one from which X-rays can be generated.

X-rays and η-rays: Radiation hazard from X-rays can be there if equipment are operating at high voltages, higher than 15,000–16,000 V. Gamma rays are electromagnetic radiation similar to X-rays. Unlike the latter, which are produced by machines, gamma rays are emitted from the nucleus of a radioactive atom that is in an excited state. Gamma rays travel at the speed of light and can penetrate long distances in air and tissue. X-rays and γ-rays have high penetrating power even through fairly dense materials. Long ranges in air and low density materials can injure tissue throughout the body. Like many other things, the effect of radiation depends on the dose. Very large doses, in the order of 5,000 mSv (The amount of radiation the dose received by people is measured in millisieverts (mSv) or more, can be lethal. Smaller doses can produce cancer after many years.

Sources of ionizing radiation in industry: X-rays and radioisotopes are used in non-destructive testing (NDT), medical facilities, and laboratories. β-particles are sometimes are used to neutralize static electricity from paper or textle manufacturing machines. Radioactive thorium (an α-emitter) is used thoriated tungsten welding rods, in magnesium alloys to improve strength, stiffness, and resistance to heat and also for skins of very high speed aircraft. When thorium alloys are welded, machined, or ground dusts/fumes are genrated. Precautions should be taken against ingestion with food through contaminated hands. High-power, high-voltge equipment used in communications and radar systems act as sources of ionizing radiation. Precautions against exposure should be taken when used in level control systems and as tracers.

Non-ionizing radiations: Nonionizing radiation is electromagnetic radiation that is not of sufficient energy to ionize matter, though it is capable of damaging the human body. Non-ionizing radiation can cause photochemical and thermal effects by exciting electrons in atoms to higher energy levels, and by producing molecular excitation. Lasers, radiofrequency and microwave radiation, IR radiation and UV radiation are all examples of nonionizing radiation. Ultraviolet and radiowaves are of three types: ultraviolet, infrared, and microwaves. Ultraviolet radiation is harmful and cause injuries either thermal or photochemical. Chronic exposure to UV radiation may cause premature skin aging, excessive wrinkling of the skin, skin cancer, and cataracts (opacities in the lens of the eyes).

Ozone in the atmosphere filters most of ultra violet radiations from the sun. The remaining reaching earth can still have damaging effects. Acute exposure to solar UV radiation can cause first- and second-degree burns. Principal-artificial sources for UV radiations are from electric arc welding, UV lamps, and plasma torches. Lasers, photocopying machines, germicidal lamps, and sunshine in any opaque cover gives good protection. Sun glasses are good for eye protection. Cornia and conjective of eye absorb UV radiation energy. Effects are photochemical rather than thermal.

Visible light: Has a wave length of 3.5–7.5x10–7 m. Eye injury is possible at eye absorption rates of more than 50 cal/(cm2)(min) for sustained time periods. Sources of visible light are flood lights, spot lights, high intensity lamps, and the like. Over exposures to sun on snow, sand, or large bodies of water (e.g. Oceans), welding, carbon arcs, and lasers.

Infrared radiation: Radiant energy is easily converted to heat, especially striking another body, giving rise to thermal effects. Sources in industry include high temperature processes like those involved with molten metals/glass, chemical reactions and paint/enamel drying, flames, IR heaters, lasers, and so on. IR causes redness of skin, skin burns, excessive perspiration, loss of body salts, exhaustion, heat stroke, and the like can cause cateracts in eyes and retina burns. Lasers are IR high intensities. Skin protection requires gloves, clothing, and cloth face masks. Glasses are available for eye protection.

Microwave radiation: Absorption by body increases kinetic energy of the absorbing molecules, which increases with increase in temperature. Principal hazards include inability of the body organs receiving microwave radiation to dissipate the heat energy. Temperature increases burn injures. Power densities are of the order of more than 100 mW/cm^2 for one hr or more at frequencies from 2 to $24.5x10^9$ Hz can affect the body thermally. Eye cateracts are caused for exposures > 10 mW/cm^2 for one hr or more at 2.5×10^9 Hz frequencies. Sources are microwave ovens, dryers, and heaters. High powered radar systems are used in military operations, aircraft, ships, microwave communication systems, alarm systems, diathermy equipment, and signal generators. Other hazards of microwave radiation can cause inductive heating of metals and induced currents that can produce sparks leading to ignition of flammables. Heating of metals in fields of strong radar or high powered communication transmitters has resulted in temperatures that caused burns when the metal is touched. Rings, watches, and metal bands, keys, etc., worn or carried by persons in such fields can be heated until they burn the bearer and should not be used by those working in such areas. Metal containers can also become so hot in such fields to ignite flammable or explosive materials. High currents can be induced in a microwave field. These can lead to spark generation and ignition of flammables.

Protection from microwave radiation: Equipment that produce microwave radiation can often be provided with shielding to protect users. In radars and communication equipment, it may not be possible to provide such shielding. Warning signs may be provided in such areas and on such equipment. No microwave antenna or other emitter should be inspected/worked on when it is energized. Dummy or water loads should be used when possible to absorb energy output of microwave equipment or isolate them by absorbent screening. Microwave equipment should not be pointed toward inhabited areas. Care should be excercized while touching metal objects. Flammables and explosives should be kept away from such areas.

Laser: (light amplification by stimulated emission of radiation): Lasers may emit UV, visible or IR radiation. Laser radiation has unique properties: monochromatic (1 wavelength emitted), coherent (all waves in phase), highly directional (low beam spreading), high energy density. Additional laser hazards include electrical (most lethal hazard), chemical (dyes in liquid laser media, toxic gases), x-radiation, fire (generally IR laser), ergonomic injuries.

Health Hazards from Radioactive Substances

Radioactive materials that decay spontaneously produce ionizing radiation, which has sufficient energy to strip away electrons from atoms (creating two charged ions) or to break some chemical bonds. Any living tissue in the human body can be damaged by ionizing radiation in a unique manner. The body attempts to repair the damage, but sometimes the damage is of a nature that cannot be repaired or it is too severe or widespread to be repaired. Also mistakes made in the natural repair process can lead to cancerous cells. The most common forms of ionizing radiation are alpha- and beta-particles, or gamma and X-rays. In general, the amount and duration of radiation exposure affects the severity or type of health effect. There are two broad categories of health effects, namely, stochastic and non-stochastic.

Stochastic health effects: Stochastic effects are associated with long-term, low-level (chronic) exposure to radiation. Increased levels of exposure make these health effects more likely to occur, but do not influence the type or severity of the effect. Cancer is considered by most people the primary health effect from radiation exposure. Ordinarily, natural processes control the rate at which cells grow and replace themselves. They also control the body's processes for repairing or replacing damaged tissue. Damage occurring at the cellular or molecular level, can disrupt the control processes, permitting the uncontrolled growth of cells, that is, cancer. Ionizing radiation has the ability to break chemical bonds to atoms and molecules making it a potent carcinogen. Radiation can cause changes in DNA. Changes in DNA are called mutations. Sometimes the body fails to repair these mutations or even creates mutations during repair. The mutations can be teratogenic or genetic. Teratogenic mutations are caused by exposure of the fetus in the uterus and affect only the individual who was exposed. Genetic mutations are passed on to offspring.

Nonstochastic health effects: Nonstochastic effects appear in cases of exposure to high levels (acute exposure) of radiation, and become more severe as the exposure increases. Unlike cancer, health effects from acute exposure to radiation usually appear quickly. Acute health effects include burns and radiation sickness. It can cause premature aging or even death. If the dose is fatal, death usually occurs within two months. The symptoms of radiation sickness include nausea, weakness, hair loss, skin burns, or diminished organ function. Medical patients receiving radiation treatments often experience acute effects, because they are receiving relatively high levels of radiation during treatment.

Table 3.17 gives a summary of radiation effects.

Table 3.17 Radiation effects

Exposure	*Symptoms and effects (Roentgen, R)*
0–100	No serious effects
100–200	Nausea and fatigue, possibly vomiting above 125 R. Delayed effects can reduce life expectancy
200–300	Nausea and vomiting on first day of exposure, loss of appetite, general illness/discomfort, soar throat, and spots on skin, and diarrhea
300–600	Nausea and vomiting in the first few hours of exposure, loss of hair, loss of appetite, discomfort, fever during second week, hemorrhage, inflammation of mouth and throat. Up to about 50 percent of persons may die at 450 R levels
> 600	All the above symptoms at shorter periods of exposure. Possible death upto 100 percent of exposed individuals

Factors affecting exposure and risk: Time of exposure and intensity are important factors. Longer exposure periods cause greater damage. Intensity depends on strength of source, distance, and existance and nature of shielding. Some radioactive isotopes have high intensity and are more hazardous.

$$\text{Intensity from a point source} \infty 1/(\text{distance})^2 \qquad (3.7)$$

Table 3.18 gives recommendations for shielding.

Table 3.18 Recommendations for shielding

Nature of particles	*Range in air*	*Shield*	*Type*	*Thickness*
α-particles (4 MeV)	2.8 cm	Aluminum 1/64 inch	Paper 1/64 inch	Ordinary clothing 1/64 inch
β-particles (3 MeV)	13 m	Lead 1.4 mm	Aluminum 5.3 mm	Pyrex glass 6.6 mm
				Water 14.8 mm
γ-rays				Thicknesses to reduce radiation to half its value
				Lead 7.62 mm (0.3 inch)
				Iron 12.7 mm (0.5 inch)
				Aluminum 68.58 mm (2.7 inch)
				Concrete 68.58 mm (2.7 inch)
				Water 210.82 mm (8.3 inch)

3.5 Flammability, Ignition, Fires, and Explosions

The terms *flammability* and *combustibility* are generally used in describing the relative ease with which materials ignite and burn. In general a flammable liquid burns more easily than a combustible liquid. NFPA makes the distinction between flammable and combustible liquids based on their boiling points and flash points (discussed later). While use of the term *flammability* is restricted to liquid and gaseous systems, *combustibility* is a more general term but commonly applied to solid materials, which burn more slowly than liquids and gases.

Classification of Degree of Flammability

Once ignition takes place, it is to be established whether the combustion process is sustained. A mixture of fuel and oxidant is not necessarily able to sustain combustion. Combustion may only be sustained if the heat released due to combustion is greater than that absorbed by the surroundings.

Requirements for a flame in gas–air mixture:

(i) At least a portion of the mixture must be heated to above the SIT.
(ii) Sufficient heat must be generated at the ignition point to heat the surrounding layers above the SIT. Propagation then occurs only if the ratio of fuel to oxidant is within certain limits (flammability limits).

All flammable and combustible materials will not have the same burning characteristics and need to be further classified from the point of view of fires and explosions and preventive and protective measures to ensure safety.

The US Government, NFPA and many other agencies use the following hazardous materials identification system (HMIS) standard for flamability ratings:

(i) Materials that will not burn.
(ii) Materials that must be preheated before they will ignite.
(iii) Materials that must be moderately heated or exposed to relatively high ambient temperatures before they will ignite.
(iv) Liquids and solids that can ignite under almost all temperature conditions.
(v) Materials which will rapidly vaporize at atmospheric pressure and normal temperatures, or are readily dispersed in air and which burn readily.

Combustion

Combustion is a rapid chemical reaction between fuel and oxygen coming together in suitable proportions initiated by a source of heat. It represents a self-sustaining chain of reactions consisting of physical and chemical transformations. The oxygen required for the reactions is either provided by the surrounding air in most cases or by an oxidizing agent. The reactions are often exothermic, releasing heat and often accompanied by visibly observable *flame*.

Fire can also result from the combining of such oxidizers as chlorine and various hydrocarbon vapors; oxygen is not required for a fire to take place.

Because of the high temperatures, products of combustion are usually gases, but there can be liquid or solid exhaust products. For example, *soot* is a form of solid exhaust that is present in some combustion processes. Since heat is required both to start combustion and is itself a product of combustion, one can see why combustion takes place very rapidly. Also, once combustion gets started, the heat source need not be there because the heat generated will keep the combustion process going.

To summarize, for combustion to occur three things must be present, namely, a fuel, a source of oxygen and a source of heat. Figure 3.3 represents the so-called fire triangle. The fire triangle (Figure 3.3) indicates how fires may be fought or prevented, namely, by cutting off or removal of fuel or removal of heat (usually done by spraying water on the fire) or removal of oxygen supply (usually done by foam or inert gas).

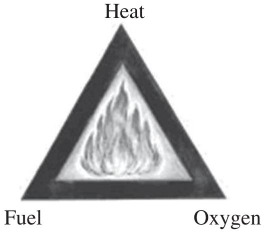


Figure 3.3 Fire triangle

The fire triangle is a simple model for understanding the ingredients necessary for most fires. It has largely been replaced in the industry by the fire tetrahedron, which provides a more complete model (Figure 3.4), described below.

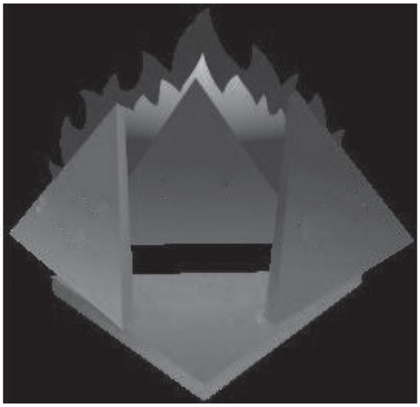


Figure 3.4 Fire tetrahydron

The fire triangle is a useful teaching tool, but it fails to identify the fourth essential element of fire, namely, the sustaining chemical reaction. This has led to development of the fire tetrahedron, a triangular pyramid having four sides (including the bottom). When the fire involves burning *metals* (known as a Class D fire in the American system of fire classifications, involving metals such as lithium and magnesium,) it becomes useful to consider the chemistry of combustion. Putting water on such a fire could result in the fire getting hotter (or even exploding) because such metals can react with water in an exothermic reaction to produce flammable hydrogen gas. Therefore, other specialized chemicals must typically be used to break the chain reaction of metallic combustion and stop the fire.

As a result of combustion, products of combustion are created and heat is released. The net amount of heat released by the combustion process involves both heat producing and heat absorbing reactions, with more heat being produced than is absorbed. One can control or stop the combustion process by controlling the amount of the fuel available, the amount of oxygen available, or the source of heat.

Combustion processes can be *rapid* and *smoldering*. *Rapid combustion* is a form of combustion in which large amounts of heat and light energy are released. This often results in a fire.

Smoldering combustion is a flameless form of combustion, deriving its heat from heterogeneous reactions occurring on the surface of a *solid fuel* when heated in an oxidizing environment. The fundamental difference between smoldering and rapid combustion is that in smoldering, the oxidation of the reactant species occurs on the surface of the solid rather than in the gas phase. The characteristic temperature and heat released during smoldering are low compared to those in the flaming combustion of a solid. Typical values in smoldering are around 600°C for the peak temperature and 5 kJ/g-O_2 for the heat released; typical values during flaming are around 1,500°C and 13 kJ/g-O_2 respectively. These characteristics cause smolder to propagate at low velocities, typically around 0.1 mm/s, which is about two orders of magnitude lower than the velocity of flame spread over a solid. Despite its weak combustion characteristics, smoldering is a significant fire hazard.

Combustion of liquid fuels: Combustion of a liquid fuel in an oxidizing atmosphere actually happens in the gas phase. It is the vapor that burns, not the liquid. Therefore, a liquid will normally catch fire only above a certain temperature, its *flash point*. The flash point of a liquid fuel is the lowest temperature at which it gives rise to ignitable flammable vapor or gas mixure in air.

Combustion of solid fuels: Ordinarily, combustible solids do not combine directly with oxygen when they burn. They give off vapor and gaseous decomposition products when they are heated and it is the vapors or gases which actually burn. Thus, before a solid can be ignited it must be heated sufficiently for it to give off flammable concentrations of vapors. There are exceptions to the general rule that a solid must vaporize or decompose to combine with oxygen. Some finely divided materials such as aluminum powder and iron powder can burn and it is probable that they do not vaporize appreciably before burning. Some metallic dusts will explode in air by light radiation alone without conduction and convection. Combustion of solid fuels, generally, consists of three relatively distinct but overlapping phases:

Preheating phase, when the *fuel* is heated to give rise to evolution of flammable gases.

Distillation phase or gaseous phase, when the mixture of evolved flammable gases (termed as *volatile matter in the case of coal or biomass combustion)* with oxygen are ignited. Energy is produced in the form of heat and light, *flame* is often visible.

Charcoal phase or solid phase, when the output of flammable gases from the material is too low for persistent presence of flame and the *charred* fuel does not burn rapidly any more but just glows and later *smolders.*

Flaming combustion is the rapid oxidation of volatile gases produced by pyrolysis. The gases that are produced by pyrolysis mix with oxygen and provide the basis for flaming combustion to occur. Flames are not attached directly to the surface of the solid fuel but are separated from it by a thin layer of vapor gas.

Smoldering/glowing combustion phase includes pyrolysis zone, glowing charred zone and the residual char and ash. Smoldering combustion typically occurs in tightly packed fuels. Although the temperatures during smoldering combustion are considerably lower than the flaming combustion, the duration of heating is much longer. The propensity of a system to burn is dependent on many factors such as fuel type, calorific value, mixture composition, pressure, velocity, turbulence, and enclosure geometry.

Flash Point

NFPA and OSHA classify liquids based on their flammability characteristics. While several properties or parameters are involved in determining flammability of a material, both the above organizations have adopted certain generalized criteria in their classification of flammable liquids based on the ease of ignition and sustained combustion. The basic requirement for these processes to take place is generation of *flammable* vapors from the liquids at or above the ambient conditions.

The two important criteria that go into the classification are *boiling point* (or *bubble point* in case of mixtures of flammables) and *flash point*. Both these criteria revolve round the ease with which vaporization takes place, in other words, vapor pressure of the liquids. It should be mentioned that flash point was selected as the basis for classification of flammable and combustible liquids because it is directly related to the ability of a liquid to generate vapor, that is, its volatility. Since it is the vapor of the liquid, not the liquid itself, that burns, vapor generation becomes the primary factor in determining the fire hazard.

Flash point of a flammable liquid is the lowest temperature at which vapors produced over the surface of the liquid are capable of *momentary* ignition/*flash* in still air, when a standard size flame is applied in a standard apparatus. At the flash point, the rate of vapor generation is not sufficient to propagate the flame for any length of time. Thus, flash point is a means of providing *early warning* for an approaching fire hazard if the temperature of the liquid exceeds its flash point.

A liquid with a flash point below ambient temperature is capable of giving rise to flammable vapor–air mixtures under ambient conditions. It is generally considered more hazardous than a liquid having a higher flash point. Many common organic liquids have flash points below room temperature, for example, acetone (−18°C) or diethyl ether (−45°C). Thus flash point is a measure of degree of flammability hazard. A higher flash point liquid may also become more hazardous if it is heated above flash point temperatures. Flash points for kerosenes are in the range of 37 and 65°C and for diesel fuel 40–50°C.

Table 3.19 gives flash points for selected substances having low flash points.

Table 3.19 Flash points for selected substances with low flash points

Material	*Flash point (°C)*
Propane	−104
Acetaldehyde	−38
Acetone	−18
Acetonitrile	6
Benzene	11
Carbon disulfide	−30
Cyclohexane	−20
Dioxane	12
Ethanol	12
Hexane	−23
Methanol	10
Methyl isobutyl ketone	16
Toluene	4

There are two methods for flash point measurements, namely, *closed cup* and *open cup* methods. In these methods, liquid is heated in the test apparatus and temperature is measured in intervals to find the lowest temperature at which a flash will be obtained when a small standard size flame is applied in the vapor zone over the liquid surface. Values of flash point for closed cup method are much lower than those for open cup method. The essential difference between the two methods is that vapors generated in a closed cup apparatus remain in contact with the liquid, attaining equilibrium with the liquid, whereas in the open-cup apparatus, vapors generated leave the liquid surface diffusing freely into the ambient air. In the case of mixtures (e.g. petroleum liquids), composition of the vapors in equilibrium with the liquid (as in the closed cup system) will be different from the vapors from an open cup apparatus. These composition effects can also influence the values of the flash points by the two methods. The methods reflect the differences in the storage methods for volatile and high boiling liquids.

Flash points are determined using ASTM or IP apparatus, which essentially involve introducing a 4 mm flame in the vapor space at regular temperature intervals to find whether there is ignition of the vapors. Details can be obtained from the above standards, revised and published periodically.

Flash points as listed in literature are apparatus dependent. For most situations flash points are conservative. Flammable liquid spills usually occur under conditions having more ventilation than those determined in a typical cup type apparatus. The problem of flash point determination is not always simple, particularly for mixtures. Viscous liquids can be heated only slowly and liquid mixtures always change their composition as they evaporate. Mixtures containing an inert inhibitor can exhibit no flash point, using the standard test procedure, but still be flammable. This anomaly can be important when one is attempting to inert a hydrocarbon–air mixture with an inhibitor.

Below flash point, flammable vapor concentrations cannot exist. There are several circumstances when flash point data may not represent the absolute minimum temperatures at which a liquid may evolve flammable vapors. When a liquid is sprayed or agitated into a mist or foam, it may become flammable by a pilot flame. As an example, investigations into a Saudi plane crash were attributed to a leak in a high pressure hydraulic *nonflammable* fluid system, due to formation of mist which lowered flammable temperature, as the cause of fire, even though ignition tests in a cup failed to ignite the liquid. This is because if vapor + mist/foam–air mixtures below lower flammability limit (LFL) contact an ignition source, the mist/foam may vaporize resulting in vapor–air compositions above LFL.

Wicking situations such as when a suspended rag soaks up a flammable liquid, may actually have a scenario-dependent flash point less than the literature value for a given ignition source. This is because the very large surface area and low thermal inertia available with some wicking materials will result in higher local vapor concentrations than those above a pool of liquid at a given temperature. Contamination of mixtures, even by small amounts of more volatile substance can cause a significant lowering of the flash point. This is the main reason for controlling flash points of side streams like kerosenes in a crude distillation unit of a refinery by the use of additional equipment such as steam strippers to remove the volatile contaminants to meet the required flash points of the product. Aging of liquids result vaporization of volatiles in a liquid mixture resulting in an increase in their flash points.

Flash point is affected by pressure and it is higher at elevated pressures. At low pressures, as in high altitudes, such as mountains, flash points are lower.

Flash point depends on the vapor pressure of the liquid and *lower flammability limit* (discussed later) of its vapor. It is considerably lower than both boiling point and *SIT* for the material. For example for methanol, flash point (closed-cup) is 11°C whereas its boiling point and self-ignition temperature are 64.7 and 385°C respectively. For hydrocarbons, closed-cup flash points can be estimated from their boiling points, using the Eqn. 3.8,

$$T_f = 0.683\, t_b - 71.7 \tag{3.8}$$

where T_f = closed-cup flash point °C.

and t_b = normal boiling point for the substance or initial boiling point (IBP) for a mixture, °C.

The formula gives approximate values of flash points and where available, experimental data should be relied upon. One method due to Prugh, involves estimation of stochiometric concentration, C_{St}, of the vapor in air based on the knowledge of molecular structure of the substances and their normal boiling points. The following equations are involved:

$$C_{St} = 83.8/(4C + 4S + H - X - 2O + 0.84) \tag{3.9}$$

where C, S, H, X, and O are number of carbon, sulfur, hydrogen, halogen and oxygen atoms, respectively, in the substance.

Alcohols: $T_b/T_f = 1.3611 - 0.0697 \ln (C_{St})$ (3.10)

Other substances: $T_b/T_f = 1.4420 - 0.08512 \ln (C_{St})$ (3.11)

T_b and T_f are normal boiling points and flash points respectively, K.

*Source: Ref. Prugh, R.W., J. Chem. Educ., 50, pp.85–89, 1973.

Flash point is the temperature at which the saturated vapor pressure is equivalent to the composition corresponding to *lower flammability limit* (LFL). For mixtures, LFL corresponding flash point is given by

$$\mathrm{LFL}_f = P_{i,fp}{}^{s}(T_f)/P \tag{3.12}$$

where $P_{i,fp}{}^{s}(T_f)$ is the saturated vapor pressure at flash point and P is ambient pressure. Flash point for a binary mixture can be estimated from Eqn. 3.13:

$$x_1\gamma_1 P_1{}^{s}/P_{1,fp}{}^{s} + x_2\gamma_2 P_2{}^{s}/P_{2,fp}{}^{s} = 1 \tag{3.13}$$

where x_i, γ_i, $P_i{}^{s}$, and $P_{i,fp}{}^{s}$ are liquid mole fraction, liquid phase activity coefficient, vapor pressure at temperature T and T_f of the component in the mixture respectively. Activity coefficients for binary and multicomponent mixtures can be estimated using UNIFAC method.

For aqueous organic solutions, like methanol—water mixtures, flash points are much higher than for the pure organic. In other words, aqueous solutions are much safer from flammability point of view. Contamination of a high flash point liquid with a more volatile flammable material, by even very small concentrations can lower flash points appreciably. Figure 3.5 illustrates schematically, effect of volatile contaminants on flash points of petroleum fractions.

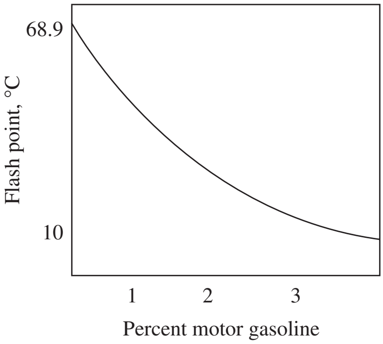


Figure 3.5 Effect of addition of motor gasoline on flash point for gas oil (only illustrative and not to scale)

Flash points referred to above are *lean mixture* flash points, which are important from safety point of view as most fires and explosions result from ingress/release of flammables into atmospheric air as a first step. There are *rich mixture* flash points, which have significance when there is air ingress into closed systems containing flammables. These are illustrated in Figure 3.7 given under discussion on flammability limits.

Classification of flammable liquids based on flash points: A *flammable liquid* is one with a flash point of less than 55°C, a *highly flammable liquid* is one with a flash point of less than 21°C (*a highly flammable solid* is one which is spontaneously combustible in air at ambient temperature or one which readily ignites after brief contact with a flame or one which evolves highly flammable gases in contact with water or moist air) and an *extremely flammable liquid* is one with a flash point less than 0°C and a boiling point of 35°C or less.

NFPA classification: Flammable liquids are classified by NFPA as Class I, which are further sub-classified, based on additional criteria that affect fire risk, as Class IA, Class IB, and Class IC—these liquids have flash points below 37.8°C (100°F) or less.

Class IA liquids are liquids that have flash points below 22.8°C (73°F) and boiling points below 37.8°C (100°F). In addition, unstable flammable liquids are treated as Class IA liquids. Typical Class IA liquids include acetaldehyde, ethylene oxide, propylene oxide, methyl chloride, ethyl chloride, ethyl ether, petroleum ether, ethyl amine, and pentane.

Class IB liquids are liquids that have flash points below 22.8°C (73°F) and boiling points at or above 37.8°C (100°F). Typical Class IB liquids include acetone, benzene, toluene, methanol, ethanol, butanol, isopropanol, acrylonitrile, acetonitrile, methyl ethyl ketone, methyl cyclohexane, ethyl acetate, ethylene glycol, n-hexane, and gasoline.

Class IC liquids are having flash points at or above 22.8°C (73°F), but below 37.8°C (100°F). Typical Class IC liquids include amyl alcohol, diethyl glycol, styrene, turpentine and naphtha. Combustible liquids are classified as Class II and Class III, which are further subclassified, based upon additional criteria that affect fire risk, as Class IIIA and Class IIIB—these liquids have flash points of 37.8°C (100°F) or more. Class I liquids are the most hazardous from a fire safety stand-point, whereas Class IIIB liquids are the least hazardous.

Class II liquids are combustible liquids that have a flash point at or above 37.8°C (100°F) and below 60°C (140°F). Typical Class II liquids include liquids such as acetic acid (glacial), cyclohexane, camphor oil, diesel fuel, kerosene, hydrazine, pine tar, and mineral spirits.

Class IIIA liquids are combustible liquids that have a flash point at or above 60°C (140°F), but below 200°F (93°C). Typical Class IIIA liquids include liquids such as aniline, benzaldehyde, dichlorobenzene, naphthalene, phenol, creosote oil, formaldehyde, formic acid, and furfuryl alcohol.

Class IIIB liquids are combustible liquids that have flash points at or above 93°C (200°F). Typical Class IIIB liquids include liquids such as castor oil, coconut oil, fish oil, and olive oil.

It is important to note that the NFPA classification system is based upon flash points that have been corrected to sea level. At *high altitudes*, the actual flash point of the liquid will be *lower* due to the reduced atmospheric pressure. This will affect the degree of fire risk when storing or handling such liquids.

DOT and UN classification: Flammable liquid: flash point ≥ 60.5°C (141°F)
Combustible liquid: flash point > 60.5°C (141°F) and < 93°C (200°F)

FM global classification Liquids that cannot be extinguished with ceiling sprinkler discharge alone:

Flash point < 93°C (< 200°F).

Liquids that can be extinguished with ceiling sprinkler discharge alone:

Flash point ≥ 93°C (200°F).

German classification: German regulations classify flammable liquids into four categories based on flash points:

Class	*Flash point*
AI	< 21°C
AII	21–55°C
AIII	> 55–100°X
B	< 21°C, soluble in water at 15°C

Table 3.20 gives a classification (R. Stahl, explosion protection, European Council directive 98/24/EC).

Table 3.20 Classification of flammable liquids

Designation of flammable liquid	*Flash point and boiling point criteria*
Highly flammable	Flash point < 0°C and boiling point < 35°C

(*Continued*)

Table 3.20 (Continued)

Easily flammable	Flash point < 0°C and boiling point > 35°C 0°C < flash point < 21°C
Flammable	21°C < flash point < 55°C

Fire point: The fire point of a flammable liquid is the lowest temperature at which the liquid, when placed in an open container, will give off sufficient vapor to continue to burn when once ignited. The fire point is usually a few degrees above the open-cup flash point. The most important use of flash and fire points is that they indicate the ability or volatility of the fluid to generate vapor under a given set of conditions. For example, if a significant leak occurs, a fluid with a lower flash point will generate more vapors, which in turh create more of a potential for fire. US Occupational Safety and Health Administration (OSHA) uses the concept of threshold quantity for highly hazardous chemicals. Threshold quantities for flammable liquids are based on their flash points and boiling points, whenever these properties are known. Threshold quantities may also be based on the flammable/combustible liquid classification or on flammability rating, Nf of NFPA.

Table 3.21 gives threshold quantities (TQ_f) for flammable and combustible liquids.

Table 3.21 Threshold quantities, TQ_f, for flammable and combustible liquids

Class	*Flammable/combustible properties to be considered*	*Threshold quantity (TQ) i (kg) on site*
F_1	Flash point < 22.8°C and B.P.< 37.8°C Class I A flammable liquids $N_f = 4$	2270
F_2	Flash point < 37.8°C and B.P. < 37.8°C Class I B and C class I B and C flammable liquids $N_f = 3$	9072
F_3	37.8°C < flash point < 60°C Class II combustible liquids	22,680

Source: Encyclopedia of chemical process design. N_f is flammability rating (NFPA).

TQ for some chemicals is too low, for example, 4.5 kg, for chloroform and for some too high, for example, 2275 kg for HCl or flammables. Table 3.22 gives threshold quantities to selected hazardous materials.

Table 3.22 Threshold quantities for selected hazardous materials

Material	*Threshold quantity (tons)*
Hydrogen sulfide	50
Chlorine	25
Phosgene	0.75
Anhydrous ammonia	200
LPG	200

(*Continued*)

Table 3.22 (Continued)

Material	*Threshold quantity (tons)*
Ethylene oxide	50
Acetylene	50
Carbon disulfide	200
Arsine	0.10
Allyl alcohol	20
Ammonium nitrate fertilizers	5,000
Dioxines	0.10
Fluorine	25
Hydrogen	50
Hydrogen cyanide	20
Methyl isocyanate (MIC)	0.15
Natural gas	200
Sulfur dioxide (liquefied)	200

Source: National Occupational Health and Safety Commission (NOHSC), Australia.

Flammability ratings for different materials are designated based on the severity of hazards involved. These are given in Table 3.23.

Table 3.23 NFPA flammability ratings, N_f

Rating (N_f)	Severity of hazard	*Description*
4	Danger	Materials that will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature or which are readily dispersed in air, and which will burn readily. This degree should include flammable gases, extremely flammable liquids, cryogenic materials, any liquid, or gaseous material that is a liquid while under pressure and have a flash point below 22.8°C (73°F) and have a boiling point below 37.8°C (100°F). Class IA flammable liquids: Materials that on account of their physical form or environmental conditions can form explosive mixtures with air and that are readily dispersed in air, such as dusts of combustible solids and mists of flammable or combustible liquid droplets.
3	Warning	Liquids and solids that can be ignited under almost all ambient temperature conditions. Materials in this degree produce hazardous atmospheres with air under almost all ambient temperatures or, though unaffected by ambient temperatures, are readily ignited under almost all conditions. This degree should include liquids having a flash point below 22.8°C (73°F) and having a boiling point at or above 37.8°C (100°F) and those liquids having a flash point at or above 22.8°C (73°F) and below 37.8°C (100°F). Class IB and Class IC flammable liquids: solid materials in the form of coarse dusts that may burn rapidly but that generally do not form explosive atmospheres with air; solid materials in a fibrous or shredded form which may burn rapidly

(*Continued*)

Table 3.23 (Continued)

		and create flash fire hazards, such as cotton, sisal, and hemp; materials that burn with extreme rapidity, usually by reason of self-contained oxygen (e.g. dry nitrocellulose and many organic peroxides); materials that ignite spontaneously when exposed to air.
2	Caution	Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur. Materials in this degree would not, under normal conditions, form hazardous atmospheres with air; but under high ambient temperatures or under moderate heating, they may release vapor in sufficient quantities to produce hazardous atmospheres with air. This degree should include combustible liquids flash point of 37.8–93.3°C. Solids and semisolids that readily give off flammable vapors.
1	–	Materials that must be preheated before ignition can occur. Materials in this degree require considerable preheating, under all ambient temperature condition, before ignition and combustion can occur. This degree should include materials that will burn in air when exposed to a temperature of 815.5°C (1500°F) for a period of 5 min or less; liquids, solids, and semisolids having a flash point above 93.4°C (200°F); this degree includes most ordinary combustible materials.
0	–	Materials that will not burn. This degree should include any material which will not burn in air when exposed to a temperature of 815.5°C (1500°F) for a period of 5 min

N_f is flammability rating (NFPA).

Flammability and Explosive Limits

Flammability limits: Flammability limits refer to the range of compositions, for fixed temperature and pressure, within which an explosive reaction is possible when an external ignition source is introduced. This can happen even when the mixture is cold. Flammability limits are given in terms of fuel concentration (by volume) at a specified pressure and temperature. Flammable gases or vapors, mixed with air or oxygen, are capable of propagating a flame on ignition, when significant quantities of fuel and oxygen molecules participate in the reaction, releasing enough energy that is capable of raising the temperature of the surrounding unreacted molecules to the levels of ignition. The probability of collisions and reaction among fuel and oxygen molecules, in a mixture containing very few molecules of either fuel or oxygen is very low. Even if there is reaction in such mixtures, the energy released will be so low that it will not be capable of raising temperature of the surrounding molecules to ignition levels. Thus, there will not be any flame propagation.

The lowest and highest concentrations of gas or vapor in air or oxygen, which upon ignition, are capable of propagating a flame through the mixture, are called *lower and upper flammability limits* respectively. The lower limit rarely differs for air or oxygen atmospheres, as the excess oxygen in the lean condition has the same thermo-physical properties as nitrogen. Below the lower flammability limit (LFL), the fuel is diluted with such an amount of excess air or oxygen that the energy released by combustion of the few fuel molecules is incapable of raising the temperature of adjacent layers of molecules to the point of ignition and a flame will not propagate through the mixture. In a similar way, above the upper flammability limit (UFL), availability of oxygen molecules for reaction with the fuel molecules will be so low, with the energy released upon reaction, again is incapable of propagating a flame through the mixture. Any concentration between LFL and UFL is capable of propagating a flame through the mixture. The concentrations falling between LFL and UFL represent the *flammability range*. Outside the flammability range, the system will not propagate a flame to any significant distance from an ignition source. Flammability limits are expressed as volume percent of fuel in the mixture. Figure 3.6 illustrates flammability limits and flammability range for hydrogen and Figure 3.7 gives comparison of flammability limits for some gases.

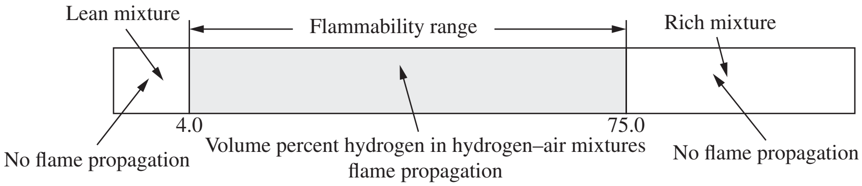


Figure 3.6 Flammability limits and flammability range for hydrogen in air under ambient conditions

The values of flammability limits differ widely for different materials. Some materials, such as hydrogen and acetylene, have wide flammability limits. That is to say, their flammability range is large. Some materials have narrow limits, examples being propane and butane, which are the main constituents of LPG. Gasoline is another example for narrow flammability limits.

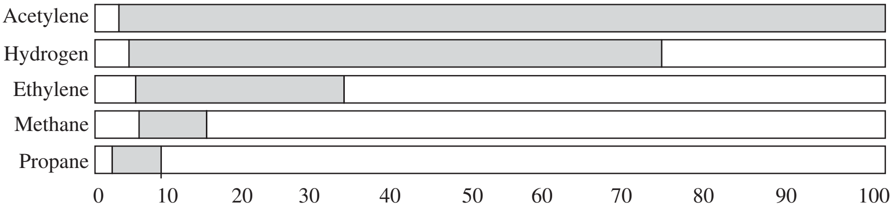


Figure 3.7 Comparison of flammability limits for some gases

Flammability range depends on ignition temperature, heat of combustion, chemical nature of the gas, heat capacities of the gases, direction of flame propagation—downward or upward (natural convection is upwards), temperature and pressure, size and shape of vessel, relative volumes of diluting gases and reactants, and the strength of the ignition source (the stronger the ignition source, the leaner the mixture that can be ignited).

The flammability range will be higher if the direction of flame propagation is upwards, the diameter of vessel is larger (lower relative heat loss to walls) and the temperature or pressure is increased. The lower and upper flammable limits of gases and vapors depend on the temperature and pressure of the mixture, the ignition source, and the concentration of the inert gases in the mixture as shown in Figure 3.8.

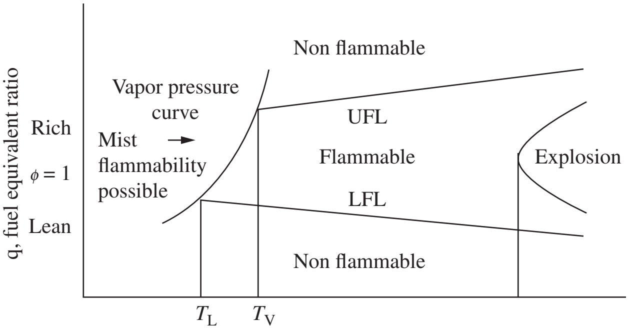


Figure 3.8 Relationships among flash points, vapor pressure, flammability limits, and SIT on a plot of mixture composition vs. temperature (illustrative only)

T_L = Lower (or lean) flash point SIT = self-ignition temperature
T_V = Upper (or rich) flash point
ϕ = Fuel equivalence ratio (FER) = $(f/a)/(f/a)_{\text{Stoichiometric}}$
f/a = ratio of fuel to air (or oxidizer) concentration
$\phi < 1$, lean mixture (excess air or oxidizer)
$\phi = 1$, stoichiometric concentration of fuel in air or oxidizer
$\phi > 1$, rich mixture (excess fuel); represents incomplete combustion

Figure 3.9 is a triangular diagram for flammability of methane–oxygen–nitrogen.

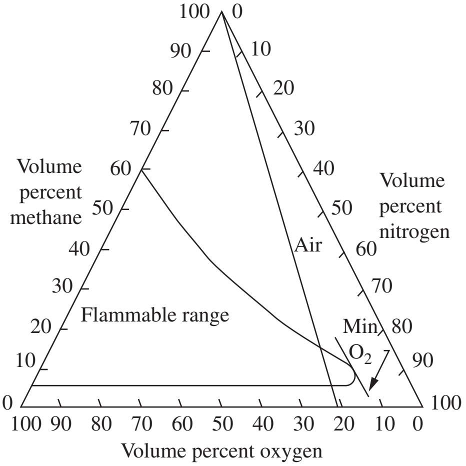


Figure 3.9 Triangular diagram for flammability of methane–oxygen–nitrogen

Figure 3.10 gives approximate relationship between temperature. Reid vapor pressure and flammability limits of petroleum products at sea level.

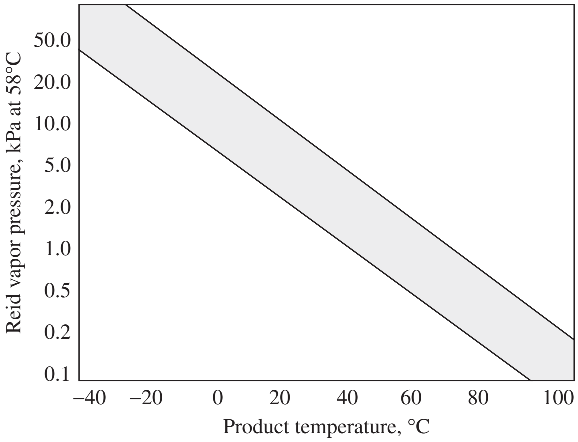


Figure 3.10 Approximate relationship between temperature, Reid vapor pressure and flammability limits of petroleum products at sea level

*__Note:__ Shaded area represents flammability range. The diagram gives an approximate estimate of the flammability range, especially near the boundaries of the shaded area.

There are flammability limits for fuel–oxygen mixtures. These limits are much wider than those for fuel–air mixtures. The applicability of flammability limits is not limited to air or oxygen. Some substances burn in chlorine or other oxidizer atmospheres having lower and upper flammability limits. Table 3.24 gives flammability limits for some materials in air/oxygen/chlorine under ambient conditions, percent v/v.

Table 3.24 Flammability limits for some materials in air, oxygen, and chlorine at ambient conditions, percent v/v

Material	*Formula*	⊥ *In air*		× *In oxygen*		× *In chlorine*	
		LFL	**UFL**	**LFL**	**UFL**	**LFL**	**UFL**
Acetylene	$HC \equiv CH$	2.5	100	---	---	---	---
Ethylene	$H_2 C = CH_2$	2.7	36	3.0	80	---	---
Propylene	$CH_3 CH = CH_2$	2.4	11	2.1	53	---	---
Ethylene oxide	$C_2 H_4 O$	3.6	100	---	---	---	---
Propylene oxide	C_3H_6O	2.8	37	---	---	---	---
Butadiene	$H_2 C = CHCH = CH_2$	2.0	12	---	---	---	---
1—Butene	$C_2 H_5CH = CH_2$	1.6	10	1.8	58	---	---

(*Continued*)

Table 3.24 (Continued)

Hydrogen	H_2	4.0	75	4. 0*	94*	4.1	89
Methane	CH_4	5.0	15	5.1	61	5.6	70
Ethane	$C_2 H_6$	3.0	12.4	3.0	66	6.1	58
Propane	$CH_3 CH_2 CH_3$	2.1	9.5	2.3	55	---	---
n-Butane	$CH_3 (CH_2)_2 CH_3$	1.8	8.4	1.8	49	---	---
Hexane	$C H_3 (C H_2)_4 CH_3$	1.2	7.4	---	---	---	---
Cyclohexane	$(CH_2)_6$	1.3	7.8	---	---	---	---
Benzene	C_6H_6	1.3	7.1	---	---	---	---
Toluene	$C_6H_5 CH_3$	1.2	7.1	---	---	---	---
Styrene	$C_6H_5 CH = CH_2$	1.1	6.1	---	---	---	---
Carbon monoxide	CO	12.5	74	16*	94*	---	---
Methanol	$CH_3 OH$	6.7	36	---	---	---	---
Ethanol	$CH_3. CH_2. OH$	3.3	19	---	---	---	---
Propanol	$CH_3.CH_2.CH_2 OH$	2.2	14	---	---	---	---
Butanol	$C_4H_{10}O$	1.4	11.2	---	---	---	---
Acetaldehyde	$CH_3 CHO$	4.0	60	---	---	---	---
Acetone	$CH_3 CO CH_3$	2.6	13	---	---	---	---
Methyl ethyl ketone	$CH_3.CO.C_2H_5$	1.4	10	---	---	---	---
Diethyl ether	$(C_2 H_5)_2O$	1.9	36	2.1	82	---	---
Methyl chloride	CH_3Cl	10.7	17.4	---	---	---	---
Vinyl chloride	$CH_2 CH Cl$	3.6	33	4.0	70	---	---
Ammonia	NH_3	15	28	15*	79*	---	---
Hydrogen sulfide	H_2S	4.0	44	---	---	---	---
Gasoline	Unleaded	1.2–1.8	7.1–8	---	---	---	---
Naphtha (Av)	---	0.8	5.0	---	---	---	---
Kerosene (Av)	---	0.7	5.0	---	---	---	---
Jet fuel (aviation kerosene)	---	0.7	4.8	---	---	---	---
Arsine	$As.H_3$	5.1	78	---	---	---	---
Silane	$Si.H_4$	1.5	98	---	---	---	---

**Irvine Glassman, combustion, Academic Press, New York, 1977. Zabetakis, M.G., Flammability characteristics of combustible gases and vapors, bulletin 627, U.S. Bureau of Mines, Washington D.C., 1965. Bodurtha, F.T., Industrial Explosion Prevention and Protection, McGraw Hill, New York, 1980.*

For many organics, particularly light paraffinic hydrocarbons, LFL decreases as molecular weight increases, as could be observed from Table 3.30. Also from the table, it is evident that flammability range in oxygen and chlorine atmospheres is far higher than that for mixtures in air, with LFL remaining essentially the same and the contribution for the increase coming from UFL. At LFL, oxygen is in excess of the theoretical value for complete combustion. The near constancy of LFL for mixtures of fuel with air or oxygen is because the excess oxygen in the lean mixture has the same thermophysical properties as nitrogen.

Acetylene decomposes explosively even at normal pressures in the absence of air, with thermal or mechanical shock and thus has no UFL. Ethylene requires high pressures and a strong ignition source for explosive decomposition. Both these gases involve positive heats of formation, H_f, for acetylene H_f is 227 kJ/mol and for ethylene it is 52.3 kJ/mol. Flammability limits are neither absolute nor unique physical properties. They are reported under standard test conditions at normal temperature and pressure.

Occurrence of flammability limits is considered to be due to a combination of heat loss from the flame region (reaction zone) due to various types of transport, plus the fact that under these limit situations, the flame temperature is so low that the mechanism of kinetics of the reaction changes.

A mixture which would not ignite at low energy levels may do so at higher energy levels. For example, a 0.2 mJ spark is not capable of igniting a butane–air mixture, initially at ambient conditions, under any circumstances. However, a 0.5 mJ spark will ignite the mixture if it is within the flammability range. With a strong spark, capable of providing 10 mJ or more energy to the mixture, flammability range becomes much wider. Materials that will not ignite under normal circumstances may ignite under the heat of a fire or welding arc.

Explosive limits: usually refer to the range of pressure and temperature for which an explosive reaction at a fixed composition mixture is possible. The composition has to be within the flammable range. Explosive limits are not to be confused with flammability limits. The reaction is usually initiated by autocatalytic (some times called self-heating) reaction at those conditions, without any external ignition source. In practical terms, this means that the mixture needs to be sufficiently hot. Explosive limits are pressure–temperature boundaries for a specific mixture ratio of fuel and oxidizer and separate the regions of slow and fast reaction. Fast reaction is a must for a flame to propagate. As an example, a stoichiometric mixture of hydrogen and oxygen at ambient conditions will support a flame because an ignition source initially brings a local mixture into the explosive regime and the established flame through diffusive mechanisms, heats fresh mixture to a high enough temperature to be explosive. Thus, in the early parts of the flame, the mixture follows steady reaction and in the later parts explosive reactions. Explosive limits may exist for many different mixture ratios, other than stochiometric ratio.

Detonation limits: Detonation limits are the range of composition within which detonations have been observed. Detonation limits are a strong function of mixture composition, initial pressure and temperature but usually considered to be narrower than the flammability limits. In addition, detonation limits are much more strongly

Table 3.25 Flammability and detonation limits in air and oxygen for selected substances

Material	*Flammability limits*				*Confined detonations*				*Unconfined detonations*			
	In air		**In oxygen**		**In air**		**In oxygen**		**In air**		**In oxygen**	
	LFL	**UFL**	**LFL**	**UFL**	**LEL**	**UEL**	**LEL**	**UEL**	*LEL*	*UEL*	*LEL*	*UEL*
Acetylene	2.5	100	---	---	4.2	50	2.9	88.8	---	---	6.7	68
Ethylene	2.7	36	3.0	80	3.32	14.7	4.1	60	---	---	9.2	51
Propylene	2.4	11	2.1	53	3.55	10.4	2.5	50	3.5	8.5	6.7	37
Ethane	3.0	12.4	3.0	66	2.87	12.2	3.6	46.4	4	9.2	11	39
Propane	2.1	9.5	2.3	55	2.57	7.37	2.5	42.5	3	7	7	31
Butane	1.8	8.4	1.8	49	1.98	6.18	2.05	38	2.5	5.2	---	---
Hydrogen	4.0	75	4.0	94	18.3	58.9	15	90	---	---	---	---
Methanol	6.7	36	---	---	---	---	9.5	64.5	---	---	---	--
Benzene	1.3	7.1	---	---	1.6	5.55	1.55	36	---	---	---	--
Diethyl ether	1.9	36	2.1	82	2.8	4.5	2.6	> 40	---	---	4.7	29
Ammonia	15	28	15	79	--	--	--	--	--	--	--	--

Source:(partial): Nettleton, M.A., Gaseous Detonations-Their Nature, Effects and Control, Chapman and Hall, New York, 1987.

dependent on the ignition source, confinement, and the physical size of the experiment than flammability limits. The ability to initiate and propagate a detonation requires a set of critical conditions to be satisfied and despite extensive research into the subject, the limits are empirical in nature.

As in the case of flammability limits, there are fuel–oxidizer mixture ratios which are not capable of propagating detonations. Thus, there are lower and upper fuel concentrations beyond which detonations are not possible. These concentrations are called *lower and upper explosive or detonation limits* (LEL and UEL). Flammability limits are sometimes called *deflagration limits*. Depending upon whether the combustion wave is a deflagration or detonation, there are flammability or detonation/explosive limits. Detonation limits are narrower than flammability limits. The following materials are capable of detonations in air, hydrogen, acetylene, ethylene, methane, benzene, cyclohexane, naphthalene, methanol, acetone, diethyl ether, carbon tetrachloride, chloroform, and trichloroethylene, to mention some of such materials.

It is frequently suggested that a substance is more liable to undergo detonation if it has a *triple bond* or if its flammability range is wide. Table 3.25 gives detonation limits for some substances in air and oxygen, along with their flammability limits.

Detonation limits in oxygen are much wider than those in air as is the case with flammability limits. It is also evident from the table that detonation range for a given material, is much narrower than its flammability range.

The detonation limits of an unconfined mixture are narrower than for confined detonations. Detonation limits reported in the literature should be treated, and applied to industrial situations, with great caution. Literature values can be lower or higher than those in an industrial plant conditions.

Detonation limits are affected by the size, shape, and geometry of the enclosed spaces. Detonation limits are typically measured in small vessels or tubes. Detonation limits tend to widen as the size of the vessel increases.

All mixtures are more susceptible to detonation when mixed with oxygen alone. The resulting detonation will have a higher detonation velocity, pressure and detonation product temperature than an equivalent detonation in air Diluents tend to narrow the detonation limits, particularly the upper limit. Relatively large amounts of diluent can be needed to suppress detonability. Significantly, more diluent is required at higher temperatures.

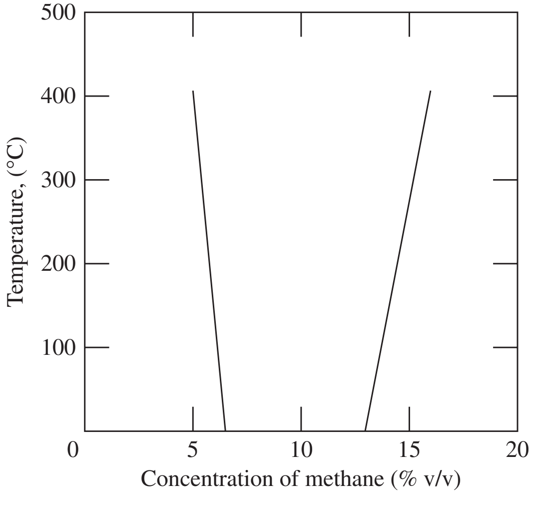
Detonations are also possible for some materials in atmospheres of oxidizers other than oxygen. Table 3.26 gives detonation limits for some organics in chlorine.

Table 3.26 Detonation limits in chlorine

Material concentration (mol%)		
	LEL	**UEL**
Methane	10	40
Propane	5	40
Methyl chloride	10	70

Flammability limits for sprays and mists: These are two-phase heterogeneous systems and vapor phase concentrations of fuel in fuel–oxidizer mixtures vary greatly. Flammability limits for sprays and mists are not well understood. The most important difference, as far as flammability limits are concerned, between a fuel mist–air mixture and a fuel vapor–air mixture is that UFL for a mist is much higher than that for a vapor. This is because combustion of this type will always contain rich and lean regions due to the heterogeneous nature of the system unlike vapor phase combustion. Thus, for rich mist–air mixtures, a large quantity of liquid fuel can pass through the flame un-evaporated. As droplet size in a mist becomes smaller, behavior of the fuel mist–air mixtures approach LFL for vapor–air mixtures. It is not commonly realized that mists of flammable liquids at temperatures well below their flash points can be as flammable as vapor–air mixtures. Vapor flammability region is of importance only at temperatures above flash point, whereas mist flammability extends below this temperature.

Effect of temperature on flammability limits: Increase in temperature increases rate of reaction. Thus, it is reasonable to expect that the flammability range should be broadened with increase in temperature. Increased temperatures normally result in a decrease in LFL and increase in UFL, thus widening the flammability range. The variation in LFL and UFL are linear but small for hydrocarbons in air. For light paraffinic hydrocarbons in air, if temperature is increased to about 100°C, the decrease in LFL and increase in UFL would be about 8 percent of the respective limits at ambient temperatures. Higher mixture temperatures reduce the amount of heat that must be transferred from the combustion zone to un-burnt gases to maintain flame propagation. Figure 3.11 illustrates effect of temperature on flammability limits for methane in air.



Closed tube 2.5 cm dia 150 cm long;
downward propagation of flame

Figure 3.11 Effect of temperature on flammability limits of methane in air

For the first 10 members of paraffinic hydrocarbons (methane to decane) in air, taking 1,300°C as the approximate flame temperature, effect of temperature on LFL can be represented by Eqn. 3.14:

$$L_t/L_{25} = 1 - (t - 25)/(1300 - 25) \tag{3.14}$$

where L_t and L_{25} are LFL values at t°C and 25°C, respectively.

Another form of the equation is

$$L_T = L_{298}\,[1 - \{314(T - 298)/L_{298}\ \mathrm{LCV})] \tag{3.15}$$

where L_T = LFL (percent fuel by volume) at temperature, T, and LCV = lower CV of fuel (MJ/kmol)

For methane, below ambient temperatures down to—155°C (e.g. LNG spills), LFL can be estimated from Eqn. 3.16:

$$\mathrm{LFL} = 5.0 + 0.0052\,(25 - t) \tag{3.16}$$

Another correlation makes use of net heat of combustion (Modified Burgess—Wheeler Law), Eqn. 3.17

$$L_t/L_{25} = 1 - 0.2388\,(t - 25)/H_c \tag{3.17}$$

where H_c is net heat of combustion in kJ/mol.

UFL can be estimated at temperatures other than ambient for C_1–C_{10} paraffinic hydrocarbons, in the absence of cool flames, using modified Bergess–Wheeler law:

$$U_t/U_{25} = 1 + 0.2388\,(t—25)/H_c \tag{3.18}$$

where U_t and U_{25} are UFL values at t°C and 25°C

Figure 3.12 gives effect of temperature on LFL for different paraffinic hydrocarbons.

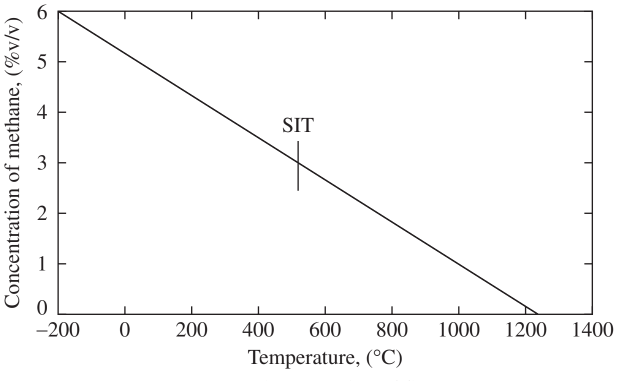


Figure 3.12 Effect of temperature on LFL for different paraffinic hydrocarbons

Effect of pressure on flammability limits: As natural gas is handled at high pressures, knowledge of effect of higher pressures on flammability limits becomes important. Increase in pressure generally increases flammability range. The effect is only marginal on LFL. Effect of increased pressures on LFL for ethane is given in Table 3.27.

Table 3.27 Effect of pressure on lower flammability limit for ethane

Pressure (MPa) gauge	0.00	0.69	1.72	3.45	5.17	6.90
LFL, percent v/v	2.85	2.80	2.70	2.55	2.40	2.20
Percent decrease in LFL	–	1.75	5.20	10.50	15.80	22.80

Table 3.28 gives effect of increase in pressure on UFL for methane and natural gas.

Table 3.28 Effect of increase in pressure in increasing upper flammability limit for methane and natural gas (approximate values)

Gauge pressure (kPa)	0	500	1,000	1,500	2,000	2,500
	15	17	20	25	31	42

In general, below atmospheric pressure, LFL is essentially constant, down to about 5.0 kPa. Below 5.0 kPa, flame does not propagate. This might probably be due to wall quenching in the experimental tube with decreased interaction of the molecules in the rarefied atmospheres. Effect of vacuum conditions, involving depressurization and evacuation will help during shut-downs of high pressure equipment. For simple low molecular weight paraffinic hydrocarbons, it appears that UFL increases almost linearly with pressure at lower pressures and tapers off to constant levels at higher pressures. For propane–air mixtures, UFL increases from 9.5 to 26 percent when pressure is increased from 0.101 to 0.69 MPa gauge (100 psig) but increases only to 32 percent on further increase in pressure to 1.38 MPa gauge (200 psig). Figure 3.13 illustrates effect of pressure on flammability limits of natural gas in air.

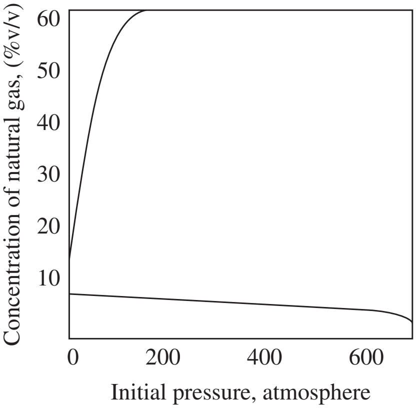


Figure 3.13 Effect of pressure on flammability limits of natural gas in air

As pressure is reduced, flammability range narrows down. For methane in air, as pressure is reduced below atmospheric pressure, the limits continue to narrow down and finally merge into each other, making flammability range zero at very low pressures, as illustrated in Figure 3.14.

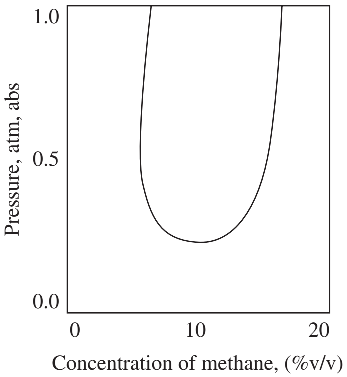


Figure 3.14 Effect of pressure (below atmospheric) on flammability limits of methane in air

This behavior of lowering of the flammability range at low pressures is influenced by the quenching effects of the tube in which experiments are carried out. Wider tubes are found to be decreasing the narrowing effect as pressure is decreased. The experimental limits might better be termed as limits of flame propagation in a tube of specified diameter. For several saturated hydrocarbons, over a pressure range of 0.1–20.7 MPa, effect of pressure on UFL can approximately be estimated by Eqn. 3.19:

$$U_P \approx U + 20.6\,(\text{Log}\,P + 1) \tag{3.19}$$

where U_P = UFL at the absolute pressure of P MPa
U = UFL at 0.101 MPa

Effect of oxygen concentration: Oxygen concentration, over and above that in normal air, has very little effect on LFL. UFL increases significantly with oxygen enrichment of ambient air. Eqn. 3.20 provides an approximate relationship between UFL in oxygen-enriched atmospheres and UFL in ambient air.

$$\text{UFL}_{\%\ \text{Oxygen}} \approx \text{UFL} + 70\,[\log\,(\%\ O_2) - 1.321] \tag{3.20}$$

where percent O_2 v/v ranges from 20.95 (in normal air) to 100.

Table 3.29 gives flammability limits for selected materials in air and oxygen.

Table 3.29 Flammability limits for selected materials in air and oxygen

Material	*LFL*		*UFL*	
	In air	**In oxygen**	**In air**	**In oxygen**
H_2	4	4	74	94
CO	12	16	75	94
NH_3	15	15	28	79
CH_4	5	5	14	61
C_3H_8	2	2	10	55

Estimation of flammability limits: Care is necessary in using flammability limit data. LFL required determining amount of flammable gas–air mixture resulting from a plant leak can probably be obtained quite readily because data are usually available at ambient conditions and accuracy required is not high. But the limits required to maintain concentration of flammable gas–oxygen mixture entering a reactor just below the flammable range under other pressure and temperature conditions needs greater consideration, because data may not be available so readily for these conditions, but they must be accurate. For such situations, experimental generation of such data must be part of the process development stage prior to design.

When experimental data are not available, flammability limits might be estimated using certain correlations which are mostly empirical. The estimated values, however, might be considered to be approximate. As LFL is the most important limit industrially, being having a direct bearing to plant leaks which are frequently responsible for fires and explosions in industry, estimated values may be adequate when process compositions are far below LFL values. A rule of thumb for organics in air states that LFL is about 55 percent of their stochiometric concentration, C_{st}, and UFL about 330 percent of C_{st} In other words, if concentration of fuel in air is reduced to about half that required for complete combustion, the mixture fails to ignite. For organics with only C, H, and O, the stoichiometric composition and LFL can be estimated using the following equations:

Combustion equation:

$$\mathrm{C_X\,H_Y\,O_Z} + [x + (y/4) - (z/2\,)]\,\mathrm{O_2} \rightarrow x\,\mathrm{C\,O_2} + y\,H_2\,\mathrm{O} \tag{3.21}$$

Equation for air required for complete combustion:

$$\text{Air} = 4.77\ [x + (y/4) - (z/2)]\ \text{mol/mol fuel} \tag{3.22}$$

Nitrogen in air at stoichiometric mixture composition:

$$N_2\ (\text{from air}) = 3.77\ [x + (y/4) - (z/2)]\ \text{mol/mol fuel} \tag{3.23}$$

$$C_{st} = (100\%\ \text{v/v})/[4.77\,x + 1.19\,y - 2.38\,z + 1] \tag{3.24}$$

$$\text{LFL} \approx (55\%\ \text{v/v})/[4.77\,x + 1.19\,y - 2.38\,z + 1] \tag{3.25}$$

Example: Toluene $C_6\,H_5\,C\,H_3$

$$x = 7\ y = 8\ z = 0$$

Substituting in Eqn. 3.24, $C_{st} = 2.28\%$ v/v

With Eqn. 3.24 LFL ≈ 1.25% v/v. (exponential value = 1.2)

For many hydrocarbon–air mixtures, LFL is given as follows:

$$\text{LFL} \times H_C \approx 4.354 \times 10^3 \tag{3.26}$$

where LFL is percent v/v and heat of combustion, H_C is in kJ/mol.

One equation for the estimation of LFL relates the number, N, of oxygen *atoms* required for complete combustion of one molecule of gas or vapor, to LFL:

$$\text{LFL} = 100/(4.85\ \text{N} - 1.425),\ \%\ \text{v/v} \tag{3.27}$$

For example, combustion of propane follows the equation,

$$C_3\,H_8 + 5\,\mathrm{O_2} \rightarrow 3\,\mathrm{CO_2} + 4\,\mathrm{H_2\,O}$$

One mol of propane requires 5 mols of oxygen for complete combustion ($N = 10$). From Eqn. 3.26,

LFL = 100/(4.85 × 10 − 1.425) = 2.12 (exponential value is 2.1)

The following empirical equations are frequently used for preliminary estimation of flammability limits:

$$\text{LFL} = 0.55\ C_{\text{st}} \tag{3.28}$$

$$\text{UFL} = 3.5\ C_{\text{st}} \tag{3.29}$$

One method to estimate LFL from flash point is:

$$\text{LFL} = (\text{vapor pressure at flash point, mmHg})/760\ \text{mmHg} \tag{3.30}$$

Vapor pressure can be estimated using Antoine equation.

LFL generally decreases as molecular weight increases. On a mass basis, LFL values for hydrocarbons are fairly uniform at about 45 mg/L air at 0°C and 101.325 kPa (1 atm), as illustrated in Table 3.30.

Table 3.30 Comparison of LFL values between volume percent and mass basis

Substance	*Molecular Wt*	*LFL (%v/v)*	*LFL (mg/liter) at (0°C) and (Atm Pr)*
Ethane	30	3.0	41
Propane	44	2.2	44
Hexane	86	1.1	43
Toluene	92	1.2	50

Some observations: Alcohols and other oxygenated substances have higher values of LFL and consequently more safe from flammability point of view. Low-molecular-weight materials have slightly lower values of LFL. LFL rarely differs for air or oxygen atmospheres, as the excess oxygen in the lean condition has the same thermophysical properties as nitrogen.

Flammability limits for mixtures: Most materials in normal circumstances exist as mixtures rather than as pure compounds. For mixtures, flammability limits can be estimated using Le Chatelier principle:

$$L_{\text{mix}} = 100/\sum_{i=1}^{n} (y_i/L_i) \tag{3.31}$$

$$U_{\text{mix}} = 100/\sum_{i=1}^{n} (y_i/U_i) \tag{3.32}$$

where L_{mix} and U_{mix} are the flammability limits for the mixtures and L_i and U_i are the pure component flammability limits, percent v/v. y_i is the volume percent of component *i* in the flammable gas/vapor mixture. Le Chatelier principle may not be applicable for nonideal mixtures involving chemically dissimilar species such as H_2S and CS_2.

Example:

Mixture composition, percent v/v: propane 1.5, butane 0.8, and pentane 0.5. Calculated values of LFL using Eqn 3.31 Propane 2.1, butane 1.8, and pentane 1.4.

Equations 3.29 and 3.30 are reasonably good for mixtures of paraffinic gases. It is only approximate for mixtures containing H_2, H_2S, and unsaturated hydrocarbons. It is even less accurate for mixtures of flammable gases with steam or inerts.

If one of the components in the mixture is not flammable, then a different formula must be used.

$$L'_1 = L_1\, x\; 100/(100 - x_{dil}) \qquad (3.33)$$

$$L'_2 = L_2\, x\; 100/(100 - x_{dil}) \qquad (3.34)$$

where L_1 and L_2 are LFL and UFL of pure components and L'_1 and L'_2 are LFL and UFL for flammables containing the diluent.

If the diluent is air,

$$L'_2 = 1000L_2/[100x_{flm} + L_2\,(100 - x_{flm})] \qquad (3.35)$$

If the diluent (other than air) contains oxygen,

$$L'_2 = 2100L_2/[21x_{flm} + L_2(x_{O2} + 0.21x_{flm} - 21)] \qquad (3.36)$$

respectively in the mixture.

When calculating the flammability limits of a mixture with a number of flammables and diluents, then the flammability of the pure flammable mixture (*minus* diluent) is first calculated. Then the effect of the diluent is calculated afterwards.

Examples: Calculate the flammability limits of a mixture of 25 percent CO, 40 percent H_2, and 35 percent CH_4.

Calculate the flammability limits of a mixture of 25 percent CH_4, 45 percent H_2, 10 percent CO, 10 percent CO_2, and 10.0 percent N_2.

Effect of diluents and suppressants: Inert gases affect flammability limits and suppress flammability. As increasing amounts of a noncombustible gas or vapor are added to a flammable gas or vapor mixture in air or oxygen, the limits approach one another and finally merge. Inert diluents such as CO2, N2, or Ar merely replace part of O_2, but all of them do not have same suppressive power.

It is found that the order of efficiency is the same as the order of heat capacities of the inert gases, that is, $CO_2 > N_2 >$ Ar. (approximate values of C_P are respectively, 43.26, 28.03, and 20.79 kJ/(kmol K).

In general, it is found that the minimum oxygen percent that will permit flame propagation in mixtures of CH_4, O_2, and CO_2, is 14.6 percent. If the diluent is N_2, the minimum oxygen content is less and equals 12.1 percent and in the case of argon, it is 9.8 percent. Other types of diluents are far more effective than inert gases. For example, halocarbons are most effective, their effectiveness being in the order of $CCl_4 > CO_2 > N_2 >$ Ar. Halocarbons affect actual combustion mechanisms rather than flame temperature. These affect both LFL and UFL. Halocarbons, however, have adverse environmental effects and their use is being discouraged.

A higher specific heat gas present in sufficient quantities will reduce the final temperature and in this sense reduces the rate of energy release which must sustain the rate of flame propagation.

Variation in concentrations of flammables: In a fuel–air mixture, exact concentration at any point is uncertain. The average fuel–air mixture composition may be below LFL. Density differences may cause stratifications resulting in concentrations exceeding LFL at certain points/levels in the mixture. For heavier gases, for example, concentrations may exceed LFL in pits, trenches, sumps and other low level points. Similarly, lighter gases may collect under roofs and ceilings of structures. Flame propagation may be possible in both cases even though the average concentrations are below LFL. Temperature variations can also be responsible for such changes with additional complications such as fog and mist formation.

A good rule of thumb in safety is that a good ventilation system should provide sufficient air so that any flammable mixture arising will be diluted to a fuel concentration of less than *one-fourth* of LFL for that particular fuel.

Table 3.31 gives limiting values of oxygen percentage concentrations (LOCs) along with minimum percent inert gas to be added to fuel–air mixtures for complete suppression of flammability of light paraffinic hydrocarbons.

Table 3.31 Maximum permissible oxygen (LOC) and minimum inert gas required to be added for complete suppression of flammability of light paraffinic hydrocarbons in air, percent v/v

Material mixtures	***Maximum permissible O_2 (LOC)***		***Minimum inert gas to be added to fuel-air mixtures***	
	N_2 as diluent	**CO_2 as diluent**	**Percent N_2**	**Percent CO_2**
Methane	12.1	14.6	38	24
Ethane	11.0	13.4	46	30
Propane	11.4	14.3	43	30
Butane	12.1	14.5	---	---
Pentane	12.1	14.4	---	---
Ethylene	10.0	11.5	50	41
Propylene	11.5	14.0	43	30
Butadiene	10.0	13.0	---	---
Hydrogen	5	5.2	---	---
Cyclopropane	11.5	14	---	---
Carbon disulfide	5	7.5	---	---
Ethanol	10.5	13	---	---
Methyl ethyl ketone	11	13.5	---	---
Methyl ether	10.5	13	---	---

In general, light hydrocarbons will not propagate flame if O_2 in mixtures of such compounds with inert gas and air, is about 10 and 12 percent v/v with N_2 and CO_2 respectively as the inert gases. CO_2 is a better flame suppressant than N_2. Many mixtures can be made nonflammable by the addition of about 30 percent CO_2 or 40 percent N_2. However, nitrogen is generally used as inerting medium. Carbon dioxide in the presence of moisture can give rise to corrosion problems. Limiting oxygen concentration (LOC) that is, the oxygen concentration below which no combustion is possible, can be estimated using Eqs 3.37 and 3.38. The calculation involves the LFL of the fuel and the stoichiometric ratio fuel/oxygen for complete combustion:

$$y_{\text{fuel}} + x_{O_2} -> a_{CO_2} + b_{H_2O} \tag{3.37}$$

LFL = Z% v/v fuel in air

$$\text{LOC} = (\text{LFL})(x/y), \text{ percent v/v } O_2 \text{ in nitrogen} \tag{3.38}$$

This gives a slightly more conservative value than experimentally determined LOCs, so one will be on the safe side. Normally, if one stays below 10 percent O_2, it will be alright for most chemicals, except hydrogen (LOC = 4%).

Water vapor can also be used as an inerting medium provided temperature in the gas/vapor space is high enough to prevent condensation. Also, water may contaminate some processes. Evaporation of water in fire-fighting rapidly removes heat as latent heat plus sensible heat thereby quenching the flames. Flue gases may also be used for suppression of flammability, but care is necessary in the choice of fuel as sulfur dioxide and some other gases if present in the flue gases can give rise to corrosion or toxic problems.

Sometimes inert powders are used to suppress flammability (used in fire fighting). Due to their large heat capacities, they absorb considerable quantities of heat to reduce speed and temperatures of flames leading to stoppage of flame propagation. Some halogen-containing compounds can also be used as inerting materials at relatively low concentrations. Effectiveness of halocarbons is in the order, $CCl_4 > CO_2 > N_2 > Ar$. Halogen effectiveness for flame quenching follows the pattern, I > Br > Cl. Halocarbons affect actual combustion mechanisms rather than flame temperature alone and affect both LFL and UFL. UFL is more sensitive to inert diluents than LFL. Some of the longer chain halons are effective as flame suppressants.

In the combustion mechanisms involving halocarbons, OH radical plays an important part. Burning process can be effectively stopped by reacting OH radical with either HBr, HI, or HCl.

Experimental determination of flammability limits: Several factors such as ignition source, diameter and length of test apparatus, direction of flame propagation influence values of flammability limits. For example, upward flame propagation usually gives lower values of LFL, widening the limits slightly, than downward or horizontal propagation.

A tube, with an inside diameter of 51 mm and a length of 1.8 m, is mounted vertically with the upper end closed and the bottom end open to the atmosphere. The gaseous mixture is placed in the tube and ignited at the bottom end. If the flame extinguishes somewhere in the tube during propagation, the mixture is said to be non-flammable. The limits are determined by varying the mixture composition in successive experiments. Upward propagation in a tube of this type usually gives smaller values of LFL and wider limits (which are conservative from safety point of view) than downward propagation. A flame, as a rough approximation, cannot propagate downward in a mixture if the convection current it produces is faster than the flame speed. 51 mm was chosen as the diameter of the tube as decrease in diameter below this value narrows down the limits (due to *quenching effects*) of the tube walls and further increase in diameter causes only a slight widening of the measured limits.

Explosive limits for dusts: Like gas or vapor mixtures in air, dust suspensions have lower and upper explosive limits, LEL and UEL. For gases, LEL, and UEL are well defined. For dusts, UEL is difficult to determine experimentally, since uniformity in concentration is almost impossible to get at higher concentration ranges. LEL is often called *minimum explosible concentration* (MEC) which, to some extent, depends on particle size. Explosive limits are expressed as g/m3. MEC *is the smallest concentration of dust suspended into a given volume of air that is capable of ignition and sustaining flame propagation, producing a pressure at least twice as high as the initial pressure at ignition.* Below LEL, particles are separated by relatively large distances and heat liberated by oxidation of single particle is not sufficient to ignite adjacent particles. Above UEL (usually in the range of 5–10 kg/m3) particles are densely packed, limiting access for the oxygen needed for combustion, and thereby quenching flame propagation. Within the explosive range (between LEL and UEL), actual dust concentration affects severity of the explosion. Theoretically, the most severe explosion effects might arise at stoichiometric concentrations; but unlike gases, dust explosions normally leave a portion of partially burnt material.

Table 3.32 gives minimum explosible concentrations (MECs) for selected dusts.

Table 3.32 Minimum explosible concentrations for selected dusts, g/m^3

Dust	*Dp (μm)*	*MEC*	*Dust*	*Dp (μ m)*	*MEC*
Wheat flour	---	50	Asphalt	---	25
Maize starch	12	30	Sulfur	20	30
Rice	---	50	Caprolactam	---	70
Sugar	---	15	Nylon 11	---	5
Coffee (instant)	---	150	Polystyrene	---	20
Milk powder	83	60	HDPE	---	10
Vitamin C	---	70	Polyurethane foam	---	30
Acetyl salicilic acid	---	15	Phenol formaldehyde Resin	---	15
Acrylonitrile polymer	---	40	Polyethylene, high density	---	10
Azo dye (yellow)	10	60	Epoxy resin	26	30
Benzoic acid	---	11	Sponge iron	---	100
Coal, 37% VM	---	55	Aluminum	29	30
(Standard Pitts-burgh)	---	---	Magnesium	28	30
Carbon black	10	60	Zirconium	10	10

Note: Where particle size is not mentioned, particles are usually at less than 150 μm size. Most materials have MEC values in the range of 30–125 g/m^3. These concentrations are sufficiently high that a 2-m-thick cloud can prevent seeing a 25 watt bulb on the other side of the cloud.

Limiting oxygen concentration (LOC) to prevent explosion of a given dust varies from dust to dust and depends also on the inert gas used to reduce oxygen percentage in the suspending medium. LOC is the oxygen concentration below which no explosion takes place. For many organic materials the LOC for nitrogen inerted systems lies between 9.0 and 14.0 percent oxygen. If CO_2 is used in place of nitrogen, the LOC typically rises by 1–2 percent due to its higher heat capacity. This does not apply to some metals which may even burn in CO_2. As discussed earlier, the diluent used to reduce oxygen content is effective in proportion to its molar heat capacity. As in the case of flammable gases, normally used inert gases with dusts are N_2, CO_2, and Ar. In some cases flue gases or steam can be used. CO_2 is a more effective diluent than N_2. At high temperatures (to prevent condensation), water vapor is as effective as CO_2. With the exception of metal powders, for most combustible dusts, flame propagation at any concentration, can be prevented by reducing oxygen to 11 percent v/v using CO_2 and to 8 percent using N_2 as inert gas. A rule of thumb used for inerting is given by Eqn. 3.39:

$$N_O = 1.3\ C - 6.3 \tag{3.39}$$

where N_O and C are maximum concentrations of oxygen percent v/v, to prevent ignition for N_2 and CO_2 as inert gas respectively. Metal powders require less oxygen concentrations to be maintained for effective inerting. Maximum permissible oxygen content to prevent dust cloud ignition at high temperatures, are much less.

For carbonaceous dusts, 3–4 percent oxygen may be the limiting concentration for effective inerting against ignition by high temperature sources. Argon and helium are preferred diluents for metal dusts. Many metals react with carbon dioxide or nitrogen. The hydrides of thorium, uranium, and zirconium, however, are preferably inerted with CO_2.

When moisture is the inerting medium, percentage moisture required in the dust to prevent ignition varies from dust to dust. For coal dust with 37 percent volatile matter (Pittsburgh coal), 16 percent moisture is required to prevent ignition. For corn starch, the percentage is 19 and for paper dust it is 35. High moisture content inhibits creation of a dust cloud. Inert dusts added as diluents to combustible dusts, wherever quality requirements permit or product dust is a waste material, also act as explosion inhibitors by interfering with the oxygen diffusion process to the active sites of the combustible dust and by acting as heat sinks. Examples of diluent dusts are stone dust, salt (NaCl) dust, gypsum ($CaSO_4$), limestone ($CaCO_3$), and sodium bicarbonate ($NaHCO_3$). Halons and dry powders such as sodium bicarbonate or mono-ammonium phosphate are used effectively as flame suppressants. Most widely used halon is Halon 1011 (CH_2ClBr). Other halons are Halon 121 ($CBrClF_2$) and Halon 1301 ($CBrF_3$). Water is particularly effective for hydrophilic dusts. About twice as much water as halon or dry powder is required for effective suppression.

In industry, uniform concentration of dust suspensions is highly unlikely. Local concentrations vary widely due to gravitational and turbulence effects as well as non-uniformity in particle size. It is therefore not a good practice to assume that there will be no dust explosion hazards if operations are carried out well above the probable UEL. LEL can be a useful guide for those situations where dust to air ratio can be controlled. Unlike gas/vapor–air mixtures, dust–air mixtures are visible. Before dust concentrations reach LEL, visibility is reduced to a few meters, making breathing difficult within the dust cloud. A rule of thumb is that if one can see his/her outstretched hand in front of his/her face, the dust cloud is not above LEL. In many industrial dust handling operations inclusive of grinding operations, the cloud concentrations seldom exceeded 7 percent of LEL for many dusts. A cloud with concentrations above LEL is likely to exist frequently, only in locations where energy has been added to the dust.

Tests for minimum explosible concentrations are carried out in a vertical tube apparatus with dispersion of the dust in the upward direction in the tube. Electrically heated wire coil or an electric spark is used as ignition source. Successive tests are carried out with reduced amounts of dust until no explosion occurs in at least 10 consecutive tests for a given concentration.

Particle size affects minimum explosible concentrations. In general for dusts other than metal dusts, minimum explosible concentrations decrease with decrease in particle size. This is mainly because the interfacial area between air and particles increases resulting in increased combustion rates. Also, tendency for the particles to get air borne will also increase. At small particle sizes (less than 75 μ m), the effect will be marginal. Exceptions are metal dusts, which, when ground finely in air, progressive size reduction can result in a product containing proportionately more oxide, which exhibit a reverse trend on minimum explosible concentrations.

Moisture content influences minimum explosible concentration. Increase in moisture content increases minimum explosible concentration, mainly due to the increased tendency for the dust particles to form agglomerates which are more difficult to disperse and partial utilization of the input heat energy for the vaporization of the moisture, limiting energy available for initiation of combustion.

Hybrid mixtures: In some situations, flammable gases, air and dust suspensions exist by design or accident. These mixtures are called hybrid mixtures. Presence of flammable gas has strong influence on the burning and explosion characteristics of dusts. A combustible dust mixed with a flammable gas and air will explode more violently than dust in air alone, even though the concentrations of flammable gas or dust in air, are very low and incapable of supporting flame propagation in gas–air and dust–air systems. Hybrid mixtures exhibit positive synergism with respect to explosibility, even in such systems where concentrations of dusts are below LEL for the dust in air and concentration of gas in air is below LFL. Also non-combustible dusts or combustible dusts having particle sizes too large to permit an explosion in air, are capable of exploding in the presence of a flammable gas, even if the gas is at a concentration in air below its LEL.

Minimum explosible concentration for a hybrid mixture containing a solvent vapor may be estimated using Eqn. 3.40, which is based on Le Chatelier principle with corrections for practical situations.

$$\mathrm{MEC} = \frac{0.8\,\mathrm{MEC_d}}{1 + (G/100)\,[(\mathrm{MEC_d}/\mathrm{LEL_s}) - 1]} \tag{3.40}$$

where MEC = minimum explosible concentration of dust for the hybrid mixture, g/m^3.

$\mathrm{MEC_d}$ = Minimum explosible concentration of dust in dust–air mixtures, g/m^3

$\mathrm{LEL_s}$ = LEL for the solvent vapor in air expressed as g/m^3.

G = Mass of solvent vapor in unit volume of vapor, dust and air mixture, expressed as wt. percent dust

$$\text{Mass of solvent-free dust per unit volume} = [(100 - G)/100]\ \mathrm{MEC} \tag{3.41}$$

$$\text{Mass of solvent per unit volume} = G\ \mathrm{MEC}/100 \tag{3.42}$$

Example 1

Sunflower meal dust is contaminated with 1.0 percent by wt. of hexane. Estimate minimum explosible concentration of sunflower meal dust for its hybrid mixture with hexane vapors and air.

Given: $G = 1.0$ $\mathrm{LEL_s} = 42$ g/m^3 $\mathrm{MEC_d} = 250$ g/m^3

$\mathrm{MEC} = (0.8)\ 250/[1 + 0.01(250 - 1)/42\ ] = 188.8$ g/m^3

Example 2

Cottonseed meal contaminated with 1.5 percent hexane.

Given: $G = 1.5$ $\mathrm{LFL_s} = 42$ g/m^3 $\mathrm{MEC_d} = 55$ g/m^3

$\mathrm{MEC} = (0.8)\ 55/[1 + 0.015\ (55 - 1)/42] = 43$ g/m^3

Above examples show that minimum explosible concentrations for the *hybrid mixtures* are *far below* those for dust–air mixtures, with the result that hazards are much higher for cases where a flammable/explosible gas/vapor is present in explosible dusts with access to air or oxygen.

Minimum oxygen concentration (MOC): LFL is based on air but actually it is O2 that is important. Often in industry inerting is used to dilute the O2 concentration. Due to this reason, one finds the parameter, MOC in literature. Below MOC the reaction cannot generate enough energy to heat the entire mixture to the extent required for self-propagation.

Figure 3.15 is a summary of dust explosion requirements (adopted from CSB).

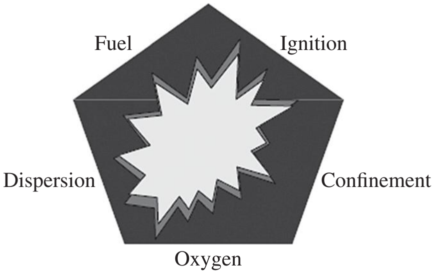


Figure 3.15 Summary diagram for dust explosion requirements

Burning Velocity and Quench Effects

Burning velocity and flame speed are important parameters for the assessment of flammability. Burning velocity is defined as the velocity at which the unburned gases move through the combustion wave in the direction normal to the wave surface. Burning velocity is a property of the gas–air mixtures (that is normal combustion velocity or laminar flame speed) only whereas flame speed depends on factors such as turbulence, pressure waves, and the like.

Flame speed, *S*, is defined as velocity of the flame relative to a stationary observer that is, the ground or another fixed frame. The burning velocity, *U*, is the velocity of the flame front with respect to the unburned gas immediately ahead of the flame. The actual flame speed in combustion of a flammable mixture is higher and often very much higher than the burning velocity. If detonation occurs, the flame speed is higher by orders of magnitude than the burning velocity.

A dimensionless number, the *Weaver flame speed number*, is used to characterize flame speed. It is simply calculated as $U/U_{(H2)}$. Its value is always less than 100 percent.Turbulence has a profound effect on flame speed increasing it significantly. At low levels of turbulence, the flame thickness (order of 0.6 mm at NTP) is smaller than the turbulent eddies. It behaves like a wrinkled laminar flame. At very high levels of turbulence the turbulent eddies are of similar size to the flame thickness. Hence turbulence occurs within the flame front giving highly enhanced combustion and very large flame speeds. Flame speed for most hydrocarbon fuels is very similar (around 0.4 m/s). This is because all hydrocarbons are quickly pyrolyzed to smaller sized molecules before combustion and hence behave in a similar manner

The relation between flame speed, *S*, and burning velocity, *U*, is

$$S = U + u \tag{3.43}$$

where u is velocity of the unburned gas just ahead of the flame. For stoichiometric hydrocarbon–air mixtures S is of the order of $8{*}U$. Figure 3.16 illustrates flame propagation in a tube.

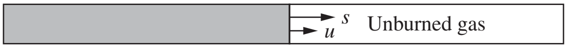


Figure 3.16 Flame propagation in a tube

The rate of combustion of a flammable mixture is affected by the burning velocity. It is in effect the velocity at which a gas–air mixture issuing from a Bunsen burner burns back onto the burner. It is given by the equation,

$$U = V/A \tag{3.44}$$

where U = Burning velocity, cm/s
A = area of flame front cone, cm^2
V = Volumetric gas flow rate, cm^3/s

Mallard—Le Chatelier equation relates burning velocity to reaction rate and thermal diffusivity and is given by:

$$U \approx (\alpha\, \mathrm{RR})^{0.5} \tag{3.45}$$

where α is thermal diffusivity, $(\lambda/\rho C_p)$ (3.46)
λ is thermal conductivity and RR is reaction rate.

Taking flame speeds to be independent of pressures, which is the case for most hydrocarbon–oxygen systems with the overall order of two for the reaction, the simplified equation is given by:

$$U \approx (e^{-E/RT_f}) \qquad (3.47)$$

where T_f is the highest temperature (flame temperature) and E is activation energy.

Laminar burning velocity gives a good indication of the combustion characteristics of a fuel. It is very sensitive to mixture composition. The maximum is normally on the rich side of stoichiometric composition.

Burning velocity depends on concentration of flammable gas in air or oxygen. It is affected by temperature and pressure. Increase in temperature and pressure increases burning velocities. For every gas there is a maximum burning velocity at a given temperature and pressure. Effect of mixture composition on burning velocity of methane in air and oxygen at atmospheric pressure is illustrated in Figure 3.17, showing a large difference between influence of air and oxygen atmospheres.

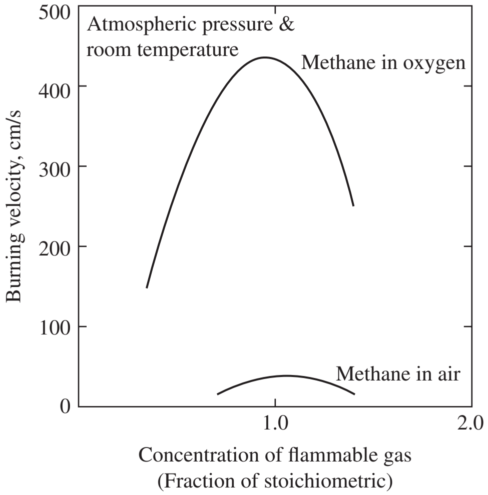


Figure 3.17 Effect of mixture composition on burning velocity of methane in Air and Oxygen

* **Source** Zabetakis, Bureau of Mines Bulletin 627, 1965

The maximum burning velocity obtained at atmospheric pressure and temperature is referred to as the maximum fundamental burning velocity.

In general, burning velocities for paraffinic hydrocarbons range from a few cm/s near the flammability limits up to about 45 cm/s near the stoichiometric mixture. For these hydrocarbons in oxygen the corresponding values are about 125 and 425 cm/s, respectively. Laminar burning velocity tends to increase with temperature. The increase is more dramatic in mixtures with relatively high burning velocities, such as hydrogen/oxygen.

Table 3.33 gives maximum burning velocities for selected materials in air and oxygen. It should be noted that H_2 has the highest burning velocity and flame speed.

Table 3.33 Maximum fundamental burning velocities for selected materials in air and oxygen

Material	*Maximum burning velocity (cm/s)*	
	In air	**In oxygen**
Hydrogen	320	1175
Acetylene	173	1140
Ethylene	68.8	550
Methane	36.4	393
Ethane	40.1	---
Propane	45	390
n-Butane	40.5	---
n-Hexane	38.5	---
Benzene	40.7	---
Carbon disulfide	58	---
Ethylene oxide	108	---
Methanol	56	---

Burning rate: The burning rate [kg/s] is the amount of fuel consumed by the combustion process per unit time. The burning rate is a measure of the rate of energy release in an explosion. The burning rate may also be defined as mass of fuel consumed per unit time and volume.

Quenching effects: Flame may be extinguished by quenching. Such quenching may be due to heat loss (local cooling) to unburnt gas or to a solid surface. It is also due to radical termination. Quench effects alter flammability limits and play a role in ignition phenomena. Flame propagation is suppressed if the flammable mixture is held in a narrow space. Flame in a tube is quenched by affecting the two mechanisms which permit flame propagation, that is, diffusion of species and of heat. Tube walls extract heat. The smaller the tube size, the greater the surface area to volume ratio within the tube and thus the greater the heat loss. Smaller tube sizes increase the number of collisions of the active radical species with the wall and with the greater the number of species destroyed. The condition and material of construction of the tube wall affect the rate of destruction of the active species. Increasing temperature decreases quenching distance and increasing pressure increases the quenching distance.

There is a minimum diameter for the apparatus used for measuring flammability limits such that below this diameter, the flammability range measured will be narrower and inaccurate. If the space is sufficiently narrow, flame propagation is completely suppressed. The largest diameter at which flame propagation is completely suppressed is known as *quenching diameter*. For an aperture of slot like cross-section, there is a critical slot width. The term *quenching distance* is some times used as a general term covering both quenching diameter and critical slot width.

The following empirical equation gives the relationship between quenching diameter and critical slot width:

$$D_{\text{II}} = 0.65\ D_{\text{o}} \tag{3.48}$$

where D_{II} is critical slot width and D_{o} is quenching diameter.

The quenching diameter and quenching length are very important parameters needed for the design of dry deflagration and detonation flame arresters.

Stability limits of laminar flames: These are of two types:

(i) One type governs ability of the mixture to support flame propagation. This includes flammability limits and quenching distance.
(ii) The second type is concerned with flow conditions, particularly for flow through tubes. This includes the phenomena of flash back, blow off and the onset of turbulence.

Quenching in a tube affect the flame propagation by affecting the two mechanisms, namely, diffusion of species and transfer of heat. The smaller the tube, the greater the number of collisions of the active radical species with the wall and the greater the number of these species destroyed. Condition and material of construction of the tube wall affect the destruction of these active species.

Increasing the temperature decreases the quenching distance and increase in pressure increases quenching distance.

There is a *maximum experimental safe gap (MESG)* that prevents transmission of an explosion occurring within a container to a flammable mixture outside.

Table 3.34 gives MESG values for selected materials in air.

Table 3.34 MESG values for selected materials in air, mm

Material	*MESG*	*Material*	*MESG*	*Material*	*MESG*
Hydrogen	0.20	Carbon disulfide	0.20	Acetylene	0.37
Ethylene oxide	0.59	Ethylene	0.65	Propylene oxide	0.70
1,3-Butadiene	0.79	Methyl ethyl ketone	0.84	Diethyl ether	0.87
Tetrahydrofuran	0.87	n-Pentane	0.89	Ethanol	0.89
Hydrogen sulfide	0.90	Carbon monoxide	0.91	Propylene	0.91
Ethane	0.91	Methanol	0.92	n-Butanol	0.91
Propane	0.92	n-Pentane	0.93	n-Hexane	0.93
Acetaldehyde	0.92	Cyclohexane	0.94	Vinyl chloride	0.96
n-Butane	0.98	Benzene	0.99	Acetone	1.04
Methane	1.14	Ethylene dichloride	1.82	Ammonia	3.18

Note: The hazard of the gases increases from explosion group IIA–IIC. The requirements for the electrical apparatus increase accordingly to these explosion groups.

MESG values for electrical equipment: Group IIA materials > 0.9; Group IIB materials 0.5–0.9; Group IIC materials > 0.5

It must be emphasized that the above values relate to stationary flames. If the gas flow is in the direction of flame propagation, a smaller gap is needed to quench the flame and, conversely, if the gas flow is in the opposite direction, a larger gap will effect quenching. If the gas velocity is high enough, a condition can occur in which a flame propagating against the flow is stabilized at a constriction and causes local overheating.

For some materials such as acetylene, hydrogen, and carbon disulfide, MESG values are very small. MESG values for gas mixtures can be estimated using Le Chatelier principle. Quenching is of practical interest in a number of ways. The stabilization of flames on burners is related to quenching. These quenching effects are important in the design of flame-proof equipment and flame arresters. The presence of un-burnt fuel in car exhaust may be attributable to quenching.

Figure 3.18 illustrates use of flange and threaded joints for flame quenching.

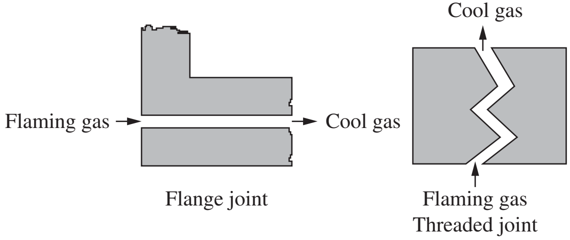


Figure 3.18 Flange and threaded joints

Longer path permits use of wider gaps. Threaded joints are preferred as the path in such joints can be longer. Moreover, a faulty thread can be more easily detected than a fault in a flange joint. Screwing is not possible for a faulty threaded joint.

Ignition

Ignition is considered to be the process of initiating flame propagation or an explosion by energizing fuel and oxidizer molecules so that they collide with each other at sufficient velocity to initiate the reaction, fast enough for a flame to propagate. Ignition requires favorable initiating conditions, which involve sufficient heat input to the system that covers the initial energy demand of the chain reactions of the combustion process. It is the first step of the self-sustaining process of combustion. It may occur as *piloted ignition* (or forced ignition) if the phenomenon is caused by any external ignition source like an electric spark or a flame, or it may ignite by itself, *self-ignition or autoignition*, if the phenomenon is the result of reactions taking place in the combustible material itself, coupled with heat release.

In a pure adiabatic system, if one assumes an Arrhenius expression defines kinetics, then the system is reacting at every temperature, no matter how slowly. In this case it is not possible to define uniquely the ignition temperature. An ignition time for a system can be defined at a given temperature. This time is usually meant to specify that interval for a given initial fraction of reactants to be consumed. This time, the time it takes for the reaction of the fuel vapor and air to reach a degree of reaction and thus temperature, so that the products are *luminous*.

When there are heat losses (nonadiabatic case) ignition temperature is defined as the lowest temperature at which the rate of heat loss from the system is over-balanced by the rate of heat generation by reaction. Here, time is not important since very long times can prevail before a rapid temperature rise is observed (i.e. a flame or an explosion is generated).

One definition for ignition to be a self-perpetrating exothermic reaction that is initiated at the temperature of incipient oxidation and that increases the temperature of the reactants above the initial air temperature until an explosion, flame, or sustained glow occurs. *Ignitability* of a fuel is that characteristic which determines the ease with which the fuel may be brought to a condition of self-supporting, active oxidation. The ignitability is governed not only by the inherent chemical characteristics of the fuel that determine its rate of oxidation at various temperatures but also by the physical characteristics of the fuel and its surroundings that determine the rate at which it can be heated. Among these physical characteristics are size of the pieces of the fuel, specific heat of the fuel, thermal conductivity of the pieces and the aggregate, rate at which the oxygen or air is brought into contact with the fuel and the rate of heat loss to the surroundings. Chemical and physical changes, such as melting and decomposition of bituminous coal, may occur as the fuel is heated.

Ignition can take place when the rate of heat production by a self-sustaining chemical reaction exceeds the rate of heat loss to the surroundings. There is no direct relationship between the heat quantity needed for ignition and the ignition temperature, because although the chemical composition of the components in the combustible system is an essential parameter of ignition temperature, it is considerably influenced by the sizes and shapes of materials, the pressure of the environment, conditions of air flow, parameters of ignition source, the geometrical features of the testing device, etc. The ignition mechanism of materials involves their physical state, namely, gas, liquid, or solid. The ignition temperature of gas varies with its concentration and is reduced by pressure increase. Substitution of oxygen for air has little effect implying the process is more governed by the Arhennius expression than concentration.

It is an important empirical statement that the mixtures of gases and air are capable of ignition in a certain range of concentrations only. This is valid also for vapors. For ignition to occur with *liquids*, these must have the formation of a vapor space above their surface that is capable of burning. The released vapors and the gaseous decomposition products mix with the air above the surface of liquid or solid material.

Most *solid* materials take up energy from any outer ignition source either by conduction, convection or radiation (mostly by their combination), or are heated up as a result of the heat producing processes taking place internally that start decomposition on their surfaces.

If heat is conducted away sufficiently rapidly, the temperature may be reduced below the ignition point and combustion ceases. Even rapidly burning explosive mixtures may be *quenched* by sufficient cooling. The turbulent flows that arise in the mixture and/or the diffusion help the oxygen to reach the molecules, atoms and free radicals on and above the surface, which are already suitable for reaction. The particles induced enter into interaction, resulting in the release of heat. The process steadily accelerates and as the chain reaction starts, the material comes to ignition levels and burns.

The combustion in the layer under the surface of *solid* combustible materials is called *smoldering*, and the burning reaction taking place on the interface of solid materials and gas is called *glowing*. Burning with flames is the process in the course of which the exothermic reaction of burning runs in the gas phase. This is typical for the combustion of both liquid and *self-ignition temperature (SIT).*

Flammable liquids, vapors, and gases in mixtures with air or oxidizer , whose compositions lie inside the flammability range , can also be ignited by simply raising their temperature by heating without the use of ignition sources such as an electric spark or a flame. Many chemicals decompose (breakdown) when heated.

The self-ignition temperature (SIT) of a substance, whether liquid, solid, or gas, is the *lowest* temperature at which the chemicals formed by decomposition begin to cause self-sustained combustion in air with no other source of ignition. It is some times called autoignition temperature (AIT).

SIT is not a property of the substance. It can vary by 100°C or more depending on the test method used. Therefore literature values may be rough estimates and intended to be guides, not as fine lines between safe and unsafe conditions. For example, measured value depends on the apparatus used and also on the composition of the mixture:

Measured value is very much apparatus related, (NFPA data):

Benzene in quartz flask, 571°C and in iron flask, 678°C.

CS_2 in 200 ml flask, 120°C and 1,000 ml flask, 110°C, and 10,000 ml flask 96°C. Hexane with different apparatus, 225°C and 510°C.

Measured value also is concentration dependent (NFPA data):

C_5 in air at 1.5 percent, 548°C, 3.75 percent 502°C, and 7.65 percent, 476°C.

Precautionary measures are necessary to avoid fires and explosions. SIT has no unique relationship to either *flammability limits* or *flash points*. SIT of mists can be lower than the flash point of the liquid (e.g. caused by decomposition reactions). SIT may be characterized in some way by the *spontaneous ignition temperature*. This is defined as the temperature above which combustion, once initiated, will maintain itself and below which *active* combustion cannot occur.

SIT depends on several variables such as structure of the fuel molecules , fuel–air mixture composition, initial fuel–air temperature, temperature and heating rate of the heated surface, oxygen content in air, pressure, presence of materials that catalyze the reactions, nature, area, shape and orientation of the surfaces, residence time or *ignition delay,* and flow conditions.

Measured value is very much related to the apparatus used. Examples include (NFPA data): For benzene in quartz flask, it is 571°C and in flask it is 678°C.

CS_2 in 200 ml flask 120°C, 1,000 ml flask 110°C and 10,000 ml flask it is 96°C. Hexane with different apparatus:225°C and 510°C. SIT usually has a minimum near the stoichiometric composition of fuel–air mixtures. Oxygen–enriched atmospheres have a tendency to lower SITs. In oxygen, SIT may be up to 300°C below the one in air. SIT decreases with increase in pressure. Gases/vapors may oxidize catalytically on hot surfaces below their SITs and outside normal *flammability limits* , releasing heat. Presence of NO_2 lowers SIT, due to the catalytic action of NO_2. Lagged/dusty surfaces have much lower SITs than the reported values.

Gasoline vapors have SITs of about 270°C (515°F) on surfaces but if the surface is reduced to that of a thin wire, its value can be as high as 595°C (1100°F). Also, the values on convex or flat surfaces are higher than the reported values. When the flammable mixture reaches SIT, ignition will not be instantaneous but requires a finite time for the absorption of heat from the slower reactions by the surrounding unreacted mixture, triggering a *reaction runaway*, increasing the heat generation rate over that of its dissipation rate. When heat dissipation is impeded, for example, inside a lagging, temperature increases further, leading to a self-propagating flame or explosion. If heat is conducted away sufficiently rapidly, the temperature may be reduced below the ignition point and combustion ceases. Even rapidly burning explosive mixtures may be *quenched* by sufficient cooling.

Flow conditions influence the heat dissipation rate. SIT of a solid is influenced by its physical condition and the rate of heating. In general, SIT values depend on the following:

(i) Percent composition of gas–air or vapor–air mixtures.
(ii) Shape and size of the space where ignition occurs.
(iii) Rate and duration of heating.
(iv) Catalytic or other effects of the material used for the container.

Figure 3.19 Illustrates the relationship among flash point, vapor pressure, flammability limits and SIT on a plot of fuel concentration vs. temperature.

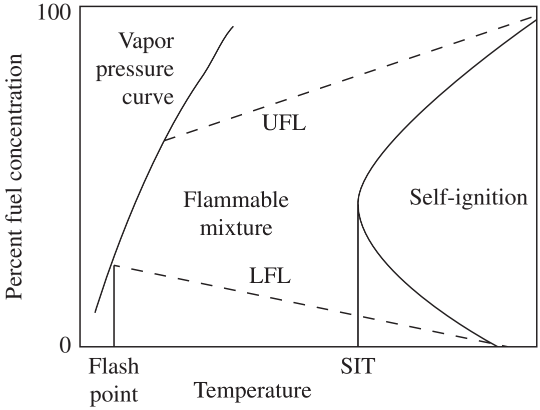


Figure 3.19 Relationships among flash point, vapor pressure, flammability limits, and SIT

At temperatures below SIT, slow reactions may be occuring. As temperature is increased, at some high value of temperature, self–ignition occurs as illustrated in Figure 3.20. The SIT curve passes through a minimum as mixture composition is changed. SIT usually has a minimum near the stoichiometric composition of fuel–air mixtures. Heavy petroleum products like diesel oils, lube oils, fuel oils and long chain hydrocarbons, for example, waxes, have lower SITs than light distillates like gasoline, naphtha, a kerosene.

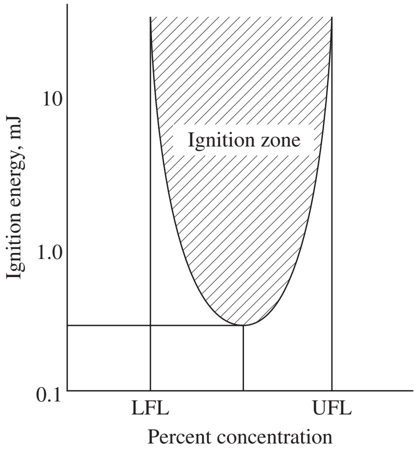


Figure 3.20 Typical relationship between ignition energy and mixture composition

Most common flammable and combustible liquids have SITs in the range of 300–550°C. Some have very low SITs. Carbon disulphide is notable for its low SIT of 90°C. A glowing light bulb or a steam line is enough to ignite CS_2. Diethyl ether has also relatively low SIT of 160°C and can be ignited by a hot plate. Gases like diborane and phosphine have extremely low SITs and require special precautions for handling.

In diesel engines temperature is raised sufficiently by compression only for combustion. The increase in temperature due to compression may lead to explosions due to the lubricating oils reaching their SIT values and catching fire in air compressors. Table 3.35 gives SITs for some materials.

Table 3.35 Self-ignition temperatures of selected materials in air at atmospheric pressure

Material	*SIT (°C)*	*Material*	*SIT (°C)*
Acetaldehyde	175	Styrene	490
Carbon disulphide	90	p-Xylene	530
Acetylene	305	Diborane	38–52
Ethylene	490	Phosphine	100
Propylene	460	Hydrazine	270
Hydrogen	400	Diethyl ether	160
Methane	540	Acetone	465
Ethane	515	Methanol	385
Ethanol	365	Iso-propanol	399
Propane	450	Iso-octane	447
n-Hexane	223	n-Pentane	260
Carbon monoxide	677	Ammonia	651

(*Continued*)

Table 3.35 (Continued)

Hydrogen sulfide	260	Phosphorous	34
Benzene	562	Sulfur	243
Toluene	536	Carbon	400
Cyclohexane	245	Characoal	349
Gasoline	268	Titanium dust layers	382–510
Kerosene	220	Titanium dust clouds	332–588
Naphtha	550	Riffle powder	288
Light hydrocarbons	650	Wood	300
Heavy hydrocarbons	750	Anthracite (glow point)	600

Ignition energy: Energy in the form of heat is required to produce vapors and gases by vaporization or decomposition of solids and liquids and intimately mix them with oxygen in air or oxidizer through diffusion and mass transfer processes to initiate chemical reactions among the molecules. To energize the molecules of oxygen and flammable vapors, by raising their temperature and hence reaction rates to a level at which combustion reactions release sufficient energy to sustain combustion process, that is, flame propagation in the surrounding mixture.

This energy is called *ignition energy*. The amount of energy required to cause combustion varies greatly for different fuels and mixture compositions. Hydrogen, acetylene and carbon disulphide can be ignited by tiny sparks or simply by static electricity generated as the gases or vapors discharge from pipes into air. Other materials, such as ammonia and methylene chloride, require such large amounts of energy to be ignited that they are sometimes considered nonflammable. If the mixture composition falls outside the *flammability limits*, there will not be any ignition and flame propagation, even if the energy supplied is very large. A minimum value known as the *lowest minimum ignition energy (LMIE)* or simply as the *minimum ignition energy (MIE)* is exhibited approximately half-way between the flammability limits.

The LMIE for most flammable vapors in air is between 0.1 and 1.0 mJ.

Minimum ignition energy (MIE) is defined as the minimum energy that can ignite a mixture of a specified flammable material with air or oxygen, measured by a standard procedure. Depending on the specific application, there are several standard procedures for determining MIE for gases, vapors, and dust clouds. The common element in all procedures is that the energy is generated by an electrostatic spark discharge (ESD) released from a capacitive electrical circuit. The exact circuit components and the arrangement of electrodes between which sparks are generated are the principal differences between the methods.

From Lewis and von Elbe the relationship between the ignition energy of the fuel vapors and their concentration will be similar to that shown by the U-shaped curve (shaded area) in Figure 3.20. The fuel is most sensitive to ignition approximately midway between the lower and upper flammable limits and that the spark energy required to ignite the vapor increases rapidly as it approaches these limits. Figure 3.21 gives ignition energy curves for benzene and ethylene oxide in air.

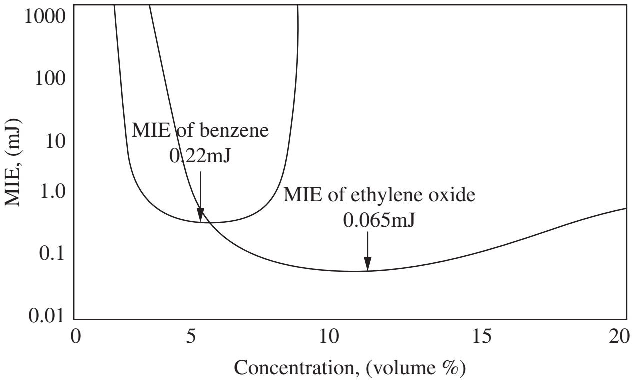


Figure 3.21 illustrates the contrast in the ignition energy curves for benzene and ethylene oxide, the later requiring much lower energies for ignition and wider flammability range, with ignition energy requirements increasing with concentration at a much slower rate.

The energy requirements will pass through minimum values that are approximate to the stoichiometric concentrations. Deviation from the stoichiometric composition to leaner or richer side depends on the chemical structure of the gas or vapor. For most hydrocarbons, MIE deviates to the richer side. Increased molecular weight of the fuel results in increased shift of MIE to the richer side. Exceptions are gases like methane, hydrogen and acetylene for which the shift will be to the leaner side. Figure 3.22 illustrates ignition curves as a function of their concentration in air.

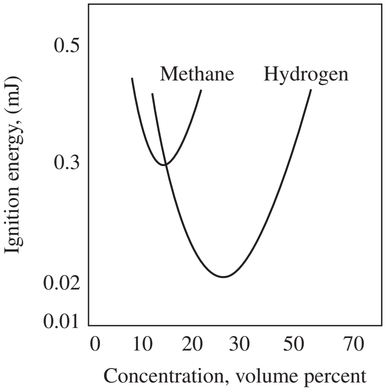


Figure 3.22 Ignition energies for hydrogen and methane as a function of their concentration in air

If the atmosphere is oxygen-rich (in excess of normal air), the sensitivity to ignition is significantly increased. This will be in terms of both an extended flammable range and greatly reduced ignition energy requirements.

Minimum spark ignition energy in air and oxygen, at 25°C and 1.0 atmosphere, are given in Table 3.36 for selected materials. Replacing air by oxygen illustrates how easy it is to ignite fuel/oxygen mixtures.

Increased oxygen concentrations result in a drastic reduction in MIE. For propane, for example, MIE decreases from 0.25 mJ in air to 0.002 mJ in oxygen.

Table 3.36 Minimum spark ignition energies in air and oxygen of selected materials at 25°C and atmospheric pressure, mJ

Material	*MIE in air*	*MIE in O_2*
Carbon disulphide	0.009 (7.8)	---
Hydrogen	0.011	---
Acetylene	0.017	0.0002
H_2S	0.068	---
Ethylene	0.07	0.001
Ethylene oxide	0.065	---
1,3-Butadiene	0.125	---
Methyl acetylene	0.12	---
Methanol	0.14 (14.7)	---
Propylene	0.28	---
CO	< 0.3	---
Methane	0.3	0.003
Ethane	0.26	---
Propane	0.25 (5.2)	0.002
n-Butane	0.25 (4.7)	---
Hexane	0.24 (3.8)	---
n-Heptane	0.24 ((3.4)	---
n-Pentane	0.22	---
Diethyl ether	0.2	0.0013
Ethyl acetate	0.48	---
Methyl ethyl ketone	0.28	---
Isopropanol	0.65	---
Benzene	0.22 (4.5)	---
Toluene	0.24 (4.1)	---
Xylenes	0.2	---
Cycohexane	0.22	---
Cyclopropane	0.18	---
Vinyl acetate	0.7	---
Acetone	1.15 (4.5)	0.006
Gasoline	0.8	0.0024

(*Continued*)

Table 3.36 (Continued)

Ammonia	680	---
Methylene chloride	10,000	---
Phosphorus (red)	0.2	---
Sulfur	15	---
Fine sulfur dust	≈ 1.0	---
Coal (37% VM pittsburgh standard)	60	---
Charcoal	20	---
Lignin	20	---
Soot	15	---
Asphalt	25	---
Corn flour	20	---
Grain dust	30	---
Sugar	30	---
Rice	40	---
Wheat flour	50	---
Instant coffee	120	---
Skimmed milk	50	---
Acetyl salicylic acid	16	---
Aspirin	25–30	---
Paracetamol	10	---
Vitamin C	60	---
Benzoic acid	12	---
Polyethylene	10	---
High density polyethylene	30	---
Polyurethane foam	20	---
Methyl methacrylate	15	---
Epoxy resin	9	---
Phenol–formaldehyde	10	---
Nylon	20–30	---
ABS	30	---
Polystyrene	15	---
Polycarbonate	25	---
Cellulose	35	---
Cellulose acetate	20–50	---
Caprolactam	60	---
Sponge iron	40	---

(*Continued*)

Table 3.36 (Continued)

Aluminum (6 μ m)	13	---
Magnesium	40–80	---
Chromium	140	---
Tantalum	120	---
Zirconium	5	---
Thorium	5	---
Thorium hydride	3	---
Uranium	5	

Note: Figures in brackets are the corresponding vapor compositions in volume percent. Data from different sources and values differ from source to source. With dusts there is potential hazard arising from ignition due to static electricity. In majority of processes involving dusts, static electricity will almost certainly be generated.

Temperature and pressure affect ignition energies. Increase in temperature results in a decrease in spark ignition energy, because less heat input is required from the electrostatic discharge to create the activation energy needed to initiate combustion reactions. For example, as an illustration for propane, ignition energy decreases from 1.17 to 0.14 mJ over a temperature range of 40–200°C and for propylene oxide it decreases from 0.24 to 0.09 mJ over a temperature range of 25–180°C.

MIE generally decreases as pressure increases because the flammable atmosphere has more potential energy at higher pressures. Approximately, ignition energy is inversely proportional to the square of pressure. For example, decreasing pressure to about half increases MIE by a factor of about 4 to 5.

Vacuum reduces molecular collisions thereby decreasing reaction rates, that is, energy release rates. Unless energy inputs are increased, ignitions will not occur at low pressures.

Figure 3.23 illustrates pressure effects on ignition energy requirements for H_2 in air.

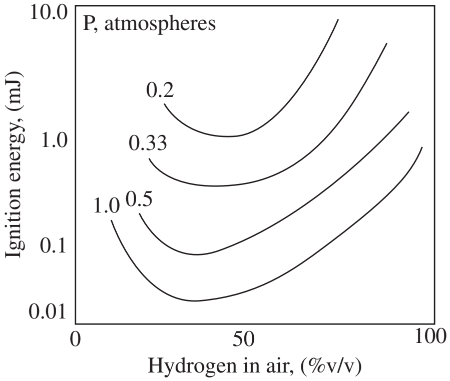


Figure 3.23 Effect of pressure on ignition energy of H_2 in air

Most data on ignition energies are for fuel gases/vapors in air (21 percent O_2 and 79 percent N_2 and other inert gases). If nitrogen in air is replaced by other inert gases, ignition energy is affected, the effect being related to the heat capacities of the inert gases.

Figure 3.24 shows the effect of replacing nitrogen in air by other inert gases, on ignition energy.

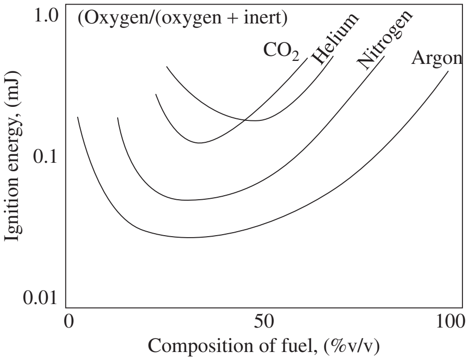


Figure 3.24 Effect of inert gas on ignition energy

If an inert gas is added to the fuel–air mixtures, in other words, with decreasing percent of oxygen in the mixture, MIE increases for gas–air as well as dust–air mixtures. CO_2 is more effective as an inert gas in raising requirements of ignition energy than N_2 or othr inert gases as shown in the figure. However use of CO_2 as a diluent involves static electricity generation as explained under ignition sources. Moreover, CO_2 in the presence of moisture gives rise to corrosion problems to equipment. Because of these reasons, nitrogen is preferred as an inerting gas.

Ignition energies for sprays and mists are much higher than those for gases and vapors, as part of the spark energy supplied to the mixture is used up in vaporizing the droplets , at least partially , before ignition occurs. The energy supplied by the spark to vaporize the droplet and then ignite the mixture may be 20–30 times greater than that for gases and vapors. For *sprays and mists*, ignition energy decreases with decrease in droplet size. This is expected as the droplet surface area per unit volume of the mixture increases with decrease in droplet diameter. This is illustrated for petroleum fuels in Figure 3.25.

In the limiting case where droplet size is infinitesimally small, the mixture behaves like a vapor–air mixture with ignition energies approaching those for gases or vapors.

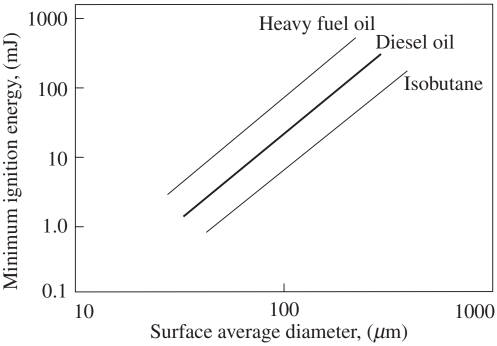


Figure 3.25 Effect of droplet diameter on MIE of typical petroleum products (schematic)

When the liquid is in the form of a pool , ignition is more difficult compared to ignition when it is in the form of a spray or mist because of the tremendous difference between the interfacial areas between the two. Much of the energy supplied from an external source is lost during the process of slow vaporization from a pool compared from a mist. For example , some *nonflammable* hydraulic oils fail to ignite when a flame is brought to the surface of the liquid pool. However for instance , when such oils leak from a high-pressure hydraulic transmission line through pin holes, they form into a fine spray and may ignite when a flame of comparable strength is brought near the spray.

To sum up: For flammable gases in air, the *lowest minimum ignition energy* (LMIE) is found *near* the stoichiometric composition (not necessarily at stoichiometric composition) and minimum ignition energy increases as the fuel composition increases or decreases from the LMIE. For most flammable dusts, minimum ignition energy is about 10 mJ, although wide variability is expected depending on the dust type, particle size and distribution.

With increase in temperature and/or pressure, minimum ignition energy *decreases*. Minimum ignition energy *increases* with increase in inert composition. Minimum ignition energy *decreases* with decrease in droplet sizes for mists and sprays of flammable liquids. Minimum ignition energy is related to *quenching distance* (*discussed elsewhere*) and experiments show that this relationship can be expressed by Eqn. 3.49

$$\mathrm{MIE} = \mathrm{C}\ \mathrm{d}^{2} \tag{3.49}$$

where *d* is quenching distance (discussed elsewhere) and C is a constant which has the same value for most hydrocarbon–air mixtures. Also, MIE is related to *burning velocity, Su* (*discussed elsewhere*), thermal conductivity of the gas–air mixture, *k* and flame temperature *T*, by the following equation:

$$\mathrm{MIE} \infty\ k\ (T_{\mathrm{f}} - T_{\mathrm{O}})/\mathrm{Su} \tag{3.50}$$

k = thermal conductivity of the gas–air mixture
Su = burning velocity of the fuel
T_{f} = flame temperature , *K*
T_{O} = ambient temperature , *K*

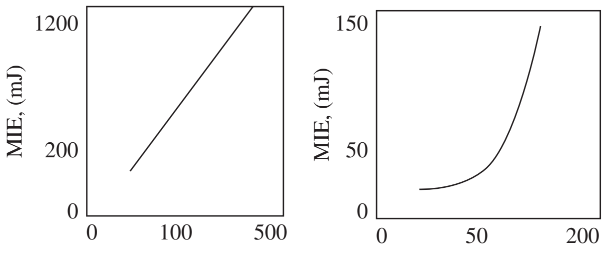
Ignition energies for dusts: Energy requirements for ignition of even the more easily ignited industrial dusts are around 20 times more than those for typical gases/vapors. Only a few dusts, for example, hydrides of zirconium, uranium, and thorium ignite at energies below 10 mJ. These dusts are capable of spontaneous ignition at room temperatures under some conditions.

The reported ignition energies are not exact but may be considered as a measure of relative sensitivities of dusts to ignition, even if they are not minimum values. Unless otherwise stated, the reported ignition energies are for *dust clouds*. Ignition energies for *dust layers* are much higher in magnitude. Ignition energies for some dusts are incorporated in Table 3.36 along with ignition energies for gases and vapors.

Minimum ignition energies for dusts are influenced by their chemical nature, particle size and shape, moisture content, temperature, turbulence, oxygen concentration, homogeneity of the suspension, and the test method used. In general, particles above 400 μm sizes will not ignite. Moderate amounts of moisture will not markedly influence ignition energy but as moisture content increases, ignition energies increase considerably.

This is because the energy supplied is partly utilized in vaporizing the moisture and also the vapors produced (in the case of carbonacous dusts with volatile matter) will contain water vapor which inhibits dispersion of the dust and explosion severity.

Particle size determines the exposed surface area that greatly influences MIE requirements for ignition of dust clouds as illustrated in Figures 3.26 (a) and (b).



(a) Cellulose acetate molding power (b) Polyethylene dust

Figure 3.26 Effect of particle size on MIE

Figure 3.27 illustrates influence of moisture content on minimum ignition energy of corn starch.

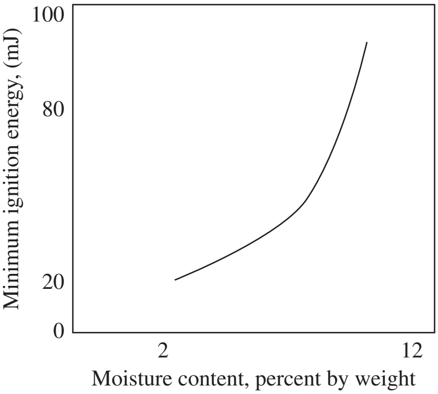


Figure 3.27 Influence of moisture content on MIE for corn starch

Turbulence increases the heat losses from the ignition source and consequently the MIE for a dust cloud typically increases with increasing turbulence. Most dusts will not burn if the air pressure is reduced below 50 mbar. Reducing the oxygen concentration in air increases the energy required for ignition. Most organic materials cease to be ignitable in the range 9–14 percent O_2. The MIE reduces if the O_2 concentration in the air is increased above 21 percent.

Many dusts must be at their stoichiometric (C_{St}) concentration, or higher for an explosion to occur and optimum concentrations can be 2–3 times the C_{St} volatiles in the dusts may influence minimum ignition energies. For *hybrid mixtures* of dusts and flammable gases in air, ignition energies are considerably lower.

With dusts there is potential hazard arising from ignition due to static electricity. In majority of processes involving dusts, static electricity will almost certainly be generated. One source of static electricity is from charged personnel. Precautions against static electricity must be taken. (*Discussion on generation and control of static electricity is given under the topic, ignition sources*).

Ignition delay: When temperature of a material is raised to its self-ignition value in a flammable atmosphere, ignition will not take place instantaneously. There is a finite time delay before ignition takes place. The mixture requires certain residence time, as in chemical reactions, before the molecules of the mixture attains the necessary collision rates for the transformation of the rate of slow reactions into fast rate to trigger ignition and flame propagation. The time period between attaining SIT and actual ignition is called *ignition delay*. Above SIT, as temperature is increased, ignition delay decreases. Close to SIT, this delay may be several minutes and as temperature exceeds SIT, delay decreases and ignition may take place within a fraction of a second.

Figure 3.28 illustrates effect of temperature on ignition delay. Below SIT, the delay is infinite and rapidly decreases as temperature exceeds SIT.

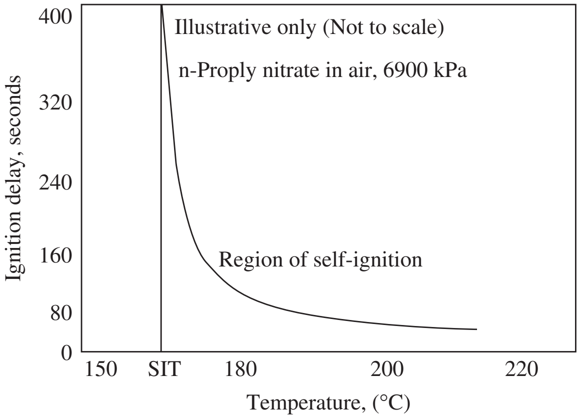


Figure 3.28 Effect of temperature on ignition delay

Ignition delay depends on nature of fuel. Paraffinic fuels involve smaller ignition delays. Smaller ignition delay periods are desirable in diesel engines and furnaces. Larger delays lead to accumulation of fuel in the confined space of a diesel engine or furnace. When ignition takes place under these circumstances, particularly at cold start-up of furnaces, all accumulated fuel ignites at once, leading to furnace explosions. Precautions are to be taken in burner management and light up procedures to avoid these hazards.

In some oil burning furnaces and kerosene stoves, cold fuel, air or surfaces have caused failures to ignite even when a strong ignition source, such as a flame, was used. The oil and kerosene vapors increased steadily. Repeated attempts at ignition finally warmed up the fuel enough to permit ignition which caused serious explosions in furnaces. For this reason, such furnaces are equipped with *blow out panels*, to relieve pressure before tubes, walls, drums, etc., can be damaged.

Degree of Flammability

The degree of hazard involved due to flammability depends on a number of properties of the materials that include ignition characteristics such as self-ignition temperature (SIT), ignition energy and ignition delay, flash point, flammability limits, burning velocity and explosion characteristics. Factors such as turbulence and interfacial area between the reactants also influence flammability characteristics of the materials.

Self-Heating

Many solid materials can exhibit self-heating, which–if unchecked–can progress to a fire or even explosion. And even if the situation does not get that far, it is likely to affect the output of the process, in terms of degradation of product quality. Recognizing that a product in powder or granular form can self- heat is the first step in controlling the risks associated with self-heating. Some materials can self-heat at ambient temperatures, especially in large scale storage, but for most materials the hazards arise when they are heated.

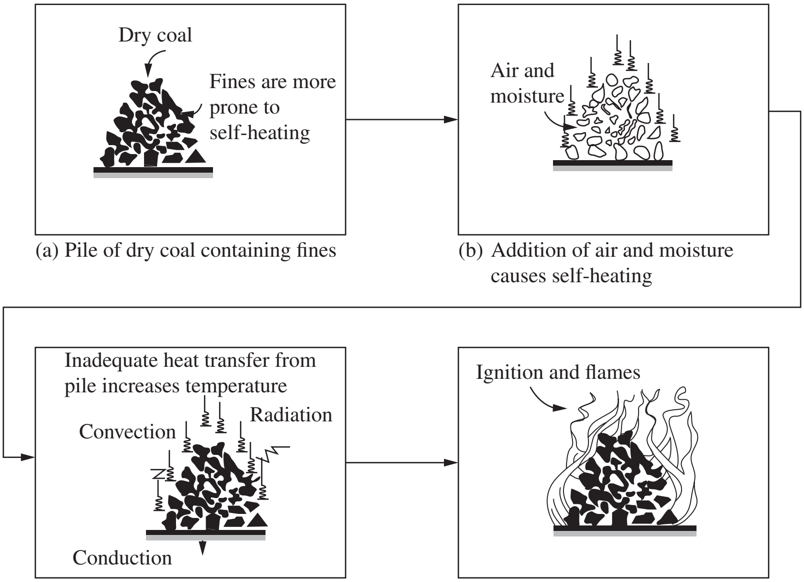
Self-heating can arise by one of two different mechanisms: by exothermic (heat releasing) chemical reactions and by exothermic decomposition. The chemical reactions are often the same as what occurs during a fire or explosion: an oxidation reaction with the oxygen in the air. At the start of the self-heating process, the reaction is very slow, like steel that oxidizes with atmospheric oxygen to form rust. Decomposition happens in a material that is unstable, and the material will fall apart while releasing heat. A significant difference between the two mechanisms is that decomposition does not require additional reactants and is therefore largely independent of the environment, while an oxidation reaction only happens if certain conditions are present, making it more difficult to predict its occurrence without detailed experimental studies.

Steps involved in self-heating process:

Step 1. Rate of heat generation exceeds rate of heat loss: If a material undergoes an exothermic chemical reaction (or multiple reactions) or decomposes exothermically, the temperature of the material will rise due to the heat released from the exothermic reaction or decomposition. In the meantime, some of the heat is lost to the environment. If the rate of heat loss exceeds the rate of heat generation, the temperature of the material will be the same as the ambient temperature, otherwise, it will increase. Due to the poor thermal conductivities of many solids, a large portion of the reaction heat is retained in the powder.

Step 2. Resulting temperature rise further increases chemical reaction rate exponentially: The temperature rise of the material due to the exothermic reaction will further increase the chemical reaction rate, which in turn will cause the temperature to increase further. The increase of material temperature also results in an increase in the rate of heat loss. However, the rate of heat loss increases linearly with temperature, while the chemical reaction rate, and thus the heat generation rate, increases exponentially with temperature. Consequently, the heat generation rate will exceed the rate of heat loss and the temperature of the material will rise higher. This process is referred to as self-heating. Self-heating begins at a temperature at which the rate of heat generation is greater than the rate of heat loss and this temperature is called the exothermic onset temperature.

Figure 3.29 illustrates the process of self-heating and ignition of coal.



(a) Pile of dry coal containing fines

(b) Addition of air and moisture causes self-heating

(c) Heat-transfer mechanisms

(d) Ignition and fire

Figure 3.29 Self-heating and fire in a pile of coal

*__Source__: *DOE Handbook 1081, Primer on Spontaneous Heating and Pyrophoricity*, December 1994.

Table 3.37 gives some known self-heating materials.

Table 3.37 Some self-heating materials with high risk of ignition

Material	***Transport and storage***	***Precautions***	***Remarks***
Charcoal	Bulk and bags	Keep dry; Provide ventilation	Prepare with care and age wetting and subsequent drying to be avoided
Bituminous coal	Bulk	Store in small piles, avoiding high temperatures	Self-heating depends on origin and nature. Highly volatile coals are particularly prone to self-heating

(*Continued*)

Table 3.37 (Continued)

Material	*Transport and storage*	*Precautions*	*Remarks*
Colors in oily fabrics	Drums, cans, and glass	Contact with rags and other cellulosics	May be very dangerous if fabrics are impregnated
Corn meal feeds	Bulk and bags	Moisture content kept under safe levels cure before storage	Contains appreciable quantity of oil which has severe tendency to self-heat
Linseed oil	Tank cars, drums, and cans	Contact with fibrous cellulosics to be avoided	Contaminated rags in piles are extremely dangerous
Varnished fabrics	Boxes	To be kept cool and ventilated	Thorough drying is safe
Oiled fabrics and silk	Rolls, bales and boxes	Thorough drying before packing and storage	Thorough drying and compact packing avoiding air ingress are safe

Source: NFPA

Flammability Hazards of Cryogenic Fluids

Cryogenic fluids are finding increasing applications, not only in space applications, but also in many chemical industry applications, which include liquid air separations for producing oxygen and nitrogen, hydrogen handling, LNG and LPG handling and the like. Several types of situations exist that may result in a flammability hazard from cryogenic fluids including fire, oxygen-enriched air, liquid oxygen, and explosion due to rapid expansion. Flammable gases such as hydrogen, methane, liquefied natural gas, and carbon monoxide can burn or explode. Hydrogen is particularly hazardous. It forms flammable mixtures with air over a wide range of concentrations (4–75 percent by volume). It is also very easily ignited.

Liquid hydrogen and liquid helium are both so cold that they can liquefy the air when contact occurs. For example, liquid air can condense on a surface cooled by liquid hydrogen or helium. Nitrogen evaporates more rapidly than oxygen from the liquid air. This action leaves behind a liquid air mixture which, when evaporated, gives a high concentration of oxygen. This oxygen-enriched air presents the same hazards as oxygen. Liquid oxygen contains 4,000 times more oxygen by volume than normal air. Materials that are usually considered noncombustible, such as carbon and stainless steels, cast iron, aluminum, zinc, and teflon (PTFE), may burn in the presence of liquid oxygen. Many organic materials can react explosively, especially if a flammable mixture is produced. Clothing splashed or soaked with liquid oxygen can remain highly flammable for hours. Lubricating oils, greases and graphite and accumulated impurities such as methane, ethane, ethylene and acetylene in distillation units, in air separation plants create potential explosion hazards. Hydrocarbons have very low solubility in liquid oxygen and therefore settle out as solids, which can explosively react with oxygen.

Flammability of a material strongly depends on the partial pressure of oxygen in the air. Flammability limits, burning velocities, ignition energies and quenching effects are strongly affected by the oxygen concentrations. Increased oxygen levels increase UFL, and burning velocities markedly, and reduce ignition energy requirement and quenching distances. Some of the most serious oxygen-related incidents have involved damaged oxygen hoses leaking into confined spaces, where welding and burning operations were taking place. Without adequate venting or pressure relief devices on the containers, enormous pressures can build-up. The pressure can cause BLEVEs. Unusual or accidental conditions such as an external fire, or a break in the vacuum which provides thermal insulation, may cause a very rapid pressure rise. The pressure relief valve may not be able to handle this increased pressure. Therefore, the containers must also have another back-up device such as a rupture disc.

Precautions in liquid air separation units include elimination of combustibles in the construction and operation of the plant, use of clean air, avoidance of build-up of contaminants in liquid oxygen, and safe disposal of liquid oxygen. The use of grease, hydrocarbon lubricants, graphite, gaskets, and seals that react with oxygen should be avoided.

Table 3.38 gives a summary of general information on hazardous materials.

Table 3.38 General information on hazardous materials

Name of material
Other names
Chemical structural formula
Purity
Concentration for detection of odor, taste
Uses
Important characteristics
Corrosivity, incompativity with other materials
Color codes
Packaging labels
General description of health hazards: Exposure effects, TLV_{TWA}, TLV_{STEL}, TLV_C, toxicity hazard ratings, etc.
Procedures for first aid and personal hygiene
General description of fire hazards: Flammability limits, self-ignition temperature, ignition energy, burning velocity, quenching distances, NFPA flammability ratings (N_f), explosibility, etc.
Reactivity hazards: NFPA reactivity rating (N_r)
Fire fighting methods
Precautions in use and handling for different quantities and locations
Suitable methods of storage
Suitability of electrical equipment
Action in the event of spillage
Environmental considerations
Statutory regulations covering storage, transportation, and use

Ignition Sources

The phenomena supplying heat energy may be grouped into four fundamental categories as to their origin:

(i) *Thermal sources*: Open flames, hot surfaces, self-ignition, compression, IC engines, plasmas, etc.
(ii) *Mechanical sources*: Frictional heat, friction sparks, vibration, metal fracture, etc.
(iii) *Energy sources from chemical reactions*: Heat energy generated during chemical reactions (oxidation reactions, reaction of metals with halocarbons, thermite reaction, reactions involving thermally unstable materials, decomposition reactions including nuclear reactions, polymerization, heat of adsorption, heat of combustion, heating, reactions with water and incompatible materials, etc.
(iv) *Electrical sources*: Electrical heat energy (static electricity, resistance heating, induction heating, heat from arcing, electric sparks, heat generated by lightning strikes, stray currents, electromagnetic radiation, high voltage transmission lines, etc.

Several sources of energy to initiate combustion reactions might be present in the process industry. The most frequently encountered ignition sources form the basis for the following discussion.

Open flames: Open flames may be the simplest and most frequently present ignition source. These include the following:

- Process flames (present by intent) → Burner flames in boiler and process furnaces, incinerators, flare stack flames, burning pits, waste burning, matches, etc.
- Accidental flames → Small process fires like pump, fires resulting from leaks and spills from oil and gas pipe lines, flange and insulation (lagging) fires, hot soot from stacks, ignition of dead grass by, for example, Sun rays, smoldering waste material (e.g. soaked in oil), matches, lighters, cigarettes, etc.
- Hot work, such as welding, cutting, hot tapping and grinding activities, is a potential source of ignition. In welding, for example, this applies not only to the welding flame or arc but also to material ignited by the welding. Hot work accounts for an appreciable proportion of ignition incidents. In the vast majority of cases the material ignited is in the equipment being worked on. It is relatively rare for hot work to be the source of ignition of a vapor cloud. It is necessary to exercise close control of hot work by training, supervision and use of a *permit system*.

Hot surfaces: Large part of process equipment operate at high temperatures Furnace walls, steam lines with defective or lost insulation, faulty operation of rotating equipment, for example, heated bearings, frictional heat of belt-driven equipment, etc., are examples for hot surfaces.

- Size, shape and surface area of the hot surface greatly influence energy input to the fuel–air mixtures.

- Some surfaces remain hot even though lagged.
- Exposed surface temperatures are to be limited to about 50°C below S.I.T. of flammables likely to be present in the area by intent or accident.
- Flammables may oxidize catalytically on hot surfaces below their S.I.T.s (e.g. Presence of NO_x can act as a catalyst) and outside their normal flammable range, releasing additional chemical energy, further increasing surface temperatures, triggering flame propagation or explosion in air.
- In diesel engines temperature is raised by intent, sufficiently by compression for ignition of fuel to occur. Lubricating oils used in air compressors have ignited in the presence of hot surfaces, leading to explosions.

Adiabatic compression: Adiabatic compression increases temperatures of gases and vapors which act as ignition sources for flammables. Sometimes shock waves are generated giving rise to fires and explosions.

Vehicles: Vehicles are potential sources of ignition. Hot engine surfaces and exhaust gases with products of incomplete combustion giving rise to glowing soot particles provide the necessary energy for ignition of any gases/vapors accidentally released in the plant areas. Diesel engines, extensively used in locomotives, fork-lift trucks, cranes, generators, dumpers, etc., are particularly hazardous. There have been cases of vehicles drawing flammable vapors through air intake resulting in flames issuing out of exhaust.

Exhausts of vehicles in hazardous areas are fitted with *flame arresters* which are regularly subjected to inspection and maintenance for possible blockages. Flame-proofing of air inlet and exhaust systems with effective follow-up maintenance is required for use in hazardous areas.

In extremely hazardous areas, detectors for flammable vapors are installed on the vehicles with warning systems for drivers to immediately stop the engines. Certain devices are capable of stopping an I.C. engine before dangerous conditions develop, for example, exhaust issuing out flames.

Mechanical/frictional sparks: Sparks from machining, grinding, dropping or banging of tools, chains and sparks resulting from friction in moving machinery, for example, braked steel wheels skidding on rails, chipping concrete, abrasive wheels or discs used for metal cleaning or grinding, etc.

Sparking due to presence of foreign material in moving parts of equipment, loose misaligned fan blades, displaced rotor bars of an induction motor touching stator.

Sparks from metal tools, abrasive grinding wheels, falling objects, hammers, spanners, cigarette lighter flints, etc., In areas with high flammability hazards, *non-sparking* tools/materials made from copper–beryllium alloys, bronze or brass may be used.

Precautions in their use include keeping them and the surfaces on which they are used clean to avoid grit coming in between, from giving rise to sparks. Tools made from these materials are soft and can deform easily and slip when force is applied. Regular inspection is necessary.

Lightning: Lightning is another potential ignition source on process plants. Lightning has been a significant ignition source for storage tank fires. Radio frequency (RF):

The possibility exists those radio frequency transmission from strong sources such as large military transmitters may act as an ignition source on process plants. The conditions for RF ignition of a flammable mixture to occur are: (i) electro-magnetic radiation of sufficient intensity, (ii) a structure capable of acting as a receiving aerial, and (iii) a mechanism for creating an incendive spark. The transmitter may be fixed or mobile. Mobile transmitters include vehicles, ships, and aircraft. Other sources include microwave energy, ionizing radiation, optical radiation, ultrasonics, and electro-magnetic radiation.

Arson, sabotage, and terrorism: Arson and sabotage happen due to employee dissatisfaction, political issues, mental disorders of employees, etc. Terrorism is relatively recent entry which occupies central stage in present times.

Chemical energy

- Light metals such as magnesium, aluminum, and titanium, when struck obliquely against rusted steel, produce sparks that are partly due to release of energy from chemical reaction and partly due to friction. A thermite reaction releases heat which might give rise to sparks:

  $$2\,\mathrm{Al} + \mathrm{Fe_2\,O_3} \rightarrow \mathrm{Al_2O_3} + 2\,\mathrm{Fe} + \mathrm{Heat}$$

- Hot pipelines and vessels coated with aluminum paint when struck by hammers or tools produce incendive sparks. Aluminum paint on un-lagged steel surfaces at temperatures above 120°C should be avoided and where such paint is used, a priming coat of zinc-rich paint on a blast-clean surface is recommended.

  Similar result produces sparks by striking slightly rusted steel with a smear of light metal or alloy or aluminum paint. The reaction is due to oxygen present in the iron oxide rust, which involves high heat of reaction. Siliceous materials also provide O_2 necessary for such chemical energy releases. Chemically clean steel does not produce such sparks. Use of paints containing such materials should be avoided in locations giving rise to flammable hazards.
- Metals treated with strong oxidizers, such as concentrated acids, show increased tendency to produce sparks and ignite under impact or friction. This is because of the reduction in activation energy required when an oxidizer, stronger than air is present.

Spontaneous ignition or self-heating: Spontaneous combustion is the ignition of a combustible material caused by the accumulation of heat from oxidation reactions. Fires started by spontaneous combustion are caused by the following mechanisms: Spontaneous combustion or self-heating: Spontaneous heating is the slow oxidation of an element or compound which causes the bulk temperature of the element or compound to rise without the addition of an external heat source. Spontaneous heating may be the result from direct oxidation of hydrocarbons (for example, oils, coal, and solvents) or it may occur because of the action of micro-organisms in organic materials.

The chemical reactions generating heat spontaneously imply the risk of ignition and burning as *internal ignition sources*. The materials inclined to spontaneous heating and spontaneous ignition may, however, become *secondary ignition sources* and give rise to ignition of the combustible materials in the surroundings.

Pyrophoricity: Pyrophoric substances ignite instantly upon exposure to air (atmospheric oxygen). A pyrophoric substance may be a solid, liquid, or gas. Most materials are not pyrophoric unless they are in a very finely divided state. Although there are some pyrophoric liquids and gases, most pyrophoric materials are metals.

Hypergolic reactions: Whereas pyrophoricity is concerned only with the spontaneous combustion of a material when exposed to air (atmospheric oxygen), a hypergolic reaction describes a material's ability to spontaneously ignite or explode upon contact with any oxidizing agent. Hydrazine (N2H4) is an example of a hypergole that reacts spontaneously with many oxidizing agents. An example is highly concentrated nitric acid is hypergolic with numerous fuels such as rocket propellants. Accidental mixing of these reactants is hazardous.

Whether spontaneous heating leads to ignition depends on several factors:

(i) The rate at which heat is generated and removed from the material being oxidized.
(ii) The ignition temperature of the porous combustible solid, hydrocarbon, or any gases liberated by oxidation.
(iii) The specific surface area of the material exposed to an oxidizer.
(iv) The amount of moisture present in the atmosphere and the porous combustible material.

For spontaneous ignition to occur, the rate of heat being generated through oxidation must exceed the rate of heat removal by conduction, convection, and radiation (thermal). As the temperature of the material begins to rise, the rate of heat generation will often increase. The result is a *runaway reaction* which ultimately causes ignition. If the rate of heat removal exceeds the rate of heat generation, the material will cool and will not ignite. The rate of heat removal may be increased through physical contact with a thermally conductive surface, by rotating piles of combustibles to cool hot spots, and by circulating inert gases through the piles to cool hot spots and displace oxygen. Some materials react readily with oxygen of the atmosphere, igniting and burning even without an ignition source. Ignition may be immediate or may take minutes or hours. Fire can also result from the combining of such oxidizers as chlorine and various hydrocarbon vapors; oxygen is not required for a fire to take place.

- The chemical reactions generating heat spontaneously, (self-heating and pyrophoricity (e.g. iron sulfide scales in crude oil storage tanks, heat of reaction or polymerization leading to runaway reactions, etc.) imply the risk of ignition and burning as *internal ignition sources*. Pyrophoric materials ignite spontaneously on exposure to air even under ambient conditions.
- Most materials are not pyrophoric unless they are in a very finely divided state. Although there are some pyrophoric liquids and gases, most pyrophoric materials are metals.
- Pyrophoric iron sulfide scales, formed from reaction of dissolved or entrained H_2S present in crude oils in storage tanks, transfer lines,

separators and heat exchangers, may glow red hot under dry and warm conditions, becoming a source of ignition. These scales may be removed periodically under *dampened* conditions, avoiding contact with air.

Pyrophoric iron sulfide is formed by the conversion of iron oxide (rust) into iron sulfide in an oxygen-free atmosphere where hydrogen sulfide gas is present (or where the concentration of hydrogen sulfide (H_2S) exceeds that of oxygen). The individual crystals of pyrophoric iron sulfides are extremely finely divided, the result of which is that they have an enormous surface area-to-volume ratio.

- When the iron sulfide crystal is subsequently exposed to air, it is oxidized back to iron oxide and either free sulfur or sulfur dioxide gas is formed. This reaction between iron sulfide and oxygen is accompanied by the generation of a considerable amount of heat. The heat released is so much that individual particles of iron sulfide become incandescent. This rapid exothermic oxidation with incandescence is known as pyrophoric oxidation and it can ignite nearby flammable hydrocarbon–air mixtures.

  Most commonly, pyrophoric iron fires occur during shut-downs when equipment and piping are opened for inspection or maintenance. Instances of fires in crude columns during turnarounds, explosions in sulfur, crude or asphalt storage tanks, overpressures in vessels, etc., due to pyrophoric iron ignition are not uncommon.
- The materials inclined to spontaneous heating and spontaneous ignition may, however, become secondary ignition sources and give rise to ignition of the combustible materials in the surroundings.
- Although some gases (e.g. hydrogen phosphide, boron hydride, and silicon hydride) and liquids (e.g. metal carbonyls and organometallic compositions) are inclined to spontaneous ignition, most spontaneous ignitions occur as surface reactions of solid materials. Gases like arsine (AsH_3), phosphine (PH_3), diborane (B_2H_6), silane (SiH_4), which are used in manufacture of microelectronics, ignite spontaneously in air.
- Spontaneous ignition, such as all ignitions, depends on the chemical structure of the material and the level of dispersity.
- Spontaneous ignition of liquids is also promoted if they come into contact with air on solid materials of large specific surface area. Fats and especially unsaturated oils containing double bonds, when absorbed by fibrous materials and their products, and when impregnated into textiles of plant or animal origin, are inclined to spontaneous ignition under normal atmospheric conditions. Cellulosic materials such as damp grain dusts, wood chips, textiles, combustible rags impregnated with oils or solvents (e.g. cotton waste used for cleaning) etc., are more prone to spontaneous ignition. The large specific surface enables the local accumulation of reaction heat and contributes to the increase of temperature of material above spontaneous ignition temperature.
- Spontaneous ignition of glass wool and mineral wool products produced from non-combustible fibers or inorganic materials covering large specific surfaces and contaminated by oil have caused very severe fire accidents.
- Activity of moulds, bacteria on moist materials increases temperatures.

- Coal is a notable example of self-heating and poses ignition hazards when stored in thick piles. The oxidation of coal is a solid–gas reaction, which happens initially when air passes over surface of coal. The amount of surface area of coal that is exposed is a direct factor in its heating tendency. Many times, segregation of the coal particle sizes is the major cause of heating. The coarse sizes allow the air to enter the pile at one location and react with the high surface area fines at another location. When there is just sufficient air flow for the coal to absorb most of the oxygen from the air and an insufficient air flow to dissipate the heat generated, the reaction rate increases and the temperatures may eventually exceed self-ignition temperature. The most important aspects of coal storage are minimizing the flow of air through the pile and minimizing the amount of finely divided coal in the pile.
- Phosphorous, a pyrophoric material, is explosive when mixed with oxidizing agents, e.g. alkali metals such as sodium, potassium, magnesium, lithium, zirconium, plutonium, thorium, and hafnium have a tendency to ignite spontaneously. Other examples of pyrophoric metals include magnesium, titanium and calcium. Mineral wool products produced from noncombustible fibers or inorganic materials, having large specific surfaces and contaminated by oil, have initiated spontaneous ignition (e.g. *Lagging fires*—discussed later) and caused very serious fire accidents. The slow oxidation reactions of the oil surrounded by the insulating material prevents heat dissipation, thereby increasing temperature, which, in turn, increases reaction rates with attending additional heat releases, triggering *runaway reactions* and ignition.
- Reaction rates double for about every 10°C rise in temperature. Self-heating reactions may also produce flammable gases, which may lead to gas explosions in process vessels or compromise product quality. The exothermic onset temperature is influenced not only by the chemical and physical properties, such as chemical reaction kinetics and heat of reaction, but also by other factors, including the following:
- Dimension and geometry of the solid bulk
- Ambient air flow
- Availability of oxygen in the bulk
- Additives and contaminants

Explosions are likely with finely divided particles resting particularly on hot surfaces.

Other ignition-prone examples include hot materials from process (must be cooled before sending to storage), hot deposits in dryers (cause of frequent explosions in dryers), cleaning rags soaked in oil or paint, premature admission of air into hot vessels containing organic residues, materials like phosphorous, sodium or potassium, zirconium powder, etc., exposed to air.

Precautions against spontaneous ignition include avoiding external heat sources, like steam lines, coming in contact with piles of materials in open, severely restricting O_2 supply to such piles, long and narrow storage bins to facilitate heat dissipation, frequent cleaning of deposits in dryers and good house keeping to prevent rubbish accumulation.

Static electricity: Static electric charge is created when two objects or materials that have been in contact with each other are separated. When in contact, the surface electrical charges of the objects try to balance each other. This happens by the free flow of electrons (negatively charged particles) from one object to the other. When the objects separate, they are left with either an excess or a shortage of electrons. This causes both objects to become electrically charged.

Static electricity is one of the least understood and most difficult ignition sources to control. It is by nature unpredictable and therefore difficult to detect. Similar operations can produce different levels of static on different days. It is a major cause of fires and explosions in many industries. Fires and explosions attributable to static may actually be increasing in frequency due to increased product purity and process intensification involving high turbulence conditions.

Static electricity generation is involved in handling and processing of solids, fluids and hybrid mixtures. Static electricity, essentially surface phenomena, involving a low current and high voltage, is produced when contact between dissimilar bodies causes disturbance of the charge along the interface. When there is no disturbance at the interfaces, positive and negative charges balance each other as illustrated in Figure 3.30. The actual mechanism by which liquids are believed to become electrostatically charged is known as double layer charging. Figure 3.30 illustrates electrical double layer at liquid–liquid and solid–liquid interfaces.

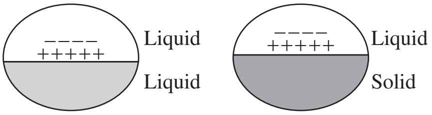


Figure 3.30 Electrical double layer at liquid–liquid and solid–liquid interfaces

The disturbance causes electrons to be pulled from the surface of one material and relocated on the surface of the other material.

- Separation of the bodies can leave excess charge, positive or negative, on each body. The material that loses electrons ends up with an excess of positive (+) charges. The material that gains electrons ends up an excess of negative (−) charge on its surface.
- Receiving or gaining electrons depend on the rank of the materials in *tribo-electric series*. This ranking is based on the *work function* of the electrons, which is a measure of the work required to remove an electron from a surface during contact electrification. A material having a higher electron work function, will have a propensity to receive electrons and thus become negatively charged. Conversely, materials having a lower electron work function will have a propensity to donate electrons and thus become positively charged. The greater the difference in the electron work functions of the contacting surfaces, the greater the magnitude of charge generated on separation.

Table 3.39 gives electron work functions for selected materials:

Table 3.39 Triboelectric series of selected materials

Material	*Electron work function (eV)*
Poly-tetra-fluoro-ethylene (PTFE)	5.75
Polyethylene (PE)	4.9
Polystyrene (PS)	4.9
Polycarbonate	4.8
Polymethyl methacrylate (PMMA)	4.68
Polyvinylacetate (PVA)	4.38
Poly-2-vinylpyridine-styrene	4.27
Polyethylene oxide	3.95–4.5

Source: Cross, J.A., Electrostatics—Principles, Problems, and Applications, Adam Hilger, IOP, Bristol, UK, 1987.

- If the bodies are good conductors of electricity, the charge moves quite freely and both bodies are effectively restored to their originally uncharged condition through the last points of contact at separation.
- When one or both bodies are either poor conductors, such as very dry or hydrophobic materials, or *insulated* good conductors, *excess charge* is retained on each body *after separation*.

  When generated excess charge accumulates on an object/body to a level above the *ionization potential* or *breakdown strength* of the air above the liquid, air adjacent to a charged liquid or solid surface is ionized, giving rise to discharge from the liquid surface as a *spark*. Ionization potential for air is 3×10^6 v/m. The energy of the spark can initiate an explosion if the liquid is flammable and the composition of vapor and air in the vicinity is in the flammable range.
- Shocks to personnel can cause injury. For a person to experience such a shock, the electrostatic potential created must be 3,500–4,000 V.

Some typical measured static charges caused by various actions are shown in Table 3.40.

Table 3.40 Typical measured static charges, volts

Action/item	*Voltage generated*	
	Low humidity	*High humidity*
	(10–20%)	*(65–90%)*
Walking on carpet	35,000	1,500
Walking on vinyl floor	12,000	250
Work chair padded with urethane foam	18,000	15,000

(*Continued*)

Table 3.40 (Continued)

Polythene bag picked up from bench	20,000	12,000
Worker at bench	6,000	100

Source: www.tpub.com

Static charge is greater during the winter months due to low humidity. When the relative humidity is high, some materials can absorb moisture, as a result of which the surface can become semiconductive. The static charge will then remain low or even disappear entirely as a result of the (semi)conductive surface. In order for static electricity to be a source of ignition, the following conditions must be fulfilled:

(i) The rate of charge generation must exceed the rate of dissipation, so charge can accumulate.
(ii) A static discharge must coincide in time and space with a flammable atmosphere. The effective energy of the static discharge must exceed the ignition energy of the local mixture.
(iii) A locally ignited flame must propagate into a surrounding flammable atmosphere.

Electrostatic discharges can be spark discharges, brush discharges or propagating brush discharges, cone discharges or lightning-like discharges. Spark discharges are highly energetic, capable of easy ignition of many flammables.

Brush discharges involve multiple brush like channels and can cause ignition of flammables with MIE up to 4 mJ. Brush discharges, which are limited in energy, will present an ignition hazard in the presence of flammable gases and vapors and possibly hybrids but are unlikely to ignite dust clouds.

Propagating brush discharges involve charges on both sides of the surfaces, releasing high levels of energy, as much as 2–3 J. Propagating discharges are capable of giving rise to leaks by puncturing or pin holing glass and PTFE linings in piping and vessels.

Cone discharges are sometimes referred to as *bulking brush discharges* and occur across the surface of bulked powder in storage silos, containers, and hoppers. They can also occur deep within the powder heap. Conditions for cone discharges are a charged powder of resistivity exceeding 1010 ohms. In grounded metal silos the discharges travel radially towards the silo wall across the surface of the powder cone during filling and may have an effective energy of up to 20 mJ. Particle size and charge density will both affect the resultant ESD energy. Large vessels produce higher energies and cone discharges are not normally observed in volumes below 1 m^3. In some cases this type of electrostatic discharge has been initiated by adding solvent to a vessel containing charged dry granular product. This practice is clearly dangerous and should not be undertaken unless it is certain that the product is uncharged.

Due to their higher energy content, propagating brush discharges and cone discharges can ignite dust clouds. Sparks, from ungrounded conductors, however, remain the most common source of electrostatic ignition in industry.

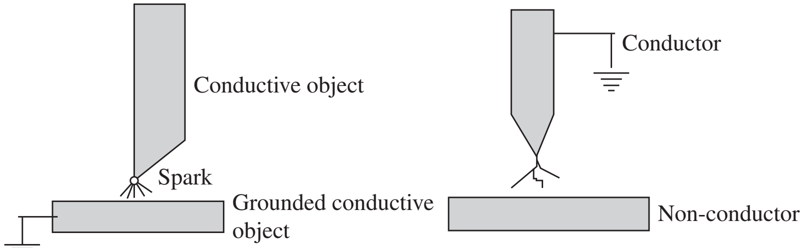
Types of discharges, their causes, energy levels and ignition capabilities and precautionary measures are summarized in Table 3.41.

Table 3.41 Types of electrostatic discharges and their characteristics

Type	*Cause*	*Approx energy (mJ)*	*Main measure against ignition*
Spark	Nonbonded conductive part	10^3 (0.5 CV^2 J)	Bonding
Brush	Conductive electrode with	≤ 5	With fuel present, prevent large radius in an electric field
Propagating brush	Very high charging of nonconductor, preferably in contact with a conductor	Up to 10^4	Prevent combination of nonconductor and limit charge of nonconductor
Conical pile	Fast accumulation of highly charged nonconductive particles, especially large sizes, d > 1 mm	Up to 10 per charge	Prevent charge of discharge accumulating product
Lightning-like discharge	High charge accumulating in large volume	≥ 10^6	Reduce charge of nonconductor or limit d to 3 m

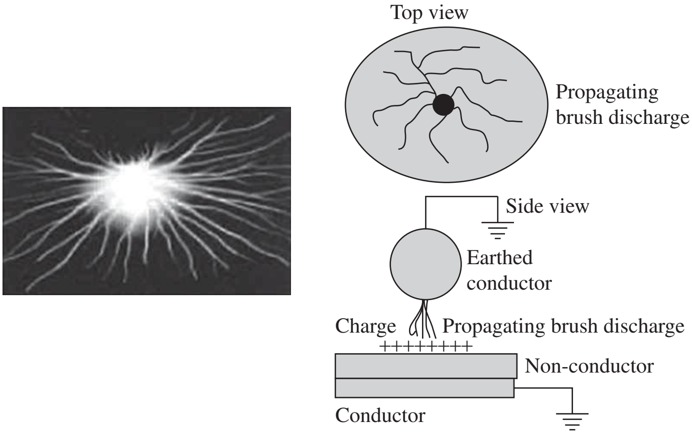
Note: Brush discharges can ignite flammable gases and vapors but not dusts. Other types of discharges are capable of igniting flammable gases, vapors, and dusts.
Source: Reinhard E. Bruderer, "Use Bulk Bags Cautiously", CEP, May 1993.

Figure 3.31 is illustrative of different types of discharges.



(a) Spark discharge between two conducting objects

(b) Brush discharge between a conductor and non-conductor



(c) Propagating brush discharge

Figure 3.31 Different types of discharges

As resistivity is the primary criterion for static problems, one way to classify liquids is based on electrical conductivities:

In petroleum industry, developments in processing technologies and specifications lead to fuels having conductivities below 5 C.U. (*Ultra-low conductivity)*, giving rise to increased static problems.

Table 3.42 gives conductivities of high, medium and very low resistivity liquids.

Table 3.42 Electrical conductivities of selected materials, pS/m (C.U.)

Material	*Conductivity*	*Comments*
Low or non-conducting liquids, light petroleum distillates, hexane, heptane, benzene, toluene, xylene, CCl_4, ethyl ether, etc.	< 100	Strong charge accumulators
Semi-conducting liquids, crude oils and residues, trichloroethylene, etc.	100–10^4	Charge dissipates rapidly
Conductive liquids	> 10^4	Charge dissipates very rapidly (in < 0.05 s)
Water and acids like H_2SO_4, ethanol, methanol, isopropanol, methyl ethyl ketone, isobutyl ketone, ethylene glycol, ethyl acetate, phenol, etc.	-	Charge accumulation only when water drops are surrounded by non-conducting fluids

Note: *pS is picoSiemen;* 1.0 *conductivity unit, C.U.* = 1 *pS/m* = 1×10^{-12} Siemens/m*;* 1.0 *Siemen* = 1.0 *Mho*

Above classification, based on conductivities, is from NFPA 77.

Relaxation is the process by which electrons leave negatively charged regions and flow to the ground or to a positively charged ions, when charged surfaces are separated. Based on the liquid resistivities and turbulence conditions, charge dissipation requires certain residence periods in the equipment. This period is termed as r*elaxation time* or *charge decay time, which is the time taken for the charge developed to its original* or *selected standard value, usually 37 percent of its original value*. It is inversely proportional to conductivity. High-resistivity flammable liquids are particularly hazardous as charge dissipation takes a very long time.

Table 3.43 gives relaxation times for selected liquids.

Table 3.43 Charge relaxation times for selected liquids

Liquid	***Charge relaxation time (s)***
Conductive liquids (conductivities > 10^4 pS/m)	
Distilled water	7.1×10^{-7}
Ethanol (25°C)	1.6×10^{-3}
Methanol (18°C)	6.6×10^{-6}
Isopropanol (25°C)	5×10^{-7}
Ethylene glycol	2.9×10^{-6}
Methyl ethyl ketone (25°C)	1.6×10^{-6}
Methyl isobutyl ketone	$> 2.2 \times 10^{-5}$
Phenol	8.7×10^{-5}
Semiconductive liquids (conductivities 100–10^4 pS/m)	
Trichloroethylene	0.037
Methylene chloride	0.018
Nonconductive liquids (conductivities < 100 pS/m)	
Benzene, purified	~ 100
Toluene	21
Xylenes	~ 100
Hexane, purified	~ 100
Heptane, purified	~ 100
Carbon tetrachloride	~ 100
Styrene monomer	2.2

Source: NFPA 77.

Some systems giving rise to static electricity problems

Handling flammable fluids: Examples involving electrostatic problems include operations such as pipeline flow, particularly two phase turbulent (e.g. oil flow containing water droplets or gas bubbles) and high velocity flow, tank filling, particularly splash filling, water droplet settling through oil in storage tanks, entrainment separation, droplet formation on expansion during vapor leaks or depressurization of equipment or escape of liquefied gases to atmosphere, steam cleaning or purging of tanks and vessels, steam leaks, agitation, mixing and blending, liquid-liquid extraction, pump cavitation involving vapor bubbles in liquids, etc.

Explosions involving large tankers have occurred during cleaning operations due to static electricity.

Turbulent flow results in more charge than laminar flow and pipes with rough internal surfaces tend to produce more charge than smooth surfaces, even when the roughness is on too small a scale to affect the state of turbulence. This may be due to roughness providing more surface area than a smooth surface of the same macroscopic dimensions.

Charging can also occur in flow through glass, rubber and plastic pipes. Glass can exhibit wide variations in conductivity. An insulated conductor can become charged by a steam jet impinging on it. An example is charging of wire mesh covering on an insulated piping. An example of liquid–liquid systems giving rise to high static accumulation is the case of suspended water droplets (conducting liquid) surrounded by low conductivity liquids such as hydrocarbon distillates in pipeline flow act as charge collectors and charge accumulation in the receiving vessel increases as much as 50 times under highly turbulent conditions. If the wet oil contains gas or air the vapor space in the discharging tank may acquire increased charge accumulation with possibility of sparking.

Exposed agitator blade in a mixer (Figure 3.32)*, due to its high tip speed, is capable of causing sparking in the vapor space of a mixer*.

Handling, dispersions, emulsions, sprays, mists, foams, and aerosols are some operations involving static problems.

Ventilation is one of the most effective ways to prevent the formation of flammable mixtures in buildings and enclosed spaces.

Figures 3.33, 3.34, and 3.35 illustrate the phenomena of charge accumulation in a storage tank.

The charge dissipates slowly through the liquid to the earthed vessel

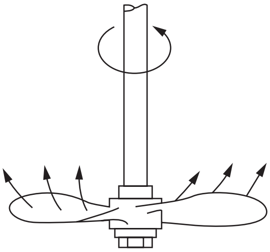


Figure 3.32 Agitation and mixing

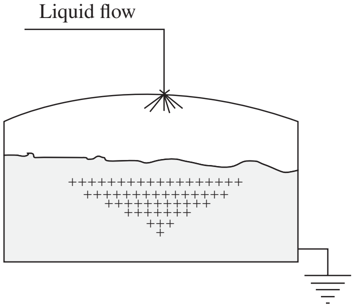


Figure 3.33 Charge accumulation at the center of liquid in a tank

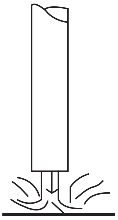
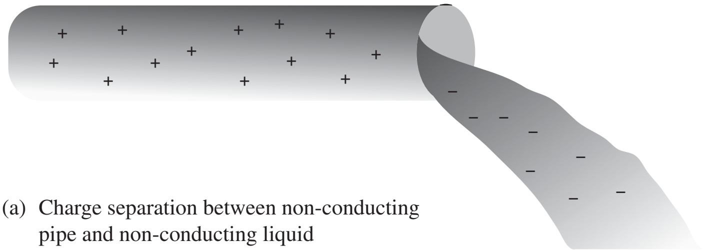
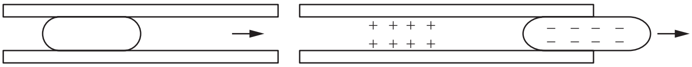


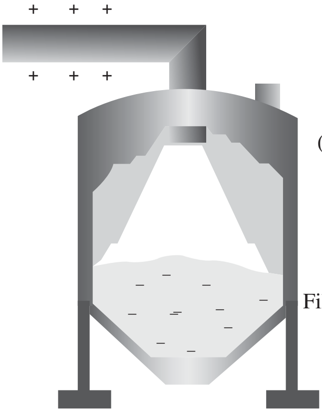
Figure 3.34 Splash filling



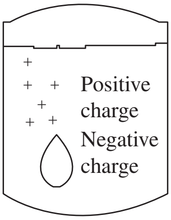
(a) Charge separation between non-conducting pipe and non-conducting liquid



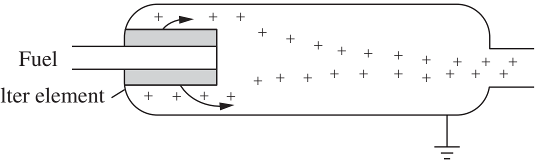
(b) Charge separation in two-phase flow



(c) Charge separation between equipment and product



(d) Charge separation during water droplets settling through a light petroleum product in a tank



(e) Charge separation in a filter

Figure 3.35 Charge separation

Ignition of flammables can occur if discharge, rather than dissipation, occurs into the flammable atmosphere as illustrated in Figure 3.36.

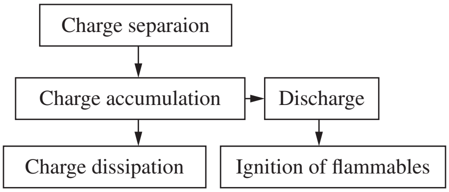


Figure 3.36 Charge dissipation or ignition of flammables

The degree of static hazard increases if the pipe line or container is non-metallic, for example, plastic, and/or fluids are of high resistivity (e.g. hydrocarbon distillates such as gasoline, naphtha, kerosene, etc., are strong static generators) or the container is conductive but not properly earthed.

Solid–fluid systems: Filtration (oil or gas filters, strainers, etc.,) slurry and suspension handling, fluidization, pneumatic conveyance of powders, centrifuging, surface coating, drying. Filters, for example, because of their large surface area, can generate 10–200 times the charge generated in the same piping system without filtration. When the pore or screen size in a filter is less than 150 μ m (more than 100 mesh per inch) a hazardous charge level is likely to be generated, particularly if the filter or screen is partially plugged.

Static hazards with filters can be reduced by contacting filters and fluid simultaneously on both sides, using separate layers of filters in series rather than one thick layer to obtain a required filtration capability, avoiding use of filters of highly charged materials such as zeolites, and flowing fluid through filter in the reverse direction after filtration to allow more rapid charge exchange.

Extremely high rate of charge generation can occur during *surface coating* processes involving low conductivity flammable solvents and particulates.

Solid–solid systems: Powder handling operations → A powder has a large exposed surface area per unit mass and since electro-statics is a surface phenomenon there is a propensity to generate and store high levels of static charge. Grinding, sieving, powder mixing, pneumatic conveying, cyclones, silos, containers and bags, drums, chutes, funnels, rotary valves, bag dump hoppers and scroll feeder systems, conveyor belts made of rubber, leather, or other insulating materials, driers, sand blasting, etc., involve dusts and dust clouds with high potential for charge generation. Particle size plays an important role, smaller particle sizes generating more charges, not only due to increased surface area per unit volume but also due to increased mobility.

Intensive charging of the conveyed material and pipeline is possible during pneumatic powder transfer. It should be ensured that pipelines used for pneumatic conveying are made from metal with good earth bonding. Resistance to ground for all conductive components should be < 10 ohms.

All operators loading powder should be grounded so that their resistance to ground is $< 1 \times 10^8$ ohms. The use of insulating coatings should be avoided on the inner surfaces of metal containers and pipelines. Plastic flanges should be used with plastic transfer lines. Use of coating or sheathing on pipelines constructed of insulating material should be avoided.

Antistatic plastic or paper bags in or around flammable gases, vapors or dusts having minimum ignition energies of < 4 mJ should be used. Powders should be discharged into the container or silo via intermediate loading equipment, for example, a cyclone fabricated from conductive material to reduce velocities and earth charge. Alternatively, rotary valves, bag dump hoppers, or scroll feeder systems can be employed.

Human body movement involving contact with charged objects, movement of clothing, footwear, manual handling, electrically isolated operators are some examples for static hazards. Wool is an excellent generator of static electricity. For example, brisk walk on a woolen carpet with shoes may generate a potential difference of up to 10,000 V.

Sliding, pouring, nonconducting conveyor belts, belt drives (static generation occurs when the belt separates from the pulley), reeling of plastic/paper, plastic liners, drying equipment involving solids movement, manufacture, handling, and application of semiconductor devices and micro-electronic systems. Even low levels of static generation, as low as 35 V, will be detrimental to semiconductor devices and operation of digital circuitry, micro-processors, etc.

Large sheets of plastic involve high accumulation of static electricity. When clear plastic tape is pulled from a roll, the end of the tape almost always exhibits static effect. Figure 3.37 shows different cases of charge separation in solid–solid systems.

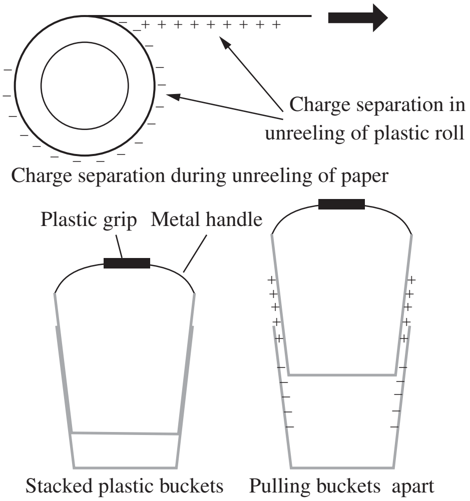


Figure 3.37 Charge separation in some solid–solid systems

When stackable, plastic objects such as chairs, buckets, or funnels are pulled apart, a separation of electrostatic charge often occurs so that opposite sign charge accumulates on the surfaces being separated. This phenomenon, illustrated below, has been implicated in a number of ESD ignitions involving flammable liquids. A plastic bucket with an insulating grip on the metal handle is likely to stay charged when held by its handle.

Figure 3.37 illustrates charge separation in some solid–solid systems.

***Source:** Triboelectric charging of common objects by Thomas B. Jones (internet)

Hybrid systems: In many industrial situations, a dispersed flammable dust may coexist with traces of flammable vapor. In such cases ignition might take place with less ignition energy than for dusts alone.

Electrostatic discharges in powder handling operations: The generation of electrostatic charges in powder occurs due to stripping or collecting electrons on the surfaces of materials. This can occur in any of the following mechanisms:

Tribo-electrically—Friction or rubbing of powder materials over each other and over materials of construction.

Induction—Passing through a high voltage field.

Thermionic (Heating)—Driving electrons off due to heat and differential temperatures.

Contact—Powder impacting or contacting a surface with residual ES charge.

Solidification—Meltable powders receiving charge during solidification (e.g. TNT).

Vaporization of liquids: The ignition sensitivity of a powder will depend on its physical condition and chemical nature. As the particle size reduces, usually the ESD ignition energy goes down. If the powder is suspended in a dust cloud, lower ignition energies are expected. Precautions against static hazards: There are four basic approaches against static hazards as follows:

(i) elimination of flammable atmosphere.
(ii) control of charge generation.
(iii) control of charge accumulation.
(iv) minimization of spark discharge.

Elimination of flammable atmosphere: Elimination of flammable atmospheres should be the primary objective. The following examples are illustrative of some situations that result in flammable atmospheres where they would not be typically expected:

Using floating roof storage tanks, with the roof bonded to tank shell and operating transfer lines full to eliminate vapor space

Inerting vapor space of vessels with nitrogen blanketing

Avoiding leakages by good maintenance

Avoiding switch loading of petroleum products in tank cars, which is the most frequently cited cause of static incidents

Vapors from the previous high or intermediate vapor pressure cargo in an empty tank mixed with air can be in the flammability range.

Inerting of vapor space during switch loading eliminates this hazard.

Contamination from inadequate flushing of product lines and other equipment before another product is introduced.

Filling vapor space with over-rich vapor, by flushing with initial inerting with nitrogen

Extremes in product temperatures, which can give rise to vapor generation. Evolution of flammable solvent vapors in drying equipment

Conditions that produce mists or foams

Explosion protection and proper venting of tanks and vessels

Proper ventilation of buildings and enclosures

Elimination of ignition sources in areas of likely flammable atmospheres. For example, use of cell phones should be avoided in such areas

Control of charge generation: Turbulence in non-conducting or poorly conducting liquid systems increases chances of charge generation.

(i) Maintaining low flow velocities in piping of liquids with high static hazards, below 1.0 m/s for liquids with an immiscible component (e.g. two phase flow) and 7.0 m/s or 0.5/d m/s (*d* = inside pipe diameter in meters), whichever is less for liquids in single-phase flow
(ii) Using alternative alloy steel piping and components in place of items made from PTFE, polyethylene, PVC and other electrically insulating

materials with flammable fluids. Items of concern include containers, drum liners, PTFE lined piping, tools, etc. Making a material suitable by applying conducting coatings on static-generating materials

(iii) Providing unrestricted flow passage with use of full bore valves, for example, ball valves

(iv) Avoiding splash filling and free fall of liquids into tanks, which gives rise to charged mists and foams, by providing diverters to direct the discharge of liquid down the side of the grounded vessel being filled, or by submerging fill pipes below the liquid level in the vessel. Care is to be taken that the submerged fill pipe does not disturb any settled water layer at the bottom of the storage tank. Regular draining of the water from tank bottoms helps avoid this situation. Whether top or bottom loaded, splashing or spraying should be avoided by limiting the filling velocity to 1.0 m/s until the loading outlet is submerged to a depth of either two pipe diameters or 15 cm (6 in) of liquid, whichever is larger. Transition from slow start to normal pumping rate might be achieved automatically using a special loading regulator tip, which shifts rate when submerged to a prescribed depth. The product of flow velocity and inside diameter of the filling pipe may then be increased to (velocity)(diameter) ≤ 0.38 m^2/s for pure liquids such as toluene, whose vapor will normally be in the flammable range throughout filling. When loading volatile products such as gasoline, whose vapor concentration can be shown to rapidly exceed the upper flammable limit during tank filling, the (velocity)(diameter) product may be increased to 0.50 m^2/s. In the case of rail tank cars, whose capacities are much higher than road tankers, a larger diameter loading line might be considered to allow faster loading rates without increasing the vd product.

(v) Mist generating operations should be avoided.

(vi) In *tank filling* operations the following additional precautions prevent spark discharges:

Avoiding loose floating conductive objects or debris inside the container.

Gauge rods or side wall probes should be connected to the bottom.

Gauge tapes, sample containers or thermometers should not be lowered into the tank vapor space. Conducting metal dip tapes can acquire static charge by induction, when brought into an electric field over a charged liquid. Avoiding objects which have sharp corners or pronounced curvature, which are known to cause intensification of charge strength. Thus protrusions from shell or roof of a tank or a suspended metal dip tape, used for level measurement, may act as probes to intensify charge strength locally.

(vii) Avoiding use of two phase flows → for example, (a) free-flowing steam to inert or clean a potentially flammable vapor space, as wet steam (two phase) is known to be a static generator, (b) pumping light hydrocarbon liquids with water droplets or solid particles, and (c) use of CO_2 fire extinguishers, which give rise to mixtures of solid CO_2 particles surrounded by gaseous CO_2 and generate static charges. Before the *inerting* action of CO_2 becomes effective, risk of ignition of flammables cannot be ruled out.

(viii) Substituting nonpolar solvents by polar solvents that are more conducting, in solvent extraction processes.

Control of charge accumulation: Electrostatic charges accumulate when they are generated at a higher rate then they dissipate. The ability of a charge to dissipate from a liquid is a function of the following:

(i) Conductivity of the material or its environment or both
(ii) Conductivity of the container
(iii) Bonding and earthing/grounding of the container

- Giving enough relaxation time for the static charge to discharge, especially downstream of filters and pumps, typically 30 s for high resistivity flammable liquids and 100 s for liquids with conductivities < 5 pS/m. High viscosity liquids also require increased relaxation times. Locating filters in piping away from storage tanks. *Providing a relaxation chamber or increased pipe diameter or length between the filter and the point of discharge dissipates the generated charge*.
- Avoiding high charge generating filter media such as zeolite beds, using separate layers of filters in series rather than one thick layer to obtain the required filtration capability or reverse flow of liquids through filters after filtration to reduce charge accumulation are other examples to reduce static hazards from filters.

  Reducing liquid resistivity: Use of commercially available ionic agents (anti-static additives) in concentrations of 0.6–6 ppm helps reduce charge accumulation in light petroleum distillates. The additive does not prevent charge generation, rather it increases the rate of charge dissipation by increasing liquid conductivity. Sometimes, charged ions of opposite polarity are injected. One disadvantage of anti-static additives is that the salts, polymers and other ingredients that comprise them are sometimes incompatible with pharmaceutical and food applications. In such cases, the use of a conductive liquid, such as alcohol or ketone may be considered. In order to be effective, these liquids need to be added in much higher concentrations, typically, of the order of 10–20 v percent or more. Such liquids must be miscible with the non-conducting liquid under process and should not add to the flammability problems. For example, the addition of MEK to xylene may greatly increase the ignition hazard owing to the lowering of flash point.
- *Inerting* vapor space in blending and mixing operations involving high resistivity liquids. In blending operations involving liquids with different resistivities, liquid with lower resistivity should be added first wherever possible, so that the resulting blend will have higher conductivity than the higher resistivity liquid being added. Inert gas concentration in the vapor space should be such that the oxidant concentration is brought down to below the *limiting oxidant concentration (LOC)*, to prevent fires and explosions.

Limiting the speed at the tip of an agitator to a maximum of 1.0 m/s should be the first consideration in mixing and agitation involving high static hazards. If greater agitator tip velocities are required by the process, an effort be made to raise the conductivity of the mixture above 50 pS/m with the use of an antistatic additive or inerting vapor space of the mixer. Air, steam, or other gases should not be used for agitation as they can produce high levels of charge in liquids, mists, or foams. For liquids having conductivities less than 50 pS/m, sampling or gauging should not be done during operations. Sufficient time, after stopping the operation, be allowed for relaxation of the charge.

- *Polar solvents*, being more conductive than nonpolar solvents, should be the recommended choice in systems with high static generation.
- Using *conducting belts, shafts*, etc., in drives and conveyors with proper earthing arrangements.
- *Humidification* of the *environment around units/equipment* where high charges can develop, particularly with non-conducting objects with relative movement, controls charge accumulation. Very low or high temperatures, with resulting *low humidity (dry air or gases)*, will increase the generation and accumulation of the charge both while it is being generated and during the normal relaxation period. Cold and dry weather can produce the ideal conditions for a static discharge.

  Under high humidity levels, above about 30 percent, charge tends to dissipate due to increased conductivity of air. Most fires resulting from static ignition arose when atmospheric humidities were less than the above levels. Over 60–70 percent humidities, charge tends to drain away. High humidity provides a *film of moisture* on the surfaces of equipment which conducts away the generated charge, as in *bonding*. A relative humidity between 40–60 percent is recommended for a typical work area.
- *Bonding*: Bonding involves making electrical connection between two conducting objects to maintain same potential. If one or both bodies involved is/or not conducting/poorly conducting, bonding becomes ineffective. Bond circuit resistance should typically be 1.0 ohm or less and should not exceed about 10 ohms. Bonding across flanges is a good practice, even though bolts serve the same purpose and should include often overlooked items such as metal rims on nonconductive containers, spray nozzles, probes, and so on. Earthing/grounding is to drain away any charge to earth from the objects bonded together or other equipment/structures. Resistance to earth should be less than 10 ohms.

Earthing can be classified as system earthing and equipment earthing. System earthing is essential to the proper operation of the system, whereas equipment earthing concerns the safety of personnel and plant. A key function of equipment earthing is to provide a controlled method to prevent the build-up of static electricity, thus reducing the risk of electrical discharge in potentially hazardous environments.

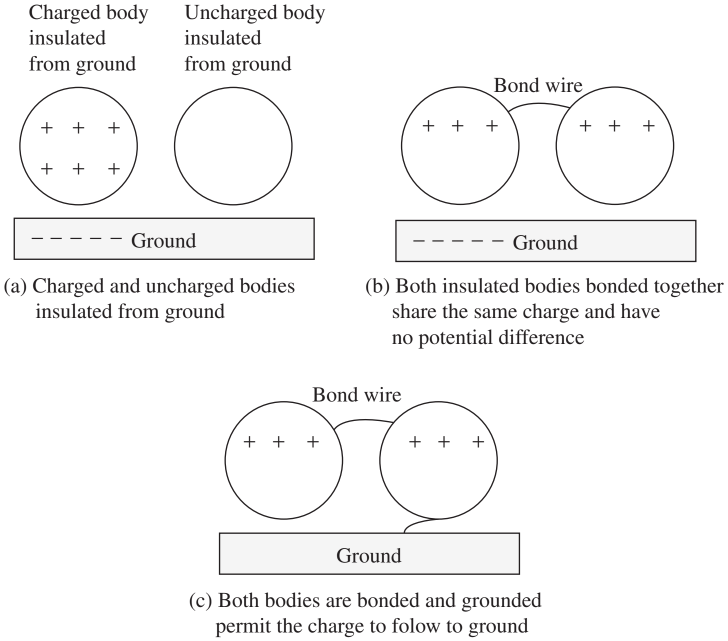
One method of discharging static electricity from nonmetallic piping is by wrapping a copper wire around the pipe in a helix and attaching it to an earthing rod at approximately 500-foot intervals.To avoid a spark from discharge of static electricity during flammable liquid filling operations, a wire bond should be provided between the storage container and the container being filled, unless a metallic path between the container is otherwise present. Above ground tanks used for storage of flammable liquids do not have to be earthed unless they are on concrete or on nonconductive supports. Wires should be un-insulated so they may be easily inspected for mechanical damage and should never be painted. When flexible hoses are employed, measures that can be adopted include:

Where velocities exceed 1.0 m/s hoses should be made of conductive material or non-conductive material with embedded fine wire mesh. The mesh should be bonded to the metal flanges or coupling of the hose; If a metal hose with a liner is used, the metal mantle and copper strip or wire is used in bonding and earthing. Some things to avoid in an earthing system are underground pipe that has a cathodic protection system, nonconducting materials, or any electrical discontinuities such as gaskets. flanges or couplings must be bonded to each other. The electrical resistance between the two couplings must not be higher than 10^6 ohms. This resistance is to be measured at regular intervals.

- Bonding and earthing versus individual earthing: A series of conductive components might be bonded together and the bonded system then earthed. Alternatively, each conductive component might be individually earthed. The first option will probably require a shorter total length of cable and a neater appearance. However, in certain cases it is preferable to earth each conductive component individually, since loss of a single bonding connection might otherwise result in isolation of a system of conductors. Vibration, corrosion, and maintenance activities might give rise to loss of bonding. Periodic inspection becomes necessary to avoid such situations. Bonding is particularly important when low vapor pressure stocks are loaded into cargo tanks that previously contained high vapor pressure products (switch loading).
- Care should be exercised to avoid spark promoters, such as unbonded conducting objects (i.e. metallic sample cans or loose conductive objects), within a tank compartment. A tank gauging rod, high level sensor, or other conductive device that projects into the cargo space of a tank truck can provide a place for a brush discharge to occur above the rising liquid. If these devices are conductive they should be bonded securely to the bottom of the tank by a conductive cable or rod to eliminate a spark gap, or placed in a gauging well that is bonded to the compartment.
- Bond wires may be insulated or un-insulated. An un-insulated bond wire permits ready visual inspection for continuity of the bond. Insulated bond wires should be electrically tested or inspected periodically for continuity. The entire bond circuit, including clamps and connectors, should be included in the continuity test. Bond circuit resistance should typically be 1.0 ohm or less.

Figure 3.38 illustrates the principles involved in earthing and bonding:

- Even if a metal container, having a high resistivity liquid is earthed, there is still a possibility of charge accumulation on the surface of the liquid, due to poor conductivity through the liquid to the container wall. If this accumulated charge builds up high enough, a static spark with sufficient energy to ignite a flammable air–vapor mixture can occur when the liquid level approaches an earthed probe or when a probe is lowered into a tank for sampling or gauging. Conductive fluids should be grounded while filling insulated containers.



(a) Charged and uncharged bodies insulated from ground

(b) Both insulated bodies bonded together share the same charge and have no potential difference

(c) Both bodies are bonded and grounded permit the charge to folow to ground

Figure 3.38 Principles involved in earthing and bonding

– Earthing and bonding should include agitators, baffles, flanges, valves, other internal parts as well. Operations such as flowing, pouring, steaming, and blasting should be properly grounded.

Static charge accumulation on linings may result in *pin hole* lining damage in equipment such as plastic, enamel or glass-lined reactors. If iron acts as catalyst for the reactions, rapid enlargement of pinholes can occur triggering runaway reactions. These need to be fitted with a path to earth to allow for relaxation of charge from the vessel contents. Suitable approaches may include a tantalum patch or a conductive discharge outlet and valve below the liquid level. Static dissipative linings and coatings are available for lining such vessels and stirrers. Use of earthing rods when loading powders into bins with insulating liners, excluding foreign objects from entering grinders to avoid frictional heating and sparking. Avoiding insulated conductors in situations where static hazard exists, for example, wire mesh covering over insulation on steam lines (leak can cause static accumulation on wire mesh).

- *Vehicles* often generate static, which when used in plant atmospheres involving flammables, might create ignition hazards from static electricity, besides giving rise to chances of ignition from hot exhaust streams. Static charge caused by separation of nonconductive tire treads from the pavement can raise a tank truck potential up to 100 kV, depending on road surface roughness, vehicle speed and tire tread resistance. This typically occurs on dry roads when tire treads have a resistivity of 10^9–10^{12} W-m. When the road surface is a good insulator, such as asphalt in dry weather, both the truck and the road surface can retain high potentials for significant periods after the truck has stopped. On stopping, charge drains rapidly through the tires to ground and potentials typically decrease to a non-hazardous level in about 10 s. Lowering the tire resistance to below 10^9 W avoids the hazard of high truck potentials. *Nonstatic* tires were shown both to decrease the peak potential on the truck and increase the rate of charge dissipation once the truck came to rest. Carbon black used in tires, drains the charge. Some times hanging chains also drain off static.
- Control of static charge on personnel: The human body is an electrical conductor and can accumulate a static charge if insulated from ground. This charge can be generated by contact and separation of footwear with floor coverings, by induction, or by participation in various manufacturing operations. Where ignitable mixtures exist, a potential for ignition from the charged human body exists, and means to prevent accumulation of static charge on the human body might be necessary.
- Steps to *prevent charge accumulation* include use of conductive flooring and footwear, personnel grounding devices and antistatic or conductive clothing, plastic or paper bags and gloves, antistatic coatings on surfaces for the operating area with flammable gases, vapors, dusts and hybrid mixtures having minimum ignition energies (MIEs) of 4 mJ or less reduce/eliminate static hazards. Low resistance polymeric materials are available for footwear, flooring, belts, tyres, hose, etc. Regular monitoring and upkeep for resistivity changes in the antistatic materials is necessary. Resistance of footwear can increase with accumulation of debris on footwear. Regular inspection will be necessary. Conductive foot wear *should not be used* where a possibility for electrocution by line voltages exists.
- Sensitive electronic components and computer boards require protection from electrostatic discharge during handling, shipping, and assembly. Anti-static packaging materials like conductive polyethylene and sophisticated laminates with very thin metalized films, have created a multimillion dollar packaging industry.
- Use of static eliminators/neutralizers: If the atmosphere in the surrounding area of the charged object is ionized, the object will attract a supply of ions of opposite sign. They will, in turn, neutralize the charge, preventing build up of high potentials. The action of air ionizers is to add very nearly equal numbers of positive and negative ions to the air in order to provide charge carriers that increase the electrical conductivity of the air. If only a small percent of the air molecules are ionized (~1–100 millionth percent),

the time for static discharge is reduced from hours to seconds. Use of air ionization to bleed surface charge off of insulators and ungrounded conductors is an effective method to reduce static risks.

- Air ionizers are widely used by the disk drive manufacturing industry. Most use either corona discharge or natural radiation (alpha) techniques to generate air ions.
- Corona method involves the use of high voltage (~5–20 kV) The voltage is applied to a set of sharp points, an intense electric field is established in the very near (~100 mm.) of the points. This field accelerates free electrons to a sufficiently high energy to allow them to ionize molecules that they collide with. When the voltage on the point is positive, positive ions are repelled into the environment and when the point is negative, negative ions are delivered.
- The use of ionizing radiation to make ions is one of the techniques used for electrostatic management. While several forms of ionizing radiation sources are available, only appropriate sources are used for static control.
- Other methods include use of A.C. or D.C. to produce air ionization.
- Ionization has been successful by the use of radioactive substances, needle point metal combs, static neutralizers to discharge static from nonconductive materials, such as fabric, rubber, or plastic sheeting and belts.
- Instruments for measuring static charges : Instruments like gold leaf electroscope and neon tube tester are activated either by separation or glow to indicate presence of small charges when brought near the object.

Minimization of spark discharge: In addition to bonding and earthing discussed above, use of reduced fluid velocity through media and reduced friction-conductive media minimize filter element spark discharge. Spark promoters in tanks and vessels should be removed or grounded. Sufficient relaxation period should be allowed before sampling and gauging.

In order to assess and avoid static hazards in a particular process, operation or plant, the following diagnostic audit will be a useful tool:

Is there a flammable atmosphere?
Find flash point.
Does contact take place?
Test powders.
Is charge generated?
Could charge accumulate?
Do discharges have enough energy?
Compare minimum ignition energies with discharge types.
Liquid flow rates, velocities and turbulence?
Measure resistivities/conductivities.
Study the plant/process/operation.
Carry out on-site measurements.

To sum up:

Virtually all manufacturing processes which involve sensitive flammable materials will contain some of the elements necessary for an electro-static ignition hazard to exist. More often than not the process runs trouble-free—the generation and accumulation of electrostatic energy is unseen and discharges, if they occur, may be low in energy and remain unnoticed. A simple change in the properties of the materials, process or operating procedures however may be all that is necessary to complete the chain between charge generation and ignition. The consequences of an ignition are of course often catastrophic. In the battle against static electricity, it is important to be vigilant and to carefully consider the consequences of any changes to material, plant and process.

Lightning: Lightning is a complex phenomena. Characteristics of lightning vary with terrain, altitude, latitude, and time of the year. Electrical storms involve the relatively slow movement of heavily charged clouds that set up an electrostatic field over a large, surface area below the cloud. The field induces an opposite charge, which moves along with the cloud, on the surface of the earth equipment and structures and usually occurs at a relatively slow rate. Initial discharge may be from cloud to cloud, at different potentials or from charged cloud to earth involving a low current and high voltage. This discharge ionizes the path to the ground, thereby providing a good conducting path for the very energetic discharge that follows, which is extremely destructive to objects in its path.

Stringent precautions are required to prevent accumulations of static electricity and to give protection against lightning. Standard copper strip (25 mm × 3 mm section or equivalent) is usually employed for the main earthing system. This should be connected to at least one copper-earthing rod that has been tested and shown to have a total resistance to earth of <10 ohms. Proper earthing and bonding used in industrial equipment is adequate for lightning protection. Metallic tanks, equipment and structures commonly found in the petroleum industry that are in direct contact with the ground (i.e. no non-conducting membranes) have proved to be sufficiently well grounded to provide for safe propagation to ground of lightning strokes.

Metallic equipment that does not rest directly on the ground but is connected to a grounded piping system is usually safe for propagation to ground of lightning strokes. One device for protection consists of elevated rods and earth wires which provide a cone of protection. If the apex of the cone corresponds with the highest point of the conductor and the radius of the base equals the height of the cone, protection is provided for structures in the area. The resistance path to earth needs to be low (< 70 ohms).

Structures made of insulating materials such as wood, plastic, brick, tile, or non-reinforced concrete are typically not inherently grounded for lightning protection. They can be protected from direct-stroke lightning by means of properly designed lightning protection systems.

Stray Currents: The term stray current applies to any electrical current flowing in paths other than those deliberately provided for it. Such other paths include the earth, pipe lines and other metallic objects or structures in contact with the earth. A stray current may be continuous or intermittent, uni-directional or alternating, and is usually distributed among a number of available parallel paths.

Stray currents can accidentally result from faults in electrical power circuits, leakage currents, high voltage railway networks, cathodic protection systems or galvanic currents resulting from the corrosion of buried metallic objects. While stray current voltages are typically not high enough to spark across an air gap, intermittent charges can result in a spark that would ignite a flammable mixture, if present.

If a gas or light oil pipeline, which handles heavy stray currents, is severed, arcing may occur at the point of separation, creating an ignition hazard. Where stray currents are known or suspected, a short, heavy gauge bond wire or jumper should be connected across the point where the line is to be separated. To be effective, the bond must have a low electrical resistance (typically less than 2.0 ohms). The wire must be attached to the pipe in a way that provides minimal electrical resistance. Figure 3.39 illustrates bonding of a valve.

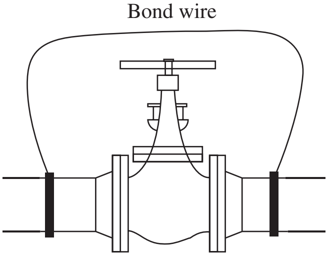


Figure 3.39 Stray current bypass

If stray currents are present in wharf piping, connecting and disconnecting a hose of a ship may produce arcs because the resistance of the hull of the ship to ground (water) is exceedingly low. In such circumstances, the stray currents in the hose of the ship can be reduced in magnitude by providing a low resistance ground for the wharf piping.

Tanker loading and unloading—Electric arcs/sparks are possible while connecting/disconnecting the flanged joint of the hose between tanker and shore. An insulated flanged section inserted into the loading line is an effective method of preventing stray current flow. To prevent static build-up, bonding and earthing should be ensured. Rail tracks at loading racks for flammables should be earthed.

Electricity: Difference between static electricity and electric current: These are two separate phenomena, both involving electric charge and may occur simultaneously in the same object. Static electricity is a reference to the electric charge of an object and the related electrostatic discharge when two objects are brought together that are not at equilibrium. An electrostatic discharge creates a change in the charge of each of the two objects. In contrast, electric current is the flow of electric charge through an object, which produces no net loss or gain of electric charge. Although charge flows between two objects during an electrostatic discharge, time is too short for current to be maintained.

Hazards due to electricity include shock to personnel, ignition of flammables, overheating or damage to equipment and cabling, electrical explosions and inadvertent activation of equipment. Electrical safety involves protection of plants and equipment from fires and explosions as well as personnel from shocks, burns and electrocution leading to injury and death.

Injury and death: The effects of electric shock depend upon the type of circuit, its voltage, resistance, current, pathway through the body, and duration of the contact. Effects can range from a barely perceptible tingle to immediate cardiac arrest. The following table shows the general relationship between the degree of injury and amount of current for a 60-cycle hand-to-foot path of one second's duration of shock. The table also illustrates that a difference of less than 100 mA exists between a current that is barely perceptible and one that can kill. Muscular contraction caused by stimulation may not allow the victim to free himself or herself from the circuit, and the increased duration of exposure increases the dangers to the shock victim. For example, a current of 100 mA for 3 s is equivalent to a current of 900 mA applied for 0.03 s in causing ventricular fibrillation. The so called low voltages can be extremely dangerous because, all other factors being equal, the degree of injury is proportional to the length of time the body is in the circuit.

Table 3.44 gives effects of electricity on human body.

Table 3.44 Effects of electric current on the human body

Current (milli-amperes)	*Reaction*
1 mA	Perception level. Just a faint tingle
5 mA	Slight shock felt; not painful but disturbing. Average individual can let go. However, strong involuntary reactions to shocks in this range can lead to injuries
6–25 mA (women)	Painful shock, muscular control is lost
9–30 mA (men)	This is called the freezing current or *let go* range
50–150 mA	Extreme pain, respiratory arrest, severe muscular contractions.* Individual cannot let go. Death is possible
1,000–4,300 mA	Ventricular fibrillation (the rhythmic pumping action of the heart ceases.) muscular contraction and nerve damage occur. Death is most likely
10,000 mA	Cardiac arrest, severe burns, and probable death

If the muscles are excited by the electric shock, the person may be thrown away from the circuit.

***Source:** W.B. Kouwenhoven, Human Safety and Electric Shock, *Electrical Safety Practices*, Monograph, 112, Instrument Society of America, p. 93. 1968. Reproduced from OSHA 3075, 1997.

The most common shock- related injury is a burn. Burns suffered in electrical accidents may be of three types, namely, electrical burns, arc burns and thermal contact burns. *Electrical burns* are the result of the electric current flowing through tissues or bone. Tissue damage is caused by the heat generated by the current flow through the body. *Arc or flash burns*, on the other hand, are the result of high temperatures near the body and are produced by an electric arc or explosion. *Thermal contact burns* are those normally experienced when the skin comes in contact with hot surfaces of overheated electric conductors, conduits, or other energized equipment.

Ignition, fires, and explosions: Electrical equipment can be a source of ignition energy required for fires and explosions. The normal operation of switches, circuit breakers, motor starters, contactors and plugs, and receptacles release this energy in the form of arcs and sparks as contacts open and close, making and breaking circuits.

Lighting fixtures, motors, electric heaters which include flexible heaters, panel heaters, heating cables, radiators, etc., batteries, and other overheated electrical appliances produce heat and become sources of ignition if surface temperatures exceed the ignition temperature of the particular gas, vapor or dust in the atmosphere.

It is also possible that an abnormality or failure in an electrical system could provide a source of ignition. Loose contacts in wiring and other fixtures (e.g. a loose lamp in a socket), overloaded circuit, multiple use of single terminals by multi-conductors, missing cabinet doors, improperly fixed fuse and circuit breakers, damaged conduits, dirty motors, use of flexible cords in place of permanent wiring, insulation deterioration and failures, etc., can be the source of both arcing and heat. Arcs can ignite combustible material like plastic insulation or produce flying sparks which can ignite combustibles at some distance.

As mentioned under *hot surfaces* as ignition sources, the surface must be hot as well as large enough to heat fuel–air mixture to self-ignition temperatures. In other words, ignition can occur even if the temperature is lower, if the surface area is large compared to volume of fuel–air mixture. An example is the space within a motor is small compared to the area of the hot internal surface. If flammable mixture fills this space, ignition may occur if the mixture is at the self-ignition temperature. If sparking is involved in the motor, hazard is much higher.

Approaches toward electrical safety are (i) elimination of flammable atmospheres, (ii) location of electrical equipment governed by codes and practices, and (iii) regular inspection and maintenance.

Flammable atmospheres: Degree of hazard from electrical ignition sources depends on the nature of flammable atmospheres both in terms of types of flammable materials present or likely to be present in the location (s) as well as their conditions of existence, for example, state of existence and concentrations in the surrounding environments. The materials may be in the form of flammable gases/vapors, flammable liquids, combustible dusts, or ignitable fibers.

3.6 Flames, Fires, and Explosions

A *flame* can be considered to be a fast, self-sustaining chemical reaction occurring in a discrete reaction zone. Reactions between fuel and oxidizer might be taking place at ambient temperatures but these are normally very slow. For a flame to propagate, the reaction must be fast, which requires higher levels of energy input to the system. The energy input is normally in the form of heat, which is provided by the reaction itself or by an external source. In some cases unstable compounds like acetylene or hydrazine, light and mechanical shock can induce the fast reactions.

Flames emit radiant energy at specific wave length bands depending on the combustion chemistry of the fuel involved. In most cases, some portion of the emitted radiant energy is visible to the human eye as the glowing, gaseous portion of a fire, which is typically referred to as its flame.

The hottest flames are not always the brightest. For example, hydrogen exhibits a high flame temperature. However, it combines with oxygen when burning to form water, and has an almost invisible flame under ordinary circumstances. When hydrogen is absolutely pure and the air around it is completely free of dust, the hydrogen flame cannot be seen, even in a dark room. This presents a hazard in welding operations involving hydrogen flames as some one may step on it unwittingly with serious consequences.

In order to gain a better understanding of flames, a burning candle can be used as an example. When the candle is lit, the heat of the match melts the wax, which is carried up the wick and vaporized by the heat. As it is broken down by the heat, the vaporized wax combines with the oxygen of the surrounding air and produces heat and light in the form of a flame.

The candle flame consists of three zones, which are easily distinguished. The innermost, non-luminous zone is composed of a gas/air mixture at a comparatively low temperature. In the second luminous zone, hydrogen and carbon monoxide (two of many products from the decomposition of the wax) react with oxygen to form combustion products, which include water and carbon dioxide. In this zone, the temperature of the flame is in the range of 590–680°C, which is sufficiently intense to dissociate the gases in the flame and produce free carbon particles. These particles are heated to incandescence and then consumed. Outside the luminous zone is a third, invisible zone in which the remaining CO and H_2 are finally consumed. This zone is not visible to the human eye.

Behavior of a flame is an important factor in the consideration of causes and effects of fires and explosions in process plants. Flames in a process plant are either intentional or accidental. Examples of intentional flames include flames on burners, incinerators and flare stacks.

For any flame to materialize, there should be contact between fuel and oxygen or oxidizer along with energy input necessary for initiating propagation of the flame.

Premixed and diffusion flames: A premixed flame is one in which air (normal source of oxygen) is mixed with the combustible gas by some mechanical device prior to combustion, as in the case of the Bunsen burner. In premixed flames, fuel gas and air (normal source of oxygen) are mixed together prior to ignition. If mixing occurs rapidly compared with combustion reactions, burning is homogeneous. Gas–air mixtures that flow in the Bunsen burner tube involve low velocities and the resulting flames are called laminar flames.

In diffusion flames, fuel and oxidizer are initially unmixed. The process of diffusion of fuel and oxidizer molecules toward each other provides the necessary contact between them prior to ignition and flame propagation. In diffusion flames, mixing is slow compared to combustion reaction rates, that is, mixing controls burning. The distinctive characteristic of a diffusion flame is that the burning rate is determined by the rate at which the fuel and oxidizer are brought together in proper proportions for the reaction to take place. In all cases of diffusion flames, there is a holding region or film in which a small premixed flame is established due to diffusion process. The rest of the flame consists of a region bounded on one side by the oxidizer with fuel absent and on the other side by fuel with oxidizer absent. Between these boundaries, fuel and oxidizer diffuse toward each other and products of combustion diffuse outward. The region between these boundaries is the combustion zone.

Unlike pre-mixed flames, diffusion flames have a wide region over which mixture composition changes due to diffusional processes. There is a concentration gradient between the two boundaries. Near the fuel boundary, concentrations are rich in fuel and temperatures are quite high due to which considerable pyrolysis and decomposition of the fuel can occur prior to complete combustion. For hydrocarbon fuels, this leads to soot formation and radiation from the hot soot particles gives rise to the typical yellow color of the hydrocarbon diffusion flames.

Both pre-mixed and diffusion flames can be laminar or turbulent. Laminar flame propagation consists of smooth and discrete flame zone. Temperatures in laminar diffusion flames are around 1,600°C for many hydrocarbons. A diffusion flame results, for example, ignition of a fuel jet issuing into air. Candle flame is an example of laminar diffusion flame. The fuel comes from the wax vapor, while the oxidizer is air. They do not mix before being introduced, by *diffusion*, into the flame zone. A diffusion flame is one in which the fuel and oxygen diffuse from opposite sides of the reaction zone (flame).

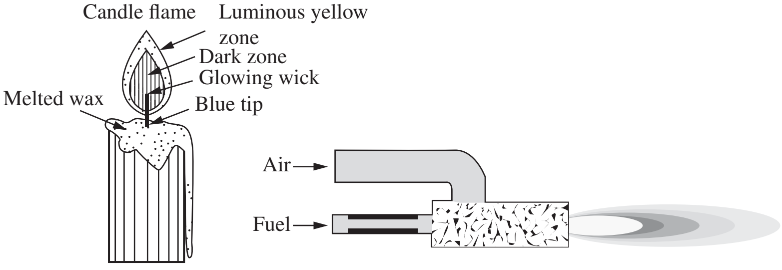
Turbulent flow can be roughly described by characterizing the *scale* and *intensity* of turbulent fluctuations in the flow. Scale represents an average eddy size at that location in the turbulent flow. Intensity relates to the magnitude of the fluctuating velocities relative to a mean velocity of the flow. It is usually defined as the root mean square of the fluctuating component of the velocity.

In turbulent flames rate of consumption of combustible mixture increases greatly. Unlike laminar flames, turbulent flames are often accompanied by noise and rapid fluctuations of the flame envelope. Premixed turbulent flames are produced when a laminar flame encounters a region where the flow ahead of the flame is turbulent. High intensity turbulence ahead of the flame can lead to extremely high effective combustion rates. This is extremely important to the development of the explosion process during an accidental explosion.

In diffusion flames such as *pool fires*, turbulence that interacts with the flame can be generated by the flame itself and the free convection induced by buoyancy. Specifically, there is a critical size above which a diffusion flame is no longer laminar in character and turbulent transport processes become important to the rate at which fuel is being consumed.

In highly turbulent diffusion flames, reaction rates are comparable with those found in premixed flames. Heat release rates in turbulent diffusion flames are far higher than in laminar flames and temperatures may approach 2,000°C. Both these factors, namely, high heat release rates and high temperatures, mean that turbulent diffusion flames have potentially much more damaging source of of heat. However, turbulent diffusion flames do not, in general, lead to explosions.

Diffusion and pre-mixed flames are illustrated in Figure 3.40.



Laminar diffusion flame

Pre-mixed flame

Figure 3.40 Diffusion and pre-mixed flames illustrated

Most turbulent premixed flames are from combustion systems, for example, boilers, furnaces, etc. In such systems, the air and the fuel are premixed in some burner device.

Most unwanted fires fall into the category of turbulent diffusion flames. Since no burner or other mechanical device exists for mixing fuel and air, the flames are diffusion type.

The main concern in fire applications is with diffusion flames, as contrasted to premixed flames where fires and oxidants are premixed or brought together to the combustion region. At high turbulence in diffusion flames, kinetics, and diffusion may be of roughly equal importance.

Cool flames: Mixtures of hydrocarbons and oxygen react very slowly below 200oC. As temperature is increased a variety of oxygen-containing compounds begin to form. Further increase in temperature CO and H2O predominate in the products. H2O2, CH2O (formaldehyde), CO2 and other compounds begin to appear. At 300–400oC, faint light often appears which may be followed by one or more blue flames that successively traverse the reaction vessel. These light missions, called cool flames are followed by an explosion.

Above upper flammability limit, *cool flames* may occur. Low-temperature oxidation gives rise to hydro-peroxides that decompose giving rise to cool flames. *Cool flames* progress slowly and give out very little light making it difficult to notice them, but if they reach a place where concentrations are suitable, that is, within the flammable range, they may change into normal flames. Cool flames normally occur at higher pressures, exceptions being acetaldehyde and diethyl and divinyl ethers which have cool flame zones at normal pressures.

Flame propagation in sprays and mists: Liquids, whether in pool form or in droplet form, will not burn as such but first they will have to change to vapor/gas phase. Rate of vaporization and combustion depends on rate of heat transfer from flame front to interface and rates of diffusion of reactants towards each other and products of combustion away from the reaction zone. Combustion reactions are very fast compared to heat and mass transfer rates. In other wards, heat and mass transfer rates are the controlling factors in droplet burning.

Plant leakages involving liquids may be either in the form of jets or sprays. Sprays result from leaks from high pressure sources. Jets may turn into sprays when they hit solid surfaces. Liquids inside a tank will form droplets as they hit its walls. For example, this might happen in splash filling of tanks or when the tank is in a moving vehicle. Entrainment of oil drops in air can take place, for example, in compressed air lines and atomized fuel injection systems. If the droplets are small, they do not settle down easily and give rise to mists. Flashing of hot liquids followed by quenching of vapor with a cold gas can lead to condensation and mist formation. For example, rupture of a hot oil line could result in considerable mist formation by such a flash-quench operation. Higher hydrocarbons are particularly prone to mist formation.

Sprays and mists increase interfacial area between the liquid and air, thereby increasing heat and mass transfer rates, resulting in vaporization rates several times over those from normal liquid surfaces. When droplet sizes are very small, less than 10 µ m, mixture will behave as a gas/vapor–air mixture. For small droplets, the mist will evaporate almost completely (particularly so if the fuel volatility is high), before a flame reaches the location of the droplets. In this situation, a fuel mist–air mixture will burn essentially like a premixed fuel vapor–air mixture and the flame will look somewhat like a premixed laminar flame.

As molecular weight of fuel increases and volatility decreases, rate of vaporization of fuel droplets, as they pass through the preheat zone of the flame, decreases markedly and the flame becomes a series of diffusion flames surrounding individual droplets. This phenomenon is further reinforced if the droplet sizes are large. For droplet sizes above 10 µm, flame propagation depends on the ratio of droplet diameter to distance between drops that continue to burn behind the flame front.

Flame propagation in dust clouds

Differences between premixed gases and dust clouds: In dust clouds, as opposed to premixed gases, inertial forces can produce fuel concentration gradients (displacement of particles in relation to gas phase). Furthermore, thermal radiation may contribute significantly to the heat transfer from the flame to the unburnt cloud, depending on the type of particle material (e.g. light metals).

It has often been assumed that the laminar burning velocity of a given dust cloud is a basic combustion property of the cloud, which is closely related also to the burning velocities at various defined levels of turbulence and hence to the flame propagation through that type of cloud at large.

Classes of fires: *Class* A fires are those which involve ordinary combustible materials such as wood, paper or cloth. These fires should be extinguished by using a dry chemical extinguisher. Water is effective in extinguishing these types of fires.

Class B fires are those which involve flammable liquids, gases, oil, paint and greases. Either dry chemical or carbon dioxide extinguishers should be used to extinguish these types of fires.

Note: flammable liquids may re-ignite after being extinguished. Water should not be used.

Class C fires are those which involve electricity. Either dry chemical or carbon dioxide extinguishers should be used to extinguish these types of fires. Water should not be used.

Class D fires are those which involve combustible metals such as magnesium or sodium. Water can react with sodium and other alkali metals explosively, therefore water should not be used. Also CO_2 extinguishers are unlikely to be able to contain a Class D fire.

Explosion, Deflagration, and Detonation

An explosion is defined as uncontrolled combustion producing a rapid increase in temperature and pressure. *Explosion* involves release of energy over a sufficiently small time and in a sufficiently small volume, generating a pressure wave of finite amplitude traveling away from the source. This energy may have originally been stored in the system in a variety of forms, for example, chemical, nuclear, electrical or pressure energy. Release of this energy is not considered to be explosive unless it is rapid and concentrated enough to produce a pressure wave. Explosive gas or gas mixture is one which permits rapid energy release as compared to most steady, low temperature reactions. Natural explosions can result from forest fires, volcanic eruptions, lightning, meteors, etc.

Intentional explosions are those resulting from condensed phase high explosives, blasting, military operations, pyrotechnics, vapor phase high explosives, propellants, gun powders, nuclear devices, laser sparks, sparking, etc.

Accidental explosions in process industry continue taking place in spite of preventive and protective measures adopted by modern process industry, due to reasons of inadequacy of the measures as well as deficiencies in their implementation. Explosions can occur inside process equipment or piping, in buildings or off-shore installations, in open process areas or in unconfined areas, or in nuclear power plants. The consequences of explosions range from no damage to total destruction of the facility. Accidental explosions are of concern to process industry and are classified and discussed in the following paragraphs.

Figure 3.41 gives typical classification of accidental fires and explosions.

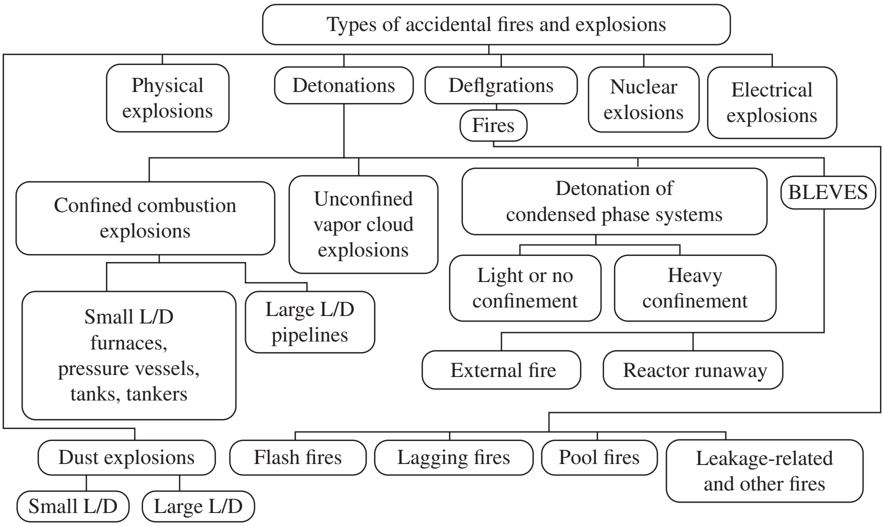


Figure 3.41 Classification of accidental fires and explosions

Damage from an explosion may result from the rupture of a container and its fragments, a shock wave, heat or fire or release of toxic gas. A compressed gas container or boiler rupture, due to high pressure, is often called a *physical explosion* and the effects may be similar to those from an explosion due to chemical reaction. Physical explosions can be detonative.

The energy released by a physical explosion can be estimated from the Brode equation:

$$E = (P_i - P_f)V/(\gamma - 1) \text{ joules} \tag{3.51}$$

where P_i = Initial pressure, N/m^2
P_f = Final pressure, N/m^2
V = Vessel volume, m^3
γ = Ratio of specific heats, C_p/C_v

Examples of physical explosions include bursting of a vessel containing high pressure compressed liquids, vapors or steam, introduction of molten material into cooling liquids or into a container with moisture content and rapid/violent mixing of materials at drastically different temperatures. Spilling of LNG on water, mixing of molten steel/slag with water are other examples.

Examples of explosions involving flammable or reactive substances include *gas and dust explosions, unconfined vapor cloud explosions, condensed material explosions, boiling liquid expanding vapor explosions (BLEVEs) and runaway chemical reactions*.

Condensed material explosions are typically associated with propellants and high explosives which involve high energy content per unit volume or unit mass. Most energetic condensed phase explosive mixture is stoichiometric mixture of liquid hydrogen–liquid oxygen having energy content of 16,700 kJ/kg. Condensed phase explosions are detonations with velocities ranging from 1.5 to 8 km/s. Condensed phase detonations can be classified into those with light or no confinement or with heavy confinement.

Examples of detonations with no or light confinement include detonations during manufacture, transport, storage and use of high explosives. An example of such detonation in a process involves detonation of accidental accumulation of highly sensitive vinyl acetylene in a distillation column, accumulation of nitrogen trichloride in a chlorine vaporizer, when Cl_2 was allowed to vaporize to dryness in it or in reactors in which hazardous impurities are allowed to accumulate. Heavy confinement of explosives results in less damage due to blasts, for example, use of blast resistant bunkers.

Boiling Liquid Expanding Vapor Explosion (BLEVE)

Among the most damaging of accidents that can occur in a chemical process plant is a BLEVE. A BLEVE occurs when a pressure vessel containing a liquid above its normal boiling point and under pressure is exposed to heat so that the metal looses strength and fails catastrophically. For a BLEVE to occur there must be a total loss of containment and significant vaporization. The failure of the vessel is often caused by an external fire exposure, as illustrated in Figure 3.42.

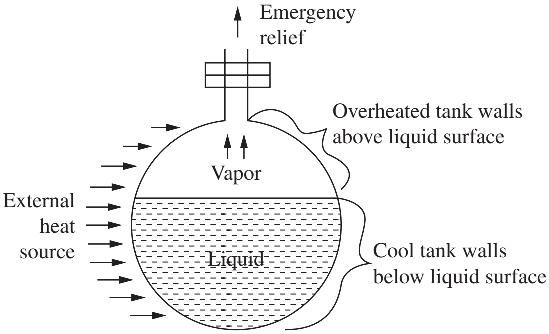


Figure 3.42 Conditions which can lead to development of a BLEVE

On such failure the pressure immediately drops to atmospheric and the liquid boils, generating a large quantity of vapor. Even if the relief system is adequately sized and functioning, nonwetted portions of the high pressure vessel can overheat and lose its strength leading to catastrophic vessel failure. On rupture of the vessel, which develops slowly because of its ductile nature, small number of large fragments is produced. Rapidly vaporizing liquid (flash vaporization) rockets the fragments to large distances at relatively high initial velocities. Vessel fragments may fly apart with great force causing injury or death to people as far away as 300 m or more. The damage is caused by the pressure wave from rapid expansion of the released vapor and from flying pieces of the vessel and piping. Pressure of the escaping vapors can injure people or damage buildings and structures. Escaping gas/vapor might result in a fire, causing further damage. The escaping fluids might mix with air and explode, producing a second pressure wave which might further cause damage. Even with nonflammables such as steam from boilers, damage might be considerable.

Flash vaporization from bulk liquid, being a relatively slow process, very little pressure rise is involved in a blast wave.

If the substance released is a fuel, BLEVE can result in very large fire balls. The major consequences of a BLEVE, in order of decreasing importance, are: the thermal radiation from the resultant fire ball causing skin burns to exposed personnel and ignition of nearby combustibles, the fragments produced when the vessel fails and the blast wave produced by the expanding vapor/liquid.

A BLEVE can occur for many reasons, including excessive pressure in the vessel, damage to a pressurized vessel from mechanical impact such as collision of ship containers, tank cars containing butane, propane, and propylene, corrosion or exposure of the pressurized vessel to external fire. Overfilling of vessels caused spillages leading to fires and BLEVES. In all the reported incidents, overpressure protection was absent.

A vessel exposed to external fire may fail below its design pressure, if the vapor space of the vessel is exposed to flames, which heat and weaken the metal causing failure. Runaway self-reactions led to over pressurization, overheating failure due to rupture of containers containing overheated volatile liquids above their boiling points leading to BLEVE incidents.

BLEVEs are a concern because of the large potential for damage at many installations. For example, a BLEVE at a 1,760 m^3 (15,000 bbl) propane sphere (equivalent to a sphere diameter of roughly 15 m (50 ft) could cause damage as far away as 4,160 m (13,650 ft). Such an incident, even if it can be contained within the boundaries of the facility, will result in significant damage, since the radii for fragmentation damage and for radiation damage to equipment would each extend to about 914 m (3,000 ft). Examples involving BLEVES include rail road tanker accidents involving high vapor pressure liquids such as LPG, propylene, and vinyl chloride monomer Some times a fire in a plant can cause BLEVES from storage tanks, drums, etc. Hot water tanks with water stored at high pressures can also result in a BLEVE. BLEVE is a possibility from release of flammable gas or vapor as a result of a leakage.

Preventive design features to be incorporated against BLEVEs include protection from overpressure and overfill, spill containment, fire protection, isolation by remote control, equipment spacing, sloping the ground away from fixed containers, insulating the containers in which liquids above their boiling points are held, water spray systems, depressurization provisions, and other measures. Water spray fire protection systems, such as fixed deluge systems or fire water nozzles are an effective way to keep the vessels and associated piping cool enough to maintain their mechanical integrity on fire exposure.

One proposition to prevent BLEVEs is construction of baffles inside the normal walls of a storage vessel which provide flow channels between baffles and the external wall. Fire exposure causes immediate boiling of the liquid near the walls and the resulting vapor *pumps* the liquid throughout the flow channel. This inherently passive process is claimed to be cooling the walls, preventing overheating the walls and thus preventing development of a BLEVE.

Deflagration and Detonation

Deflagration consists of a rapid reaction during which heat is transferred progressively from a reaction zone to the nearby reactants whose temperature is then raised to a point at which they too react. The rate at which deflagration proceeds is high but involves a subsonic wave (in which the burning velocity is less than the velocity of sound in the unburned gas ahead of the flame) sustained by a chemical reaction. In practice the velocity depends on the degree of confinement and the size and shape of the flammable mixture.

Assuming that the un-burnt gas is stationary, the flame propagates into the un-burnt gas at *laminar burning velocity*, which is a fundamental parameter, whose value reflects the reactivity of the mixture. If the un-burnt gas is turbulent, the burning velocity can increase and is then called the *turbulent burning velocity*. The rate of deflagration is controlled by diffusion of heat and reactive species from the reaction zone to the unburnt material.

The words combustion wave, flame and deflagration wave are normally used interchangeably. Deflagrations velocities are of the order of 1–1,000 m/s and pressure rises are of the order of 7–10 bar, starting at ambient pressure, for deflagrations involving hydrocarbon mixtures. A deflagration is a combustion reaction and involves only flames (fires).

The behavior of a flame front (leading surface of a flame) is dependent on a number of variables such as type of fuel, fuel–air mixture, pressure, temperature, turbulence, and propagation in unconfined and confined spaces.

A *deflagration* may develop in the atmosphere as an *unconfined deflagration*, or in an enclosed area, typically a piping system, as a *confined deflagration*. Detonations and overdriven detonations are most commonly encountered in closed piping systems.

A confined deflagration starts at low speed and pressure. As the flame front propagates in the pipe, its speed and associated pressure increase. In long or complicated (multiple bends) pipe runs the flame accelerates until it transitions through an overdriven detonation state into a stable detonation. Flame propagation in a confined space is illustrated in Figure 3.43.

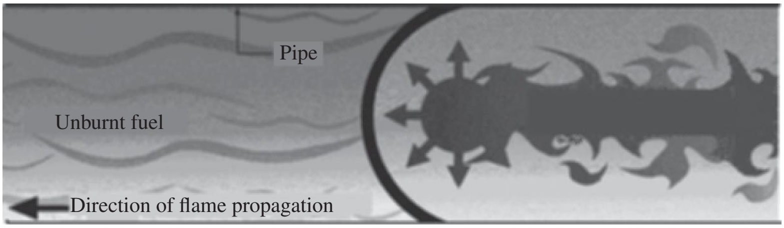


Figure 3.43 Flame propagation in a pipe

In a closed vessel/confined space containing a fuel/air mixture, the deflagration pressure increase at the flame front is very approximately given by 1.2 M^2, where M is the Mach number (i.e. the deflagration speed divided by the speed of sound in the un-burnt mixture). Once the deflagration speed approaches speed of sound, a shock wave will form.

If the velocity through the reacting mixture reaches sonic or higher velocities, then the explosion is called *detonation*. A shock wave will be generated and sustained by the energy of the chemical reaction in the highly compressed explosive medium in the wave. The shock compression heats the gas and triggers the combustion process. Detonation wave is a three-dimensional shock wave followed by the reaction zone.

An explosion does not necessarily require the passage of a combustion wave through the expanding medium whereas an explosive gas mixture must exist in order to have either deflagration or detonation. That is, deflagrations and detonations require rapid energy release and explosions do not require the presence of a wave form.

Explosive medium may support either a deflagration or detonation wave depending mainly on confinement and mixture ratio. The primary result of an ordinary thermal initiation appears always to be a flame, which propagates with subsonic speed. Where conditions are such that the flame causes adiabatic compression of the still un-reacted material ahead of it, the flame accelerates leading through transition from deflagration to detonation. In deflagrations, hot gases *move away* from the wave whereas in detonations *they follow* the wave.

Characteristics of detonations involve supersonic velocities, with high pressure shock wave, *ahead* of the reaction zone. Adiabatic gas compression results self-ignition.

Detonation is the most devastating form of gas explosion. Unlike deflagration, detonation does not require confinement or obstructions in order to propagate at high velocity. For detonations involving hydrocarbons, typical velocities are of the order of 1,850 m/s for fuel/air mixtures and 3,000 m/s for fuel/oxygen mixtures. These velocities may be higher where hydrogen is the fuel.

In a detonation, a high-pressure shock front travels approximately 1–10 mm ahead of the reaction zone. Because chemical reaction rates depend exponentially on temperature, extremely rapid combustion occurs. High pressures arise from the strength of the shock.

The initial pressure rise of a steady detonation is at a maximum close to the stoichiometric concentration, and decreases as the mixture approaches the detonation limits. Typical maximum detonation pressures are 15–19 times the initial pressure for stoichiometric fuel/air mixtures, and 25–30 times the initial pressure for stoichiometric fuel/oxygen. Turbulence can increase these pressures dramatically.

Flame temperatures in detonations are of the order of 1,600 K (for lean mixtures) to 3,000 K for stochiometric mixtures. For mixtures in oxygen, the maximum temperature increases to more than 4,000 K and can be as high as 10,000 K. In a detonation, a high pressure shock wave travels approximately 1–10 mm ahead of the reaction zone, the reaction zone being the flame itself (in a fast deflagration, the reaction zone lags much further behind the shock wave). Because chemical reaction rates depend exponentially on temperature, extremely rapid combustion occurs. High pressures arise from the strength of the shock.

Deflagration transition to detonation (DDT), propagation and transmission of detonation waves, depend strongly on the reactivity of the gas cloud as well as on the geometry/environment in which the gas cloud is located. There are two extremes regarding the geometry/environment, a gas cloud inside a pipe and a gas cloud in the open.

Detonation incidents in the chemical industry frequently involve DDT. A deflagration flame in a detonable mixture (typical velocity 1.0 m/s) can be accelerated to detonation by turbulence induced by friction with pipe walls, obstructions like pipe bends, etc. Turbulence accelerates the flame because it wrinkles the flame front, which increases its surface area and therefore increases the rate of reaction. This results in a shock forming ahead of the flame as the flame approaches sonic velocity. The shock front acts like a piston, heating and compressing the unburnt gas ahead of the flame. Eventually the un-burnt gas self-ignites, and a detonation wave is formed ahead of the flame. This occurs at a flame speed of approximately 1,000 m/s. The transition distance in a pipe is in the range of L/D of 10–60 (for a highly reactive gas like acetylene, it is 3).

Very reactive fuels such as hydrogen, acetylene and ethylene in air and other fuels in oxygen-enriched atmospheres, are particularly susceptible to DDT. In a confined space, such as a closed vessel, a high flame velocity is not a requirement for generation of pressure. In a closed vessel there is no or very little relief (i.e. venting) of the explosion pressure and therefore even a slow combustion process will generate pressures. Pressures increase significantly when a detonation reflects off a solid wall. For example, for ethylene/air the peak pressure increases instantaneously from approximately 18 to 45 bar.

Detonation can produce large numbers of small fragments due to brittle failure. However, large distorted and twisted fragments can be produced if the vessel is sufficiently strong.

In a gas explosion involving hydrocarbon-air mixtures within flammability limits, set off by ignition from a weak source, the flame will normally start as a laminar flame with a velocity of the order of 3–4 m/s. If the cloud is unconfined and unobstructed the flame is not likely to accelerate to velocities of more than 20–25 m/s and the overpressure will be negligible if the cloud is not confined. In a building or in the open with obstructions such as process equipment, the flame may accelerate to several hundred meters per second. When the gas is burning, the temperature will increase and the gas will expand by a factor of up to about eight or nine. The unburned gas is pushed ahead of the flame and the laminar flame turns into a turbulent flame. The effective burning rate will increase and the flow velocity and turbulence ahead of the flame increases further. This causes flame acceleration and high explosion pressures and in some cases transition to detonation.

Damage resulting from an explosion depends on factors like type of fuel and oxidizer, concentrations within the cloud and size of the cloud, location and strength of the ignition source, size, location and type of explosion venting areas, location of the structures likely coming within the path of flame propagation and emergency response and other explosion mitigation provisions.

A useful indicator of the susceptibility of a material to detonation is its maximum experimental safe gap (MESG) value. The lower the MESG, the more easily a material will detonate, that is, gases in Group IIC are most susceptible.

Examples of materials that can detonate in air are hydrogen, acetylene, ethylene, ethylene oxide, ethane, and propane.

Summary of factors that favor detonations:

(1) Low MESG value.
(2) Proximity to stiochiometric composition.
(3) Pipe diameter not much above critical diameter. For a given mixture, there is a critical pipe diameter, below which detonation will not occur. This is because, in a sufficiently narrow pipe, there is not enough room for the detonation's cellular structure to exist.
(4) Pipe length to diameter ratio is critical ratio for diflagration to detonation transition (DDT). The critical ratio is approximately 3.0 for very sensitive fuels such as acetylene or ethylene in air, and varies from approximately 10–60 for other fuels in air.
(5) Obstacles and bends. These increase turbulence, so decrease DDT run up distance and encourage overdriven detonations.
(6) Confinement. Detonation limits are wider in confined than in unconfined areas, but there is some evidence that detonation limits are wider in larger vessels.
(7) Elevated temperature. This widens detonation limits, particularly the upper limit.
(8) Elevated pressure. This widens detonation limits, particularly the upper limit.
(9) Oxygen enrichment or presence of other reactive oxidants.
(10) Absence of diluents.

Unconfined Vapor Cloud Explosions (UCVCEs)

Vapor cloud explosions generated from a release of flammable vapor can, under certain conditions, explode with possible widespread damage to plant and property and injury to people. A massive spill of flammables into the open atmosphere can lead to the following sequence of events:

(i) Dissipation harmlessly without ignition. Dispersion without ignition, is not necessarily nonhazardous, as some substances are toxic as well as flammable. Cloud will spread from too rich, through flammable range to too lean. Cloud will disperse through natural convection. Slow leaks give time for cloud to disperse naturally without finding an ignition source.

(ii) Ignition immediately on release leading only to a fire. Edges start to burn through deflagration (steady state combustion). If cloud is small enough with little confinement it cannot explode.

(iii) Ignition after dispersion over a wide area leading to a large fire.

(iv) As in (iii) except after start of the burning, flame propagation takes place through the fire, which accelerates to give rise to UCVCE producing a angerous blast wave. Flame velocity will increase with containment and turbulence. If velocity is high enough cloud will detonate. Confinement prevents combustion products escaping, giving higher local pressures even with deflagration. Creates turbulence, a precursor for detonation. Terrain can cause confinement.

UCVCEs can be most dangerous as happened in Flixborough explosion, which caused death of 28 employees and caused extensive damage to the plant and surrounding area. Onsite leaks have a much higher potential for UVCE than offset leaks. Vapor systems need very large failures to cause UVCE.

In an unconfined space, upon ignition of a fuel gas/vapor, the flame moves outwards toward unburned gas. The expanding flame front forms a narrow layer between the unburned gas and products of combustion. A pressure pulse forms in front of the flame. Both chemical and mechanical energy contribute to the formation of the pressure pulse.

Chemical energy: Heat generated from combustion increases the temperature and pressure of the gas in front of the flame.

Mechanical energy: The product gas expands outward due to the increased temperature and pressure.

The pressure pulse dissipates as the flame expands in the unconfined space. Usually, the velocity of the flame front in an unconfined space is subsonic, resulting in a deflagration.

Flixborough explosion provided an opportunity to investigate consequences of explosions, especially in the areas of unconfined vapor cloud explosions, control room location, plant, and equipment modifications and use of materials of construction, to cite a few aspects.

A degree of confinement or congestion, that is, the presence of obstacles or obstructions within the vapor cloud, is necessary for hydrocarbon vapor clouds to produce significant blast effects. It is, however, possible for significant blast effects to arise in situations where an explosion is initially confined, such as within vessels or pipe work and propagates into an unconfined cloud. In this situation, the jet of flame emerging from the confined area creates turbulence in the unconfined cloud, generating a turbulent mixture and high flame speeds.

Obstacles within a vapor cloud generate turbulence in the gas flow ahead of the flame front, increasing the combustion rate and hence the flame speed and the explosion overpressure. Provided that the separation distance between the obstacles is not too large, this mechanism can result in increasing flame speed and pressure as an explosion propagates over a series of obstacles. The obstacles also distort the flame front as it propagates over them, increasing the flame area and thus the combustion rate.

Factors Favoring High Overpressures

Cloud composition, highly unsaturated molecules, high flammable range, low ignition energy, high flame speeds. For example, ethylene clouds give high overpressures when they burn. Stable atmospheres lead to large clouds. Low wind speed encourages large clouds. Large clouds increase probability of finding ignition source. Equipment failures where leak is not vertically upwards increases likelihood of large cloud.

Most UVCE C_2–C_6 light gases disperse readily, heavy materials do not form vapor clouds easily. The strength of the ignition source is also a factor in determining the strength of any resulting explosion. These effects are most pronounced in reactive gases, such as ethylene and least pronounced in relatively unreactive gases, such as natural gas.

Majority of UVCEs occur after the release (leak) of flashing liquids above their normal boiling temperatures, from pressurized containment, allowing rapid formation of a well-mixed vapor–air cloud. The amount of vapor released is also significant, with the destructive potential increasing with the quantity of fuel released. Examples of leakages are:

A 5 cm (2 in) diameter hole in a plant containing gasoline at atmospheric temperature and 690 kPag (100 psig) involve a leak rate of about 3.0 tons/min, but very little vapor form. There may be fire but explosion is unlikely, unless leak is inside building.

A 5 cm (2 in) hole in a plant with flammable gas (e.g. propane) at atmospheric temperature and 690 kPag (100 psig) involve a leak rate of about 0.25 ton/min (less if it has to flow through a pipeline). If the gas has unhindered escape route, it will be diluted by jet mixing and explosion will be unlikely. If the gas impinges on the ground/other equipment and loses kinetic energy, a gas cloud will form and explosion will be possible.

A 5 cm (2 in) hole in a pipe containing gasoline at 120°C and 690 kPag (100 psig), gasoline leaks at the same rate as in the first example, but it is above normal boiling temperature, that is, above 100°C. 1/8th of it will flash and most of the rest will form a spray. Large vapor cloud will form and much larger explosion possible than in the above cited cases.

Other factors, such as the fuel reactivity, the degree of confinement and congestion and the momentum of the fuel being released, are likely to be equally important, if not more so, in determining whether or not a VCE will occur on ignition. The effects of a VCE can be experienced onsite and offsite.

Table 3.45 gives damages caused by vapor cloud explosions.

Table 3.45 Damages caused to people and facilities

Peak overpressure (kPa)	*Effects*
Effects on people	
6	Knock people down
35	Rupture ear drum
100	Damage lungs
240	Threshold fatalities
340	50 percent fatalities
450	99 percent fatalities
Effects on facilities	
3. 5–7	Glass windows break
7–14	Common siding types fail
-	—corrugated asbestos shatters
-	—corrugated steel and panel joints fail
-	—wood siding, blows in
14–20	Unreinforced concrete or cinder block walls fail
20–27	Self-framed steel panel buildings collapse. Oil storage tanks rupture
35	Utility poles snap
50	Loaded rail cars overturn
50–55	Unreinforced brick walls fail

The two well-known detonation theories are those of Chapman and Jouguet (CJ) and Zel'dovitch, von Neumann and Doring (ZND). The first is based on pure gas dynamic and thermodynamic arguments, assuming infinitely fast chemistry. The CJ theory treats the detonation wave as a discontinuity with infinite reaction rate. The latter introduces finite rate chemistry. Despite the omission of detailed chemistry, CJ predictions can be very accurate. The accuracy of ZND calculations is limited by the accuracy of the chemical reaction schemes used.

The ZND model describes the detonation wave as a shock wave, immediately followed by a reaction zone (i.e. flame). The thickness of this zone is given by the reaction rate. The ZND theory gives the same detonation velocities and pressures as the CJ theory. The only difference between the two models is the thickness of the wave.

The CJ theory combines an analysis based on the conservation of mass, energy and momentum with basic thermodynamics. It is a one dimensional model and assumes that the reaction rate is infinitely fast. The representation of a detonation by this model, with an infinitely thin reaction zone, is known as an *ideal* detonation. The model neglects the high momentary pressure spike at the leading edge of the detonation wave. A CJ analysis can be used to calculate detonation properties such as velocity and pressure. Predicted values compare reasonably well with experimental data and the model is widely used.

$$\text{Average CJ pressure} \approx (\gamma M^2/\gamma+1)\, P_i \qquad (3.52)$$

where $\gamma = c_p/c_v$, M = mach number and P_i= initial pressure.

$$\text{Peak CJ pressure} = [(2\gamma \mathrm{M}^2/\gamma+1) - (\gamma - 1/\gamma+1)]\, P_i \qquad (3.53)$$

Table 3.46 gives CJ pressure and CJ velocity for some fuel–air mixtures.

Table 3.46 CJ pressures and CJ velocities for some fuel–air mixtures (initial conditions: 25°C and 1.013 bar)

	Hydrogen	*Methane*	*Propane*	*Ethylene*
CJ pressure (bar)	15.8	17.4	18.6	18.6
CJ velocity (m/s)	1968	1802	1804	1822

Source: Baker, W.E., Cox, P.A., Westine, P.S., Kulesz, J.J. and Strehlow, R.A.

Explosion hazards and evaluation, Elsevier Scientific Publishing Company (1983).

The CJ model cannot be used to calculate parameters which require knowledge of the structure of the detonation wave, such as detonation limits, initiation energy, critical pipe diameter and the thickness of the reaction zone. These so-called *dynamic detonation parameters* can be calculated (with varying degrees of accuracy) using the ZND theory.

Over-driven detonation is a detonation wave that is artificially supported above its CJ velocity and hence also has a much higher peak pressure than the CJ value. There is a rapid increase in pressure with the degree of overdriving (i.e. the increase in velocity above the CJ value). Overdriving can occur during the transition from deflagration to detonation, or during initiation by a solid explosive. This over-driven detonation can generate much higher pressures than the steady state detonation—up to 100 times the initial pressure (5 times the CJ pressure). Usually this pressure is short lived, but can be sufficient to cause local mechanical damage.

When a detonation is formed, a strong pressure wave can propagate back through the burnt gas. This is called *retonation*. It can be enhanced if it propagates back through gas that has not all been burned during the flame acceleration phase. It can reflect (for example off a closed end or bend) and travel back towards the main detonation wave. Because of the increased speed of sound in the hot burnt gases, the reflected retonation overtakes the detonation. Under appropriate conditions, a combined detonation/retonation wave front can exist for a very short time. During this time, the overdriven pressure can be between approximately 2 and 5 times the usual detonation pressure.

One empirical method that has been widely used for predicting the effects of a VCE and for quantifying the magnitude of incidents involving VCEs is the TNT (Tri-nitro toluene) equivalence method. The basis of the method is to equate the energy being released by the explosion to the mass of TNT, that on detonation, would give the same level of damage. This method uses the large body of data available for the consequence of TNT explosions to predict the consequences of explosions resulting from other sources. The first step is to establish the energy likely to be released by the explosion. This is done by combining the total available energy with an estimate of the yield of the explosion, sometimes expressed in terms of the *efficiency* of the explosion. This energy is then used to calculate an *equivalent mass* of TNT. The consequence of the explosion of this mass of TNT can then be found from various graphs and tables of data. The following example illustrates the method.

A cloud containing 1,000 kg of propane ignites, leading to a vapor cloud explosion. Estimate the overpressure at a distance of 150 m from the centre of the cloud. ΔH_c = 531kcal/mol = 2349 kJ/mol = 53.4 MJ/kg. The heat of detonation of TNT is 4652 kJ/kg so the equivalent mass of TNT for this explosion is given by:

Mass of propane × Heat of combustion of propane × efficiency factor. For this case, the efficiency factor can be taken to be 0.04, that is, 4 percent.

Therefore, TNT equivalent mass = $1000 \times 53 \times 10^6 \times 0.04/(4652 \times 10^3) = 455.7$ kg.

The overpressure is then estimated from the *scaled distance* which is a function of the actual distance from the centre of the explosion and the magnitude of the TNT equivalent mass.

Scaled distance = actual distance)/(mass TNT)$^{1/3}$, where the distance is in m and the mass is in kg. Therefore in this example, scaled distance = $150/(455.7)^{1/3} = 19.5$ mkg$^{-0.333}$.

The overpressure is then read from Figure 3.44.

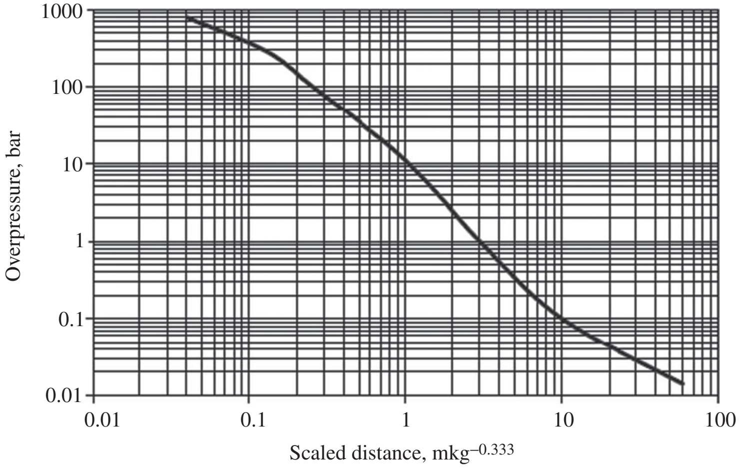


Figure 3.44 Overpressure due to explosions

Pressure Vessel Explosions

These can involve (i) simple failure, (ii) combustion-generated failure, or (iii) failure followed by immediate combustion.

Simple failure may be due to faulty design, construction or installation, corrosion, erosion or embrittlement of the materials of construction, mechanical breakdown, failure, due to blockages of control devices, inadequacies in inspection methods and schedules, human errors, or external fire exposure of the vessel. Internal pressure of the vessel increases if its contents are gaseous, weakening the material of the vessel until rupture occurs. Fragment and missile damage can be quite dangerous. There have been cases where fragments weighing tons of material were thrown to distances of a kilometer or so. Damage to the surroundings will be limited. If the contents are toxic, as in the case of an ammonia reactor/separator, toxic exposure hazards to personnel become a possibility.

Examples of combustion-generated failure include explosions in compressed air lines, fuel being lubricating oils or char deposits on the walls, or piping explosions involving acetylene caused by acetylene decomposition. The third type produces fire balls (BLEVEs), the size depending on the quantity of the fuel released.

Improperly operated or maintained pressure vessels can fail catastrophically, killing and injuring people and cause extensive damage even if the contents are benign. The conditions and factors that have played major roles in pressure vessel accidents:

(i) Operation above the maximum allowable working and test pressures
(ii) Improper sizing or pressure setting of relief devices
(iii) Improper operation of relief devices due to faulty maintenance and failure to test regularly
(iv) Failure of the vessel due to fatigue from repeated pressurization, general thinning from corrosion or erosion, localized corrosion, stress corrosion cracking, embrittlement, holes, and leaks
(v) Failure to inspect regularly
(vi) Improper repair of a leak or other defect involving welding and annealing, that embrittles and further weakens the vessel
(vii) Overpressurization and failure of the vessel due to exothermic reaction or polymerization
(viii) Vessel exposure to fire

Hazards posed by a vessel can be worse if repair welds are made without shutting down and emptying the vessel. For example, if a pressure vessel is repaired without removing the water, the quench effect of the water can embrittle the steel,

Design, fabrication, and inspection of pressure vessels are regulated through standards and rules prescribed by ASME and other standards organization,

Despite some of the most rigorous, well conceived safety rules and procedures ever put together, boiler and pressure vessel accidents continue to occur.

Summary of common causes of explosions in pressure vessels:

(i) Errors in design, construction and installation
(ii) Corrosion or erosion of materials of construction
(iii) Mechanical breakdown, failure, or blocking of automatic control devices
(iv) Failure to inspect thoroughly, properly and frequently
(v) Improper application of equipment
(vi) Lack of planned preventive maintenance
(vii) Inadequate training of operators
(viii) Human failure, such as lack of understanding, failure to follow safe operating procedures, and lack of functional coordination

Explosions in Gas and Oil Fired Furnaces/Heaters

General causes: Fuel leakage through faulty shut-off valve, repeated attempts to light pilot without intermediate purge, too low purge air flow rate, insufficient purge time, control failure, improper air–fuel ratio due to damper or fan control failure, delayed ignition due to faulty ignition equipment, faulty pilot, unstable fuel supply, inadequate oil atomization due to plugging of burner nozzle, failure of atomization steam, tube rupture extinguishing flame, opening of fuel valve before establishing pilot, etc. Summing up the causes reduces to three categories of causes: (i) inadequate purge, (ii) delayed ignition, and (iii) improper air–fuel ratio.

Explosion Hazards in Compressed Air Systems

Risk of slow oxidations taking place in compressed air systems resulting in CO formation, posing hazards to personnel, for example, when using air-driven tools in confined spaces. Many explosions are reported in literature involving compressed air systems in mines and industries. Common factors to these explosions include (i) involvement of oil-lubricated cylinders of reciprocating compressors, carbonaceous deposits/residues downstream in the immediate vicinity of the final stage outlet valves, observations of features such as faulty compressor operation and high final stage outlet temperatures prior to the explosions, and blowing of compressor piping systems at discrete points separated by different unaffected pipe lengths downstream of the compressors, are common prior to the explosions.

Mechanism of explosion propagation in compressed air systems: A very thin layer of oil in a 25.4 cm (10 inch) pipe at 890 kPa (100 psi) air pressure could support a flame process similar to gaseous detonation. Flame speeds of about 1,220 m/s (4,000 ft/s) were observed.

Passage of shock wave into piping causes heating and evaporation of the oil film to sufficient degree to support combustion. Increased volume from combustion could then reinforce shock wave and the process could be self supporting.

The turbulence behind the shock wave could be sufficient to cause removal of oil film and convert it to mist which might ignite subsequently. Sonic interactions between the shock wave and liquid surface can result in vibrations in the film which might dislodge the liquid from it.

Once the liquid leaves the walls, turbulence and evaporation may be involved although mist itself is capable of supporting flame. LFL for hydrocarbons is essentially same whether fuel is present as a vapor or mist.

Blowing open of straight runs of pipe at isolated points separated by intervals of long undamaged sections is characteristic of film detonations. For gaseous detonations, long straight runs may be ripped open from end to end.

Even with detonations associated purely with gaseous phase, local abnormally high pressures may be developed during transition from deflagration to detonation. These are associated with formation of a primary shock wave ahead of the combustion waves once the combustion wave overtakes primary shock wave, the combined wave front proceeds with uniform velocity corresponding to detonation.

With oil film detonations, the primary shock wave is responsible for the production of the explosive medium and this will always lag behind the shock front. There appears to be a delay time of about 1.0 ms between the passage of the shock wave and the first appearance of droplets near the wall. The droplets then invade the pipe at a velocity of about 20 m/s and would take approximately 4 ms to fill a 15 cm (6 in) diameter tube. This delay time of 5 ms would result in the explosive medium being produced.

Explosion Hazards in Dryers

Dryer explosion scenarios: Overheating of particulates by a hot surface is by far the most likely ignition source in dryers. In some cases, the particulates accumulate on the hot surface and forms a smoldering nest, while in other cases the hot surface temperature is sufficiently high to directly ignite the suspended dust cloud. Although particulates near the dryer inlet may be too wet to be readily ignited, particulates exiting the dryer are both dry and often suspended in concentrations above the MEC.

Other dryer dust explosion hazard scenarios include hybrid mixture formation due to vaporization of a flammable liquid, direct firing ignition sources, frictional sparks and overheating from failed bearings, misaligned fan blades, tramp metal, and electrical equipment not appropriate for atmospheres containing combustible dust clouds.

Pressure piling: If an explosion occurs in a system in which there are interconnected spaces, a situation may arise in which pressure developed by the explosion in one space causes a pressure rise in the unburnt gas in an inter-connected space, so that the enhanced pressure in the latter becomes the starting pressure for a further explosion. This effect is known as *pressure piling* or *pre-compression*. Pressure piling is a local dynamic effect that can cause high local explosion pressures.

The type of geometry that causes pressure piling is illustrated in Figure 3.45.

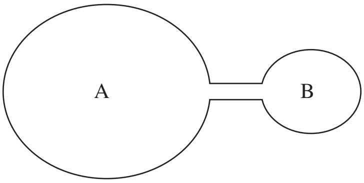


Figure 3.45 Type of geometry conducive for pressure piling

If initial explosion occurs in space *A*, this may cause pressure piling in space *B*. Then in the worst case, if final pressure in *A* is x times the initial pressure, the final pressure in *B* would be x^2 times the initial pressure in both spaces, *A* and *B*.

A particular version of such a vessel configuration, or geometry, can be represented as two or several interconnected boxes like the rooms in a building.

Pressure piling can give rise to enormous increase in maximum pressure rise in a plant. Possibility of pressure piling should be given thorough consideration in evaluating explosion effects.

A comparable but more complex situation may occur inside electrical casings where numerous wires, circuits and other components restrict the flow of gas. Explosions within such vessels is strongly affected by the characteristics of the geometry and can, under given conditions, result in very high local peak pressure and rates of pressure rise. In these situations peak pressure and rate of pressure rise can be several factors higher than in comparable explosions in single vessels. The term *pressure piling* or *pre-compression* is used to describe explosions that show such characteristic pressure development and high peak pressure.

Pressure piling occurs when a detonation propagates through a medium that has been pre-pressurized by an earlier flame, for example, in inter-connected vessels. The CJ pressure is enhanced by the precompression ratio. The pressure is further enhanced if the detonation wave reflects off a wall or propagates into a corner. Pressure waves ahead of the flame front may also be reflected, for example, by bends, obstructions or the far end of the line and merge to form a pressure wave which travels back towards the flame. This reflected shock can accelerate a deflagration to detonation and the initial pressure is increased by a factor of 2–5, due to the shock pre-compression. Both can result in devastating detonation pressures.

Dust Explosions

Dusts may be produced by grinding, milling, incidental breakage, chemical precipitation, spraying processes and the like. Manufacture of fine particles may be process objective, for example, flour milling, plastic molding powders, paint pigments, and the like. In some cases production may be secondary unwanted process, for example, producing saw dusts, breakage in pneumatic conveying, fluidization, suspension by intent, etc., Settled dusts on surfaces form grinding processes from system leaks or collecting bins and silos and give rise to hazards when dust is put to suspension through free fall or air currents. Hazard of metal dusts increase with increase in temperature whereas plastic dusts become relatively less hazardous at high temperatures as they become soften and melt, with decrease in surface area.

There is a risk of fires and explosions in all industrial plants dealing with combustible dusts, whether these dusts arise from manufacturing plants or waste generating operations. Explosions are common in grinders, pulverizers, conveying systems, dust collectors, cyclones, bag houses, electrostatic precipitators, dryers, ovens, mixers, blenders, silos, grain handling, and other equipment involving combustible dust handling and processing systems. NFPA defines combustible dust as "*a combustible particulate solid that presents a fire or deflagration hazard when suspended in air or some other oxidizing medium over a range of concentrations, regardless of particle size or shape*."

Many dusts and powders that originate from industrial processes are easily flammable. These dusts have characteristics that differentiate them such as those *explode easily*, since they carry an oxidant and do not need oxygen from the atmosphere to explode and those *ignite easily*, requiring little or no external heat to ignite.

Examples of combustible dusts include agricultural dusts like grain dusts, corn, milk powder, sugar, carbonaceous dusts such as coal, active carbons, carbon black, chemical dusts like adipic acid, sulfur, anthroquinone, pharmaceutical dusts such as aspirin, paracetamol, and metal dusts such as aluminum, iron, and zinc. Combustible particulate matter, capable of being airborne and generally having particles of less than 500 μ m, could be termed as combustible and explosive dusts. Combustible dusts that pass a 200 mesh screen can be quite disastrous.

Dusts may be produced by grinding, milling, incidental breakage, chemical precipitation, spraying, condensation from vapors of materials that condense directly to solids and other processes. Manufacture of fine particulates may be the process objective. Examples are flour milling, plastic molding powders, paint pigments, metal powders, pharmaceuticals, pesticides, dyes, and the like. In some cases, production of fines is secondary unwanted process. Dusts transported by pneumatic conveyance are always in suspension.

Combustible dusts are primarily of two types, namely, organic and metal dusts. For metal dusts, burning process is inherently simpler than it is for organic dusts because the number of intermediate steps during burning process is small, making the overall process simpler. Differences do exist based on whether the metal melts during the burning process and/or whether the oxide formed is either a solid, liquid or vapor under the combustion conditions. Unlike combustion of organics which result in the formation of carbon dioxide and water vapor, metal dusts usually produce solid oxides, consuming atmospheric oxygen, thereby increasing percentage of nitrogen in the left over gas/air. In some cases, atmospheric nitrogen will react violently with the metal to form metallic nitride, which may be unstable at high temperatures, thereby increasing rate of combustion of the dust and pressure effects of an explosion. Explosibility of metal dusts generally increase with increase in temperature.

With organic dusts, tremendous range of behaviors is possible. Devolatilization and charring can occur prior to actual heterogeneous attack of carbon residuals in the dust. If the mixture is very rich in dust, it is highly probable that only the volatiles will burn. Explosion hazard increases with increase in volatile matter in the dusts. Carbonaceous dusts with a volatile content of less than eight percent involve essentially no explosion hazard, though there may be fire hazard. The combined effect of combustion of volatiles produced and direct combustion of particulates at the solid–gas interface may result in significant, and in some cases, uncontrolled gas expansion effects. In unconfined situations, dust explosion will result in mainly localized flames and pressure effects. Under confined conditions, the expansion effects can cause severe damage to the enclosures. Under certain circumstances, fire balls are produced, if a vented explosion is large. Such fireballs extend upwards and downward similar distances.

Finely divided solid materials are more flammable than in their massive form. For example, fine powders of aluminum and iron may even ignite at ambient temperatures. Interfacial area between particles and air increases as particle size is decreased, especially so in suspended form. Finer dusts go into suspension easily with little turbulence and their residence time in air will be more, increasing chances of ignition. Materials that, if finely divided and dispersed in air can burn explosively, include most organic materials, many metals, for example, iron, aluminum, zirconium, titanium, tantalum, and some nonmetals, for example, S, Si, and P_2S_5. In particulate handling facilities such as dust collectors, fine particles are inherently concentrated, with increased ignition hazards.

Generation of dust clouds inside process equipment: In order for an explosive dust cloud to be formed from a layer/deposit, the layer/deposit must be exposed to a process that suspends the particles in the air to the extent that the dust concentration falls into the explosive range. Most often such dispersion of dust to form explosive clouds takes place *by intent* inside process equipment, for example, through handling and transportation in various process equipment (e.g. mills, dryers, mixers, bucket elevators, and other conveyors, silos, filters, cyclones, and connecting ducts).

Dust fires are of two types, namely, flaming or smoldering. Flame can be sustained if sufficient volatile matter is evolved from the dust. Volatiles may be produced from smoldering dusts or from the flame itself. Dust characteristics which affect this combustion process include volatile content, melting point, particle size and shape.

Flame may spread across dust surface or may burn down from the surface into the dust layer. If flame is able to release sufficient volatiles, it may travel quite rapidly across the surface. Otherwise its propagation over the surface is determined by the smoldering rate. Smoldering may continue into the dust layer with flame on the surface.

If particle size is sufficiently large, flame may propagate through the dust layer. In this case because of high porosity of the layer, oxygen diffusion into the layer increases rate of combustion. On the other hand, oxygen diffusion into large dust particles gives rise to slow smoldering rate. Too large particles such as massive logs make smoldering difficult to persist. Convection currents over the dust surfaces will increase burning rates.

If smoldering fire starts below the dust layer and moves up, it may burst into flames and spreads rapidly when it reaches the surface. Typical smoldering rates for wood dusts are 5 cm/s, for coal dusts 20 cm/s, with a bed depth of 1 cm. Dust deposits can undergo smoldering for long periods, with large dust piles being known to smolder for years, based on rates of oxygen diffusion into the deposit and heat loss.

Hazards may be created if there are large delays between ignition and outbreak of flames. There have been cases of dust fires breaking out unexpectedly in an industrial unit shut-down overnight or discovering a fire when a ship is unloaded.

Normally more energy is required for activating a dust explosion in air than with gases and vapors. However, once combustion starts, the energy released by the reaction produces high temperatures and pressures.

Dusts are also uniquely different from spray/mist flames because dust particle temperatures can become extremely high during the burning process. In the case of liquid mist flames, droplet temperature is limited to boiling point of liquid under the existing pressure conditions. This means that spray/mist flames can radiate significantly only from any soot that is formed in the rich mixture regions of the flame while dust flames radiate from the dust particles themselves while burning progresses. Radiative energy transport can be the dominant mechanism when the burning dust cloud becomes large and opaque.

Dust reacts very differently, depending on whether it is in a deposited layer or whether it is in a suspended dust cloud. Dust layers are liable to begin smoldering on hot surfaces, whereas a dust cloud that has been ignited locally or through contact with a hot surface can explode immediately. Dust explosions are often the consequence of smoldering dust layers which become stirred up and already carry the ignition initiation. When such a layer is stirred up, for example by mechanical cleaning methods or inappropriate extinguishing attempts, this can lead to a dust explosion.

A gas or vapor/air explosion can also stir up the dust, which then often leads to the first, the gas explosion, turning into the second, and the dust explosion. In deep coal mines methane explosions often have triggered off coal dust explosions whose consequences were more serious than those of the original explosion.

Ignition of a dust layer can result in a small explosion which creates turbulence and give rise to dust suspensions in air, which when ignited, causes a large explosion and major damage to the plant.

Secondary dust clouds inside and/or outside process equipment are generated through blast waves from primary dust explosions. The blast wave from a primary dust explosion can generate secondary explosive clouds ahead of the flame by entraining dust deposits and layers there.

Dust explosions in small L/D enclosures behave similarly to fuel vapor explosions. Dust explosions in equipment such as piping or pneumatic conveyors can involve detonations and cause considerable damage at large distances in the plant.

Most of the casualties from dust explosions occur when the initiating explosion within some equipment or enclosure breaches the equipment/enclosure and causes a secondary explosion in the surrounding building. The secondary explosion occurs when dust deposits on exposed surfaces in the building are lifted by the blast wave emanating from the breached equipment/enclosure, and then are ignited by the flame vented from the breached equipment/enclosure.

These secondary dust explosions are particularly devastating because they produce large burning dust clouds and pressures beyond the strength of most buildings. Tertiary level explosions are also possible.

Dust explosions can be deflagrations, detonations, thermal runaways, BLEVEs or physical explosions.

Generally dust explosions are *deflagrations*. Peak pressures are approximately 8 times of initial pressures. Given favorable conditions, such as long, large diameter pipe work, *energetic* dusts may *detonate*, that is, the flame front propagate into the unburnt cloud by compression caused by shock waves traveling at or above sonic velocity, with peak pressures as high as 20 times or more of the initial pressures. Coal dusts in mines can give rise to detonations.

In general, dusts with particle size above 400 μm will not ignite, that is, if the particles are larger than 0.4 mm diameter, dust explosions will not occur.

For many dusts the MIE is approximately proportional to the *cube of particle diameter*.

To sum up, the conditions required for a dust explosion are the following:

Combustible particulates sufficiently small to burn rapidly when ignited.

A suspended cloud of these combustible particulates at a concentration above the minimum explosible concentration (MEC).

Confinement of the dust cloud by an enclosure or partial enclosure.

Oxygen concentration higher than the limiting oxygen concentration (LOC) for the suspended dust cloud.

Delayed ignition source of adequate energy or temperature to ignite the suspended cloud.

Inter-vessel deflagration propagation and pressure piling does not always occur. When the deflagration does propagate into the interconnected vessels, the jet flame ignition of the dust cloud in the second vessel produces a much more rapid rate of burning and associated pressure rise. The more rapid burning and pressure rise can render explosion venting or explosion suppression systems ineffective in the second vessel. Hence, there is often a need for explosion isolation systems to supplement the installed explosion protection for an individual vessel.

The *deflagration index,* K_{St}, is used to quantify the explosion violence for a specific dust, and is needed when specifying explosion relief vents. Numerically, K_{St} is the maximum rate of pressure rise for a deflagration of an optimum dust/air mixture in a one m^3 spherical vessel, at an established level of turbulence and ignition energy.

For a specific dust, the maximum rate of pressure rise in vessels of different volumes can be predicted by the cubic law:

$$(dP/dt)_{max}\, V^{1/3} = \text{constant} = K_{St} \qquad (3.54)$$

$(dP/dt)_{max}$ is the maximum value of pressure rise per unit time in a closed vessel occurring during an explosion of a dust–air mixture of optimum concentration under specified test conditions. *V* is the volume of the vessel.

Figure 3.46 illustrates pressure rise in a confined space as a function of time in unvented and vented conditions.

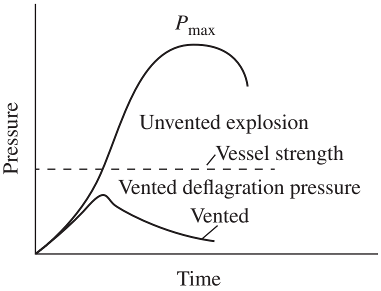


Figure 3.46 Pressure rise as a function of time in unvented and vented vessel

This rule has been shown to be effective for vessels of 20 L and greater, hence testing is normally conducted in 20 L vessels.

Many dusts and powders have been analyzed for their individual rate of combustion and combustibility. Based on these analyses, a value of K_{st} has been assigned to each dust, which indicates the *deflagration index* of the dust, expressed as bar-m/s. Higher K_{st} value indicates faster rate of combustion.

K_{St} is specific to dust and test method. It is influenced by chemical properties of the dust and oxidizer, particle size and shape and turbulence. Decreasing particle size increases K_{St}, and to a lesser degree, increases the explosion pressure, P_{max}.

The NFPA 68 Guide is a useful document that provides K_{st} values for varieties of dusts and powders. It also provides the method to calculate vent area, for vented explosions, for various applications.

K_{St} provides a basis for classification of dusts as given in Table 3.47.

Table 3.47 Classification of dusts based on K_{St}

Dust explosion class	K_{St} *(bar.m/s)*	*Severity of hazard*
St 0	0	No explosion
St 1	1–200	Weak to moderate explosion
St 2	201–300	Strong explosion
St 3	≥ 301	Very strong explosion

For example, Pittsburgh seam coal has a K_{St} value of 129 bar m/s. It is therefore considered a St 1 dust.

Dust explosions have lower and upper limits. A lower limit of explosion indicates that the concentration of dust particles is below the lower limit of explosion. Below this level, the dust concentration will not explode even on ignition. This happens because the heat produced in such a circumstance is not sufficient to affect other dust particles. Alternatively there could be a dust concentration of explosive levels but there may not be enough oxygen to start the fire.

Another general classification involves the ability to propagate a combustion wave when dust is deposited in a layer

Class 1: No self-sustained combustion
Class 2: Local combustion of short duration
Class 3: Local sustained combustion, but no propagation
Class 4: Propagating smoldering combustion
Class 5: Propagating open flame
Class 6: Explosive combustion

In the context of preventing and mitigating dust explosions safer process design could include use of production, treatment, transportation, and storage operations where dust cloud generation is kept to a minimum. One example is the use of mass flow silos and hoppers instead of funnel flow types.

Inerting the atmospheres is about 9–14 percent over equipment with dust hazards to prevent dust hazards. Maximum oxygen content in air atmospheres to prevent dust explosions

Particle sizes over 200 mesh are most explosible. A total of 40 mesh or coarser dusts are relatively safer. Maintaining high humidity, wherever possible reduces dust hazards. Buildings are kept smaller and isolated with strong walls and weak roofs so that explosions are relieved upward. Flow velocities in interconnecting piping maintained high over flame propagating velocities where possible. High velocities involve low residence times with the consequence of less chances for ignition. Suppression systems activated with infrared sensors to prevent explosion pressures from rising damaging levels, to isolate equipment and prevent spread of fire from one unit to another.

Assessment of dust explosion hazard is illustrated in Figure 3.47.

Explosion hazard rating of dusts involves two parameters, namely, ease of ignition and severity of explosion. Ease of ignition depends on minimum ignition temperature, minimum explosible concentration and minimum ignition energy. Severity of explosion depends on maximum explosion pressure and maximum rate of pressure rise.

Ignition severity = (maximum ignition temperature) (minimum ignition energy) (minimum ignition concentration) of standard Pittsburg coal/(maximum ignition temperature) (minimum ignition energy) (minimum ignition concentration) of sample dust.

Explosion severity = (maximum explosion pressure) (maximum rate of pressure rise) of sample dust/(maximum explosion pressure) (maximum rate of pressure rise) of standard Pittsburg coal dust at a fixed concentration of 500 g/m^3 for both the dusts.

Explosion index = (explosion severity) (ignition sensitivity)

Explosion index, explosion severity, and ignition sensitivity are dimensionless.

Values more than 1.0 indicate relative hazard of the dust greater than Pittsburgh coal dust.

Standard data used in these ratings:

Minimum ignition temperature = 610°C
Minimum ignition energy = 60 mJ
Minimum explosion concentration = 55 g/m^3

Maximum explosion pressure = 5.7 bar
Maximum rate of pressure rise = 159 bar/s
Concentrations used = 500 g/m^3

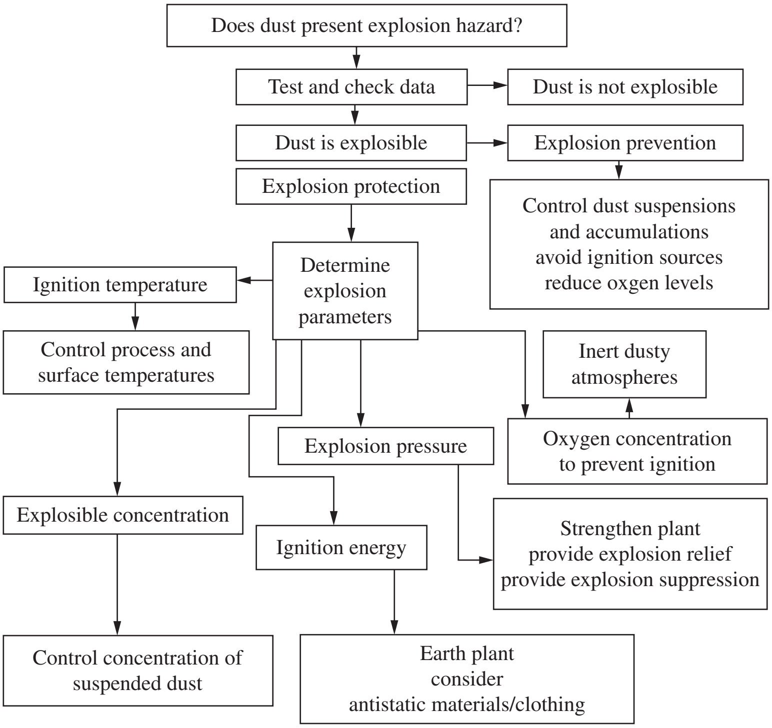


Figure 3.47 Assessment of a dust explosion hazard

Relationship between explosion hazard rating, ignition sensitivity, explosion severity, and explosion index are given in Table 3.48.

Table 3.48 Explosion hazard rating, ignition sensitivity, explosion severity, and explosion index

Relative hazard rating	*Ignition sensitivity*	*Explosion severity*	*Explosion index*
Weak	≤ 0.2	≤ 0.5	≤ 0.1
Moderate	0.22–1.0	0.5–1.0	0.1–1.0
Strong	1.0–5.0	1.0–2.0	1.0–10.0
Severe	≥ 5.0	≥ 2.0	≥ 10

Hybrid systems: In some situations, flammable gases, air, and dust suspensions exist by design or accident. These mixtures are called hybrid mixtures. Presence of flammable gas has strong influence on the burning and explosion characteristics of dusts. A combustible dust mixed with a flammable gas and air will explode more violently than dust in air alone, even though the concentrations of flammable gas or dust in air, are very low, below their LFL, and incapable of supporting flame propagation in gas–air and dust–air systems. Small amounts of flammable gas can greatly reduce the MIE for a dust to a level such that electrostatic brush discharges can ignite the hybrid cloud.

Table 3.49 gives data on combustion characteristics for some typical dust clouds.

Table 3.49 Combustion data for dust clouds

Dust	*Median particle size (mm)*	*Minimum explosible dust concentration (g/m^3)*	*Minimum ignition energy (Mj)*	*P_{max} (bar g)*	*K_{St} (bar.m/s)*
Cotton	44	100	–	7.2	24
Cellulose	51	60	250	9.3	66
Milk powder	165	60	75	8.1	90
Rice flour	–	60	> 100	7.4	57
Bituminous coal	< 10	–	–	9.0	55
Polyurethane	3	< 30	–	7.8	156
Sulfur	20	30	–	6.8	151
Toner	< 10	60	4	8.9	196

3.7 Fires

Table 3.50 lists hazards associated with fires.

Table 3.50 Hazards associated with fires

Burns from radiation from heat or fire engulfment
Asphyxiation due to oxygen depletion in the surrounding environment
Toxic exposure due to products of combustion. Composition of the products depend on the compounds present in the burning material, temperatures attained and oxygen supply to the fire
Injury and death from weakened or failed structures
Explosions

Flash Fires

Flash fire involves nonexplosive combustion of a vapor cloud resulting from a release of flammable material into the open air, which, after mixing with air, ignites. Its major hazard is from the effect of heat from thermal radiation. It involves slow deflagration of a premixed, unconfined, unobstructed gas cloud producing negligible overpressure. In a flash fire, gas burns and does not explode. Thermal effects are the main hazard from flash fires. Flash fires may cause damage to vulnerable items such as cabling but does not lead to any significant damage to equipment. Another effect is to cause sudden depletion of oxygen, which may be harmful to personnel around.

Insulation/Lagging Fires

Insulation or lagging fires are very common in process industry. Insulation fires occur when fluid leaks from flanges, valve stems, gaskets, welds, cracks in insulation pads, or instrument ports from which fluid infiltrates porous insulation such as calcium silicate or glass/mineral wool. The open structure of the porous insulation allows the fluid to spread throughout the insulation due to its wick effects from the leak.

Insulating materials which have become saturated due to leakage of flammable liquids are a potential fire hazard. The risk of combustion normally occurs at temperatures above 180°C. Routine inspection and prompt elimination of leakage is essential.

Liquids such as chlorinated paraffins, phosphatic esters are intrinsically fire resistant, but others such as liquids dosed with anti-oxydant or hydraulic fluids containing water are not, and may become combustible again if they suffer preferential loss of anti-oxidant or water, in the warm lagging.

About 6–12 percent by volume of oil in the lagging is most susceptible in the porous insulating material. Pumps, flange joints, and sample and drain points are typical leakage points leading to lagging fires. Spontaneous ignition might result upon self-heating of the fluid, making use of the air stored inside the porous insulation or due to a sudden increase in available oxygen if insulation cladding is removed or punctured. Heat generated due to oxidation of the fluid and prevention of this heat from dissipation due to the insulation effect of the lagging upsets the balance between heat generation due to exothermic reaction (oxidation) and heat loss leading to thermal runaway. Worst hazard arises from a lagging fire arises when lagging is opened up.

A common case of lagging fires can arise in the engine rooms of ships, as a result of diesel fuel soaking into the lagging around hot pipes. It is the C_{18} and higher molecular weight components of diesel fuel that are troublesome as far as the potential for lagging fires is concerned.

If the insulation is not covered by an impervious coating or other protective shield over the insulation, lagging fires result with diffusion of air into the insulation. Sometimes precast insulation pads are removed from valves and other fittings by workmen who forget to replace them after maintenance. The exposed hot surfaces become ignition sources for any leaked flammables that might come in contact with such surfaces.

Closed cell materials, such as foam glass, which resists saturation due to its closed cell structure is particularly recommended in areas of potential leakage such as near instrument connections, valve packing glands, flanges, filters, and areas of potential areas of leak points. Such insulation contain the fluid *near the leak*, reducing the fire potential of the fluid. Closed cell material should be extended 50 cm on either side of the potential leak point and weep holes should be drilled in the bottom to drain any leaked fluid. While open insulation presents more of a potential for fires, it is cheaper than closed materials. Open insulation can be installed on long piping runs where the possibility of leakage is extremely remote.

The most effective precaution against insulation fires is the identification of all potential leak points and the specification of high temperature closed cell insulation or no insulation at these points. Closed cell insulation prevents the fluid from spreading throughout the insulation. If necessary, flanges should be covered only with metal caps with weep holes, avoiding insulating these areas if possible.

Pool Fires

A pool fire involves a horizontal, upward facing, combustible fuel. Liquid fuel may burn in an open storage container or on the ground in the form of a spill. The structure of most pool fires may be split into a number of fairly well-defined zones:

- In deep pools of liquid fuel, there may be significant convective flow within the fuel which may affect the fuel vaporization rate and hence influence the *external* characteristics of the fire. The interaction between the fuel and the vessel which surrounds it (if any) may also have a significant influence over the burning behavior.
- Above the fuel there is a reasonably constantly shaped conical zone, rich in unburnt fuel vapors.
- Surrounding the cone of vapor is a zone of luminous flame, also with a reasonably constant shape.
- Above this zone is a further combustion region, but here there is intermittency and obvious turbulence in the flaming.
- Finally there is the nonreacting buoyant plume, which is generally turbulent in nature and is characterized by decreasing velocity and temperature with height and lateral position.

Fire development is generally characterized in terms of heat release rate (HRR) vs. time. The HRR is not a fundamental property of a fuel and, therefore, cannot be calculated from the basic material properties.

The most common method to measure HRR is known as *oxygen consumption calorimetry* (ASTM E134). The basis of this method is that most gases, liquids, and solids release a constant amount of energy for each unit mass of oxygen consumed. This constant has been found to be 13,100 kJ/kg oxygen consumed and is considered to be accurate within ± 5 percent for most hydrocarbon fuels. Another common method of assessing HRR is to measure the burning rate, which is also known as the mass loss rate.

Liquid fuel may burn in an open storage container or on the ground in the form of a spill. For a given amount of fuel, spills with a large surface area burn with a high HRR for a short duration, and spills with a smaller surface area burn with a lower HRR for a longer duration. When spilled, the flammable/combustible liquid may form a pool of any shape and thickness, and may be controlled by the confinement of the area geometry such as a dike or curbing. Once ignited, a pool fire spreads rapidly over the surface of the liquid spill area. The burning rate of a given fuel can also be affected by its substrate (i.e. gravel and sand) in a spill. For flammable/combustible liquids, flame spread rates range from approximately 10 cm/s to 2 m/s.

When a spilled liquid is ignited, a pool fire develops. The diameter of the pool fire depends upon the release mode, release quantity (or rate) and burning rate. In some instances, the spill is unrestricted by curbs or dikes, allowing it to spread across the ground and establish a large exposed surface area. Liquid pool fires with a given amount of fuel can burn for long periods of time if they have a small surface area, or for short periods of time over a large spill area.

Burning modes of pool fires depend on diameter of the burning pool. Table 3.51 gives relationship between pool diameter and burning mode.

Table 3.51 Burning modes of pool fires

Pool fire diameter (m)	*Description of burning mode*
< 0.05 (2 in)	Convective, laminar
< 0.2 (8 in)	Convective, turbulent
0.2–1.0 (8 in to 3.3 ft)	Radiative, optically thin
> 1 (3.3 ft)	Radiative, optically thick

The primary hazard from pool fires is thermal radiation exposure. It depends on diameter and height of fire (cylinder shape), surface emissive power (intensity). 5 kw/m^2 will cause second degree burns to unprotected skin in 30 s. Largest fires are expected with oil spills on water, since there is no effective way to confine such fires. As diameter of the fire increases, its height decreases with significant reduction in heat exposure by radiation effects.

The thermal radiation hazard from a pool fire is related mainly to the fuel type and the fire size, that is, pool diameter and flame height. More specifically, radiative heat loss is directly related to the quantities of the major combustion products (CO_2, H_2O, and CO) and soot in the flames and plume. Soot may often be the dominant influence on the absorption coefficient in large fires, and it has been established that the majority of the radiation in fire plumes (> 90 percent) is derived from the visible part of the flame, where soot particles are radiating heat.

Leakage-Related Fires

These include pump fires, valve fires, flange fires, and fires involving other components in the plant. Fire exposure of steel piping and flanges may result in rupture and release of contents of the piping. In case of fire, thermal response to nuts and bolts is essential to keep integrity of piping. Standard elastomer gasket materials melt and flow under fire conditions. Flat or spiral-wound gaskets, on the other hand, will not melt during fire exposure. Under extreme fire conditions, gasketed and ring joint flange and bolt materials may yield, and allow leakage at the flange joint. Flange bolts and nuts need to be replaced every 1–2 years and, over time, corrosion progresses to the point that the flanges need to be cut off and replaced. Installations like offshore oil platforms, refineries, process chemical facilities, and water treatment plants commonly face these kinds of corrosion problems, which can lead to leakages.

Every pipe is a potential source of leaks. The fire at Indian oil depot at Jaipur, for example, started as a result of the pipe line leakage and 50,000 kL of diesel got exposed and caught fire. Flanged joints and critical valves should be protected from fire with insulation that is clad and strapped with stainless steel. Such fires cause minor damage to the plant if detected and handled at their early stages of development. Otherwise such fires could lead to devastating fires and explosions. Jet fire is a typical leakage-related fire.

Other Fires

There have been instances of fires in storage tanks and equipment during operations and maintenance. Storage tank fires can be disastrous as quantities of flammables are often very large. Tank and equipment fires resulted, particularly, during welding operations cleared without proper *permit systems* and inadequacies in implementation of *permit systems*. Combustible residues and deposits left during cleaning operations in tanks and equipment have been generally responsible for such fires.

Pyrophoric iron sulfide deposits in crude oil storage tanks and associated piping and equipment may result in fires, if proper cleaning procedures are not followed. Most commonly, pyrophoric iron fires occur during shut-downs when equipment and piping are opened for inspection or maintenance. Instances of fires in crude columns during turnarounds, explosions in sulfur, crude or asphalt storage tanks, overpressures in vessels, etc., due to pyrophoric iron ignition are not uncommon.

This is true with column packing. Deposits and liquid films in distillation column packing are difficult to clean, especially with structured packing. There have been instances of fires in distillation columns during maintenance operations. Any hydrocarbon residues left over in the column after shut-down may remain as a thin film on the packing. The surface area of such films can be very large. Small amounts of hydrocarbons are left over even on structured packing which has low liquid hold-up characteristics. Such materials may self-heat and ignite on exposure to air.

Iron sulfide is one such pyrophoric material that oxidizes exothermically when exposed to air. It is frequently found in solid iron sulfide scales in refinery units. It makes no difference whether these pyrophoric sulfides exist as pyrite, troilite, marcasite, or pyrrhotite. It is formed by the conversion of iron oxide (rust) into iron sulfide in an oxygen-free atmosphere where hydrogen sulfide gas is present (or where the concentration of H_2S exceeds that of oxygen). The individual crystals of pyrophoric iron sulfides are extremely finely divided, the result of which is that they have an enormous surface area-to-volume ratio. When the iron sulfide crystal is subsequently exposed to air, it is oxidized back to iron oxide and either free sulfur or sulfur dioxide gas is formed.

This reaction between iron sulfide and oxygen is accompanied by the generation of a considerable amount of heat. In fact, so much heat is released that individual particles of iron sulfide become incandescent. This rapid exothermic oxidation with incandescence, known as pyrophoric oxidation, can ignite nearby flammable hydrocarbon–air mixtures. There is a greater likelihood of this reaction occurring when the process involves a feedstock with high sulfur content. The heat usually dissipates quickly unless there is an additional source of combustible material to sustain combustion. The white smoke with SO_2 gas, commonly associated with pyrophoric fires, is often mistaken for steam.

Chemical cleaning is used with pyrophoric films and deposits using agents like sodium per-carbonate (sodium carbonate peroxy-hydrate) or potassium permanganate, the later being less preferred.

3.8 Nuclear Power Plant Explosions

A nuclear power plant uses uranium fuel to produce steam for generating electricity. This process changes uranium into other radioactive materials. If a nuclear power plant accident occurs, heat and pressure build-up, and the steam, along with the radioactive materials, may be released.

A nuclear blast is an explosion with intense light and heat, a damaging pressure wave, and widespread radioactive material that can contaminate the air, water, and ground surfaces for kilometers around.

There are many hazards in the use of nuclear power plants. The most prominent of these dangers include nuclear melt-downs. There have been a number of situations in which these dangers have become real disasters, giving birth to safety and regulatory agencies.

The greatest fear about nuclear power plants is a severe accident in the nuclear reactor. When the whole system or an individual component of a nuclear power plant causes the reactor core to malfunction, it is known as a nuclear melt-down. This occurs most commonly when the sealed nuclear fuel assemblies that house the radioactive materials begin to overheat and melt. If the melt-down becomes too severe, the radioactive elements within the core can be released into the atmosphere and around the area of the power plant as happened in Chernobyl and Fukishima explosions. Because of the geometric design of the reactor cores, a nuclear explosion is impossible; however, smaller explosions such as the release of steam are possible.

3.9 Electrical Fires and Explosions

Fires can be started by electrical arcing or connections where wires are improperly spliced to other components, such as receptacle outlets and switches. Also, if heat develops in an overloaded conductor from too much current flow, a fire can be ignited. An electrical fire is one where the source is energized.

A high current electrical fault can create an *electrical explosion* by forming a high energy electrical arc which rapidly vaporizes insulation material and metal. An electrical explosion is the sudden release of energy due to a short circuit between power phases or a phase to ground.

It is important to realize that a very large amount of energy is available on the bus of most electrical panels when they are operating within their normal design parameters. For example a phase to phase short circuit on a 400 Amp, 120/208 V panel can instantaneously release over 84,000 W of energy during a fault condition and not blow the protective fuse or circuit breaker. An explosion of this magnitude will destroy the panel and can start a fire and can cause severe injuries or even death.

Far more serious explosions occur when a short circuit causes the collapse of the magnetic field in the transformer feeding a building. When this happens, there is an instantaneous release of the energy stored in the transformer in the form of a *fault* *current*. The most important aspect of designing an electrical system for a building is to make sure that the protective fuses and circuit breakers are capable of handling the *maximum available fault current*. When fault current ratings are exceeded circuit breakers weld together and are unable to clear the fault.

3.10 Fire Balls

Fire ball damage is the direct result of materials initiated through contact or engulfment by flames that are consuming fuels. A fire ball may result from the ignition of fuel–air mixtures or from the explosion of solid or chemical explosives. The explosion fire ball is short lived but the flames will persist until all of the fuel is consumed in fuel–air fires. Ignition of fuel–air mixtures above pools of spilled liquid fuels produces flames with dimensions that vary with the volume of spilled liquid, rate of spillage, nature of spillage containment surface, wind velocity, location of ignition source, and time delay before ignition. The maximum equivalent spherical radii of fire balls for a wide variety of explosives is given by:

$$D \approx 7.93\ W_f^{1/3} \tag{3.55}$$

where D = fire ball diameter, m and W_f = weight of fuel, kg

The duration of the fire ball may be estimated from the following equation:

$$t \approx 0.47\ W_f^{1/3} \tag{3.56}$$

where t is in seconds.

3.11 Fire Damage

The important fire damage parameters are thermal radiation, fire balls (flame engulfment), smoke inhalation, fire detection, and extinguishment, apart from explosion overpressures and shrapnel damage.

Table 3.52 gives thermal flux damage levels.

Table 3.52 Thermal flux damage levels

Radiation intensity (kw/m^2)	***Effect***
1. 2	Received from sun at noon
1. 6	Minimum necessary to be felt as pain
2. 1	Minimum necessary to cause pain after one min
4. 7	Causes pain in 15–20 s, injury after a 30 s exposure
11. 7	Thin, partially insulated steel can lose mechanical integrity
12. 6	Exposed wood can be ignited after long exposure
23. 0	Thin uninsulated steel can lose mechanical integrity

Source: From a risk assessment study

Smoke Inhalation

Smoke inhalation is one of the major causes of injury and death in any fire producing smoke, especially in enclosed spaces such as buildings. While smoke is less of a problem with clean gaseous fuels such as hydrogen or natural gas *in the open*, combustion involving liquid and solid fuels may give rise to serious inhalation problems. Gaseous fuel burning can still cause asphyxia when inhaled, apart from the effects of temperatures of hot combustion products.

3.12 Runaway Chemical Reactions

A reactive hazard may involve:

Impact-sensitive or thermally sensitive materials (i.e. self-reactive chemicals): When subjected to heat or impact, these chemicals may rapidly decompose, resulting in a potentially explosive release of energy.

Runaway reactions (i.e. self-reactive chemicals or mixtures): In an out-of-control reaction involving a chemical or chemical mixture, the rate at which heat is generated exceeds the rate at which it is removed through cooling media and surroundings.

Chemical incompatibility between two or more substances: These hazards occur when a chemical is suddenly mixed or comes into contact with another chemical, resulting in a violent reaction.

The worst process industry disasters worldwide have involved uncontrolled chemical reactions. Sudden thermal energy releases from exothermic decompositions and runaway reactions have contributed to serious fire and explosions in several chemical process plants. Similarly, thermal runaway had also occurred in storage and transportation of reactive chemicals. The secondary events of thermal runaway reactions can be rupture of process vessel, toxic spills and release of explosive vapor clouds or their combinations.

Reactive chemical hazards can result from any chemical reaction with the potential to release heat, pressure, or toxic reaction products in quantities too high to be absorbed or contained by the environment and equipment that holds the reacting mixture. It is a common misconception that reactive chemical incidents occur only in reactors. They can occur throughout a process such as other process equipment, waste treatment and transport facilities, storage areas and separation equipment.

It is important to distinguish between reactive chemicals and hazardous chemical reactions. The chemical substances in the process might not be considered to be reactive chemicals, but this does not mean that the process does not have reactivity hazards. Interactions of chemical substances may be more important for understanding process hazards than the reactivity of individual chemicals. *Runaway reactions* can occur from interactions among chemicals not considered particularly reactive by themselves.

Chemicals commonly involved in reactivity hazard incidents include acids, bases, oxidizers, monomers, water, organic peroxides, hypochlorite, etc.

Thermal hazards can be broadly divided into two categories, namely, energy released during desired reaction and energy released during unwanted reaction. The first of these encompasses enthalpies of reaction, crystallization, melting, and dissolution whilst the second is usually associated with heats of decomposition reaction.

An empirical parameter, *reaction hazard index*, is often used in assessing reaction hazards. The empirical reaction hazard index (RHI) based on activation energy (E_a; kcal/mol) and decomposition temperature (T_d; K) is given as follows:

$$RHI = 10T_d/(T_d + 30E_a) \tag{3.57}$$

Summary of Reaction Kinetics

In exothermic reactions, unless heat is removed, increase in temparature may lead to runaway reactions.

In homogeneous reactions, rate is increased by a factor of 2 or 3 for every 10°C rise in temperature.

For a specific reaction,

$$\text{Rate of heat generation} \propto e^{RT} \tag{3.58}$$

If only means of heat removal is an external jacket and/or or internal coil through which coolant flows at T,

$$\text{Rate of heat removal} \propto (T_r - T) \tag{3.59}$$

Hence, generation rate is exponential with reaction temperature, T_r, and removal rate is only linear. Thus a critical value of T_r will exist at which control is lost, that is, runaway occurs.

Reactions which are immeasurably slow at normal temperatures may become increasingly rapid as temperature is increased. Reaction of hydrogen and oxygen is an example. Table 3.53 gives decomposition energies of some reactive chemicals.

Table 3.53 Decomposition energies of some reactive chemicals

Chemical compound	*Characteristic bonds*	*Heat of decomposition (kJ/mole)*
Aromatic nitro	$R–NO_2$	220–410
Peroxides	C–O–O	200–340
Aromatic diazonium	$R–N_2$	130–165
Oximes	C = N–OH	110–170
Aromatic azo	R–N = N–C	100–180
Epoxides	$–CH–CH_2–O$	65–100

Heat generated from exothermic reactions is directly related to mass of reactants involved. This and the ability to take the heat away, is a very important consideration in scaling up, that is, performance of reaction in a larger scale reactor. In a conventional vertical cylindrical reactor of diameter D and length L,

$$\text{Volume (and mass) of reactants} \propto D^2L \tag{3.60}$$

$$\text{The ratio, heat transfer area/ potential heat release} \propto 1/D \tag{3.61}$$

And becomes increasingly unfavorable with size. There is a critical value for D, thus an exothermic reaction which is easily controlled on a laboratory scale, may become hazardous on a larger scale. If heat is removed through an agitated reactor using an internal cooling coil or external jacket, then if process side offers the major resistance, which is common, overall heat transfer rate depends upon the speed of the agitator, N, that is, $U \propto (N^{2/3})$ (3.62)

So, failure of agitation for any reason may result hot spots and/or runaways. Exothermic reactions frequently occur under unexpectedly uncontrolled conditions and result in ejection of reactants or explosions. Typical problems may arise because inadvertent admixture of materials. Contacting of oxydizing acids (e.g. chromic acid, nitric acid or perchloric acid) with organic matter result in a violent reaction. Unexpected reactions may be inherently hazardous because of toxic or flammable gases are generated. Generation of gas phase may give rise to pressure build-up in a confined space. Water-reactive materials are particularly hazardous as water is likely to enter into reaction systems.

Self-reacting materials can cause loss or injury by decomposing, polymerizing or rearranging in an uncontrolled manner, even without being combined with other materials. *Chemical interactions* have the potential for damaging consequences, if conditions are such that an uncontrolled chemical reaction can take place. This includes situations where chemical reactions are intended to occur (e.g. batch reactions) but something goes wrong such as a temporary loss of agitation. It also includes situations where no chemical reaction is intended, but incompatible materials are combined or mixtures are subjected to heating or other conditions that lead to an uncontrolled chemical reaction.

U.S. Chemical Safety and Hazard Investigation Board (CSB) has adopted the definition of a reactivity incident as *a sudden event involving an uncontrolled chemical reaction with significant increases in temperature, pressure, or gas evolution that has the potential to or has caused serous harm to people, property or the environment*. Reactions involving release of large quantities of heat or gas are potentially hazardous, particularly during fast decomposition and/or oxidations. These gases might be flammable, toxic or corrosive and pressurize the reactor to the point of rupture. Solid/liquid products might be thermally sensitive or shock sensitive or corrosive.

An exothermic reaction can lead to thermal runaway, which begins when the heat produced by the reaction exceeds the heat removed. The surplus heat raises the temperature of the reaction mass, which causes the rate of reaction to increase. This in turn accelerates the rate of heat generation. Increase in temperature will be considerable if large quantities of heat are generated in a short time. Many organic compounds that decompose exothermically will liberate condensable and noncondensable gases at high temperatures, which can increase pressures in the reactor. Energy released by a chemical reaction might:

Generate a blast wave, vaporize a liquid phase, increase temperature, reaction rate, initiate a secondary reaction, reach/exceed temperature, or pressure limits of the reactor, leading to rupture and release of contents.

An approximate rule of thumb suggests that reaction rates and hence the rate of heat generation doubles with every 10°C rise in temperature. Thermal runaway can occur because, as the temperature increases, the rate at which heat is *removed* increases *linearly,* but the rate at which heat is *generated* increases *exponentially*.

Figure 3.48 illustrates some reaction rates as a function of temperature (Arhenious equation) for normal reactor operation and anomalies in reaction rates.

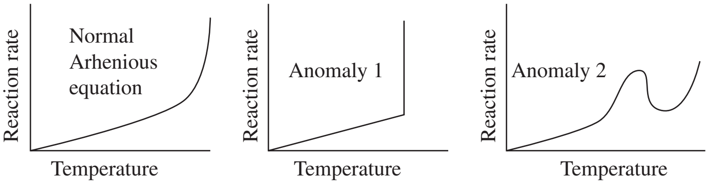


Figure 3.48 Reaction rate as a function of temperature (Arhenious equation and anomalies)

From the above curves the following conclusions can be drawn.

(i) Rapid increase in reaction rate with increase in temperature (Normal characteristic). Slow increase in reaction rate with temperature. (Some heterogeneous reactions controlled by interphase transfer by diffusion).
(ii) Very rapid increase at one point, (ignition point in onset of an explosion).
(iii) Decrease in rate at higher temperatures (characteristic of catalytic reactions)
(iv) Decrease in rate at intermediate temperatures, followed by an increase.
(v) Slow decrease in rate with increase in temperature.

To avoid runaway or an explosion, rate of addition of reactants and heat removal have to be carefully controlled and possible confusion in process control must be avoided. Kinetics and thermodynamics of reaction must be fully understood and suitable measures must be implemented. Manufacturers and users of the material liable to exothermic nature must understand and take measures to avoid runaways. Scale up may introduce heat transfer problems. Modification in reactor geometry, agitation arrangements, charging procedures, and control must also be introduced with caution.

A fire causes the temperature of a reactive material to reach the onset of a reaction runaway with little reactant consumption. This leaves more reactant to react and generate heat and pressure. The impact of this additional heating on reaction rates is exponential. Many materials (such as monomers) are stored with inhibitors. Fire exposure can deplete the inhibitor, when this happens, the runaway reaction can proceed at a much higher rate than the rate at the runaway onset temperature. The *fire flux* is therefore an important design variable for a reactive system.

Insulation is commonly used to minimize heat input to a vessel when it is exposed to fire. However insulation will also minimize heat loss from the vessel during a reaction runaway. In the case of fire exposure, the insulation will *prevent* the vessel contents from cooling after the fire is put out, and this may lead to a reaction runaway. If insulation is used, it should be considered how the vessel is drained, cooled, inhibited, or used in the process before the reaction runaway starts.

The pressure rise that is associated with a rise in reaction temperature is a critical factor. The rise in vapor pressure with temperature is one aspect but the generation of non-condensable gas from decomposition or side reactions is a major contributory cause in the majority of chemical plant explosions. Careful study of any possible temperature deviation is necessary to ensure that the pressure rise that can accompany this is understood and can be managed.

One of the major causes of reactivity incidents is a misunderstanding of the changes in the reaction properties upon scale-up. It is important to understand that changes in the scale of a reaction can radically affect the thermal properties and that the size and shape of any chosen reactor system should be carefully considered to ensure that adequate cooling capacity is maintained. Moving an apparently *safe* process to a larger scale without fully investigating the reactor/reaction properties has caused several incidents.

Failure to scale up properly and to take appropriate precautions may lead to the loss of process control which in turn may result in a runaway exothermic reaction and/or the generation or release of toxic materials. There have been a number of such failures in the past which have led to multiple fatalities, severe damage to property, environmental damage and business loss.

Once control of the reaction is lost, temperature can rise rapidly leaving little time for correction. The reaction vessel may be at risk from over-pressurization due to violent boiling or rapid gas generation. The elevated temperatures may initiate secondary, more hazardous runaways or decompositions. When pressures greater than the design pressure of the reactor are generated, there is likely to be an explosion. The types of explosions that may result depend on the confinement of the reactive material, its energy content, its kinetic parameters, and the mode of ignition.

Runaway reactions result from some type of upset in process control, for example, loss of adequate cooling due to scale formation on heat transfer surfaces, pump problems, and the like, inadequate mixing, too much or wrong composition of catalyst, etc. High-pressure liquid phase in a reactor can lead to a BLEVE.

Endothermic reactions may not have obvious reactivity hazards, but should nevertheless be expected to be associated with reactivity hazards.

Since energy is being added to carry out such reactions, the final products will have a greater internal energy content than the starting materials, the products themselves may pose a reactivity hazard. In addition, an endothermic reaction may be reversible under certain conditions and thus may result in a potentially hazardous exothermic reaction.

Table 3.54 summarizes types of chemical reactivity.

Table 3.54 Summary of types of reactivity

Main category	*Sub-category*
Readily self-reacts	Polymerizes
–	Decomposes
–	Rearranges
–	Condenses
Readily reacts with common environmental substances	Reacts with nitrogen, oxygen or water
–	Reacts with ordinary combustibles
–	Reactors with materials of construction
Readily reacts with other chemicals	Reacts with acids or bases reacts with hydrogen

In order to determine the hazards of a reaction, information on the chemistry and thermo-chemistry of the reaction needs to be understood. This includes the possibility of thermal decomposition of raw materials, intermediates, products and by-products, whether exothermic runaway can occur and the rate and quantity of heat and gas produced by the reaction.

The explosion hazards from runaway reactions are governed by the thermodynamics and kinetics of the thermal process. Theoretical prediction of limiting temperature is difficult due to process complexities. Further, the kinetic data obtained through laboratory techniques, at conditions far away from runaway situation, are often not valid for assessing the runaway behavior of exothermic processes.

Thermal hazard assessment basically relies on identification of dangerous process conditions, process deviations and thermal sensitivity of reaction mixtures and products.

When dealing with mixtures of chemicals containing energetic structures (e.g. double or triple bonds, nitro groups, peroxides, ethers, strained ring structures, heterogeneous ring structures, etc.) one should be aware that reactions and decompositions may occur in mixtures at lower temperatures than might be expected based on the stability characteristics of the pure materials. Thermal stability testing may be the only way to recognize stability problems in many cases.

It is interesting to recall an incident involving a chemical reaction and fire in a chemical solution in a railway wagon which remained on the siding for nearly two months (also mentioned elsewhere). There was segregation within the solution with two layer formation, triggering a reaction at the interface with heat evolution and explosion. This incident demonstrates hidden hazards involved in mixtures of chemicals which are otherwise *not reactive between each other*.

In order to determine possibility of runaway reactions, steps to be used in assessment include literature data and calculations to give preliminary information, basic screening tests, such as differential scanning calorimetry, isothermal calorimetry (mainly to measure reaction kinetics and heats of reaction), adiabatic calorimetry (mainly to examine runaways) and relief vent-sizing tests. Reaction calorimetry has been traditionally employed for characterizing the heat evolved during a chemical process.

Reaction calorimetry is usually a heat flow technique allowing the reacting mixture to remain at the processing temperature whilst measuring the heat evolved. In calorimetric measurements, a small amount of the sample is heated over a temperature range, usually of 30–400°C, and temperature, pressure, and time data are recorded. This information is then used for alarm settings, relief sizing, and modeling.

In recent times *power compensation calorimetry* has become more popular. In this technique the temperature of the coolant liquid is maintained slightly below the reaction temperature, a separate heater within the vessel is then used to supply the correct amount of heat to obtain the correct temperature. The power consumed by this heater is then altered during the reaction to maintain isothermal conditions and the changes in power reflect the power output of the reaction. The advantage of this technology is that the thermal transfer area critical to measurement is that of the power compensation heater not the vessel wall and therefore fewer calibrations are needed.

Scanning calorimetries (differential scanning calorimetry (DSC) and differential thermal analysis (DTA)) are normally employed to study temperature (or time) initiated processes and as such are frequently used to investigate thermal decomposition processes.

A substance or mixture is potentially capable of deflagration if it has a calculated enthalpy of decomposition more than 1,000 J/g, and is considered capable of detonating if it has a calculated enthalpy of decomposition in the absence of oxygen more than 3,000 J/g.

Reaction runaways can involve both the desired reactions and undesired secondary reactions. Materials which are unstable, polymerize, peroxide forming, pyrophoric, water-reactive, and oxidizers give rise to reactive hazards.

Table 3.55 gives examples of such materials.

Table 3.55 Examples of materials which give rise to reactive hazards

Unstable (decomposing)	TNT, dibenzoyl peroxide, ethylene oxide, and acetylene
Thermally sensitive	Picric acid, hydrogen peroxide (concentrated) shock-sensitive, and explosive
Polymerizing	Acrylic acid, styrene, 1, 3-butadiene
Pyrophoric	Phosphorus and silane
Peroxide-former	1, 3-butadiene, isopropyl ether
Water-reactive	Sodium, sulfuric acid, and acetic anhydride
Oxidizer	Chlorine and nitric acid

General causes of uncontrolled reactions are summarized in Table 3.56.

Table 3.56 General causes for runaway reactions

Unexpected introduction of a reactant, catalyst, or other material
Extended reaction and/or cycle time favoring auto-catalytic reactions
Materials added in wrong sequence
Wrong material used or added
Too much material added. Accumulation of reactants due to reaction is rate-limited
Too little or no material added
Material added too rapidly
Material added too slowly
Contaminated feed material
Entry of water into reactor involving water-reactive materials
Wrong catalyst added
Excess catalyst or promoter added
Insufficient or no catalyst added
Catalyst addition delayed

(*Continued*)

Table 3.56 (Continued)

Inadequate inhibitor added
Excess inhibitor added
Unexpected depletion of an inhibitor or other material
Inhibited material frozen
Material transferred out of reactor too soon
Material transferred to wrong location
Blocked transfer pump
Inadequate cleaning or purging before introducing feed to reactor
Equipment purged with air instead of inert gas
p_H control lost
Cooling/refrigeration lost or inadequate
Heat added
Fire exposure or external heating of the vessel or storage tank
Hot work in area or on equipment containing self-reactive material
Abnormal energy input due to electrical sparking/arcing, friction or impact
Heating lost
Incoming material too cold
Incoming material too hot
Heating delayed
Leakage of heat transfer fluid
Fouling of heat transfer surfaces. Lack of adequate heat removal
Start of agitation delayed
Insufficient or no agitation. High local temperature caused by loss of, or insufficient mixing
Excess agitation
Power input to agitator lost
Sudden, or rapid mixing of previously separate phases
Phase separation of a previously homogeneous mixture
Level control lost
Vessel overfilled
Over-pressurization of the reactor/system
Pressurization of an enclosure by an oxidizing gaseous intermediate
Vent pressurized
Vent blocked or not opened
Air leak under vacuum

Summary of Checklist for Reaction Hazard Identification

(i) Knowledge of the heat of reaction for the intended and other potential chemical reactions. All potential reactions that could occur in the reaction mixture should be identified and the heat of reaction of these reactions be understood.

(ii) Knowledge of the maximum adiabatic temperature for the reaction mixture. If the maximum adiabatic reaction temperature exceeds the reaction mixture boiling point, the reaction is capable of generating pressure in a closed vessel and safeguards should be evaluated to prevent uncontrolled reaction and the need for emergency pressure relief systems should be evaluated.

(iii) Determination of the stability of all individual components of the reaction mixture at the maximum adiabatic reaction temperature.

(iv) Understanding the stability of the reaction mixture at the maximum adiabatic reaction temperature.

(v) Determination of the heat addition and heat removal capabilities of the pilot plant or production reactor. Factors such as reactor fill level, agitation, fouling of internal and external heat transfer surfaces, variation in the temperature of heating and cooling media, variation in flow rate of heating and cooling fluids should be considered.

(vi) Identification of the potential reaction contaminants. Contaminants such as air, water, oil, corrosion products, trace metal ions of sodium, calcium, and others commonly present in water should be identified and their effects should be evaluated, particularly about their catalyzing effects on any decomposition or other reactions.

(vii) Consideration of the impact of possible deviations from intended reactant charges and operating conditions. The impact of loss of cooling, agitation, temperature control, insufficient solvent and reverse flow into feed piping or storage tanks should be considered.

(viii) Identification of all heat sources connected to the reaction vessel and determination of their maximum temperature.

(ix) Determination of the minimum temperature to which the reactor cooling sources could cool the reaction mixture. Potential hazards resulting from too much cooling, such as freezing of reaction mixture components, fouling of heat transfer surfaces, increase in reaction mixture viscosity reducing mixing and heat transfer, precipitation of dissolved solids from the reaction mixture, and a reduced rate of reaction resulting in a hazardous accumulation of unreacted material should be considered.

(x) Consideration of the impact of higher temperature gradients in plant scale equipment compared to a laboratory or pilot plant reactor. Agitation is almost certain to be less effective in a plant reactor and the temperature of the reaction mixture near heat transfer surfaces may be higher (for systems being heated) or lower (for systems being cooled) than the bulk mixture temperature. For exothermic reactions, the temperature may also be higher near the point of introduction of reactants because of poor mixing and localized reaction at the point of reactant contact.

(xi) Consideration of possible vapor phase reactions. These might include combustion reactions, other vapor phase reactions such as the reaction of organic vapors with a chlorine atmosphere and vapor phase decomposition of materials such as ethylene oxide or organic peroxide.

(xii) Consideration must be given to both in-process materials such as feeds, catalysts, intermediates, products, by-products, solvents, additives, and to processing aids such as heat transfer fluids, recycles, flow aids, refrigerants, fire fighting chemicals, etc., Understanding of the hazards of the products of both intended and unintended reactions. For example, possibilities of the intended or unintended reactions leading to the formation of viscous materials, solids, gases, corrosive products, highly toxic products, or materials which will swell or degrade gaskets, pipe linings, or other polymer components of a system, or accumulation of reactants and impurities should be examined.

(xiii) The rates of all chemical reactions involved or likely to be involved should be considered. Thermal hazard calorimetry testing can provide useful kinetic data.

(xiv) Particular attention be paid to aspects such as possibilities for presence of pyrophoric, spontaneously combustible, water-reactive, peroxide-forming, polymerizable, decomposable, incompatible or oxidizing materials.

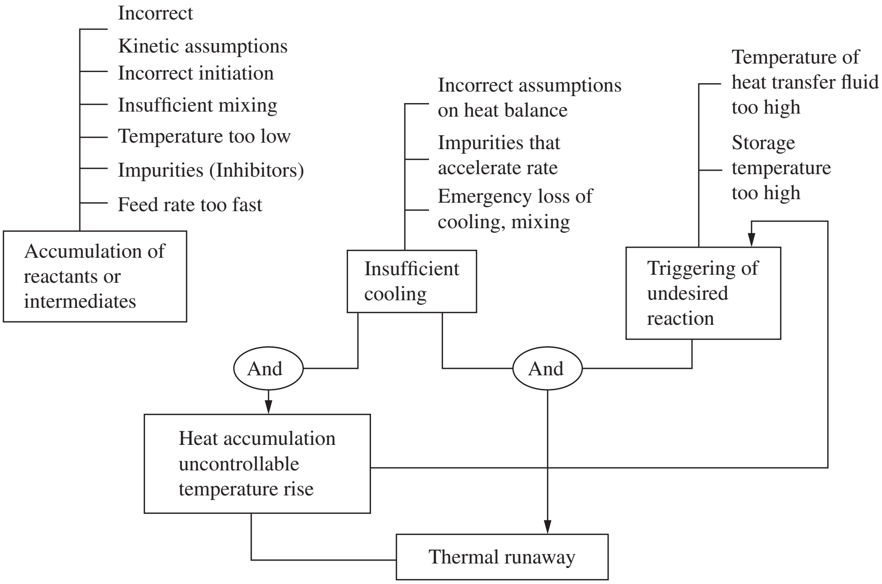


Figure 3.49 Possible causes for a thermal runaway for a batch reactor

Figure 3.49 illustrates possible causes for a thermal runaway for a batch reactor. Table 3.57 gives possible events and errors in batch reactor operations.

Table 3.57 Possible events and operator errors in batch reactor operations

Events
Agitator failure (mechanical or electrical)
Instrument failure (pressure, temperature, flow, level, or a reaction parameter such as concentration)
Failure of instrument air or electricity
Loss of inert gas blanket
Failure of relief devices (e.g. pressure relief valves or rupture discs)
Restricted or blocked vent
Leakage of materials out (e.g. due to gasket failure) or air inwards
Attainment of abnormal reaction conditions (over pressure, over temperature, segregation of reactants, excessive reaction rate, initiation of side reactions, layering)
Failure of coolant, refrigerant, or other utilities
Restriction of material flows in/out
Failure of high-or low-pressure alarms/cut-outs
Power failure affecting agitator, pumps, instruments
Emergency elsewhere on plant/site
Selected operator errors
Failure to clean, purge vessel or lines
Addition of wrong material or wrong quantities (more, less or zero)
Failure to add catalyst or other material
Addition of materials in incorrect sequence
Failure to add material (e.g. short-stop or inhibitor) at correct stage
Error in valve, switch or associated equipment operation
Spillage of material
Improper venting to atmosphere
Failure to actuate agitation at the proper time or use of incorrect speed

Source: Batch reactor hazards and their control by Phillip Carson and Clive Mumford, IChemE, 2003.

It is a measure of the intrinsic rate of potential energy release from fire or explosion resulting from chemical reaction. N_r can both qualitatively as well as rigorously be estimated. For qualitative evaluation of N_r, NFPA classification provides guidelines as given in Table 3.58 based on chemical characteristics are employed.

Table 3.58 NFPA reactivity hazard rating index, N_r

Rating	*Description*
4	Materials that in themselves are readily capable of detonation or of explosive decomposition or explosive reaction at normal temperatures and pressures. This degree should include materials that are sensitive to mechanical or localized thermal shock at normal temperatures and pressures.
3	Materials that in themselves are capable of detonation or of explosive reaction but that require a strong initiating source or which must be heated under confinement before initiation. This degree should include materials that are sensitive to thermal or mechanical shock at elevated temperatures and pressures or which react explosively with water without requiring heat or confinement.
2	Materials that in themselves are normally unstable and readily undergo violent chemical change but do not detonate. This degree should include materials that can undergo chemical change with rapid release of energy at normal temperatures and pressures or which can undergo violent chemical change at elevated temperatures and pressures. It should also include those materials which may react violently with water or which may form potentially explosive mixtures with water.
1	Materials that in themselves are normally stable, but that can become unstable at elevated temperatures and pressures or which may react with water with some release of energy but not violently.
0	Materials that in themselves are normally stable, even under fire exposure conditions, and which are not reactive with water.
Special ratings	
OX	Denotes materials that are oxidizing agents. These compounds give up oxygen easily, remove hydrogen from other compounds, or attract negative electrons.
W	Denotes materials that are water-reactive. These compounds undergo rapid energy releases on contact with water.

The rigorous method for N_r evaluation is based on the exothermic peak temperatures obtained from differential thermal analysis (DTA) or scanning calorimeter (DSC).

Table 3.59 gives threshold quantities for reactive or explosive chemicals.

Table 3.59 Threshold quantities, TQ, for reactive or explosive chemicals

Class	*NFPA reactive rating (N_r)*	*TQ (kg)*
R_1	4	1,134
R_2	3	6,804
R_3	2	22,680

Source: Encyclopedia of chemical process design.

An explosion involving a chemical reaction can either be a *deflagration* or *detonation*.

Table 3.60 summarizes information required for hazardous materials involved in the reaction processes and products.

Table 3.60 Summary of information required for hazardous materials involved in the reaction processes

General description of hazards	–
Range of incompatible chemicals. Any incompatibility with air and/or water	–
General description of precautions	–
Fire fighting methods	–
Regulations	–
Sources of advice on precautions	–
Characteristics: evaluate as appropriate under all process conditions	–
Formula (chemical structure)	–
Purity (identity of any contaminants), physical state, appearance, other relevant information	–
Concentrations, odor, detectable concentration, taste (analytical methods)	–
Physical properties	–
Molecular weight	Particle size and size distribution
Vapor density	Foaming/emulsification characteristics
Specific gravity	Critical temperature/pressure
Melting point	Expansion coefficient
Boiling point	Surface temperature
Solubility/miscibility (with water; in general)	Joule–Thompson effect
Viscosity	Caking properties
Corrosivity	
Contamination factors (incompatibility); oxidizing or reducing agent; dangerous reactions	
Flammability data	
Flash point	Vapor pressure
Fire point	Dielectric constant
Flammability limits (LFL/UFL)	Electrical resistivity
Ignition temperature	Electrical group
Spontaneous heating	Explosion properties of dust

(*Continued*)

Table 3.60 (Continued)

Toxic thermal degradation products in a fire	
Reactivity (instability) information	
Acceleration rate calorimetry	Drop weight test
Differential thermal analysis (DTA)	Thermal decomposition test
Impact test	Self-acceleration test
Thermal stability	Card gap test (under confinement)
Lead block test	JANAF
Explosion propagation with detonation	Critical diameter
Pyrophoricity	–
Toxicity information	–
Toxicity hazard rating	–
Hygiene standard (TLV, IDLH, ceiling limits, etc.)	
LD_{50}	
Biological properties	–
Exposure effects	–
Inhalation (general)	Respiratory irritation
Ingestion	Respiratory sensitization
Skin/eye irritation	Skin sensitization
Carcinogenicity	Mutagenicity
Teratogenicity	–
Radiation information	–
Radiation survey	–
Alpha, beta, gamma, and neutron emission	–

Source: Batch reactor hazards and their control by Phillip Carson and Clive Mumford, IChemE, 2003.

3.13 Incompatible Materials

All potential material interactions should be examined for incompatibilities. Even if the materials are relatively nonhazardous by themselves, potentially dangerous interactions may occur when mixed. Interactions between chemicals and other materials with which they come in contact can be examined in pairs by using an interaction matrix as illustrated in Figure 3.50.

NH_3 anhydrous ammonia	combustible; toxic vapor; cryogenic liquid spill					
Cl_2 chlorine	explosive NCl_3 formed with excess chlorine or heat	oxidizer; toxic vapor; cryogenic liquid spill				
HF anhydrous hydrogen fluoride	heat generation, liberating toxic vapors	heat generation, liberating toxic vapors	strong acid; corrosive; toxic vapor and liquid			
I_4H_6 1,3-butadiene	heat generation, violent polymerization	fire, toxic gas generation	heat generation, violent polymerization	flammable; peroxidizes; polymerizes decomposes		
Fe, etc. carbon steel	none predicated	iron/chlorine fire if above 250°C (or 100°C with impurities)	hydrogen blistering between steel laminations	none predicted	material of construction	
H_2O 150# steam	heat generation, liberating toxic vapors	none predicted	heat generation, liberating toxic vapors	antioxidant consumed, leading to polymerization	none predicted	elevated pressure, temperature
combined with...	**NH_3** anhydrous ammonia	**Cl_2** chlorine	**HF** anhydrous hydrogen fluoride	**C_4H_6** 1,3-butadiene	**Fe, etc.** carbon steel	**H_2O** 150# steam

Figure 3.50 Example interaction matrix for identifying process hazards

***Note:** Descriptions along diagonal are properties of materials by themselves.

***Source:** DOE Handbook Chemical Process Hazard Analysis, February 1996. Chemicals can usually be grouped into five main categories, namely, flammable/combustible, acid, alkaline or basic, oxidizer and reactive. These groups are incompatible with each other and must be handled and stored separately.

Table 3.61 provides some examples of incompatible materials, that, when mixed together, can create a fire or explosion hazard.

Table 3.61 Examples of incompatible materials

Group A	*Group B*	*Hazard on mixing A an B*
Acids or bases corrosives	Reactive metals such as aluminum, beryllium, calcium, lithium, potassium, magnesium, sodium, zinc powder	Fire

(*Continued*)

Table 3.61 (Continued)

Solvent or reactive	Acids, bases, reactive metals organic materials such as alcohols, aldehydes, nitrated hydrocarbons	Explosion
Flammable liquids	Acids, bases, oxidizers, poisons	Fire, explosion or violent reaction
Flammable compressed gases	Oxidizers	Fire, explosion or violent reaction
Cyanide and sulfur mixtures	Acids	Fire
Oxidizers such as chlorates	Flammable liquids, flammable solids	Explosion
chlorine, chorites, chromic acid	or combustible wastes	–
hypochlorites, nitrates	–	–
perchlorates, permanganates	–	–
peroxides	–	–

Table 3.62 gives examples of water reactive chemicals, giving rise to toxic gases.

Table 3.62 Examples of water reactive chemicals

Name of chemical	*Toxic gases produced on contact with water*
Potassium cyanide	HCN
Sodium cyanide	HCN
Acetone cyanohydrin	HCN
Sodium hydrosulfite	H_2S, SO_2
Zinc hydrosulfite	H_2S, SO_2
Sodium phosphide	PH_3
Calcium phosphide	PH_3
Magnesium aluminum phosphide	PH_3
Aluminum phosphide	PH_3
Uranium hexafluoride	HF
Chlorosilanes	HCl
Lithium nitride	NH_3
Phosphorous pentachloride	HCl
Phosphoric acid	HF
Chlorosulfonic acid	HCl
Acetyl chloride	HCl

Hazardous wastes/spills: A spill is generally considered hazardous waste if it contains any of the following characteristics:
Ignitable: A flash point of less than 60°C (140°F).
Corrosive: A p_H of less than or equal to 2.0, or greater than or equal to 12.5, or corrodes steel at a rate greater than 6.35 mm per year at 55°C.
Reactive: Unstable, reacts violently with water; is sufficiently cyanide or sulfide bearing to produce toxic gas; is capable of detonations or forms potentially explosive mixtures with water.
Toxic: If the material tests positive and is above a certain concentration for 39 contaminants that the EPA has listed in Federal Regulations (e.g. certain pesticides, benzene, heavy metals, such as lead or mercury) and halogenated organic substances, such as pentrachloro phenol and trichloroethylene.

3.14 Material Safety Data Sheets

Material safety data sheets (MSDS) provide data on properties of individual materials relevant to hazards likely to be posed by materials in the workplace. These sheets should be made available to employees by the managements. An idea of the kind of information one should expect to find in MSDS is briefly described in the following paragraphs.

1. **Product identification:** The manufacturer or distributor listed should be able to provide detailed information on the hazards of the material(s) covered by the MSDS. This should include trade name, commonly used synonyms, chemical names with formulae for pure chemicals, brand name and chemical family name for mixtures, and TLVs. One component of a multi-component product might be listed because of its toxicity, another for its flammability, and a third for its reactivity.

   Toxic hazard data should be stated in terms of concentration, mode of exposure, or test, and animal used; that is, 100 ppm LC_{50} rat, 25 mg/m^3 LD_{50} oral mouse or permissible exposure limit from published sources. Flammable or reactive data should be included as well as flash point, shock sensitivity, or brief data to indicate the nature of the hazard.
2. **Physical data:** This section is one of the most important and useful sections on the MSDS both for assessing how hazardous the substance is and how completely the MSDS is filled out. This is especially true for solvents. The data in this section should be for the total mixture or product. The data should include:

   Boiling point or ranges of boiling points for mixtures,

   Vapor pressure (A high vapor pressure indicates that a liquid will evaporate easily. The term *volatile* is used to describe a liquid that evaporates easily. This is important to know because it indicates that air concentrations can build up quickly when the material is worked with in its liquid form. Materials with high vapor pressures can be especially hazardous in enclosed areas or in an areas with poor air circulation. Even materials with lower vapor pressures may pose an inhalation hazard because the method of handling (e.g. spraying versus brushing) also affects the concentration in air.

Percent volatile by volume refers to the percentage of a liquid or solid that evaporates at room temperature. The higher the percentage the faster the substance will evaporate.

Evaporation rate is the rate at which the material evaporates compared either to ether that evaporates very quickly or to butyl acetate that evaporates very slowly. The chemical which is used for comparison (ether or butyl acetate) should be listed, If a substance has an evaporation rate greater than one, it evaporates more easily than the chemical it is compared to; if the rate is less than one, it evaporates more slowly than the chemical it is compared to.*Vapor density* is the relative density or weight of a vapor or gas compared with an equal volume of air. If the vapor density of a substance is less than one, it will tend to rise in air; if the vapor density is greater than one, it will sink in air. Substances with high vapor densities pose a particular problem because they will collect in the bottom of tanks, pits, trenches, and sumps.

Specific gravity refers to the ratio of the weight of a volume of liquid to the weight of an equal volume of water at a specified temperature. If a substance has a specific gravity greater than one, it will sink in water; it if has a specific gravity less than one, it will float on water.

Solubility in water refers to the percentage by weight of the substance that can be dissolved in water. Less than 0.1 percent is considered negligible; 0.1–1 percent is slight; 1–10 percent is moderate and more than 10 percent is appreciable; and if it can be dissolved in all proportions, it has complete solubility.

Appearance and odor may help identification of the substance. It should be noted that relying on odor to indicate whether there is a hazardous concentration of the substance in air. Some substances can reach hazardous levels and not have a noticeable odor.

The information in the *Physical Data Section* is useful for the control of toxic vapors. Boiling point, vapor density, percent volatile, vapor pressure and evaporation are all useful for designing proper ventilation systems. This information is also useful for design and use of adequate fire and spill containment equipment and procedures.

Fire and explosion data: Working with flammables, solvents, peroxides, explosives, metal dusts and other unstable substances, this section is important. If the product does not pose a fire hazard, this should be stated in this section.

Flash point and self-ignition temperature should be listed.

Flammable liquids: The flash point and flammable limits are the most important when related to the boiling point, vapor pressure, percent volatile and evaporation rate.

Fire extinguishing media means what kind of fire extinguisher to use. If the substance is not flammable and/or is completely inert, the MSDS should say so.

Special firefighting procedures *and unusual fire and explosion hazards* would need to be described for any combustible material. Some concentrated corrosives, calcium carbide or reactive metals, must not have water applied in case of fire.

3. **Reactivity data:** The information in this section will assist in determining safe storage and handling of hazardous, unstable substances. Instability or incompatibility of the product to common substances such as water, direct sunlight, metals used in piping or containers, acids alkalis, etc., should be listed here.

   Incompatibility: Common materials or contaminants which the specific material could be expected to come into contact with and which could produce a reaction should be listed here. Conditions to avoid should also be listed.

   Hazardous decomposition products should list products released if the substance is exposed to aging, heating, burning, oxidation, or allowed to react. The shelf life of the product should also be listed in this section when applicable. Although some materials are innocuous in their original form, when they are exposed to the conditions such as aging, burning etc., they may form hazardous products.

   Hazardous polymerization is a reaction with extremely high or uncontrolled release of energy. If the substance contains any catalyst and vehicle it may indicate that hazardous polymerization can occur.
4. **Health hazard information:** Health hazard data should be the combined estimate of the hazard of the total product. This might be stated as a time weighted average concentration, permissible exposure limit (PEL) or TLV. Other data, such as LD50, might be used.

   Routes of exposure should contain information about the potential hazard from absorption of the product, the severity of the effect, and the basis for that determination. The basis might be animal studies, analogy with similar products, or human exposure. Routes of exposure should list common effects by route of exposure, usually by inhalation or absorption by skin contact. It should include chronic and acute effects, as well as information on carcinogenicity, teratogenicity, or mutagenicity If inhalation is a primary route of exposure, high vapor pressure, high volatility usually pose more of an inhalation problem than chemicals with low vapor pressure and low volatility. Use of proper respiratory protective devices become relevant for necessary ventilation requirements. If skin contact or absorption is a problem, proper protective equipment like gloves and eye and skin protection should be specified. Effects of overexposure should indicate relevant signs, symptoms, and diseases that could result from acute and chronic exposure to the hazardous substances.

   Emergency and first aid procedures should contain treatment information that could be used by paramedics and individuals trained in first aid. Any substance with a TLV should have emergency first aid procedures listed for acute exposures, especially if the material has a low TLV. Note to physician should include special information that would be important to a doctor including required or recommended preplacement and periodic medical examination, diagnostic procedures, and medical management of overexposed employees.
5. **Spill or leak procedures:** Detailed procedures and protective clothing and equipment and/or ventilation to be used for cleaning up a spill and safe

disposal should be indicated here. For example, if a material has a low TLV, is highly volatile, is flammable, unstable and has severe effects of overexposure listed then very specific procedures on handling a spill or leak need to be spelled out. This section should state whether the substance is incompatible with common clean up procedures or media (such as water).

Waste disposal methods: If labeling and special handling of clean-up residue is necessary, that should be stated along with the appropriate method of disposal, for instance, sanitary landfill, incineration, etc.,

6. **Special protection information:** Respiratory protection: If respirators are required or recommended, the type and class should be stated, such as *supplied air or organic vapor cartridges* or suitable for dust, etc. If protective clothing is required, the type and material of that clothing should be indicated.

   Ventilation: If the substance is very volatile and the TLV is low, local exhaust ventilation, which captures contaminants at the point where they are generated, is probably the most effective control. Mechanical, general or dilution ventilation is not recommended for chemicals with a low TLV, especially if they are highly volatile or have high evaporation rates.

   Protective gloves: If gloves are recommended, the type should be specified. Chemical family should be checked to make sure proper gloves are being recommended.

   Eye protection: First aid procedures may be listed, such as flooding with water. If splashes may occur, eye protection and eyewash facilities should be recommended.
7. **Special precautions:** How to label the substance, or required signs to be posted might be listed here, as well as any information on safety or health that has not been covered in other sections of the MSDS.

Example of material safety data sheet

1. Chemical product and company identification

Matheson Tri-Gas, Inc. Emergency Contact: 959 Route 46 East Chemtrec 1-800-424-9300

Parsippany, New Jersey 07054-0624 Information Contact: 973-257-1100

Substance: Ethylene Oxide

Trade Names/Synonyms: Mtg MSDS 34; Oxirane; Dihyrooxirene; Dimethylene Oxide; Epoxyethane; 1, 2- Epoxyethane; Ethene Oxide; Eto; Eo; Oxacyclopropane; Oxane; Oxidoethane;

Alpha, Beta-Oxidoethane; Oxiran; Rcra U115; Stcc 4906610; Un 1040; C2h4o; Mat09520; Rtecs Kx2450000

Chemical Family: Epoxy

Creation Date: January 24 1989 Revision Date: June 16 2005

2. Composition, Information on Ingredients

Component: Ethylene Oxide Purity: 99.7 percent CAS Number: 75-21-8

Component: Acetaldehyde Purity: < 0.1 percent CAS Number: 75-07-0

Component: Acetic acid Purity: < 0.1 percent CAS Number: 64-19-7

Component: Water Purity: < 0.1 percent CAS Number: 7732-18-5

1. Hazards identification:
NFPA Ratings (Scale 0–4): Health = 3 Fire = 4 Reactivity = 3
Emergency Overview:
Color: Colorless
Physical form: Gas
Odor: Sweet Odor

Major health hazards: Harmful if inhaled or swallowed, skin burns, eye burns, respiratory tract, irritation, central nervous system depression, allergic reactions, cancer hazard (In humans)

Physical hazards: May explode when heated. Flammable gas. May cause flash fire.

Potential health effects:

Inhalation:

Short-term exposure: Irritation, Lack of Sense of Smell, Tearing, Nausea, Vomiting, Diarrhea,

Difficulty Breathing, Irregular Heartbeat, Headache, Drowsiness, Symptoms Of Drunkenness, Disorientation, Bluish Skin Color, Lung Congestion, Lung Damage, Kidney Damage, Paralysis, Reproductive Effects, Convulsions

Long term exposure: Cancer

Skin contact:
Short-term exposure: Irritation (possibly severe), allergic reactions, blisters
Long-term exposure: Same as Effects Reported In Short Term Exposure

Eye Contact:
Short-term exposure: Irritation (possibly severe), frostbite, tearing
Long term exposure: Same as effects reported in short term exposure

Ingestion: Short-term exposure: Irritation (possibly severe), sore throat, nausea, vomiting, diarrhea, stomach pain, chest pain, headache, drowsiness, symptoms of drunkenness, bluish skin color

Long term exposure: Liver damage, cancer

2. First aid measures

Inhalation: If adverse effects occur, remove to uncontaminated area. Give artificial respiration if not breathing. If breathing is difficult, oxygen should be administered by qualified personnel. Get immediate medical attention.

Skin contact: If frostbite or freezing occur, immediately flush with plenty of lukewarm water (41–46oC). Do not use hot water. If warm water is not available, gently wrap affected parts in blankets. Get immediate medical attention.

Eye contact: Wash eyes immediately with large amounts of water, occasionally lifting upper and lower lids, until no evidence of chemical remains. Get medical attention immediately.

Ingestion: Contact local poison control center or physician immediately. Never make an unconscious person vomit or drink fluids. When vomiting occurs, keep head lower than hips to help prevent aspiration. If person is unconscious, turn head to side. Get medical attention immediately.

Note to physician: For inhalation, consider oxygen. For ingestion, consider gastric lavage and activated charcoal slurry.

3. Fire fighting measures: *Fire and explosion hazards*: Severe fire hazard. The vapor is heavier than air. Vapors or gases may ignite at distant ignition sources and flash back. Vapor/air mixtures are explosive.

Extinguishing media: Alcohol resistant foam, carbon dioxide, regular dry chemical, water

Large fires: Use alcohol-resistant foam or flood with fine water spray.

Fire-fighting: Let burn unless leak can be stopped immediately. Move container from fire area if it can be done without risk. Fight large fires from a protected location or safe distance. Stay away from the ends of tanks. For fires in cargo or storage area: Cool containers with water from unmanned hose holder or monitor nozzles until well after fire is out. If this is impossible then take the following precautions: Keep unnecessary people away, isolate hazard area and deny entry. Let the fire burn. Withdraw immediately in case of rising sound from venting safety device or any discoloration of tanks due to fire. For tank, rail car or tank truck,

Evacuation radius: 1,600 m. Do not attempt to extinguish fire unless flow of material can be stopped first. Flood with fine water spray. Do not scatter spilled material with high pressure water streams.

Apply water from a protected location or from a safe distance. Cool containers with water spray until wet.

After the fire is out. avoid inhalation of material or combustion by-products. Stay upwind and keep out of low areas. Evacuate if fire gets out of control or containers are directly exposed to fire. evacuation radius: 1,600 m. Water may be ineffective.

Flash point: –29°C

Lower flammable limit: 3 percent

Upper flammable limit: 100 percent

Self-ignition: 429°C

6. Accidental release measures

Water release: Keep out of water supplies and sewers.

Occupational release: Avoid heat, flames, sparks and other sources of ignition. Stop leak if possible without personal risk. Reduce vapors with water spray. Do not get water inside container.

Small spills: Flood with water. Large spills: Dike for later disposal. Remove sources of ignition. Keep unnecessary people away, isolate hazard area and deny entry. Notify local emergency planning committee and state emergency response commission for release greater than or equal to RQ (U.S. Sara Section 304). If release occurs in the U.S. and is reportable under Cercla Section 103, Notify the National Response Center at (800)424–8802 (USA) or (202)426–2675 (USA).

4. Handling and storage: *Storage*: Store and handle in accordance with all current regulations and standards. Subject to storage Regulations: U.S. OSHA (29 CFR 1910.106). Protect from physical damage. Store below 30°C. Store outside or in a detached building. Avoid contact with light. Store in a cool, dry place. Use diking sufficient to contain total contents plus 10 percent. Store with flammable liquids. Keep separated from incompatible substances.

Grounding and bonding required. Keep separated from incompatible substances. Notify state emergency response commission for storage or use at amounts greater than or equal to the TQ (U.S. EPA Sara Section 302). Sara Section 303 requires facilities storing a material with a TQ to participate in local emergency response planning (U.S. EPA 40 CFR 355.30).

5. Exposure Controls, Personal Protection

Exposure limits:

Ethylene oxide:

1 ppm OSHA TWA
5 ppm OSHA excursion limit 15 min
0.5 ppm OSHA action level
1 ppm ACGIH TWA
0.1 ppm (0.18 mg/m^3) NIOSH Recommended TWA 10 hr (Not to exceed)
5 ppm (9 mg/M3) Niosh Recommended Ceiling 10 min

Ventilation: Provide local exhaust or Process Enclosure Ventilation System. Ensure compliance with applicable exposure limits.

Eye protection: Wear Splash Resistant Safety Goggles with a Faceshield. Provide an emergency eye wash fountain and quick drench shower in the immediate work area.

Clothing: For the gas: Wear appropriate chemical resistant clothing. For the liquid: Wear appropriate protective, cold insulating clothing. Wear appropriate chemical resistant clothing.

Gloves: For the gas: Wear appropriate chemical resistant gloves. For the liquid: Wear insulated gloves.

OSHA regulated substances: U.S. OSHA (29 CFR 1910.1047).

Respirator: The following respirators and maximum use concentrations are drawn from NIOSH and/or OSHA.

50 ppm

Any air-purifying respirator with a full face piece and a canister providing protection against this substance.

2,000 ppm

Any supplied-air respirator with a full face piece that is operated in a pressure-demand or other positive pressure mode. Any supplied-air respirator operated in a continuous-flow mode.

For unknown concentrations or immediately dangerous to life or health(IDLH)

Any self-contained breathing apparatus that has a full face piece and is operated in a pressure-demand or other positive-pressure mode.

Any supplied-air respirator with full face piece and operated in a pressure-demand or other positive-pressure mode in combination with a separate escape supply.

Escape Any air-purifying respirator with a full face piece and a canister providing protection against this substance. Any supplied-air respirator with a full face piece that is operated in a pressure-demand or other positive pressure mode.

Any supplied-air respirator operated in a continuous-flow mode.

Any self-contained breathing apparatus that has a full face piece and is operated in a pressure-demand or other positive-pressure mode.

Any supplied-air respirator with a full face piece that is operated in a pressure-demand or other positive pressure mode.

6. Physical and chemical properties

Physical state: Gas
Color: Colorless
Odor: Sweet odor
Molecular weight: 44.06
Molecular formula: $(CH_2)_2$-O
Boiling point: 13°C
Freezing point: −111°C
Vapor pressure: 1095 mm Hg @ 20°C
Vapor density (Air = 1): 1.5
Specific gravity (Water = 1): 0.8824 @ 10°C
Water solubility: Soluble
p_H: Not applicable
Volatility: 100 percent
Odor threshold: 500 ppm
Evaporation rate: Not applicable
Viscosity: 0.0095 c^P @ 20°C
Coefficient of water/oil distribution: Not applicable
Solvent solubility:

Soluble: Alcohol, ether, acetone, benzene, carbon tetrachloride, and organic solvents

7. Stability and reactivity

Reactivity: May decompose explosively when heated above 427°C.

Conditions to avoid: Avoid heat, flames, sparks and other sources of ignition. Containers may rupture or explode if exposed to heat

Incompatibilities: Acids, combustible materials, bases, metal salts, metal oxides, amines, halo carbons, metals, cyanides, oxidizing materials

Hazardous decomposition:

Thermal decomposition products: Oxides of carbon

Polymerization: May polymerize violently or explosively. May polymerize when heated. Avoid contact with incompatible materials.

8. Toxicological information

Ethylene oxide:

Irritation data:

1 Percent/7 sec Skin-human; 18 mg/6 hr Eyes-rabbit moderate

Toxicity data:

800 ppm/4 hr Inhalation-rat LC_{50}; 72 mg/kg oral-rat LD_{50}

Carcinogen status: OSHA: Carcinogen; Known Human Carcinogen; IARC: Human limited evidence, animal sufficient evidence, Group 1; ACGIH: A_2 -suspected human carcinogen

Local effects:

Irritant: Inhalation

Corrosive: Skin, eye

Acute toxicity level:

Toxic: Inhalation, ingestion

Target organs: Immune system (sensitizer), central nervous system

Tumorigenic data: Available.

Mutagenic data: Available.

Reproductive effects data: Available.

Additional data: Alcohol may enhance the toxic effects.

9. Ecological information

Ecotoxicity data:

Fish toxicity: 84,000 ug/L 96 hr LC_{50} (Mortality) Fathead minnow (Pimephales promelas)

Invertebrate toxicity: 490,000 ug/L 48 hr LC50 (Mortality) Brine Shrimp (Artemia Sp)

10. Disposal considerations

Subject to disposal regulations: U.S. EPA (40 Cfr 262). Hazardous waste number(s): U115. Dispose in accordance with all applicable regulations.

11. Transport information

U.S. DOT (49 Cfr 172.101):

Proper shipping name: Ethylene Oxide

ID number: UN1040

Hazard class or division: 2.3

Labeling requirements: 2.3; 2.1

Quantity limitations:

Passenger aircraft or railcar: Forbidden

Cargo aircraft only: Forbidden

Additional shipping description: Toxic-inhalation hazard zone D

Canadian transportation of dangerous goods:

Shipping name: Ethylene oxide

UN number: Un1040

Class: 2.3; 2.1

12. Regulatory information

U.S. regulations:

CERCLA sections 102a/103 hazardous substances (40 Cfr 302.4):

Ethylene oxide: 10 Ibs RQ

Acetaldehyde: 1,000 Ibs RQ

Acetic acid: 5,000 Ibs RQ

Sara Title III Section 302 Extremely hazardous substances (40 Cfr 355.30):

Ethylene oxide: 1,000 Ibs TPQ

Sara title III section 304 Extremely hazardous substances (40 Cfr 355.40):

Ethylene oxide: 10 Ibs RQ

Sara title III Sara sections 311/312 Hazardous categories (40 Cfr 370.21):

Acute: Yes

Chronic: Yes
Fire: Yes
Reactive: Yes
Sudden release: Yes
Sara title III Section 313 (40 Cfr 372.65):
Ethylene oxide
OSHA process safety (29Cfr 1910.119):
Ethylene oxide: 5,000 Ibs TQ
Acetaldehyde: 2,500 Ibs TQ
State regulations:
California Proposition 65:
Known to the State of California to cause the following:
Ethylene oxide
Cancer (July 01, 1987)
Female reproductive toxicity (February 27, 1987)
Acetaldehyde
Cancer (April 01, 1988)
Canadian regulations:
WHMIS classification: ABD1
National inventory status:
U.S. Inventory (TSCA): Listed on inventory
TSCA12(B*) Export Notification*: Not listed
Canada Inventory (DSL/NDSL): Not determined
16. Other information
Note: Above refers to U.S. laws and other countries may have their own laws.

3.15 Annexure

NFPA Health, Flammability, and Reactivity Hazard Ratings

Table 3.63 gives NFPA health, flammability, and reactivity hazard ratings for selected materials.

Table 3.63 NFPA hazard ratings for selected materials

Material	*Health*	*Flammability*	*Reactivity*
Acetone	1	3	0
Acetylene	0	4	3
Ammonia (anhydrous)	3	1	0
Ammonium nitrate	0	0	3
Aniline	3	2	0
Arsine	4	4	2
Benzene	2	3	0

(*Continued*)

Table 3.63 (Continued)

Beryllium powder	3	1	0
Bromine	3	0	0
Butane	1	4	0
Butanol	1	3	0
Calcium	3	1	2
Carbon disulfide	3	4	0
CO	3	4	0
Chlorine	4	0	0
Chloroform	2	0	0
Chromic acid	3	0	1
Coal tar pitch	0	1	0
Cyclohexane	1	3	0
Diborane	4	4	3
Diethanol amine	1	1	0
Dimethyl amine	3	4	0
Endrin (dry)	2	0	0
Ethane	1	4	0
Ethanolamine	3	2	0
Ethanol	0	3	0
Ethylene	1	4	2
Ethyl ether	1	4	1
Ethylene glycol	1	1	0
Ethylene oxide	3	4	3
Fluorine	4	0	3
Formaldehyde	3	4	0
Gasoline	1	3	0
Heptane	1	3	0
Hexane	1	3	0
Hydrogen	0	4	0
H_2S	4	4	0
HCl	3	0	0
Isobutane	1	4	0
Isopentane	1	4	0
Isoprene	1	4	2
Isopropanol	1	3	0

(*Continued*)

Table 3.63 (Continued)

Lithium	3	2	2
m-Xylene	2	3	0
Methane	1	4	0
Methanol	1	3	0
Methyl ethyl ketone	1	3	0
Methyl isobutyl ketone	2	3	1
Methyl isocyanate (MIC)	4	3	2
Naphtha	1	3	0
Natural gas, liquefied	3	4	0
Nickel carbonyl	4	3	3
Nitric acid	3	0	0
Nitrobenzene	3	2	1
Nitrogen, liquefied	3	0	0
NO_x	3	0	0
Nitroglycerine	2	2	4
Nitromethane	1	3	4
o-Xylene	2	3	0
Oxalic acid	3	1	0
Oxygen, liquid	3	0	0
p-Xylene	2	3	0
Pentane	1	4	0
Perchloric acid	3	0	3
Petroleum, crude	1	3	0
Petroleum ether	1	4	0
Phenol	4	2	0
Phosgene	4	0	1
Phosphine	4	4	2
Phosphoric acid	3	0	0
Phosphorus, white or yellow	4	4	2
Potassium	3	1	2
Potassium cyanide	3	0	0
Propane	1	4	0
Propanol	1	3	0
Propylene	1	4	1
Propylene oxide	3	4	2
Silane	1	4	3

(Continued)

Table 3.63 (Continued)

Sodium	3	3	2
Sodium hydroxide	3	0	1
Styrene	2	3	2
Sulfur	2	1	0
SO_2	3	0	0
Sulfuric acid	3	0	2
Tetraethyl lead	3	2	3
Toluene	2	3	0
Trichloroethylene	2	1	0
Trinitrotoluene (TNT)	2	4	4
Turpentine	1	3	0
Vinyl chloride (VCM)	2	4	2
o-Xylene	2	3	0

Table 3.64 is a summary of representative hazardous chemicals.

Table 3.64 Summary of some chemicals and their hazards

Ammonia	Toxicity and fire
Chlorinated hydrocarbons	Toxicity
Cyano compounds	Toxicity
Multi-bond hydrocarbons	Fire and explosion
Epoxides	Explosion
Hydrides and hydrogen	Explosion
Metal acetylides	Explosion
Nitrogen compounds	Explosion
Oxygenated compounds of halogens	Explosion
Oxygenated manganese compounds	Explosion
Peroxides	Fire and explosion
Polychlorinated biphenyls	Environmental
Polycyclic aromatic hydrocarbons	Environmental

Table 3.65 shows reactive chemical combinations.

Table 3.65 Reactive chemical combinations

A	+	***B***	***Hazardous event***
Acids	Chlorates, chlorites, hypochlorites		Spontaneous ignition
–	Cyanides		Toxic/flammable gas
–	Fluorides		Toxic gas

(*Continued*)

Table 3.65 (Continued)

–	Epoxides	Heat/polymerization
Combustibles	Oxidizers	Explosion
–	Anhydrous chromic acid	Spontaneous ignition
–	Potasium permanganate	Spontaneous ignition
–	Sodium peroxide	Spontaneous ignition
Alkali	Nitro-compounds	Easy to ignite
–	Nitroso-compounds	Easy to ignite
Ammonium salts	Chlorates/nitrates	Explosive salts
Alkali metals	Alcohols	Flammable gas
–	Glycols	Flammable gas
–	Amides	Flammable gas
Alkali metals	Amines	Flammable gas
–	Azo compounds	Flammable gas
–	Di-azo compounds	Flammable gas
Inorganic sulfide	Water	Toxic/flammablee gas
Metals	Explosives	Heat/explosion
–	Polymerizable compounds	Polymerization

Review Questions

1. What are the hazards associated with different forms of energy?
2. Name some potential hazardous processes.
3. What are the hazards associated with human health? What substance was responsible to cause large number of deaths during Bhopal disaster?
4. What are the different toxic substances present in the environment? Name different systemic effects on human beings.
5. Nickel carbonyl is one of the most poisonous substances. In which industry it is formed and under what circumstances?
6. What are neurotoxins? Give examples.

   What are the reasons mercury processes are replaced by membrane processes in caustic soda manufacture?
7. What are the different ways by which toxic substances enter human body?
8. What are teratogens, mutagens, and carcinogens? What effects they cause to human health?
9. What are the different measures of toxicity? Explain.
10. What are the differences among acute, chronic and sub-chronic effects of toxicity? Explain.
11. What are different types of toxic effects? What are the characteristics of each of these effects? Give examples of materials that give rise to each of such effects.

12. Illustrate how different concentrations of ammonia exposures affect human health.
13. Compare ammonia, chlorine, and carbon monoxide in their toxic characteristics. Illustrate by means of suitable diagrams, effects of exposure to chlorine.
14. In what ways do reduced oxygen concentrations in the working environments affect worker exposures?
15. What are the different indices available from different sources? What values of SHI are considered to indicate extreme toxicity?
16. What are NFPA health hazard ratings? What are the rating numbers, categories, and description of the degrees of the hazards?
17. Give EPA toxicity classifications and their consequences on health.
18. What is toxicity index? Give the equation and what is its utility?
19. What are threshold quantities and how do they influence hazard severity?
20. What are the health hazards associated with exposure to cryogenic fluids?
21. What types of hazards affect health of personnel involved in welding operations?
22. What are the biological hazards that contribute to ill health? How these can be reduced in working environments?
23. What are the different effects of exposure to noises?
24. How thermal radiation levels influence health?
25. What is ionizing radiation? What are the different types of ionizing radiations? What are the sources of ionizing radiation in industry?
26. What are the health hazards associated with exposures to radioactive substances?
27. What is hazardous material identification system, HMIS, standard for flammability ratings? Explain.
28. What are fire triangle and fire tetrahedron? What are the basic differences between the two? Give diagrams for the two.
29. (a) What is the difference between rapid and smoldering combustion process? Explain.
    (b) What are the distinct phases in the combustion of solid fuels?
30. (a) How are liquids classified by NFPA and OSHA?
    (b) Define flash and fire points. Which are more significant from safety point of view?
31. (a) What are open cup and closed cup methods for flash point determination methods?
    (b) Which of the two is significant for use with high boiling fuels? Why?
32. (a) Under what circumstances a “non-flammable” hydraulic liquid can become flammable?
    (b) How do rags used in maintenance operations influence flash points of liquids that are soaked in the rags? Explain giving reasons.
    (c) What are the contaminants that can give rise to lowering flash points from literature values?
33. (a) Give an empirical equation for estimation of flash points. For what types of liquids such a formula is applicable?
    (b) The normal boiling point for a liquid is 80°C. Estimate its flash point.
34. What is C_{st}? Give an empirical formula for the estimation of C_{st} for mixtures of fuels containing carbon, hydrogen, sulfur and halogen atoms?
35. Give NFPA classification for liquids based on flash points.

36. What are the NFPA ratings for flammability? Describe.
37. (a) What are flammability limits? Which of these limits are more significant from safety point of view in open plant leaks?
    (b) Illustrate flammability limits for binary mixtures by means of a suitable diagram.
    (c) Which of the following fuels have (i) wide and (ii) narrow flammability ranges? (iii) which ones are more hazardous?
38. What are the factors on which flammability range depends?
39. (a) What are the factors that influence flammability limits? Illustrate how flammability limits are dependent on temperature and pressure.
    (b) Estimate limiting oxygen concentration for butane. LFL for butane is 1.9 percent by volume. Use the stochiometric formula.
40. (a) What are explosive limits? How these are different from flammability limits?
    (b) What are detonation limits? Name some materials that are capable of detonations.
41. Give a typical triangular diagram representing flammability range.
42. Why UFL for sprays and mists is much higher than that for vapor–air mixtures?
43. Give some correlations for estimation of flammability limits.
44. What are MEC and LOC? For what types of mixtures, these are significant?
45. Give an equation for inerting combustible dust-air mixtures.
46. (a) What is burning velocity? How burning velocity and flame speed differ? Explain.
    (b) Give an equation relating burning velocity and flame speed.
    (c) Illustrate, by means of a diagram, effect of mixture composition on burning velocity
47. (a) What are quench effects? Give an equation relating quenching diameter and slot width through which flame propagation occurs.
    (b) What are the mechanisms that affect flame propagation?
    (c) What is MESG? In what way MESG is important? How does MESG is important in design? Compare flange and threaded joints in piping.
48. What is self-ignition temperature (SIT)? What factors influence SIT? How is it important in diesel engines?
49. (a) What is ignition energy? Name some substances which have low ignition energy? Are they more hazardous than those having higher ignition energies and how?
    (b) How are ignition energies for dusts different from gases?
50. How is minimum ignition energy related to quenching distance? Give the relationship.
51. (a) What is ignition delay? What is the effect of temperature on ignition delay?
    (b) What are the hazards involved with ignition in furnaces? How does ignition energy plays an important role in furnace ignitions?
52. (a) What are the causes for self-heating? What are the mechanisms involved in self-heating.? Illustrate by means of a diagram.
    (b) What are the precautions that help burning of coal heaps stored in a coal-fired power plant?
53. What are the various ignition sources likely to be present in industrial operations?
54. (a) What is static electricity? What are the different causes in its generation in industrial operations?
    (b) What are the different types of static discharges? Explain.
    (c) What is relaxation?

55. (a) Name some systems in industrial operations that give rise to static ignition problems.
    (b) What are the precautions to eliminate static ignition problems? Explain.
56. What are the effects of electricity on human body?
57. What can be the instances which can result in stray currents?
58. What are the characteristics of hydrogen flames? What additional hazards are attributed to hydrogen flames, over and above normal flames?
59. (a) What are the essential differences between premixed and diffusion flames?
    (b) Is a pool fire diffusion or premixed flame?
    (c) Illustrate by means of a diagram, diffusion and premixed flames.
    (d) Are fires in industry premix or diffusion types?
60. (a) What are the special features of fires involving sprays and mists?
    (b) What are the causes for the formation of droplets/mists in plant leakages?
    (c) does such leaks involving hydrogen could result in the formation of sprays and mists? Explain.
61. Discuss the classification of fires, stating the types of materials involved in different classes of fires.
62. Classify accidental fires and explosions. Illustrate. Give examples of different accidental explosions
63. What are BLEVES? Under what circumstances BLEVES can result?
64. (a) What are the differences between deflagration and detonation? In what way MESG value indicates whether an explosion could be detonation?
    (b) Name some materials that can give rise to detonations.
    (c) Give a summary of factors that favor detonations.
65. Illustrate flame propagation in a pipe.
66. What are UVCEs? The Flixborough explosion involves an UVCE? What are the causes that can lead to UVCEs?
67. What are the causes for the development of high pressures during the occurrence of an UVCE?
68. What are the two detonation theories? Discuss.
69. What is TNT equivalent method? Explain.
70. What are the types and characteristics of pressure vessel explosions?
71. What are the conditions and factors that plays a major role in pressure vessel explosions?
72. What is the mechanism involved in explosions in compressed air systems?
73. (a) What is pressure piling? Explain.
    (b) Illustrate, by means of a diagram, the type of geometry of the equipment that causes pressure piling.
    (c) What are the consequences of pressure piling?
74. Give examples of combustible dusts resulting from different industrial operations. What types of explosions can result from burning of dusts? How are combustible dusts classified? What is K_{st}?
75. (a) What are ignition severity, explosion severity, and explosion index?
    (b) State the relationships among explosion rating, ignition sensitivity, explosion severity, and ignition index for combustible dusts.

76. (a) What are different types of fires from industrial context?
    (b) What are insulation fires? How do they occur? What precautionary steps help reduce such fires?
77. What circumstances give rise to pool fires? What hazards are possible from pool fires?
78. What are the scenarios that give rise to leakage fires? Does a jet fire arise from leakages?
79. (a) How pyrophoric iron sulfide deposits in crude oil storage tanks, piping, and distllation column packings can be causes for fires?
    (b) What are the precautionary measures involved in clean up of such deposits?
80. What are the hazards involved in the use of nuclear power? Give examples if accidents arising from nuclear reactors?
81. What are electrical fires? How they are caused?
82. (a) Give an equation for the maximum equivalent spherical radii of fire balls. For what types of materials such an equation is applicable?
    (b) How does the duration of the fire ball can be estimated? Give an equation.
83. (a) What are the important parameters involved in fire damage?
    (b) What is meant by a runaway reaction? Under what circumstances a reaction runaway occurs?
84. What are the common causes for reaction runaways?
85. What are the possible events and operator errors that can lead to hazardous situations in batch reactors?
86. What is NFPA reactivity hazard rating index? Describe.
87. Give examples of incompatible and water reactive materials.
88. (a) What is MSDS? What is its utility? What are the sources for information on MSDS?
    (b) Give MSDS for a typical hazardous material
89. What is the UFL of a gas mixture composed of 1.0 percent methane, 2 percent ethane and 3 percent propane by volume at 50°C and 2 atm.
90. Find the inherent hazrds of acetone cynohydrin, C_4H_7NO.

Key words for internet searches

ACGIH, OSHA, NOISH, EPA, U.S.
Department of labor, AIHA, ANSI, U.S. Navy, DOT

***Note:** *Vast number of sites are given in Appendix A of the book for the purpose of use in internet searches for key words by enterprising teachers, students, industry professionals and managements.*

Chapter 4

Process and Plant Hazards

Learning Objectives

4.1 Hazards of Pressure
4.2 Causes for Overpressures
4.3 Flow Deviations
4.4 Effects of Leakages/Releases
4.5 Hazards of Temperature
4.6 Cryogenic Fluids
4.7 Vibration and Noise
4.8 Human Errors
4.9 Ergonomics

* * *

4.1 Hazards of Pressure

Many basic operations in the chemical process industries run at high pressures. Steam generating units, compressors, polymerization, and chemical reactions are carried out, for example, at pressures of thousands of kPa.

Principal causes of incidents involving pressure systems include the following:

> Poor equipment and/or system design, poor maintenance of equipment, an unsafe system of work, operator error, poor training/supervision, bad installation, and inadequate repairs or modifications.

Hazards of high-pressure vessels include the following:

> Leakage or failure of pressure vessels, design defects, failure of relief systems, lack of hydraulic testing, lack of proper instrumentation or instrumentation failure, lack of nondestructive testing (NDT), corrosion of vessels, lack of routine inspections, and attempt of pneumatic testing.

The risk from failure of pressure systems and equipment is dependent on a number of factors, which include the following:

> The type of fluid or gas and its properties, the suitability of the equipment and pipe work and that contains it, the age and condition of the equipment, the complexity and control of its operation, and the skills and knowledge of the people who design, manufacture, install, maintain, test, and operate high-pressure equipment and systems.

The following conditions and factors have played major roles in pressure vessel accidents:

- Operation above the maximum allowable working and test pressures.
- Improper sizing or pressure setting of relief devices.
- Improper operation of relief devices due to faulty maintenance and failure to test regularly.
- Failure of the vessel due to fatigue from repeated pressurization, general thinning from corrosion or erosion, localized corrosion, stress corrosion cracking, embrittlement, holes and leaks.
- Failure to inspect frequently enough.

- Improper repair of a leak or other defect involving welding and annealing that embrittles and further weakens the vessel. Hazards posed by a vessel can be worse if repair welds are made without shutting down and de-inventorying the vessel. If a pressure vessel is repaired without removing the water, the quench effect of the water can embrittle the steel.
- Exothermic reaction or polymerization.
- Vessel exposure to fire.

Some of the special considerations for high pressure work are as follows:

Hydrogen, which increases in temperature as it expands (negative Joule Thompson effect). This can result in fire at leaks in a system. High-pressure valves must be designed so that adjustment of the stuffing box nut will not result in forceful ejection of the stem assembly.

When discharged suddenly, pressure relief valves as well as rupture discs can generate large vibratory forces that are transmitted into process piping. A good design practice is to eliminate bends in the piping from these devices in favor of straight runs. Adequate support is necessary. It is also important to size rupture discs of different blowing pressures such that a holder for a low pressure disc does not receive a higher rated one.

Some installations are subject to significant levels of vibration or to thermal expansion and will require suitable support to accommodate the resulting stresses. The scheduled maintenance of relief valves is often inconvenient because production must stop. For this reason, one sometimes encounters installations with fittings to blank off the safety valve, and allow production to continue while the valve is serviced. This runs completely counter to the rationale for installing relief valves, and should not be tolerated. Similarly, no design should the flow intended for a relief valve to be manifolded.

Because of the high pressure load, large vessel closures can require large diameter bolts. To give adequate tightening, it may be necessary to provide for hydraulic tensioners to stress the bolts.

Mechanical linkages are frequently required in valves, agitated reactors and other components. Alignment is very important. Adequate cooling and special lubrication may be required for the sophisticated agitator shaft seals commonly used.

High pressure vessels generally have rounded shapes, to minimize the existence of corners and sharp bends where pressure could affect the integrity of the material most easily. The use of finite element analysis programs has become widely used in designing such vessels. These programs are able to calculate the stresses and pressure points in many complex types of vessel geometries. Much of the equipment for high pressure operations is fabricated from high strength alloy steels.

Overpressure development is one of the most serious hazards leading to explosions in a process plant. Failure of a vessel or piping can lead to a sequence of events that result in a disaster. Boilers and pressure vessels have many potential hazards in common, as well as hazards unique to their specific operations. These vessels hold gases, vapors, liquids, and solids at various temperatures and pressures, ranging from almost a full vacuum to pressures of thousands of kPa. In some applications, extreme pressure and temperature changes may occur in a system in rapid succession, imposing special strains.

Deviations in steam parameter has implications on the following:

Changes in the steam pressure and temperature change the enthalpy of the steam. Temperature of superheated steam plays a major role in the available enthalpy, however pressure also changes enthalpy and if the reduction in pressure is significant there will be considerable increase in enthalpy. The problem is mainly the specific volume of steam; reduction in pressure increases the specific volume. This leads to higher steam pipe and tube velocities thus increasing the pressure drop by a square function. Due to increase in superheated steam pressure drop at lower operating pressure and higher steam flow changes in drum pressure from design will be to a reduced extent. However, it will depend on the amount of reduction in operating pressure and the amount of increase in steam flow. The saturation temperature of water drops with pressure and so the sensible heat addition required reduces.

The rupture of a pressure vessel occurs when the total expansive force acting to cause the rupture exceeds the strength of the vessel. Rupture of a piping system under pressure produces a blast wave. Overpressure can injure personnel and damage facilities. Overpressure is the localized increase in the atmospheric air pressure associated with the passage of a shock wave. The overpressure that accompanies failure of a piping system causes harm that is a function of the magnitude and the duration of the shock wave.

Typical damaging effects from overpressures are the following:

- 2.76 kPa [0.4 psig]: Limited minor structural damage to buildings,
- 3.4–6.9 kPa [0.5–1 psig]: Glass shattering with body penetrating velocities
- 4.8 kPa [0.7 psig]: Minor damage to house structures 6.9 kPa [1 psig]: Partial damage of house structures (made uninhabitable); 95 percent ear drum protection with ear plugs. Stored energy powers the shock wave. Part of the energy that goes into compressing a gas up to the test pressure of a piping system is released suddenly if the piping system ruptures. Several different ways to estimate the theoretical amount of stored energy that is converted into blast overpressure and acceleration of fragments of the ruptured vessel have been proposed. The most common methods of estimating stored energy release assume isentropic expansion, isothermal expansion, and/or thermodynamic availability. The isentropic expansion model gives the lowest energy release estimate, the isothermal model gives the highest estimate, which can be as high as twice that for the isentropic model, and the availability model gives an intermediate value.

Rupture of a piping system may occur due to either ductile fracture or brittle fracture. When the input of heat from the pressure vessel equals that removed by the fluid flowing out, equilibrium is reached and pressure remains constant. If the fluid flow output is prevented or restricted so it is inadequate to remove all the excess heat supplied, the temperature and pressure in the vessel will increase. If adequate supplies of fresh fluid are not provided, any vapor can turn to dry gas and then increase in pressure. If a safety device is not provided or is inadequate to limit gas pressure to safe value, the strength of the vessel might be exceeded, causing it to fail.

Several accidents resulted from *rocketing of gas cylinders* when the gas is released due to accidental dropping of the cylinders, or broken valves. Such cylinders, traveling at high velocities caused damage to buildings, structures, and equipment. The thrust generated by the gas can be 20–50 times the weight of the cylinder.

When liquid nitrogen becomes gaseous it expands approximately 700 times and replaces the oxygen in the air and can lead to asphyxiation of people around.

Whipping of unsecured flexible hoses can also generate injury and damage. Examples are unsecured hoses which start whipping when, for example, a high pressure pump is started to load a ship with oil or other liquid cargo. Whipping lines can tear through and break bones, metal, gas, and water lines, or anything that comes in contact. A thin leaking sheet of compressed gas may cut through the human body. Very high pressure water jets are known to have the ability to cut through steel. No attempt should be made to grab and restrain a whipping line. Valve that controls flow through the hose should be shut.

Water hammer is caused by a sudden stoppage of liquid flow so a shock effect occurs. The mass of liquid has momentum. If the flow is terminated abruptly by closing a valve at the downstream end of a line, the momentum of the liquid is transformed into a shock wave (water hammer) which is transmitted back upstream through the liquid, because liquids are practically incompressible. The energy shock involved may be adequate to break fittings and lines, especially if they are made of brittle materials which do not stand shock well. To avoid damage to liquid lines, the use of quick closing valves should be avoided. If they must be used, the shock can be alleviated by a suitable air chamber or surge tank connected to the lines slightly upstream of the valve. Start-up of steam or compressed gas lines after shut-downs can damage the lines if draining of condensate and clean up of dirt is not properly carried out. When the valves on the lines are opened, slugs of flowing condensate may hit bends and other parts of the lines/downstream equipment, damaging violent water hammer may result.

Exposure of human beings to high pressures can give rise to syndromes such as *oxygen poisoning* and *nitrogen poisoning* leading to narcotic effects. Most commonly known effect of high-pressure exposures is the resulting decompression effects during release of the pressure to atmospheric pressure. High-pressure exposures can act on the body fluids and tissue, making entry of these fluids into cavities of the body. If decompression is not properly handled, *dysbarism and decompression sickness* can result. Disbarism involves physical disturbances in the body caused by variations in exposure. The causes for this type of sickness are release of dissolved gases, like O_2, CO_2, and N_2, in blood and expansion of free gas in the body cavities. O_2 and CO_2 are chemically bound (reversible reaction) in the blood stream, whereas N_2 is in dissolved form and is the main cause of dysbarism. These exposure effects can occur among divers in deep waters, involved in repair and salvage operations with off-shore oil and gas facilities and underwater pipelines. At sea level partial pressure of nitrogen in air is 570 torr (mm Hg). At higher pressure, more nitrogen dissolves in blood stream. As a diver goes down, more nitrogen and excess oxygen dissolves. These gases are released during rapid ascent of divers from deep waters, causing damage to the body (e.g. joint/muscle pains, bone pains, difficulty in breathing, effects on nervous system, etc.) and the rise should be slow to avoid rapid release of the gases in the blood stream which results in body damage. *Low pressures* such as those encountered in confined space entry can result in oxygen deficiency to the body and also expansion of gases into the cavities of the body. Such expansion of gases can cause severe pain. Workers entering a low pressure area experience decompression similar to release from high pressures. Human body, on exposure to low pressures at high altitudes attempts to adjust to low pressures through increase in respiration, bringing more oxygen to the respiratory system and also increasing red blood cells.

Vacuum can be as hazardous as pressure. Development of vacuum can be very destructive unless design is done to withstand external pressure. A storage tank may catastrophically collapse under conditions of even slight drop in pressure below atmospheric. It is not uncommon for a storage tank to collapse by the suction of a pump drawing liquid from the tank, due to blockage of tank vents. Much of the damage caused by the high winds during hurricanes/tornados, is due to the negative pressures. Buildings are designed to take positive pressures but not to resist negative pressures that may be generated on the lee side when the winds pass over. Although the actual pressure difference is small, the area over which the negative pressure may act is very large, resulting in a considerable force. When the pressure inside the vessel is lower than atmospheric pressure, the force acts inward, with sometimes spectacular results. A tanker was being steam cleaned and, at the end of the job, the hatches were closed. With no vacuum breaker fitted, as the steam condensed, the tanker imploded. In another incident, a tanker was being pumped out with all the hatches closed and the vacuum breaker failed to operate. In another case, a tank was being painted and the painters had covered the vent with plastic sheeting. When operations started to empty the tank, it collapsed before the plastic sucked through. It sometimes takes a vacuum of only a few cm of water to collapse a tank. One should be aware of blockages and trapped pressure.

Causes for creation of vacuum in storage tanks include too fast pumping out of the contents, blocked vents, weather effects such as exposure to rain and snow resulting condensation in the vapor space, rusting of steel in a storage tank isolated, resulting in oxygen depletion in vapor space otherwise filled with air. Figure 4.1 illustrates operations that cause bursting/collapse of atmospheric storage tanks.

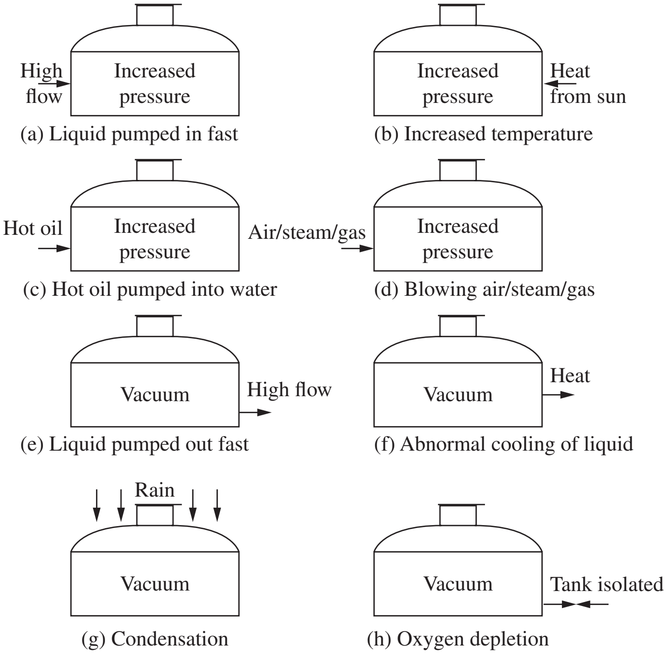


Figure 4.1 Operations that cause bursting/collapse of atmospheric storage tanks

Example: A 3-m diameter drum in a refinery was sucked in by internal vacuum when the steam condensate collection drum half full with hot water was rapidly cooled. The hot water temperature was 100°C and the drum under slight positive pressure, vented to atmosphere. A small amount of flash steam escaped through this 5 cm vent line. Before collapse, the condensate flow into the drum is interrupted and as a result, water level in the drum rapidly dropped. The operator opened a large valve to fill the drum with water at 25°C, to compensate the drop in level. The cold water rapidly condensed the steam and vacuum was created inside the vessel. Air was sucked in through the 5 cm vent line, but not fast enough to prevent collapse. A large sized vent line could have saved the situation.

Another example: A large intercontinental ballistic missile was moved in an aircraft from the high altitude location, where it was manufactured, to sea level location from where it was to be launched. Propellant tanks were sealed before shipment to prevent entry of moisture/contaminants. The internal pressure is that of prevailing atmospheric pressure at the high altitude facility. When the aircraft landed at sea level site, where pressure is much higher, the difference in pressures between the two sites caused the tanks collapse as the tanks were not designed to withstand the high external pressure.

4.2 Causes for Overpressures

Overpressure is the result of an imbalance or disruption of the normal flows of material and energy that causes the material or energy, or both, to build up in some part of the system. The failure of a device or of a group of components can lead to overpressurization and subsequent adverse events, such as fire, explosion, spill, or release. Changes in action of fluid moving equipment, for example, failure of a pump or compressor, surge in compressors.

Change in flow rate, for example, full or partial closure of a valve on pump discharge. Blocked discharge: This can occur when any vessel, pump, compressor, fired heater, or other item of an equipment, which, on closure of a block valve at outlet either by mechanical failure or human error. This will expose the vessel to a pressure that exceeds the maximum allowable working pressure (MAWP), and a pressure relief device is required unless administrative procedures to control valve closure such as car seals or locks are in place. Changes in heat input, for example, fire exposure, heat from sun, heat input from associated equipment, and so on. Contact between different materials, for example, hot oil and water. Entry of a volatile fluid into a system.

Fire exposure: Fire may occur in a hydrocarbon processing facility, and create the greatest relieving requirements. All vessels must be protected from overpressure by pressure relief valves, except as below:

> A vessel which normally contains no liquid, since failure of the shell from overheating would probably occur even if a pressure relief valve were provided. Vessel (drums or columns) with ≤ 0.6 m (2 ft) in diameter, constructed of pipe, pipe fittings or equivalent, do not require pressure relief valves for protection against fire, unless these are stamped as coded vessels. Heat exchangers do not need a separate pressure relief valve for protection against fire exposure since they are usually protected by pressure relief valves

> in interconnected equipment or have an open escape path to atmosphere via a cooling tower or tank. Vessels filled with both a liquid and a solid (such as molecular sieves or catalysts) not require pressure relief valve for protection against fire exposure. In this case, the behavior of the vessel contents normally precludes the cooling effect of liquid boiling. Hence rupture discs, fire-proofing and de-pressuring should be considered as alternatives to protection by pressure relief valves.

According to API RP 520 and 521 standards, a fire-exposed area is within an area of 232 and 465 m^2 (2,500–5,000 ft^2), and below a height of 7.6 m (25 ft) above the grade. In this scenario, the exposed vessel is blocked in. Potential vapors resulting from the fire must be relieved using a PRV on the vessel, or via a vent path that remains in a locked-open position between the vessel and an adjoining vessel.

Changes in heat output, for example, loss of condenser cooling water.

Utility failure: Failure of the utility supplies to processing plant will result in emergency conditions with potential for overpressure of the process equipment. Utility failure events include electric power failure, cooling water failure, steam supply failure, instrument air or instrument power system failure, and the like.

Electric power failure normally causes failure of operation of the electrical drive equipment. The failure of electrical drive equipment such as electric pump, air cooler fan drive will cause the reflux to a distillation column lost and lead to the overpressure at the overhead drum. Cooling water failure occurs when there is no cooling water supply to cooler or condenser. It will cause immediate loss of the reflux to a distillation column and vapor produced from the bottom of the column accumulated at overhead drum will lead to overpressure. Failure of control system such as loss of supply of instrument air to control valve will cause control loop interrupted and lead to overpressure in process vessel. To prevent instrument air supply failure multiple air compressors with different drivers and automatic cut-in of the spare machine requires properly located pressure relief valve.

Check valve failure: A check valve is normally located at a pump outlet. Malfunction of the check valve can lead to overpressure in the vessel. When a fluid is pumped into a process system that contains gas or vapor at significantly higher pressures than the design rating of equipment upstream of the pump, failure of the check valve from this system will cause reversal of the liquid flow back to pump. When the liquid has been displaced into a suction system and high pressure fluid enters, serious overpressure will result.

Thermal expansion or contraction: For example, liquid density changes in a pipeline. If isolation of a process line on the cold side of an exchanger can result in excess pressure due to heat input from the warm side, then the line or cold side of the exchanger should be protected by a relief valve. If any equipment item or line can be isolated while full of liquid, a relief valve should be provided for thermal expansion of the contained liquid. Low process temperatures, solar radiation, or changes in atmospheric temperature can necessitate thermal protection. Flashing across the relief valve needs to be considered. Tube rupture in a heat exchanger involving high pressure fluid on tube side. Chemical reaction, for example, runaway reactions, operator error.

Overfilling of tanks: Overfilling process vessels and tanks has been one of the causes of a number of serious accidents in process industry. A spill of flammable material such as gasoline can form a dense flammable vapor cloud that can grow and spread at ground level until it finds an ignition source which can cause explosions. In many overflow incidents there has been failure of level instrumentation and high level alarms.

Examples: Control valve on nitric acid feed line to a batch reactor is stuck open, resulting overfilling of the vessel. Steam regulator to jacket fails, leading to overpressurization of the vessel. Failure of coolant system to a reactor leading to reaction runways.

Pressure deviations can, not only lead to overpressure or under-pressure, but also to changes to flow and level.

Some causes of pressure deviations in LNG or LPG processes: Composition change, overfilling of storage vessels, power failure, loss of cooling or refrigeration, water ingress, flash vaporization, instrument air failure, control valve or control system failure, human error, abnormal heat input due to malfunctioning of pump bearings, recirculation, etc., heat exchanger tube rupture or other equipment failure, blocked outlets, relief system inadequacies due to thermal changes, fire exposure. Table 4.1 gives a summary of typical reasons for pressure deviations in the operation of a process plant.

Table 4.1 Summary of typical reasons for pressure deviations

Thermal expansion and contraction in liquid-filled equipment and pipe work with isolation values closed. When liquid is blocked in a vessel or pipeline, external heat input can cause liquid temperature, and hence volume, to rise. This can be caused by the following: liquid that is blocked in a pipeline and is being heated, the cold side of a heat exchanger being filled while the hot side is flowing, or a filled vessel at ambient temperature that is being heated by direct solar radiation. PRVs used in these cases can be easily analyzed and sized
Abnormal heat input—This failure can be caused by the supply of heating medium, such as fuel oil or fuel gas to a fired heater, being increased; heat transfer occuring in a new and clean heat exchanger after revamp; control valve for the fuel supply failing to fully open; or supply pressure of the heating steam being changed from normal range to maximum pressure. As a general rule, when sizing a PRV, maximum heat-duty assumed for the abnormal case should be no more than 125 percent of normal heat duty.
Abnormal vapor input—Abnormal vapor input can be caused by the failure of the upstream control valve to fully open, or upstream-relieving or inadvertent valve opening. The required relieving capacity must be equal to or greater than the amount of the vapor accumulation expected under the relieving conditions.
Loss of absorbent flow—When gas removal by absorbent is more than 25 percent of the total inlet-vapor flow, an interruption of absorbent flow could cause pressure to rise in the absorber. The PRV should be sized base on the net accumulation of the vapor at the relieving conditions.

(*Continued*)

Table 4.1 (Continued)

Entrance of volatile materials—The entrance of a volatile liquid, such as water or light hydrocarbons into hot oil during a process upset, can cause instantaneous phase expansion. Instead of relying on PRVs, processes should be properly designed with the use of double block valves, the avoidance of water-collecting pockets and use of steam condensate traps and bleeds on water connections.
Runaway reactions—Runaway reactions tend to accelerate with rising temperature; extremely high volumes of non-condensable with high energy can cause the internal pressure of a vessel or pipeline to rise rapidly. PRVs may not provide sufficient relief, so vapor depressurizing systems, rupture disks and emergency vents are preferable.
Exchanger tube rupture—Required relief capacity should be greater than the vapor generated because of heat build-up in the system.
Accumulation of non-condensables—Accumulation can result from blocking of the normal non-condensable vent or accumulation in the pocket of a piping configuration or equipment. Because this can result in a loss of cooling duty, PRV analysis should be handled the same way.
Constant displacement pumps feeding a vessel with outlets blocked off.
Heat addition from sun/fire exposure— Blockages due to fouling, carbon deposits in furnace tubes, migration of crumbled packings in distillation/absorption equipment, freezing in vent lines, etc. The closure of a block valve on the outlet of a pressure vessel can cause the vessel's internal pressure to exceed its maximum allowable working pressure if the source pressure exceeds the vessel design pressure. Blocked outlets can be caused by control valve failure, inadvertent valve operation, instrument-air or power failure, and other factors. A PRV must have sufficient capacity to pass a fluid flow rate that is equivalent to the difference between those of the incoming fluids and the outgoing fluids. Utility failures can include general power failure, partial power failure, loss of instrument air, loss of cooling water, loss of steam, and loss of fuel gas or fuel oil. For these cases, a flare header should be designed and sized based on the maximum relief load that could result from a potential utility failure. Cooling-duty losses can include the following: loss of quench stream, air-cooled exchanger failure, loss of cold feed and loss of reflux. Relieving capacity should be calculated by performing a heat balance on the system, based on the loss of the condensing duty. Failure of cooling water pump to a condenser.
Upstream relieving—When an upstream vessel is relieving by discharge fluid to a downstream vessel, the downstream vessel should be designed to handle the pressure and volume of the incoming stream without overpressurizing. If the upstream vessel does not have adequate relief capacity, the downstream vessel should have a PRV of its own. When two vessels are connected by an open path and the first has its own PRV and discharges to a flare header, the second will experience the impact from the relieving pressure of the first vessel and should be analyzed accordingly.

(*Continued*)

Table 4.1 (Continued)

Process control failure—This situation refers to the failure of process controllers, such as programmable logic controllers and distributed control systems. The potential impact of failure of every control loop should be analyzed, as well as the impact if one loop fails but all others remain active. As a general rule, the required relief capacity must be greater than the vapor generated because of heat buildup in the system.
Valve malfunction—Check valve malfunction results in backflow, which can be from 5 to 25 percent of the normal flowrate. Required relief capacity should be based on this.
Inadvertent valve operation results in a valve position that is opposite from normal operating conditions, which is largely caused by human error and can be avoided by careful operation.
Control valve failure to open or close is caused by electronic- or mechanical signal failure. This typically will affect just one valve at a time and should be analyzed on a case-by-case basis.
Contact between hot and cold material and hot oil and water.
Premature admission of cold liquids into a hot vessel.
Admission of water into a vessel containing highly miscible vapors such as NH_3.
Freezing in vent lines.

Table 4.2 gives a summary of typical effects of pressure in the operation of a process plant.

Table 4.2 Summary of typical effects of pressure in the operation of a process plant

High pressure
Leakage and spillage
Rocketing of gas cylinders
Whipping of unsecured pressure hoses
Loss of lubrication
Loss of pressure to control systems
Contamination/formation of flammable/explosive mixtures
Entry of compressed air/gases into human blood stream
Cuts in skin, when exposed to leaking gas jets
Boiler/pressure vessel/pipeline explosions
Low pressure
Collapse of atmospheric storage tanks
Vaporization of liquids leading to formation of flammable mixtures
Ingression of air/contaminants into low pressure enclosures leading to contamination/ignition → fire → explosions
In-operation of pressure-actuated controls

4.3 Flow Deviations

Flow deviations include high, low, zero, reverse, and fluctuating flows.

Flow deviations can cause pressure, temperature, and level changes.

Causes of no flow include lack of feed material, lack of pressure difference, equipment failures, vapor lock, gassing up of pumps, pump failure, pipe failure, leakage, and blockage. Blockages can result from fouling deposits, freezing, solidification, polymerization, contamination, and the like.

Loss of flow in a fired heater: Loss of flow occurs when a series of equipment failures interrupts the flow of fluid to a heater. A pump motor loss, a coupling failure, a system pressure control valve failure or a blinded full flow filter might cause the initial failure. The second failure then occurs when fouling, burn-out or poor location causes the high temperature cut off device to miss the sudden temperature increase. As the burner or other heating element continues to impart energy into the now stagnant fluid, the temperature increases rapidly beyond SIT. If a crack develops in the heater coil or the piping connected to the heater, hot fluid is discharged into the hot atmosphere, where the fluid spontaneously ignites.

There have been several incidents involving softening and failure of heater elements due to loss of flow through the heater tubes. Misjudgment by the operators relying on temperature readings led to burn out of the tubes, causing enormous losses in terms of equipment and interruption of production.

To avoid incidents resulting from loss of flow, low flow shut-down should be included in the burner safety interlock.

Flow detectors that are immersed in the fluid are not recommended because they might fail in the open position. Pressure sensors have proved to be the most reliable for long-term service. To provide effective indication of a no-flow situation, plants can install pressure sensors across a fixed restriction such as an orifice plate or the heater itself to measure pressure drop, or as high and low discharge pump pressure monitors.

Serious fires caused by cracked heater tubes are relatively rare, but can occur. Cracks are formed by excessive thermal cycling or near hot spots that develop from internal fouling or flame impingement.

Leaking fluid will burn off immediately while the heater is operating. However, when the system is not in operation, fluid will continue to leak into the combustion chamber as a result of available head pressure from the expansion tank and overhead piping. In the most serious cases, fluid forms in a large pool inside the heater during a prolonged shut-down. When the heater is restarted, the entire pool ignites and destroys the heater.

Flame impingement will cause severe thermal cracking of the fluid that can be detected by routine fluid analysis. Heater tube fouling often is caused by deposits that result from fluid oxidation. The reaction of the hot fluid and air forms tars and sludge that coat surfaces and reduce heat transfer.

These deposits could create heater hot spots that ultimately cause cracks.

4.4 Effects of Leakages/Releases

Material contamination may degrade purity of a product. For example, oil leaking into gasoline may affect its quality.

Colored liquids/oils into food products and textiles may have damaging effects.

Loss of system fluids: For example, hydraulic actuating devices are dependant on adequate supply of fluid.

Loss of system pressure: Some pressurized systems may not be able to maintain desired pressure for their operation. For example, pneumatic/vacuum systems fail or become less effective if leaks are present.

Loss of stores: Leakage of containers may result in loss of material required for other operations/economic purposes.

Lubricant leakages will result in loss of lubrication.

Moisture leakage into air results in increase in humidity in limited atmospheres affecting effectiveness of personnel/equipment.

Leakage of cold water onto hot surfaces may cause the surfaces contract/cracks, for example, surfaces such as glass used for vacuum tubes are especially susceptible.

Leakage of low-temperature fluids onto (cold) surfaces may cause freezing/blockages.

Water or other conductive fluid contaminants leaking into electrical conductors or onto live electrical equipment may give rise to short circuits and increased shock hazards.

Leakages of flammables can lead to fires and explosions. Leakages are responsible for major disasters, as happened, for example, at Bhopal, India with leakage of methyl isocyanate. There have been several incidents which led to disasters. Leak of radioactive material at Chernobyl nuclear plant is another example of a disaster.

Leakage in a high pressure multilayer ammonia separation vessel in an ammonia manufacturing facility led to an explosion with enormous damage to the plant and economic losses in terms of production of ammonia and downstream urea in a North African industrial complex.

Leakages are usually reported especially during start-up process of a process plant. The principal reason for such leakages is that the design intent often differs from the actual conditions prevailing during start-up.

Major leaks typically involve mechanical failure of components, such as a flange joint, an expansion joint, flexible hose, pump seal, or rotary union, that allows a significant quantity of fluid to leak onto an ignition source.

To prevent leaks, plants should allow expansion joints and flexible hoses to move along their axes, never sideways. Isolation and bleed valves should be installed in the piping for each piece of equipment to make maintenance easy without requiring draining of the whole system. Welded connections (instead of threaded connections) should be used as much as possible. Valves may be installed with their stems sideways so any leaks run down the stem and away from the piping.

Releases of high pressure fluids such as LPG have taken place several times leading to explosions and fires.

4.5 Hazards of Temperature

Temperature effects on personnel can cause climatic stress, dehydration, heat stroke, heat cramps, fainting, high or low temperature burns, frostbite, etc.

Effects of high temperatures on materials:

- Decreased viscosity of lubricants resulting in increased wear.
- Gelling of oils/lubricants.
- Liquid expansion and overflow.
- Condensation of moisture and other vapors.
- Peeling of coatings on surfaces with resultant exposure to corrosion.
- Weakening of soldered seams.
- Loss of ductility of metals and increased brittleness. Accidents took place due to brittle failure of structures and bridges, break-up of ships, cracked gas pipelines, and heavy equipment.
- Loss of flexibility of plastics.
- Electrical devices might loose reliability.
- Premature operation of thermally activated devices.
- Opening/closing of electrical circuits.

Electrical resistivity of metals increases with temperature, while the resistivity of semiconductors decreases with increasing temperature.

Susceptibility to fires will increase with increased temperature. At higher temperatures, oily rags may be ignited.

Radiation from flames, molten metals and other systems operating over 500°C can cause charring, decomposition, etc. Charring can also result from exposure to a steam line, hot electronic equipment or overheated bearing.

Flammable liquid spills are more hazardous in warm and hot weather due to increased vaporization rates resulting larger volumes of fuel–air mixtures and less powerful ignition sources might be sufficient to ignite.

Reactivity and corrosivity of materials will increase with increased temperatures. Decomposition reactions can result at higher temperatures. Hydraulic fluids might decompose, generating contaminants at higher temperatures resulting in plugging orifices and other flow restrictions and lead to higher pressures in confined spaces.

Explosive reactions can lead to fires in welding operations involving inadequately cleaned tanks.

Strength of materials might reduce at higher temperatures. Expansion of materials might result in dimension changes, loosening/binding of parts, deformations, damage and failures and collapse of welded structures.

Effects of low temperatures on materials: These include the following:

- Freezing and bursting of water lines.
- Restricted flow and immobilization of moving parts.
- Contraction effects leading to cracks in metals, jamming/loosening of moving parts, etc.
- Delayed ignition in furnaces, leading accumulation of fuel causing explosions on ignition.

4.6 Cryogenic Fluids

Each cryogenic liquid has its own specific properties but most cryogenic liquids can be placed into one of three groups:

Inert gases: Inert gases do not react chemically to any great extent. They do not burn or support combustion. Examples of this group are nitrogen, helium, neon, argon and krypton.

Flammable gases: Some cryogenic liquids produce a gas that can burn in air. The most common examples are hydrogen, methane and liquefied natural gas.

LNG is cold, boiling at −161°C, and its vapors are flammable. Special low temperature metals and materials are used during liquefaction, transfer and storage. LNG is usually stored as a liquid at atmospheric pressure in special steel inner tanks with outer concrete tanks with no bottom connections. Pressurized storage and transport is not used so the dangers of catastrophic pressure vessel failure, such as boiling liquid expanding vapor explosions (BLEVES), are avoided. Natural gas is less reactive than other fuels and potential plant explosions (deflagrations) are less severe than with, say, hydrogen, propane, or ethylene.

An accidental release of LNG results in a variety of consequences. Outflow can lead to spreading, boiling, evaporation and dispersion of flammable vapors in the absence of ignition. Delayed ignition might lead to explosion if the vapors disperse into congested or confined areas, followed by flashback to the site of the original release and a sustained pool fire, depending on the pool area and release rate. Early ignition would create a pool fire but no vapor cloud explosion.

Oxygen: Many materials considered as noncombustible can burn in the presence of liquid oxygen. Organic materials can react explosively with liquid oxygen. The hazards and handling precautions of liquid oxygen must therefore be considered separately from other cryogenic liquids.

All cryogenic fluids have two properties in common, namely, they are extremely cold, and small amounts of liquid can expand into very large volumes of gas. They can produce a large amount of vapor when heated to room temperature. Explosions can occur from sudden overpressurization.

Heat flux into a cryogenic system from the environment will vaporize the liquid and potentially cause pressure build-up in cryogenic containment vessels and transfer lines. Even a small temperature rise for a cryogenic fluid can result in sharp increase in vaporization and pressure. Adequate pressure relief must be provided to all parts of a system to prevent an explosion.

The vapors and gases released from cryogenic liquids also remain very cold. They often condense the moisture in air, creating a highly visible fog. In poorly insulated containers, some cryogenic liquids actually condense the surrounding air, forming a liquid air mixture.

Liquid helium is cold enough to solidify atmospheric air. Only helium should be introduced or allowed to enter a liquid helium Dewar. Precautions should be taken to prevent air from back-diffusing into the helium.

Oxygen liquefies at a higher temperature than liquid helium or nitrogen. Consequently, oxygen can condense on the exterior of cryogenic containers or transfer lines. An explosive situation may result if this oxygen-rich liquid is allowed to soak insulating or other materials that are not compatible with oxygen.

Some oils can form an explosive mixture when combined with liquid oxygen. Surfaces where there is a possibility of liquid oxygen condensation must be thoroughly cleaned and degreased.

Within a cryogenic system, adequate relief valves must be installed for all vacuum and cryogenic vessels, and also for any cryogenic lines that have the potential to trap cryogenic fluids. Relief valves must be sized so that under worst-case failure conditions, the maximum pressure reached in any vessel is below the maximum safe working pressure (MSWP) for the vessel. Each system must be analyzed in detail to properly determine worst case failure modes and the required relief valve sized.

There are three groups of health hazards associated with cryogenic liquids: extreme cold, asphyxiation, and toxicity.

Extreme cold effects: Cryogenic liquids and their associated cold vapors and gases can produce effects on the skin similar to a thermal burn. Brief exposures that would not affect skin on the face or hands can damage delicate tissues such as the eyes. Prolonged exposure of the skin or contact with cold surfaces can cause frostbite. The skin appears waxy yellow. There is no initial pain, but there is intense pain when frozen tissue thaws. Unprotected skin can stick to metal that is cooled by cryogenic liquids. The skin can then tear when pulled away. Even nonmetallic materials are dangerous to touch at low temperatures. Prolonged breathing of extremely cold air may damage the lungs.

Asphyxiation: When cryogenic liquids form a gas, the gas is very cold and usually heavier than air. This cold, heavy gas does not disperse very well and can accumulate near the floor. Even if the gas is nontoxic, it displaces air. When there is not enough air or oxygen, asphyxiation and death can occur. Oxygen deficiency is a serious hazard in enclosed or confined spaces.

Toxic hazards: Each gas can cause specific health effects. For example, liquid carbon monoxide can release large quantities of carbon monoxide gas, which can cause death almost immediately. Toxic hazards for specific cryogenic fluids can be found in their material safety data sheets.

Some materials may become brittle at low temperatures and fail on over-pressurization or mechanical shock. Only suitable materials may be used to store or transfer liquid cryogens.

Table 4.3 gives a summary of reasons for temperature deviations.

Table 4.3 Typical reasons for temperature changes

Changes in heat input/output, e.g., loss of fuel/loss of cooling
Changes in heat transfer, e.g., fouling of heat exchangers
Heat generation, e.g., runaway reactions
Changes in flow, e.g., to a reactor/heat exchanger/furnace tubes, etc
Changes in pressure

(*Continued*)

Table 4.3 (Continued)

Rotating machinery in distress, e.g., due to mis alignment/over speed/inadequate lube flows, etc. → hot spots
Fire exposure.
Errors in charging rate/sequence to reactors
Catalyst hot spots
Mal distribution of reactants to a reactor
Inadequate mixing

Table 4.4 gives summary of typical effects of temperature.

Table 4.4 Summary of typical effects of temperature

High temperatures
Vaporization of volatiles
Increased reaction rates. General rule is that an increase in temperature by 10°C doubles the reaction rate
Runaway reactions
Increased corrosion rates
Increased pressures in vessels/enclosures
Loss of strength of materials of construction. High temperature environments can cause organic insulating materials to become brittle
Softening and failure of furnace tubes
Decomposition/charring of organics/plastic components like cable insulation, seals, etc
Loss of lubrication due to decreased viscosity of lubes
Dimensional changes due to thermal expansion. For example, clearances in a pump are critical to its operation and maximum efficiency. Heat causes the metal parts to expand, decreasing the internal clearances. Extra clearances must be added to ensure that the pump does not seize due to thermal expansion
Radiation and hot surface contact burns
Loss of worker efficiency due to exposure to hot weather
Low temperatures
Blockages due to thickening/solidification/freezing of liquids
Brittle failure of materials of construction
Significantly large contraction levels can result when materials are cooled to cryogenic temperatures. This can lead to development of interferences or gaps due to dissimilar materials, changes in alignments, strain and possible failures, etc.
Jamming/increased friction in rotating parts due to increased viscosity of lubes
Condensation of vapors in lines resulting hammer/vibration and decrease in pressures
Low temperature burns/frost bites

4.7 Vibration and Noise

Technically, vibration occurs in response to excitation forces acting on an operating machinery system. Vibration is often an indication of construction-related defects of the machine or machine parts, assembly problems, improperly installed systems, electromagnetic forces, and other factors.

Basics of sound levels:

Sound → A physical phenomenon consisting of minute vibrations, which can be sensed by the human ear by traveling through a medium such as air or water.

Noise → An unwanted sound that disturbs our activities and infringes on our enjoyment of *peace and quiet*.

Decibel (dB) → The logarithmic unit of measure for sound. Decibels are logarithmic, not linear. For example, two sources with equal sound levels increase sound level by 3 dB. 90 dB + 90 dB ≠ 180 dB, but = 93 dB.

The perception and measurement of sound involves two basic physical characteristics:

Intensity → A measure of the acoustic energy of the sound vibrations, expressed in terms of sound pressure (Volume).

Frequency → Number of times per second the air vibrates or oscillates (pitch). Noise levels of some commonly used equipment are illustrated in Table 4.5.

Table 4.5 Noise levels of some commonly used equipment

Equipment	Noise level (dB)
Lawn mover	90
Tractor	95–105
Circular saw	90–100
Jackhammer	112
Gun shot	140
Chain saw	110

Examples of noise sources:

Mechanical noise: Engine block vibration, road tire interaction, drilling, cutting and grinding, pulverizing, electric motors, bearings, gears, conveyor systems, and the like.

Flow noise: Ventilation systems, engine cooling systems, water sprays, dust scrubbers, engine intake and exhaust systems, pumps, compressors, blowers, dryers, high speed mixers, and the like.

Effects: Loss of hearing sensitivity, annoyance, distraction, contributions to other disorders, interference with other sounds, and ruptured ear drums.

Loss of hearing: Impairment that interferes with understanding of speech in sentence form (as opposed to use of test words). The frequency range for human hearing is 20 Hz to 20 kHz. Most important frequencies for speech understanding are 500–2,000 Hz. A young person with normal hearing can detect sounds in the range of 16–20,000 Hz. If noise levels are maintained within 80 dB, there will be no damage potential. Fifty percent of those exposed to 95 dB suffer hearing loss. Almost everyone will suffer hearing loss at 105 dB level exposures. Hearing protection is required for noises above 115 dB. OSHA defines 85 dB as the average noise level at which precautionary measures must be implemented by industry. It is not uncommon for noise levels in close proximity to equipment at a chemical plant to reach 100 dB or higher. Noise levels above 140 decibels will cause immediate hearing loss.

It is known that exposures to certain compounds, such as those containing lead, toluene, n-butyl alcohol, and carbon monoxide, have been linked to increased hearing loss. These exposures also combine synergistically with noise to cause increased hearing loss.

Impulsive noise: Sudden noises, for example, due to an explosion, riffle shot, impact of heavy hammer, etc. At such conditions most of the mechanisms of the ear are incapable of providing self-protection. Under shock wave of an explosion, pressures developed may be so great that ear drums might rupture. A very loud impulsive sound can cause a ringing in the ear and an immediate loss of hearing sensitivity. If there are no further similar exposures, hearing will return to normal. Loud impulsive noises can cause tightening of blood vessels which reduces blood flow. In addition, it will cause release of adrenalin into blood by the body mechanisms as a defensive measure. Impulsive noises can result in fatigues and headaches. Personal protection requires not more than 140 dB of impulsive noise levels.

Annoyance: Noise normally annoys people. Types and levels of noise for annoyance vary from person to person, and it can lead to errors in work and accidents. Examples are a slow water drip in the silence of night, an unexpected impulsive noise, or sudden impact of sonic boom which startles a person. Some types of annoying noises can also distract persons from their normal activities. Other types of distractive noises include music broadcasts on loud speakers, telephone ringing, etc. Distraction of persons engaged in hazardous work may lead to accidents. Conversation with the driver in a moving bus can distract his attention.

Other noise effects: Nervousness, psychosomatic illnesses and inability to relax, etc.

Noise effects on equipment: Noise induces fatigue in materials which can lead to failure of rotating parts, failure of steam lines, pressure vessels, containers of hazardous liquids and gases, and other stressed equipment. Vibration and mechanical shock can result in a misalignment of components or loosen fixings and may cause loss of electrical contact integrity. Loosening of bolts and fasteners, breaking of lead wires, filaments, crazing and flaking of finishes, chattering of spring type contacts, valves and pointers giving false readings, loss of calibration of monitoring and measuring instruments, generation of static electricity between plastic and nonconducting surfaces are other examples.

Also metal fatigue in sensor components and cold working of wires may occur. Misalignment accelerates wear in moving parts; loose electrical contacts may lead to heat-related degradation; damage to electrical connections and displacement of insulation and connections will lead to electrical continuity/insulation problems.

Measures to reduce noise levels: Selection of equipment with low vibration and noise, for example, use of presses instead of drop hammers. Selection and operation of low speed rotating/reciprocating equipment such as pumps, fans, motors, presses, etc.

For example, large, slow moving machines may be used instead of small fast moving one with the same capacity, low fluid velocities in ducts and in liquid jets, avoiding sudden direction changes in piping and ducts, avoiding quick opening valves in liquid systems and taking other hammer-reducing measures. Care should be taken on foundations to avoid/reduce vibrations of equipment and use of tight foundation bolts, firm securing of piping to prevent rattling and the like. Vibrating parts on machinery and equipment are a common noise source. Vibration can be controlled by mounting the machinery on special rubber pads or springs, or with noise damping rubber joints between parts within the machinery. Vibration damping material can also be attached or sprayed on flat vibrating surfaces to reduce noise. Use dynamic dampers, rubber/plastic bumpers, noise-absorbing linings on air ducts and muffles on openings through which air flows, flexible mountings/couplings, resilient flooring, etc., to ensure low noise levels and failure-free operations. Using mufflers on engines is a well known method of reducing noise. Special silencers are also available for compressed air equipment and fans. A stationery noise source can be enclosed in an insulated box, booth or room. The enclosure usually has two layers—an outer layer made of heavy stiff material such as wood, metal, or concrete and an inner noise-absorbing foam layer. Some noise sources must be easy to access and cannot be fully enclosed. A flat barrier between the noise source and employees will give a small reduction in noise level. A partial enclosure will be somewhat more effective. Placing absorbing material on nearby reflective walls or ceilings also can help reduce noise levels. Noise producing operations may be isolated from others. Compressor houses in a fertilizer plant are an example. Periodic maintenance is required to minimize vibration and noise. Existing equipment and machinery will often become noisier over time if one neglects routine maintenance. Tightening nuts and bolts, adjusting engines, and oiling or greasing moving parts can reduce noise levels, sometimes dramatically.

Any hearing conservation program includes noise monitoring with sound meters in different areas of the industry or with personal dosimeters which record noise exposures of individuals with time, audiometric testing of employees every six month or annual intervals, providing the employees with hearing protective devices, with mandatory use, whenever the average noise levels exceed 85 dB, conducting awareness training programs on effects of noise, are some of the measures industry must take up. Table 4.6 gives a summary of operating deviations.

Table 4.6 Types of operating deviations

Major deviations	Pressure, temperature, flow, level
Other operating deviations	Expansion, contraction, cavitation, hammer, mechanical stress, vibration, noise, cyclic effects, loading, fouling, environmental factors, corrosion, erosion
Localized effects	Mixing, maldistribution, separation, surging, siphoning, stagnation, blockage, vortex formation, adhesion, lubrication faults, stress bearings, overheating, hot spots, sedimentation

(*Continued*)

Table 4.6 (Continued)

Loss of containment	Leakage, spillage, venting
Time effects	Contact time, control lag, sequence
Plant operations	Planned changes in operations, changes in linked plants, demand change, commissioning, start-up, shut-down, sudden changes in feed rate or quality, maintenance, inspection, utility failures such as loss of power, steam, cooling water, boiler feed water, or instrument air, equipment failure, supply failure, liquid level control malfunction, control disturbance, operator disturbance, human error, loss of communication, climatic effects, fire/explosion, terrorist attack. Emergency shut-downs and subsequent start-ups are among the greatest threats to plant safety. They divert attention from situations that could present real danger, and result in unnecessary shut-downs and re-starts
Typical errors	Wrong routing, involving failure to ensure that correct valves are in plant start-up: open and other valves closed, drain valves left open, resulting in spillage, sequential errors—for example, water added to acid instead of acid to water, overpressurizing system with valves closed, failure to complete purging cycle before admitting fuel–air mixtures, mixing cold and hot fluids leading to rapid flashing or excessive vaporization, admission of steam into a cold line full of condensate, resulting in water hammer, back-flow of material from high pressure to low pressure system, introduction of water into hot oil systems, imposing tremendous overloads on equipment*, mixing of air and combustibles inside vessels, setting wrong values for operating parameters such as agitator speed, reflux, jacket temperature, errors in furnace light-up procedures, etc.
Constructional defects	Plant incomplete, inadequately supported, not aligned, not level, not tight, not clean, incorrect materials of construction, faulty fabrication, defective components. Use of off-specification materials of construction for valves, fittings, flange bolts and other items of equipment. Use of odd-sized bolts, inadequate foundations and faulty supports, improper alignments and failure to maintain proper line slopes, low point drains and high point vents not fitted where necessary, drain lines with discharge on paved areas, slip plates not removed and spectacle plates not turned, faulty joints/use of incorrect jointing material, failure to tighten hot joints, use of pipe gaskets with no central holes, installation of check valves, rupture discs and other items the wrong way round, block valves inaccessible/installed spindle down, paint on valve stems and metal hoses, wrong connections, incorrect fabrication-weld defects and improper treatment, hardening, surface finish and tolerances, plant not clean/items left inside equipment, introduction of impurities through chemical cleaning, insulation missing damaged, loose, etc. inadequate inspection and testing, inadequate communications and coordination between contractors, engineering and design groups, and production department

Chemical reactions	Type and extent, excessive reaction rate, initiation of side reactions. unintended reactions, contaminants, abnormal reaction conditions, for example, overpressure, overtemperature, segregation of reactants, runaway reaction, catalyst problems like activity loss, fouling, poisoning, disintegration, reaction and regeneration issues, addition of wrong material or wrong quantities, addition of materials in incorrect sequence, failure to add material, for example, inhibitor, at correct stage, spillage of material, failure of coolant, refrigerant, or other utilities, failure to actuate agitation at the proper time, failure to actuate agitation at the proper time. power failure, affecting agitator, pumps, instruments, stirrer failure, mechanical or electrical, instrument failure, pressure, flow, temperature, level or a reaction parameter, for example, concentration
Material characteristics	Physical properties, phase, thermal and electrical conductivity, miscibility, particle size, moisture content, etc.
Sampling hazards	Exposures of gases, vapors and dust while collecting samples, approaching odd locations, splashes and spillages while collecting samples, exposures due to breaking of sight glasses and glass level indicators, dip gauging of flammable liquids, and dip gauging of corrosive liquids

*Note: Water has great potential to generate large volumes of vapor compared to hydrocarbons. Flashing of water is not a problem as long as the heaviest hydrocarbons are in the boiling range of 90–95°C. Serious problems arise with equipment handling boiling hydrocarbons in the boiling range of 250–550°C. Common example of crude distillation units blowing out column trays during start-ups. With flashing liquids in vacuum distillation columns damaging consequences are possible.

4.8 Human Errors

Many major accidents have been attributed to human error as a primary cause. Statistics show that in the chemical process industries accidents attributed, at least in part, to human error range between 60 and 90 percent and in the petrochemical industry, for example, oil refineries where automation is very high, human error accounts up to 50 percent. It is evident that the relative number of accidents due to human errors is on the rise while those due to technical failures are decreasing. Systems are most vulnerable to human error during manual inspections, plant start-up and shut-down, and after any modification to the original design. Simulation techniques, work flow documentation and mobile solutions all contribute to reducing human error.

Human error is defined as *departure from acceptable or desirable practice on the part of an individual that can result in unacceptable or undesirable results*. The process-related activities where errors have the most influence include design, engineering, and specifying components, commissioning, start-up and shut-down, plant operations, worker fatigue, providing and sustaining safeguards, inspection, maintenance, and repair, troubleshooting, plant modifications, poor communication, and management system weaknesses.

Human factor considerations should be incorporated in design. An increase in the difficulty of the job of an operator can lead to errors and short-cuts. For example if the operator is required to read instruments located in areas difficult to access, the operator is likely to skip access to such inconvenient locations. Feedback from operators and maintenance personnel is a useful tool for managements to improve operator performance.

The US Chemical Safety Board (CSB) cited human factor deficiencies as one of the main contributors of the catastrophic accident at the BP Texas City Refinery in March 2005. There have been several incidents involving human factors as the cause of their origin.

Typical complaints from operators

Inadequate precision of temporal information (e.g. lack of true alarm order), excessive nuisance alarms, inadequate anticipation of process disturbances, lack of real-time, root-cause analysis (symptom-based alarming), lack of distinctions between instrument failures and true process deviations, lack of adequate tools to measure, track, and access past records of abnormal situations and the like.

There are many ways to classify human error. In active errors, the mistake and its consequences are apparent immediately. In contrast, latent errors require time, conditions or another action before becoming evident.

Errors also can be random or involve human factors stemming from procedures, management practices, equipment design, or some other trigger.

People-Oriented Errors

Slips, lapses or errors in execution: Slips are actions that occur despite best intentions. They can be caused *internally* by short-term lack of attention or *externally* by distractions. Examples would include reversing numbers or letters, or mis-spelling words one knows how to spell. Slips tend to recur on routine tasks.

Capture errors: These errors occur when one goes on *autopilot*, substituting a frequently performed activity for a desired one. For example, one misses a highway exit on the way somewhere after work, taking the route home instead.

Identification errors: These occur when something is identified incorrectly. The current downsizing trend has increased the potential for this type of error, due to increased reliance on equipment, piping and instrument/electrical tagging and identification.

Impossible tasks: Some assigned tasks are unreasonably complex, impractical or even impossible to do. As a result, workers might take short-cuts or develop alternative methods that can lead to error. In general, the more complex an action, the more likely an error will be made while carrying it out. Consider a control system designed so that an abnormal condition triggers hundreds or even thousands of alarms, overwhelming operators. Drawings and distributed control system (DCS) screens that are too busy increase the potential for information overload and error.

Input or mis-perception errors: With errors of this type, the information needed to make a decision or perform a task might be misunderstood, perhaps because it has been presented in an overly complex or misleading way. Overly complex instrumentation systems are a source of this type of error. In other cases, data might be missing, forcing users to make the wrong assumptions.

Lack of knowledge: This type of error occurs when someone fails to get appropriate information from other people or departments. In operations, it could be a lack of situational awareness during abnormal conditions. Lack of knowledge leads to assumptions that are the mother of all problems.

Mindset: Mindset generally is a function of expectations and habits. All too often, people see what they expect to see, despite evidence to the contrary, particularly under high stress or time constraints. Equipment should be designed intuitively, with user habit in mind. Examples of error prone designs include a valve sequence that is not in a normal order (e.g. open valve 1, close valve 3, open valve 2, open valve 6, close valve 4, …), or, in countries in which the written word moves from left to right, a sequence that does not progress in that direction (e.g. pumps labeled C, B, and A from left to right rather than A, B, and C). Other problematic cases involve color coding in one section of the plant that does not match the scheme used in the rest of the plant.

Mindset can result from folklore, habit, faulty experience or rationalization of experience. It also can occur by applying habitual actions in the wrong situations. A number of accidents have occurred because operators did not believe their instruments.

Overmotivation or undermotivation: Over-motivation can come from being too zealous, (e.g. completing a job too quickly just to please a supervisor). Working too fast can lead to short-cuts and risk taking. High-pressure production environments with incentives, for example, can lead to these problems. Ironically, undermotivation stemming from boredom or lack of morale also can lead to short-cuts and risk taking. However, it is more likely to cause latent errors, discovered later by someone else.

Reasoning error: These errors occur when a person has the correct information to make a decision or take an action, but comes to the wrong conclusion. Lack of training and/or experience leads to this type of error.

Task assignment mismatches: These occur when workers simply are mismatched to the task at hand.

Situation-Oriented Errors

Environmental: Some errors can be caused by environment. Examples include poor location, insufficient work space, excessive vibration and noise, temperatures that are too high or too low, insufficient light, and too many distractions. Environmental conditions that can affect performance include these adverse environmental conditions can stress personnel, interfere with performance and increase the likelihood that they will commit errors while performing a task. Work conditions that require protective gear, such as confined space environments, or that require unusual physical postures, also can interfere with task performance, as may poor housekeeping.

Stress-related: Decision making under stress can lead to errors. Some sources indicate if a person is under high stress, the chances of error are as much as 50 percent. The stress might come from the decision or act, from the work environment, from other people or from outside work. High-pressure production environments, for example, can lead to operator uncertainty and stress when one of the decisions includes shutting down production. Fatigue, loss of effectiveness due to high humidity, high and low temperatures, obnoxious atmospheres. Extended working hours, contaminant entry into control rooms, hazardous material-containing equipment/storage vessels should be avoided. Life support equipment should be made handy.

Timing-related: Some errors are caused by too little or too much time. The less time a person has to make a decision or take an action, the more likely he or she is to make a mistake. Ironically, the opposite can also be true, although too little time tends to create errors of commission, and too much time yields errors of omission. Some sources indicate that if a person has too little time, the likelihood of their making error is as much as 50 percent.

System-Oriented Errors

Chain errors: Many errors are really a chain of events stemming from one root error. Often these result from blind acceptance of information from other sources such as a computer.

Procedural errors: Sometimes procedures are not appropriate for the given task. Procedures that go against current norms also might lead to confusion and errors. Procedures that are too complex, too simple or misleading also can lead to errors. Failure to follow all the steps of a procedure or adding steps would be a form of this error.

Violations: Violations are intentional errors, defined as noncompliance with accepted norms. These occur when people feel that a procedure or action is troublesome or unnecessary, or that a task is unpleasant. In the worst cases, such violations can be made with malicious intent.

Production Errors

Errors in manufacture of critical components can make a product unsafe. Errors in assembly can lead to failures/cracks in piping connections resulting in leakages. Failures in electrical connections clean and dry can give rise to short-circuits. Corrosion, dents, rough finishes and dents will create stress concentrations that could result in structural failures under operational loads.

Maintenance and Repair Errors

Mistakes in reassembly, failure to lubricate moving parts of equipment, replacement of components when scheduled are common which can lead to hazardous conditions. Maintenance personnel are subject to greater hazards than operational personnel. For example, welding operations involving used equipment may lead to toxicity and fire hazards if process materials are not completely cleaned up before such welding. Similarly failure to deenergize high-voltage lines, depressurize equipment/lines before opening for maintenance are other examples.

Operational Errors

Procedural and control errors during operation may lead to hazardous problems. Activation of a circuit inadvertently, failure to close a valve/shut-off a pump are other examples. Procedural errors, especially during emergencies when personnel are particularly stressed, are critical. Examples of such errors include inaccurate settings, pressing wrong buttons, loss of control due to excessive speed, delay in operating controls, irritability of operators during stress conditions with loss of patience in fine adjustments and slamming controls violently.

Human Error in System Design

Failure to perform a required function, for example, to complete the sequence of operations due to lack of instructions/incorrectly written procedures, too lengthy and cumbersome procedures, etc.

Failure to recognize a hazardous condition requiring corrective action. Examples are warnings/cautions/explanations and training for their compliance.

Inadequate response to a contingency due to interference between personnel in the absence of clear-cut emergency duties and adequate gap between tasks. Inability to concentrate because of unsafe conditions, unguarded equipment/hot surfaces which lead to avoidance of work. Inadequacies in reading instruments due to their positioning, poor lighting, need to interpret readings, etc. Inadvertent activation of controls or activation in the wrong order. For critical functions, controls that cannot be activated due to, for example, when a person accidentally stumbles on them. Interlocks should be provided where sequences are critical.

Faulty instruments: Operator should notify faults immediately for rectification. Periodic calibration is necessary to rectify faulty operation.

Failure to note critical indications such as visual and audible warnings to attract attention. Vibrations and noise are often cause irritation, faulty instrument readings. Providing vibration isolators, ear plugs, and noise eliminators will be of help. Human errors are reflected in the instrument design process by mistakes, specification errors, failure to communicate, lack of competency and functional errors. Often, simple steps such as developing a checklist, systematic review processes and comprehensive training can help prevent these errors. However, the current downsizing trend has sometimes limited the opportunity to catch errors before they occur.

Mistakes: Probably the most common human errors in instrument designs are mistakes. Slips are the most typical type of mistakes, but mistakes also can be due to incompetence or problems with the design systems, leading to data, drawing, informational and change errors. Complex, detailed instrument system design can lead to errors. Design document review processes and self-checking methods can help. People tend to make the same errors when dealing with details or small matters, particularly if there are no major consequences (e.g. misspelling the same word or entering data incorrectly). Table 4.7 gives a summary of different types of human errors.

Table 4.7 Summary of different types of human errors

People-oriented errors
Slips (lapses and execution errors)
Capture errors
Identification errors
Impossible tasks
Input or misperception errors
Lack of knowledge
Over or undermotivation
Reasoning error
Task mismatches
Situation-oriented errors
Environmental
Stress

(*Continued*)

Table 4.7 (Continued)

Timing
System-oriented errors
Errors by others
Procedural
Violations
System design errors
Mistakes
Specification errors
Communication breakdown
Lack of competence
Functional errors
Common errors in instrument design
Errors in construction, operation, and maintenance
Incorrectly identified or tagged equipment
Equipment improperly installed in a hazardous area
Improperly calibrated or ranged equipment
Loose terminals
Improper grounding or shielding

Figure 4.2 illustrates types of human factors that can lead to accidents.

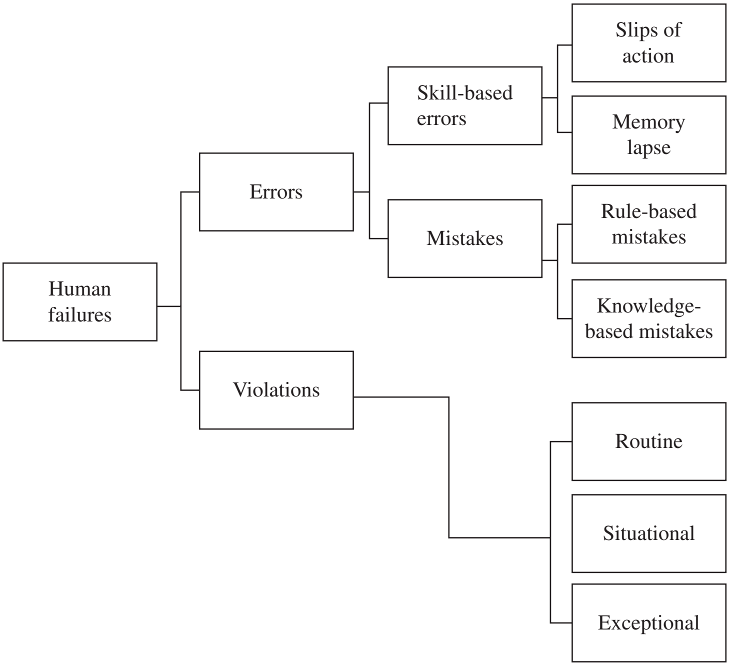


Figure 4.2 Types of human failures

Source: HSG48, Reducing Error and Influencing Behavior, p. 12 (HSE Books, 1999).

4.9 Ergonomics

Ergonomics is the science of designing the workplace environment to fit the user. Proper ergonomic design is necessary to prevent repetitive strain injuries, which can develop over time and can lead to long-term disability.

The International Ergonomics Association defines ergonomics as *the scientific discipline concerned with the understanding of interactions among humans and other elements of a system, and the profession that applies theory, principles, data and methods to design in order to optimize human well being and overall system performance*. Ergonomics is a science concerned with the *fit* between people and their work. It puts people first, taking account of their capabilities and limitations.

Ergonomics aims to make sure that tasks, equipment, information and the environment suit each worker. To assess the *fit* between a person and his work, ergonomists have to consider many aspects. These include the job being done and the demands on the worker, the equipment used (its size, shape, and how appropriate it is for the task), the information used (how it is presented, accessed, and changed), the physical environment (temperature, humidity, lighting, noise, and vibration), the social environment (such as teamwork and supportive management). Ergonomists consider all the physical aspects of a person, such as body size and shape, fitness and strength, posture, the senses, especially vision, hearing and touch, the stresses and strains on muscles, joints, nerves and the like.

Ergonomists also consider the psychological aspects of a person, such as mental abilities, personality, knowledge, experience.

Applying ergonomics to the workplace reduces the potential for accidents, reduces the potential for injury and ill health, improves performance and productivity. Ergonomics can reduce the likelihood of an accident. For example, in the design of control panels, consider the location of switches and buttons → switches that could be accidentally knocked on or off might start the wrong sequence of events that could lead to an accident. Expectations of signals and controls → most people interpret green to indicate a safe condition. If a green light is used to indicate a *warning or dangerous state* it may be ignored or overlooked.

Information overload: If a worker is given too much information he may become confused, make mistakes, or panic. In hazardous industries, incorrect decisions or mistaken actions have had catastrophic results.

Ergonomics can also reduce the potential for ill health at work, such as aches and pains of the wrists, shoulders and back. Consider the layout of controls and equipment; these should be positioned in relation to how they are used. Those used most often should be placed where they are easy to reach without the need for stooping, stretching or hunching.

Failure to observe ergonomic principles may have serious repercussions, not only for individuals, but whole organizations. Many well-known accidents might have been prevented if ergonomics had been considered in designing the jobs people did and the systems within which they worked.

Examples of some typical ergonomic problems in the workplace:

Display screen equipment:

- The screen is poorly positioned—it is too high/low/close/far from the worker, or is offset to one side.

- The mouse is placed too far away and requires stretching to use.
- Chairs are not properly adjusted to fit the person, forcing awkward and uncomfortable postures.

Understanding ergonomics at work:

- There is glare on the screen from overhead lights or windows, increasing the risk of eye strain.
- Hardware and/or software are not suitable for the task or the person using it, causing frustration and distress.
- Not enough breaks or changes of activity.

Manual handling:

- The load is too heavy and/or bulky, placing unreasonable demands on the person.
- The load has to be lifted from the floor and/or above the shoulders.
- The task involves frequent repetitive lifting.
- The task requires awkward postures, such as bending or twisting.
- The load cannot be gripped properly.
- The task is performed on uneven, wet, or sloping floor surfaces.
- The task is performed under time pressures and incorporates too few rest breaks.

Work-related stress:

- Work demands are too high or too low.
- The employees have little say in how they organize their work.
- Poor support from management and/or colleagues.
- Conflicting demands, for example, high productivity and quality.

Managing the working day:

- Insufficient recovery time between shifts.
- Poor scheduling of shifts.
- Juggling shifts with domestic responsibilities.
- Employees working excessive overtime.

Identifying ergonomic problems:

Talking to employees and seeking their views. Employees have important knowledge of the work they do, any problems they have, and their impact on health, safety, and performance.

Assessing the work system by asking questions such as:

Is the person in a comfortable position?

Does the person experience discomfort, including aches, pain, fatigue, or stress?

Is the equipment appropriate, easy to use and well maintained?

Is the employee satisfied with his working arrangements?

Are there frequent errors?

Are there signs of poor or inadequate equipment design, such as plasters on the fingers of the worker or *home-made* protective pads made of tissue or foam?

Examining the circumstances surrounding frequent errors and incidents where mistakes have occurred and people have been injured. Accident reports should be used to identify details of incidents and their possible causes.

Recording and looking at sickness absence and staff turnover levels. High numbers may result from the problems listed earlier and/or dissatisfaction at work.

Effective application of ergonomics in work system design can achieve a balance between worker characteristics and task demands. This can enhance worker productivity, provide worker safety and physical and mental well being, and job satisfaction. It is believed that ergonomic de-ciencies in industry are a root cause of workplace health hazards, low levels of safety, and reduced worker productivity and quality.

Table 4.8 summarizes the important human factors involved in safety issues.

Table 4.8 Important human factor issues involved in safety

Issue	Definition	Consequences
Organizational change and transition management	Any change to the structure, population, or distribution of roles and responsibilities of an organization that may impact safety	Can include reduction in resources, competence, or motivation to deal with:
De-manning and staffing levels	• Business re-engineering • Downsizing • De-layering	Upsets and crises Emergencies Maintenance Safety management system
	Empowerment	
	• Multiskilling	
	• Outsourcing/contractorization	
	• Mergers, de-mergers, and acquisitions	
Training, competence, and supervision	The continuing ability of individuals and teams to perform reliability and safety-related elements of their roles, responsibilities, and tasks, and for this to be demonstrable	Failure to perform to required level in related or safety-critical tasks, roles, or responsibilities
Fatigue from shift work and overtime	Impaired human reliability from fatigue	Symptoms include loss of alertness, drowsiness, loss of patience Errors include absent-minded slips, memory lapses, etc. Three Mile Island, Chernobyl, Challenger, Exxon Valdez all included fatigued staff amongst the root causes

(*Continued*)

Table 4.8 (Continued)

Alarm handling	Designing alarm systems to ensure prompt, reliable and effective operator response	Failure to identify a need to act, or failure to select an effective course of action. Texaco refinery; three-mile Island
Compliance with safety critical procedures	Selecting, designing and managing safety-critical procedures in a way that assists human reliability	Unreliable or dangerous performance of safety-critical tasks
Safety culture/blame culture	The product of individual and group values, attitudes, perceptions, competencies, and patterns of behavior that determine the commitment to, and the style and proficiency of safety management of an organization	Safety culture is widely believed to be directly related to safety performance, that is, the frequency and/or probability of accidents
Communications, for example, shift handover	Reliable and accurate communication of safety-critical or safety-related information	Risks from lack of, or inaccurate information Piper Alfa
Ergonomics:		
(a) Design of interfaces	(a) Design of systems, displays, controls, and hardware to aid human reliability	(a) Human error in operation or maintenance
(b) Health ergonomics	(b) Design of healthier, safer, and more productive work systems that benefit individuals, organizations and society	(b) Work systems that lead to accidents, ill health, and job dissatisfaction
Maintenance errors	Human errors in maintenance that lead to immediate or latent unsafe conditions	Can include loss of process integrity, or failure in service, or on demand of plant and equipment

Note: Issues compiled from interaction of HSE-HID Land Division inspectors with UK chemical and allied industry major hazard sites.

Review Questions

1. What are the different causes of overpressure development in process equipment?
2. What types of hazards can result from high-pressure operations in a process plant?
3. What are the different factors that contributed to major accidents in process industry?
4. “Normally leaks result in cooling due to expansion of fluids.” Is it true with hydrogen leaks from high-pressure vessels? In what way hydrogen leaks present special hazards? Explain.

5. What causes rocketing of gas cylinders? Explain.
6. What can be the reason for water hammer and vibration in fluid lines? What are its undesirable effects?
7. What are the hazards involved in deep sea diving? How these are eliminated/decreased?
8. In what way vacuum can be hazardous to atmospheric storage vessels? Illustrate.
9. What are the causes of pressure deviations in LNG and LPG processes?
10. Give a summary of typical reasons for pressure deviations in a process plant.
11. What are the consequences of low or decrease in flows in tubes of a process heater?
12. What are the hazards that can result from leakages in a process plant?
13. What are the ways leakages can be prevented in process equipment and piping?
14. What are the effects of high temperatures on materials?
15. What are the ways by which exposure to cryogenic fluids can create hazards to people and equipment?
16. List down typical reasons for temperature deviations in process operations.
17. What are the effects of temperature on plant/equipment operations and personnel?
18. In an ammonia plant what equipment gives rise to vibrations and noise?
19. What are the different types of noises produced in an industrial plant? Name some measures to reduce noise levels.
20. What are the common constructional defects in a plant under construction?
21. What are the process-related activities that cause human errors?
22. What was the main contributor to the catastrophic accident at the BP Texas City Refinery?
23. Name some common people-oriented human errors.
24. What are situation-oriented human errors?
25. What are the types of human errors during maintenance and repair in a plant?
26. What are ergonomics? In what type of plant operations ergonomics play an important role.

Key words for Internet searches

API RP 520, U.S Chemical Safety Board (CSB)

Note: *Vast number of sites are given in Appendix A of the book for the purpose of use in internet searches for key words by enterprising teachers, students, industry professionals and managements.*

Chapter 5

Hazard Analysis

Learning Objectives

5.1 General
5.2 Process Safety Management
5.3 Process Hazard Analysis
5.4 Hazard Analysis Methods
5.5 Checklists
5.6 Preliminary Hazard Analysis
5.7 What-If
5.8 What-If/Checklist
5.9 Hazard and Operability Analysis and Hazard Analysis
5.10 FMEA—Failure Modes, Effects
5.11 Analysis
5.12 Fault Tree Analysis
5.13 Cause and Consequence Analysis
5.14 Dow Fire and Explosion Index
5.15 Security Vulnerability Analysis
5.16 Annexure

5.1 General

A *process hazard* is an inherent chemical or physical characteristic with the energy potential for damaging people, property, and/or the environment. The keyword in this definition is *potential*. Hazards are intrinsic to a material, or its conditions of use.

Hazard is defined as a condition, event, or circumstance that could lead to or contribute to an unplanned or undesirable event. Hazard is something with the potential to cause harm to people, facilities/property and environment. Hazards are intrinsic to a material, or its conditions of use. Types of hazards include physical, chemical, biological, ergonomic, behavioral, and/or psychological.

Examples: Hydrogen sulfide—toxic by inhalation; gasoline—flammable; moving machinery—kinetic energy; pinch points

Risk is the likelihood of harm resulting from a *hazard*. Risk is defined in general terms as the product of the frequency (or likelihood) of a particular event and the (usually adverse) consequence of that event, be it in terms of lives lost, financial cost, and/or environmental impact.

Risk = probability × consequences

One of the most important steps in risk assessment is to evaluate risks, that is, to determine whether the level of risk is tolerable, or is unacceptably high and would therefore warrant some urgent attention.

Evaluation of risks will depend on the method used for estimation of the risk. Risk evaluation could be carried out qualitatively, semiquantitatively, or quantitatively.

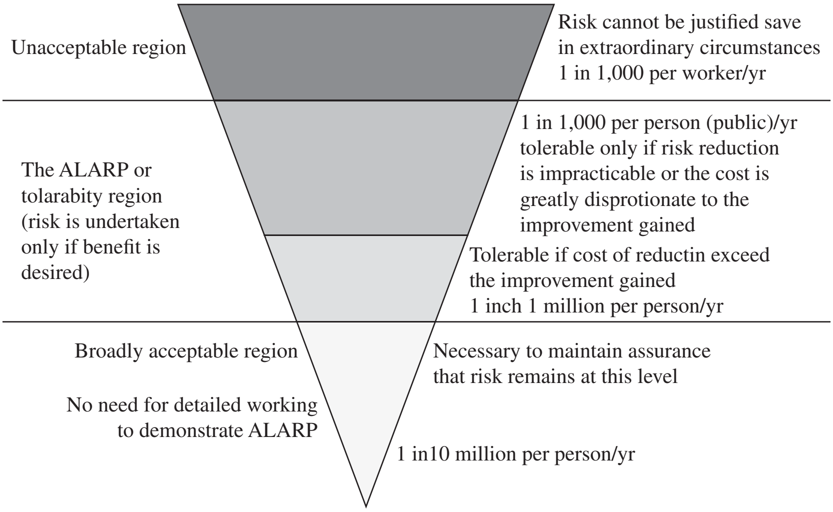


Figure 5.1 Levels of risk and ALARP

With qualitative risk, judgment is used and it is difficult to prioritize, whereas consideration is given to tolerability of risk if accidents can result from exposure to the hazard. Some criteria set the limit for maximum tolerable level of risk to a worker in a hazardous industry (e.g. nuclear installation) at 1 in 1,000 per person/yr, and the maximum tolerable limit to a member of the public as 1 in 10,000 per person/yr. Figure 5.1 illustrates levels of risk and as low as reasonably practicable (ALARP).

Factors that affect risk include people, setting, location, environment, equipment, clothing, and activity. Table 5.1 gives a classification of hazards.

Hazard vs. risk: The potential risk of a hazard is determined by its severity and how likely the hazard is to occur. Examples include improperly stored chemicals, using a more hazardous material, when a less hazardous material is available, not using the available engineering controls such as elimination of flammable and toxic atmospheres, ignition sources, inerting, etc., and not wearing personal protective equipment, when working in hazardous atmospheres, and so on.

Risk management involves the process of managing potential hazards and what could go wrong, focusing on being proactive, planning for safe activities, and adjusting them as conditions change, and focusing on what can be controlled and what cannot be controlled.

Risk assessment involves identification of hazards within the workplace, determining the likelihood that these hazards will cause harm and damage, prioritizing prevention and mitigation/control measures.

Risk analysis framework No activity is completely risk-free. Risks that cannot be eliminated must be assessed and managed. A comprehensive plan to manage risk includes policies and procedures for risk assessment, risk management, and risk communication.

Risk assessment in general includes the following steps:

Employers should carry out risk assessments as a first step in ensuring the safe and healthy workplace. All relevant risks should be systematically addressed by identifying, in particular, hazards, and major risks, taking into consideration and critically assessing existing safety controls and measures provided. Employers should carry out risk assessments as a first step in ensuring the safe and healthy workplace. All relevant risks should be systematically addressed by identifying, in particular, hazards, and major risks, taking into consideration and critically assessing existing safety controls and measures provided.

Table 5.1 Classification of hazards

Safe	No major degradation of performance; no equipment damage; no personnel injury
Marginal	Performance degradation can be counteracted/controlled without major damage/injury to personnel
Critical	Performance degradation/damage/hazard required immediate corrective action for survival of personnel and equipment
Catastrophic	Severe performance degradation/equipment loss and or death or serious injury to personnel

Note: Hazards are either accepted or corrected based on the above classification from which *acceptable* or *nonacceptable* risks can be determined.

The level of protective measures should match the level of risk. In most cases, a rough assessment should be made first, finding out the need to carry out detailed assessment, if needed. Written records of procedures and emergency plans must be maintained identifying workplace chemical and process hazards, technology and equipment used in the processes. Written safety and operating information should be provided to employees, including contract employees, and they should be trained in operating procedures by emphasizing hazards and safe practices that must be developed and made available. Such provision should include emergency response procedures. The activities of contractors working in process areas must be thoroughly reviewed and controlled to prevent them from creating a process incident and to ensure their safety should an incident take place. Employees and their representatives should be consulted on the development and conduct of hazard assessments and the development of accident prevention plans, with access to these and other records required.

A workplace hazard assessment should be performed, including as appropriate, identification of potential sources of accidental releases, identification of any previous release within the facility that had a potential for catastrophic consequences in the workplace, estimation of workplace effects of a range of releases, and estimation of the health and safety effects of such a range on employees.

Preventive and protective measures must be identified and provided. A system should be established to respond to the workplace hazard assessment findings, which shall address prevention, mitigation, and emergency responses.

Reviewing of assessments at frequent intervals with inclusion of any modifications, change of employees and managements, and the like.

Risk assessments must be *suitable and sufficient* in terms of identifying all hazards, persons and facilities at risk, and specific regulations, applying a systematic approach, inclusion of nonroutine operations, and taking existing control measures into account.

Start-up and shut-down procedures and maintenance details should be included in hazard identification and analysis measures.

A system must be developed and implemented to control any maintenance work in the process areas that involves a source of ignition (work permit systems).

Use of probabilities in risk analysis: Risk with hazardous materials consists of two elements, namely, the consequence of certain unwanted event and the probability of the consequences that will occur. Distinction should be made between three types of probabilities, namely, probability of the initiating event, probability that countermeasures provided in design function, and probability of a consequence of an accident.

5.2 Process Safety Management

Process safety management (PSM), in brief, involves the *proactive* and *systematic* identification, evaluation, and mitigation or prevention of chemical releases that could occur as a result of failures in process, procedures, or equipment. AIChE's CCPS defines PSM as *a management system that is focused on prevention of, preparedness for, mitigation of, response to, and restoration from catastrophic releases of chemicals or energy from a process associated with a facility*. The scope of a PSM can vary significantly, depending on numerous factors, including process safety information, nature of the materials involved (reactivity, toxicity, flammability, stability, physical properties, and others), nature and complexity of the process chemistry and reaction kinetics, maturity of the process (new process, old process, and existing process being modified), degree of understanding related to the process, the chemicals, the equipment (operating history), mechanical integrity, hot work, pre-startup safety review, regulatory and code compliance issues, facility siting studies, proposed modifications (to the process, the equipment, control systems, organizational structure, and administrative management systems), employee involvement, process hazard analysis (PHA), operating procedures, training, contractors, management of change, incident investigation, emergency planning and response, compliance audits, and trade secrets.

5.3 Process Hazard Analysis

Process hazard analysis, or evaluation, is one of the most important elements of the process safety management program. A PHA is an organized and systematic effort to identify and analyze the significance of potential hazards associated with the processing or handling of highly hazardous chemicals. A PHA provides information that will assist employers and employees in making decisions for improving safety and reducing the consequences of unwanted or unplanned releases of hazardous chemicals.

A PHA is an organized and systematic method to identify and analyze the significance of potential hazards associated with processing or handling highly hazardous chemicals and assess risk. The results of a hazard analysis are the identification of unacceptable risks and the selection of means of controlling or eliminating them.

A PHA helps employers and workers to make decisions for improving safety and reducing the consequences of unwanted or unplanned releases of hazardous chemicals. It is used to analyze potential causes and consequences of fires, explosions, releases of toxic, or flammable chemicals, and major spills of hazardous chemicals. It focuses on equipment, instrumentation, utilities, routine, and nonroutine human actions, and external factors that might impact a process.

Simply, PHA allows the employer to determine locations of potential safety problems, identify corrective measures to improve safety, and preplan emergency actions to be taken if safety controls fail.

PHAs must address the following:

The hazards of a process: These hazards may be identified by performing a PHA.

- Identification of previous incidents with likely potential for catastrophic consequences.
- Engineering and administrative controls applicable to the hazards and their interrelationships.
- The consequences of failure of engineering and administrative controls, especially those affecting employees.
- The influence of facility siting.
- Human factors.
- A qualitative range of possible safety and health effects on employees in the workplace caused by failure of controls.
- The need to promptly resolve PHA findings and recommendations.

A PHA analyzes potential causes and consequences of releases of toxic or flammable chemicals, fires, explosions, and major spills of hazardous chemicals. The PHA focuses on equipment, instrumentation, utilities, human actions, and external factors that might affect the process.

The selection of a PHA methodology or technique will be influenced by many factors including knowledge about the process, whether its operation for a long period of time with extensive experience or it is a new process or one that has been changed frequently by the inclusion of innovation features.

Also, the size and complexity of the process will influence the decision as to the appropriate PHA methodology to use. All PHA methodologies are subject to certain limitations. For example, the checklist methodology works well when the process is very stable and no changes are made, but it is not as effective when the process has undergone extensive changes. The checklist may miss the most recent changes and consequently they would not be evaluated. Another limitation to be considered concerns the assumptions made by the team carrying out hazard analysis. The PHA is dependent on good judgment and the assumptions made during the study need to be documented and understood by the team and reviewer and kept for a future PHA. The ideal team will have an intimate knowledge of the standards, codes, specifications, and regulations applicable to the process being studied. The selected team members need to be compatible.

The application of a PHA to a process may involve the use of different methodologies for various parts of the process. For example, a process involving a series of unit operations of varying sizes, complexities, and ages may use different methodologies and team members for each operation. Then, the conclusions can be integrated into one final study and evaluation. A more specific example is the use of a

PHA checklist for a standard boiler or heat exchanger and the use of a hazard and operability PHA for the overall process. Also, for batch-type processes a generic PHA of a representative batch may be used where there are only small changes of monomer or other ingredient ratio and the chemistry is documented for the full range and ratio of batch ingredients.

Finally, when an employer has a large continuous process with several control rooms for different portions of the process, such as for a distillation column and a blending operation, the employer may wish to do each segment separately and then integrate the final results.

5.4 Hazard Analysis Methods

Several methods are available for carrying out hazard analysis, which include checklists, what-if analysis, what-if/checklist, hazard and operability studies (HAZOP), hazard analysis (HAZAN), failure mode and effects analysis (FMEA), fault tree analysis, Dow fire and explosion index, cause and consequence analysis, security vulnerability analysis (SVA), and layers of protection analysis (LOPA), etc. Table 5.2 gives a brief summary of observations/comments on different methods of hazard analysis.

Table 5.2 Summary of observations/comments on different methods of hazard analysis

Preliminary hazard analysis	A common method for establishing a crude risk picture, with relatively modest effort. Covers selected parts of, or the entire, bow-tie, that is, the initiating events, the cause and consequence analysis
Check lists	Used to verify status of a system using a written list of items/procedures. A checklist analysis uses a written list of items or procedures to verify the status of a system. Checklists may vary widely in level of detail, depending on the process being analyzed
What-if analysis	Used to identify hazards, hazardous situations or specific accident events that could produce an undesirable consequence. What-if analysis involves the examination of possible deviations from the design, construction, modification, or operating intent of a process
What-if/checklist	Used to identify hazards, consider types of accidents that can occur in a process/activity, evaluate in a qualitative manner the consequences of these accidents, and determine whether safety levels against these potential accident scenarios appear adequate
HAZOP	A systematic analysis of how deviation from the design specifications in a system can arise, and an analysis of the risk potential of these deviations. Based on a set of *guide-words*, scenarios that may result in a hazard or an operational problem are identified. Basic concept involved in HAZOP studies is that processes work well when operating under design conditions. When deviations occur from design, operability problems and accidents can occur

(*Continued*)

Table 5.2 (Continued)

HAZAN	Hazard analysis technique consisting on essentially three steps, namely, estimating how often an incident will occur, estimating the consequences to employees, public and environment, plant and profits. Past experiences should be the basis, and if such experience is not available, similar plant experiences may be considered
FMEA	Used to examine each potential effects failure mode of a process on the system. Failure mode is the symptom, condition or fashion in which hardware fails. A simple analysis method to reveal possible failures and to predict the failure effects on the system as a whole
Fault tree analysis	A systematic, deductive failure analysis that focuses on a particular accident or undesired event called the *top event* and develops the underlying sequence of events leading to the top event.
Cause and consequence analysis	Quantifies vulnerable zone for a conceived incident and once the vulnerable zone is identified for an incident, measures can be proposed to eliminate damage to plant and potential injury to personnel.
SVA	A process in identifying and then preventing potential security weaknesses in a facility.
LOPA	A semiquantitative methodology used to ensure that process risk is successfully mitigated to an acceptable level.

5.5 Checklists

Consists of using a detailed list of prepared questions about the design and operation of the facility. Questions are usually answered *yes* or *no*. Used to identify common hazards through compliance with established practices and standards.

Checklist question categories: Causes of accidents, process equipment, human error, external events, facility functions, alarms, construction materials, control systems, documentation, training, instrumentation, piping, pumps, vessels, etc.

Checklist questions: Causes of accidents.

- Is process equipment properly supported?
- Is equipment identified properly?
- Are the procedures complete?
- Is the system designed to withstand hurricane winds?
- Facility functions.
- Is it possible to distinguish between different alarms?
- Is pressure relief provided?
- Is the vessel free from external corrosion?
- Are sources of ignition controlled?

Checklist summary: The simplest of hazard analyses; easy-to-use; level of detail is adjustable; provides quick results; communicates information well; effective way to account for *lessons learned; NOT* helpful in identifying new or unrecognized hazards; limited to the expertise of its author(s). Table 5.3 illustrates a typical checklist for process safety review.

Table 5.3 Typical process safety review checklist

	Materials
1.	What process materials are unstable or spontaneously ignitable?
2.	What evaluation has been made of impact sensitivity?
3.	Has an evaluation of possible uncontrolled reaction or decomposition been made?
4.	What data are available on amount and rate of heat evolution during decomposition of any material in the process?
5.	What precautions are necessary for flammable materials?
6.	What flammable dust hazards exist?
7.	What materials are highly toxic?
8.	What has been done to assure that materials of construction are compatible with the chemical process materials that are involved?
9.	What maintenance control is necessary to assure replacement of proper materials, for example, to avoid excessive corrosion, to avoid producing hazardous compounds with reactants?
10.	What changes have occurred in composition of raw materials and what resulting changes are in process?
11.	What is done to assure sufficient control of raw material identification and quality?
12.	What hazards can be created by failure of supply of one or more raw materials?
13.	What assurance is there of adequate raw material supply?
14.	What hazards can occur as a result of loss of gas for purging, blanketing, or inerting? How certain is gas supply?
15.	What precautions need to be considered relative to stability of all materials in storage?
16.	What fire extinguishing agents are compatible with process materials?
17.	What fire emergency equipment and procedures are being provided?
	Reactions
1.	How are potentially hazardous reactions isolated?
2.	What process variables could, or do, approach limiting conditions for hazard?
3.	What unwanted hazardous reactions can be developed through unlikely flow or process conditions or through contamination?
4.	What combustible mixtures can occur within equipment?
5.	What precautions are taken for processes operating near or inside the flammable limits?
6.	What are process margins of safety for all reactants and intermediates?
7.	What reaction rate data are available on the normal, or abnormally possible, reactions?
8.	How much heat must be removed for normal, or abnormally possible, exothermic reactions?
9.	How thoroughly is chemistry of the process known?
10.	What foreign materials can contaminate the process and create hazards?
11.	What provision is made for rapid disposal of reactants if required by plant emergency?

(Continued)

Table 5.3 (Continued)

12.	What provisions are made for handling impending runaways and for short-stopping an existing runaway?
13.	How fully is the chemistry of all desired and undesired reactions known?
14.	What hazardous reactions could develop as a result of mechanical equipment (pump, agitator, etc.) failure?
15.	What hazardous process conditions can result from gradual or sudden blockage in equipment?
16.	What raw materials or process materials can be adversely affected by extreme weather conditions?
17.	What process changes have been made since the previous process safety review?
	Operations
1.	When was the written operating procedure last reviewed and revised?
2.	How are new operating personnel trained on initial operation and experienced operating personnel kept up-to-date on plant operating procedures, especially for start-up, shut-down, upsets, and emergencies?
3.	What plant revisions have been made since the last process safety review?
4.	What special cleanup requirements are there before start-up and how are these checked?
5.	What emergency valves and switches cannot be reached readily? What procedures are there to cope with these situations?
6.	What safety precautions are needed in loading liquids into, or withdrawing them from tanks? Has the possibility of static electricity creation been adequately taken care of?
7.	What process hazards are introduced by routine maintenance procedures?
8.	What evaluation has been made of the hazards of sewered materials during normal and abnormal operation?
9.	How dependable are supplies of inerting gas and how easily can supplies to individual units be interrupted?
10.	What safety margins have been narrowed by revisions of design or construction in efforts to de-bottleneck operations, reduce cost, increase capacity, or improve quality?
11.	What provisions does the operating manual have for coverage of start-up, shut-down, upsets and emergencies?
12.	What economic evaluation has dictated whether a batch process or a continuous one is used?
	Equipment
1.	In view of process changes since the last process safety review, how was adequate size of equipment assured?
2.	Are any venting systems manifold, and if so, what hazards can result?
3.	What procedure is there for assuring adequate liquid level in liquid seals?
4.	What is the potential for external fire which may create hazardous internal process conditions?
5.	Is explosion suppression equipment needed to stop an explosion once started?

(Continued)

Table 5.3 (Continued)

6. Where are flame arresters and detonation arresters needed?
7. In confined areas, how is open-fired equipment protected from spills?
8. What safety control is maintained over storage areas?
9. In the case of equipment made of glass or other fragile material, can a more durable material be used? If not, is the fragile material adequately protected to minimize breakage? What is the hazard resulting from breakage?
10. Are sight glasses on reactors provided only where positively needed? On pressure or toxic reactors, are special sight glasses provided which have a capability to withstand high pressure?
11. What emergency valves and switches cannot be reached readily?
12. When was pertinent equipment, especially process vessels, last checked for pressure rating?
13. What hazards are introduced by failure of agitators?
14. What plugging of lines can occur and what are the hazards?
15. What provisions are needed for complete drainage of equipment for safety in maintenance?
16. How was adequacy of ventilation determined?
17. What provisions have been made for dissipation of static electricity to avoid sparking?
18. What requirements are there for concrete bulkheads or barricades to isolate highly sensitive equipment and protect adjacent areas from disruption of operations?
Piping and valves
1. Were piping systems analyzed for stresses and movement due to thermal expansion?
2. Are piping systems adequately supported and guided?
3. Are piping systems provided for antifreezing protection, particularly cold water lines, instrument connections and lines in dead-end service such as piping at standby pumps?
4. Are provisions made for flushing out all piping during start-up?
5. Are cast iron valves avoided in strain piping?
6. Are nonrising stem valves being avoided?
7. Are double block and bleed valves used on emergency inter-connections where possible cross-contamination is undesirable?
8. Are controllers and control valves readily accessible for maintenance?
9. Are bypass valves readily reached for operation? Are they so arranged that opening of valves will not result in an unsafe condition?
10. Are any mechanical spray steam de-superheaters used?
11. Are all control valves reviewed for safe action in event of power or instrument air failure?
12. Are means provided for testing and maintaining primary elements of alarm and interlock instrumentation without shutting-down processes?
13. What provisions for draining and trapping steam piping are provided?

(Continued)

Table 5.3 (Continued)

Pressure and vacuum relief
1. What provision is there for flame arresters on discharge of relief valves or rupture discs on pressurized vessels?
2. What provisions are there for removal, inspection, and replacement of relief valves and rupture discs, and at what scheduling procedure?
3. What need is there for emergency relief devices: breather vents, relief valves, rupture discs, and liquid seals? What are the bases for sizing these?
4. Where rupture discs are used to prevent explosion damage, how are they sized relative to vessel capacity and design?
5. Where rupture discs have delivery lines to or from the discs, what has been done to assure adequate line size relative to desired relieving dynamics? To prevent whipping of discharge end of line?
6. Are discharges from vents, relief valves, rupture discs, and flares located to avoid hazard to equipment and personnel?
7. What equipment, operating under pressure, or capable of having internal pressures developed by process malfunction, is not protected by relief devices and why not?
8. Is discharge piping of relief valves independently supported? Make piping as short as possible and with minimum changes in direction
9. Are drain connections provided in discharge piping of relief valves where condensate could collect?
10. Are relief valves provided on discharge side of positive displacement pumps; between positive displacement compressor and block valves; between back-pressure turbine exhaust flanges and block valves?
11. Where rupture discs are in series with relief valves to prevent corrosion on valve or leakage of toxic material, install rupture disc next to the vessel and monitor section of pipe between disc and relief valve with pressure gauge and pressure bleed-off line. Have any rupture discs been installed on discharge side of relief valve?
12. What provisions for keeping piping to relief valves and vacuum breakers at proper temperature to prevent accumulation of solids from interfering with action of safety device are provided?
Machinery
1. Are adequate piping supports and flexibility provided to keep forces on machinery due to thermal expansion of piping within acceptable limits?
2. What is separation of critical and operating speeds?
3. Are check valves adequate and fast acting to prevent reverse flow and reverse rotation of pumps, compressors and drivers?
4. Are adequate service factors on speed changing gears in shock service provided?
5. Are there full-flow filters in lube-oil systems serving aluminum bearings?
6. Are there provisions for draining and trapping steam turbine inlet and exhaust lines?
7. Are there separate visible-flow drain lines from all steam turbine drain points?
8. Are driven machines capable of withstanding tripping speed of turbine drain points?

(Continued)

Table 5.3 (Continued)

9. Are nonlubricated constructions or nonflammable synthetic lubricants used for air compressors with discharge pressures of greater than 518 kPag (75 psig) to guard against explosion?
10. What provisions are made for emergency lubrication of critical machinery during operation and during emergency shut-downs?
11. Are provisions made for spare machines or critical spare parts for critical machines?
12. Are there provisions for operation or safe shut-down during power failures?
13. Are vibration switches on alarm or on interlock for cooling tower fans provided?
Instrumentation control
1. What hazards will develop if all types of motive power used in instrumentation should fail nearly simultaneously?
2. If all instruments fail simultaneously, is the collective operation still fail -safe?
3. What provision is made for process safety when an instrument, instrumental in process safety as well as in process control, is taken out of service for maintenance? When such an instrument goes through a dead time period for standardization or when, for some other reason, the instrument reading is not available?
4. What has been done to minimize response time lag in instruments directly or indirectly significant to process safety? Is every significant instrument or control device backed up by an independent instrument or control operating in an entirely different manner? In critical processes, are these first two methods of control backed up by a third ultimate safety shut-down?
5. Has the process safety function of instrumentation been considered integrally with the process control function throughout plant design?
6. What are the effects of extremes of atmospheric humidity and temperature on instrumentation?
7. What gauges, meters, or recorders cannot be read easily? What modifications are being made to cope with or solve this problem?
8. Is the system completely free of sight glasses or direct reading liquid level gauges or other devices which, if broken, could allow escape of the materials in the system?
9. What is being done to verify that instrument packages are properly installed? Grounded? Proper design for the environment?
10. What procedures have been established for testing and proving instrument functions?
11. What periodic testing to check performance and potential malfunction is scheduled?
Malfunctions
1. What hazards are created by the loss of each feed, and by simultaneous loss of two or more feeds?
2. What hazards result from loss of each utility, and from simultaneous loss of two or more utilities?
3. What is the severest credible incident, that is, the worst conceivable combination of reasonable malfunctions, which can occur?
4. What is the potential for spills and what hazards would result from them?

(Continued)

Table 5.3 (Continued)

Location and plot plan
1. Has equipment been adequately spaced and located to permit anticipated maintenance during operation without danger to the process?
2. In the event of the foreseeable types of spills, what dangers will there be to the community?
3. What hazards are there from materials dumped into sewers of neighboring areas?
4. What public liability risks from spray, fumes, mists, noise, etc., exist, and how have they been controlled or minimized?

*Adapted from: *Guidelines for Hazard Evaluation Procedures*. Prepared by Battelle Columbus Division for The Center for Chemical Process Safety of the American Institute of Chemical Engineers. 345 East 47th Street, New York, NY. (1985).

Limitations of a checklist: When derived from handbooks or similar sources, many entries in a checklist may not be applicable to the process being studied. In other cases, process hazards may be so unusual they are not in standard checklists. Thus, it may be difficult to assure that all hazards have been analyzed. In addition, checklists may indicate that hazards exist, but not what accident scenarios are associated with them.

5.6 Preliminary Hazard Analysis

Preliminary hazard analysis (PHA) is a semiquantitative analysis that is performed for the following reasons:

1. identify all potential hazards and accidental events that lead to an accident
2. rank the identifed accidental events according to their severity
3. identify required hazard controls and follow-up actions

Several variants of preliminary hazard analyses are used, and sometimes under deferent names such as rapid risk ranking and hazard identifcation (HAZID).

Preliminary hazard analysis is used as an initial risk study in an early stage of a project (e.g. a new plant). It identifes where energy may be released and which accidental events may occur, and it also gives a rough estimate of the severity of each accidental event.

The results are used to (i) compare main concepts to (ii) focus on important risk issues, and as (iii) input to more detailed risk analyses.

It is used as an initial step of a detailed risk analysis of a system concept or an existing system, and also used as a complete risk analysis of a rather simple system. A preliminary hazard analysis considers:

(i) Hazardous components, (ii) safety related interfaces between various system elements including software, (iii) environmental constraints including operating environments, (iv) operating test, maintenance, built-in tests, diagnostics, and emergency procedures, (v) facilities, real property installed equipment and training, (vi) safety related equipment, safeguards, and possible alternative approaches, and (vii) malfunctions to the system, subsystems, or software.

Table 5.4 gives an example of a preliminary hazard analysis:

Table 5.4 Example of a preliminary hazard analysis for a fired heater

Subsystem/item	Fired heater
Operating mode	Normal operation
Hazardous element	Fuel supply
Trigger event which causes hazardous condition	No flames on burners and fuel valve open
Hazardous condition	Fuel enters heater and accumulates
Trigger event causing potential accident	Burners ignite explosively
Potential accident	Explosion and/or fire
Possible effects of the accident	Injury to personnel and damage to structure
Measures to prevent/contain occurrences	Provision of flame failure detectors and alarms. System shut-down by suitable trip system

Pros and cons of preliminary hazard analysis:

Pros: (i) Helps ensure that the system is safe, (ii) modifcations are less expensive and easier to implement in the earlier stages of design, and (iii) decreases design time by reducing the number of surprises.

Cons: (i) Hazards must be foreseen by the analysts and (ii) the efects of interactions between hazards are not easily recognized.

5.7 What-If

Experienced personnel brainstorming a series of questions that begins, "*What if…?*"

Each question represents a potential failure in the facility or misoperation of the facility

The response of the process and/or operators is evaluated to determine if a potential hazard can occur. If so, the adequacy of existing safeguards is weighed against the probability and severity of the scenario to determine whether modifications to the system should be recommended.

What-If—steps:

(i) The system is divided up into smaller and logical sub-systems.
(ii) A list of questions for a sub-system is identified.
(iii) Identify required hazard controls and follow-up actions.
(iv) Hazards, consequences, severity, likelihood, and recommendations are identified.

1. The system is divided up into smaller and logical subsystems.
2. Step (ii) through (iv) are repeated until complete.

(a) What-If question areas: equipment failures, human error, and external events.

(b) What-If—summary:

Perhaps the most commonly used method
One of the least structured methods
Can be used in a wide range of circumstances

Success is highly dependent on experience of the analysts
Useful at any stage in the facility life cycle
Useful when focusing on change review

Applications include pumping stations, oil–water separation systems, drilling operations, tank farms, liquid loading facilities, and the like.

Limitations of what-if analysis: the what-if analysis is a powerful PHA method, if the analysis team is experienced and well organized. Otherwise, because approach is a relatively unstructured one, the results are likely to be incomplete.

5.8 What-If/Checklist

A hybrid of the *what-if* and *checklist* methodologies. Combines the *brainstorming* of *what-if* method with the *structured features* of *checklist method*.

What-If/Checklist—steps:

Begin by answering a series of previously prepared *what-if* questions.

During the exercise, brainstorming produces additional questions to complete the analysis of the process under study.

What-If/Checklist—summary:

Encourages creative thinking (what-if) while providing structure (checklist).

In theory, weaknesses of standalone methods are eliminated and strengths preserved—not easy to do in practice.

Example: When presented with a checklist, it is typical human behavior to suspend creative thinking.

Limitations of what-if/checklist: combining the what-if and checklist analysis methods emphasizes their main positive features (i.e. the creativity of what-if analysis and the experience-based thoroughness of a checklist analysis) while at the same time compensating for their shortcomings when used separately. For example, a traditional checklist is, by definition, based on the process experience the author accumulates from various sources. The checklist is likely to provide incomplete insights into the design, procedural, and operating features necessary for a safe process. The what-if part of the analysis uses creativity of a team and experience to brainstorm potential accident scenarios. However, because the what-if analysis method is usually not as detailed, systematic, or thorough as some of the more regimented approaches (e.g. HAZOP study and FMEA) use of a checklist permits the PHA team to fill in any gaps in their thought process.

5.9 Hazard and Operability Analysis

The Hazard and Operability Analysis (HAZOP) process is based on the principle that a team approach to hazard analysis will identify more problems than when individuals working separately combine results. The HAZOP team is made up of individuals with varying backgrounds and expertise. The expertise is brought together during HAZOP sessions and through a collective brainstorming effort that stimulates creativity and new ideas, a thorough review of the process under consideration is made.

A HAZOP study is a structured and systematic examination of a planned or existing process or operation in order to identify and evaluate potential hazards and operability problems, or to ensure the ability of equipment in accordance with the design intent.

Table 5.5 gives HAZOP guide words and their definitions.

Table 5.5 HAZOP guide words and their definitions

Guide word	*Definition and examples*
No or not	The complete negation of the design intent occurs; no flow in a pipeline due to plugging.
More or less	A quantitative increase or decrease of some variable such as flow rate, temperature, reactivity, etc., occurs.
As well as	All the design intentions are fulfilled and something happens in addition.
Part of	Only part of design intension is fulfilled; batch reactor is partially cooled, resulting a runaway reaction.
Reverse	The logical opposite of the design intention occurs; reverse flow from a reactor to storage tank.
Other than	Something completely different than intended occurs; tank car of sulfuric acid unloaded into caustic storage tank resulting in tank failure.

The HAZOP analysis technique uses a systematic process to identify possible deviations from normal operations and ensure that appropriate safeguards are in place to help prevent accidents. It uses special guide words that are a unique feature of HAZOP analysis.

The HAZOP process is based on the principle that a team approach to hazard analysis will identify more problems than when individuals working separately combine results. The HAZOP team is made up of individuals with varying backgrounds and expertise. The leader should be experienced in using the technique, but does not necessarily need to have thorough knowledge about the actual process. The group comprises of persons who have detailed knowledge about the system to be analyzed. The expertise is brought together during HAZOP sessions and through a collective brainstorming effort that stimulates creativity and new ideas, a thorough review of the process under consideration is made. Through a HAZOP study, critical aspects of the design can be identified, that requires further analysis. Detailed, quantitative reliability, and risk analyses will often be generated in this way.

Node: Node is some specific sections of the system in which (the deviations of) the design/process intent are evaluated. A node can be a subsystem, a function group, a function, or a subfunction.

Steps: (i) Identify hazards (safety, health, and environmental), and problems which prevent efficient operation; (ii) choose a vessel and describe its intention; (iii) choose and describe a flow path; (iv) apply *guideword* to *deviation*.

Guidewords include *none, more of, less of, part of, more than, other than, reverse*. Figure 5.2 gives principle involved in a HAZOP study.

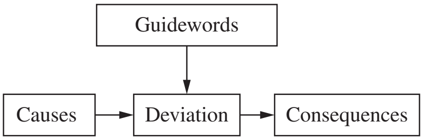


Figure 5.2 Principle involved in a HAZOP study

Deviations are expansions, such as *no flow, more pressure, less temperature, more phases than* (there should be).

To apply the HAZOP guide words effectively and to address the potential accidents that can result from the guide word deviations, the analysis team must have access to detailed design and operational information. The process systematically identifies specific engineered safeguards (e.g. instrumentation, alarms, and interlocks) that are defined on detailed engineering drawings.

HAZOP study worksheets are used to document deviations, causes, consequences, and recommendations/decisions.

Most common uses of HAZOP study:

- Used primarily for identifying hazards and operability problems of continuous process systems, especially fluid and thermal systems. Also used to review procedures and sequential operations.
- HAZOP is primarily used for processes that contain unusual, complex, or extremely hazardous materials. Examples of applications include materials with toxicity and corrosivity, processing and storage facilities involving LNG and LPG, offshore production facilities and the like.

HAZOP—Pros and cons:

- Creative, open-ended.
- Completeness—identifies all process hazards.
- Rigorous, structured, yet versatile.
- Identifies safety *and* operability issues.
- Can be time-consuming (e.g. includes operability).
- Relies on having right people in the study group.
- Does not distinguish between low probability, high consequence events (and vice versa).

Inherent assumptions of HAZOP:

- Hazards are detectable by careful review.
- Plants designed, built and run to appropriate standards will not suffer catastrophic *loss of containment* if operations stay within design parameters.
- Hazards are controllable by a combination of equipment, procedures which are *safety critical*. HAZOP conducted with openness and good faith by competent parties.

Table 5.6 gives guidewords for HAZOP studies.

Table 5.6 Guide words for HAZOP studies

Guideword	*Meaning*	*Examples*
None of	Negation of intention	No forward flow when there should be. Sequential process step omitted
More of	Quantitative increase	More of any relevant physical parameter than there should be, such as more flow (rate, quantity), more pressure, higher temperature, or higher viscosity. Batch step allowed proceeding for too long

(Continued)

Table 5.6 (Continued)

Less of	Quantitative decrease	Opposite of *More of*
Part of	Qualitative decrease	System composition different from what it should be (in multicomponent stream)
As well as	Qualitative increase	More things present than should be (extra phases, impurities). Transfer from more than one source or to more than one destination
Reverse	Logical opposite	Reverse flow. Sequential process steps performed in reverse order
Other than	Complete substitution	What may happen other than normal continuous operation (start-up, normal shut-down, emergency shut-down, maintenance, testing, and sampling). Transfer from wrong source or to wrong destination

**Source:* DOE-HDBK-1100-2004

The HAZOP study should be performed in a deliberate, systematic manner to reduce the possibility of omissions. Within a study node, all deviations associated with a given process parameter should be analyzed before the next process parameter is considered. All of the deviations for a given study node should be analyzed before the team proceeds to the next node.

Table 5.7 gives example of HAZOP study process parameters and deviations.

Table 5.7 Example of HAZOP study process parameters and deviations

Process parameter	***Deviation***	***Process parameter***	***Deviation***
Flow (rate)	No flow	Time	Too long
	High flow		Too short
	Low flow		Too late
	Reverse flow		Too soon
Flow (quantity)	Too much	Sequence	Omit a step
	Too little		Steps reversed
			Extra step
Pressure	High pressure	pH	High pH
	Low pressure		Low pH
Temperature	High temperature	Viscosity	High viscosity
	Low temperature		Low viscosity
Level	High level/overflow	Heat value	High heat value

(Continued)

Table 5.7 (Continued)

	Low level/empty		Low heat value
Mixing	Too much mixing	Phases	Extra phase
	Not enough mixing		Phase missing
			Loss of agitation
			Reverse mixing
Composition	Component missing	Location	Additional source
	High concentration		Additional destination
	Low concentration		Wrong source
			Wrong destination
Purity	Impurities present	Reaction	No reaction
	Catalyst		Too little reaction
	deactivated/inhibited		Too much reaction
			Reaction too slow
			Reaction too fast

**Source:* DOE-HDBK-1100-2004

Loss of containment deviations:

- Pressure too high
- Pressure too low (vacuum)
- Temperature too high
- Temperature too low
- Deterioration of equipment
- Inherent assumptions of HAZOP—
- Hazards are detectable by careful review.
- Plants designed, built and run to appropriate standards will not suffer catastrophic *loss of containment* if operations stay within design parameters.
- Hazards are controllable by a combination of equipment, procedures which are *safety critical*.
- HAZOP conducted with openness and good faith by competent parties.

Table 5.8 illustrates typical format for a HAZOP study worksheet.

Table 5.8 Typical format for a HAZOP study worksheet

Guide word deviation	Cause	Consequence	Safety levels	Scenario	Comments and/or actions

**Source:* DOE-HDBK-1100-2004

Figure 5.3 illustrates HAZOP procedure.

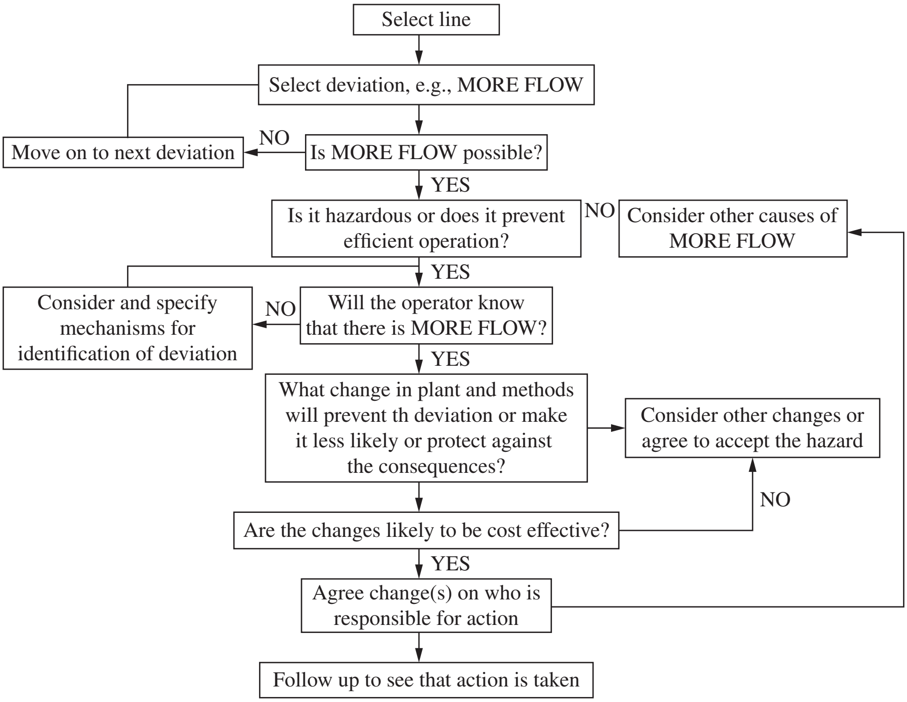


Figure 5.3 Illustration of HAZOP procedure

Figure 5.4 gives an illustrate of a typical HAZOP report.

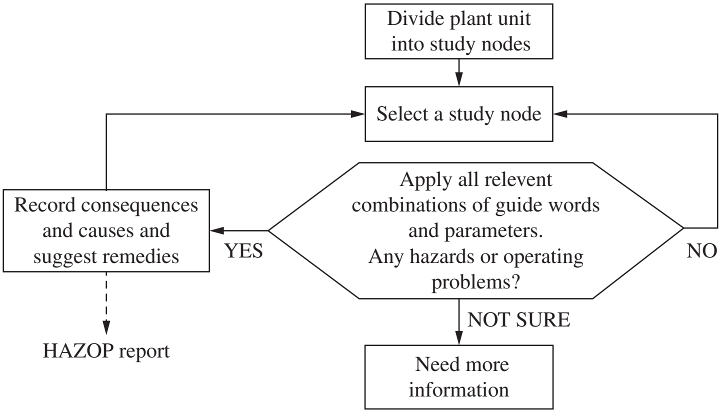


Figure 5.4 Illustration of a typical HAZOP report

Pros and cons of HAZOP:

- Creative, open-ended.
- Completeness—identifies all process hazards.
- Rigorous, structured, yet versatile.

- Identifies safety *and* operability issues.
- Can be time consuming (e.g. includes operability).
- Relies on having right people in the room.

Does not distinguish between low probability, high consequence events (and vice versa).

Limitations of the hazard and operability study: Requires a well-defned system or activity. The primary limitation of a HAZOP study is the length of time required to perform it. Because the study is designed to provide a complete analysis, study sessions can be intensive and tiring. Focuses on one-event causes of deviations. The HAZOP process focuses on identifying single failures that can result in accidents of interest. If the objective of the analysis is to identify all combinations of events that can lead to accidents of interest, more detailed techniques should be used.

HAZOP studies typically do not look at occupational hazards (e.g. electrical equipment, rotating equipment, and hot surfaces) or chronic hazards (e.g. chronic chemical exposure, noise, and heat stress).

For HAZAN, see Table 5.2.

5.10 FMEA—Failure Modes, Effects Analysis

Failure mode and effects analysis (FMEA) is a design evaluation procedure used to identify potential failure modes and determine the effect of each on system performance. These analyses (FMEAs) evaluate the ways equipment can fail or be improperly operated and the effects these failures can have. In a FMEA, each individual failure is considered as an independent occurrence with no relation to other failures in the system, except for the subsequent effects the original failure may produce. In short, FMEAs identify single failure modes that either directly result in or contribute significantly to an accident. It is a manual analysis to determine the consequences of component, module or sub-system failures. It consists of a spreadsheet where each failure mode, possible causes, probability of occurrence, consequences, and proposed safeguards are noted.

An FMEA is used to examine each potential failure mode of a process to determine the effects of the failure on the system. A failure mode is the symptom, condition, or fashion in which hardware fails. It may be identified as a loss of function, a premature function (function without demand), an out-of-tolerance condition, or a physical characteristic, such as a leak, observed during inspection. The effect of a failure mode is determined by the system's response to the failure.

Failure mode keywords: Rupture, crack, leak, plugged, failure to open, failure to close, failure to stop, failure to start, failure to continue, spurious stop, spurious start, loss of function, high pressure, low pressure, high temperature, low temperature, overfilling, hose bypass, instrument bypassed.

Severity of the worst consequence is expressed as follows:

Category i: *Catastrophic*—May cause death, or loss of system or process.

Category ii: *Critical*—May cause severe injury, major property or system damage.

Category iii: *Marginal*—May cause minor injury, minor property or system damage.

Category iv: *Minor*—Is not serious enough to cause injury, property or system damage.

Example for FMEA is given in Table 5.9.

Table 5.9 Example of FMEA involving a fuel control valve to a burner

Component	Fuel control valve
Failure or error mode	Jammed fully open
Effect of failure on	Burner continues to operate other components
Effect of failure on	Process stream temperature rises whole system
Qualitative hazard	Critical hazard classification
Qualitative assessment	Reasonably probable of failure frequency
Method of failure	Temperature increase observed/detection alarm triggered

Limitations of failure mode and effects analysis: One of the limitations is that the logic trees used are based on the probability of failure at the component level and full application is expensive.

Human operator errors are not usually examined in a FMEA, but the effects of human error are indicated by an equipment failure mode. FMEAs rarely investigate damage or injury that could arise if the system or process operated successfully. Because FMEAs focus on single event failures, they are not efficient for identifying an exhaustive list of combinations of equipment failures that lead to accidents. It is a low level analysis and typically produces very large quantities of output impossible to work with all of it.

5.11 Fault Tree Analysis

Fault tree analysis (FTA) is a failure analysis in which an undesired state of a system is analyzed using Boolean logic to combine a series of lower-level events. This method is mainly used to quantitatively determine the probability of a safety hazard.

FTA is a graphical method that starts with a hazardous event and works backwards to identify the causes of the *top event*. It is a top-down analysis.

- Intermediate events related to the top event are combined by using logical operations such as AND & OR.
- Provides a traceable, logical, quantitative representation of causes, consequences, and event combinations
- Amenable to—but for comprehensive systems, requiring—use of software.
- Not intuitive, requires training.
- Not particularly useful when temporal aspects are important.

FTA analysis involves five steps:

1. *The undesired event to study is defined:* Definition of the undesired event can be very hard to catch, although some of the events are very easy and obvious to observe.
2. An engineer with a wide knowledge of the design of the system or a system analyst with an engineering background is the best person who can help define and number the undesired events. Undesired events are used then to make the FTA, one event for one FTA; no two events will be used to make one FTA.

3. *An understanding of the system is obtained:* Once the undesired event is selected, all causes with probabilities of affecting the undesired event are studied and analyzed. Getting exact numbers for the probabilities leading to the event is usually impossible for the reason that it may be very costly and time consuming to do so. Computer software is used to study probabilities; this may lead to less costly system analysis. System analysts can help with understanding the overall system. System designers have full knowledge of the system and this knowledge is very important for not missing any cause affecting the undesired event. For the selected event all causes are then numbered and sequenced in the order of occurrence and then are used for the next step which is drawing or constructing the fault tree.
   (i) The fault tree is constructed: after selecting the undesired event and having analyzed the system so that one knows all the causing effects (and if possible their probabilities) one can now construct the fault tree. Fault tree is based on **AND** and **OR** gates that define the major characteristics of the fault tree.

Figure 5.5 illustrates a typical fault tree for an explosion as the top event.

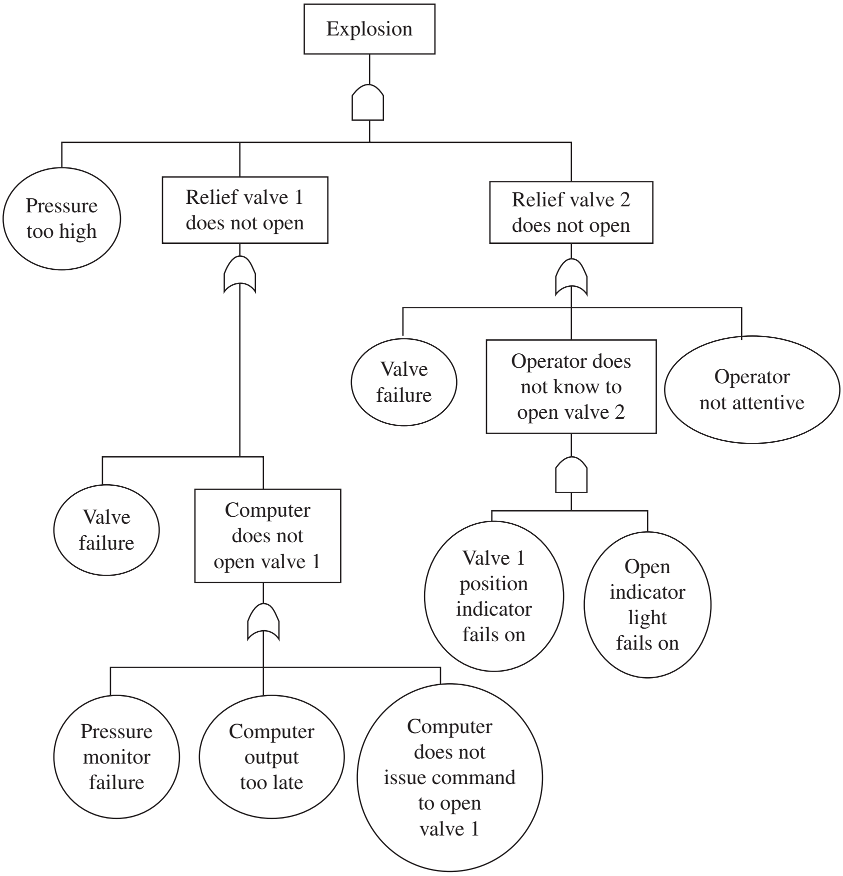


Figure 5.5 Example of FTA involving explosion as a top event

(ii) The fault tree is evaluated: after the fault tree has been assembled for a specific undesired event, it is evaluated and analyzed for any possible improvement or in other words study the risk management and find ways for system improvement. This step is as an introduction for the final step which will be to control the hazards identified. In short, in this step one identifies all possible hazards affecting in a direct or indirect way the system.

(iii) The hazards identified are then controlled: This step is very specific and differs largely from one system to another, but the main point will always be that after identifying the hazards all possible methods are pursued to decrease the probability of occurrence.

FTA is a deductive, top-down method aimed at analyzing the effects of initiating faults and events on a complex system. This contrasts with failure mode and effects analysis (FMEA), which is an inductive, bottom-up analysis method aimed at analyzing the effects of single component or function failures on equipment or sub-systems. FTA is very good at showing how resistant a system is to single or multiple initiating faults. It is not good at finding all possible initiating faults. FMEA is good at exhaustively cataloging initiating faults, and identifying their local effects. It is not good at examining multiple failures or their effects at a system level. FTA considers external events, FMEA does not. In civil aerospace the usual practice is to perform both FTA and FMEA, with a failure mode effects summary (FMES) as the interface between FMEA and FTA.

5.12 Cause and Consequence Analysis

Cause–consequence analysis is an integration of deductive (fault tree) and inductive (event tree) analyses into a single method and notation. The cause and consequences method involves the identification of the potential modes of failure of individual components and then relates the causes to the ultimate consequences for the system.

The consequences evaluated include those that represent system failure as well as those that represent other system behavior. As all consequence sequences are investigated the method can assist in identifying system outcomes which may not have been envisaged at the design stage. Cause–consequence analysis is most frequently applied to systems where the system state changes with time. Cause–consequence analysis is particularly suited to analysis of systems which include protective mechanisms.

The cause–consequence diagram is developed from some initiating event, that is, an event that starts a particular operational sequence or an event which activates certain safety systems. The cause–consequence diagram comprises two conventional reliability analysis methods, the FTA method and the event tree analysis method. The event tree method is used to identify the various paths that the system could take, following the initiating event, depending on whether certain subsystems/components function correctly or not. The fault tree method is used to describe the failure causes of the subsystems considered in the event tree part of the diagram. This relationship is shown in Figure 5.6.

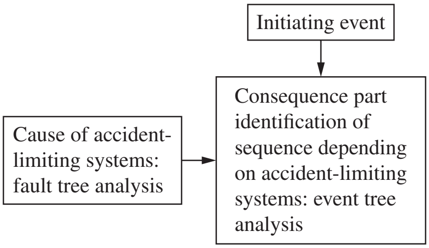
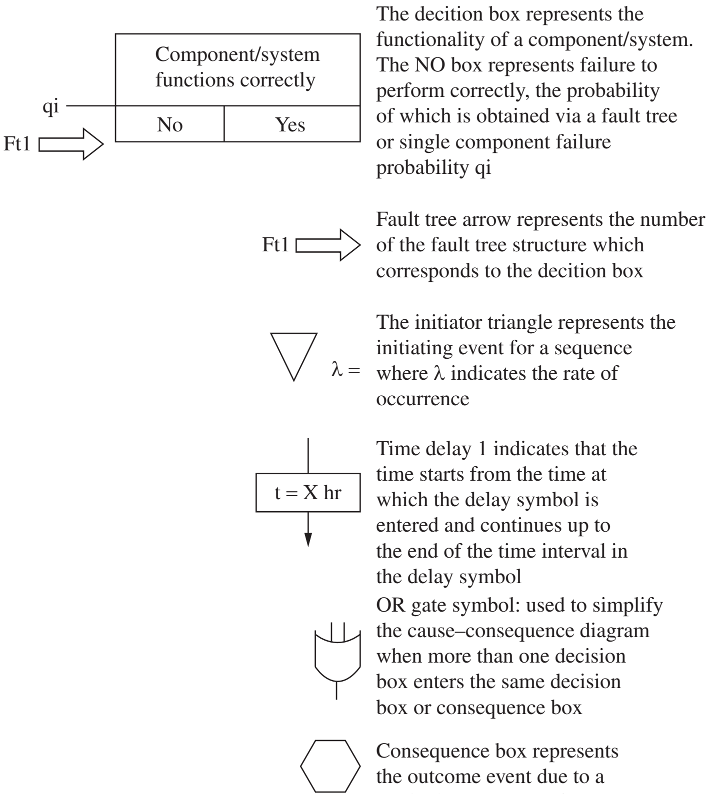


Figure 5.6 Typical presentation of cause–consequence diagram

The symbols used for construction of a cause–consequence diagram are illustrated in Figure 5.7

Advantages: Very expressive notation with high information density. Can express interactions of multiple failures and protective mechanisms. Workthrough of consequences relates failures to safety/hazard implications. Can be used for probabilistic analysis (though this is very complex, however, some tools exist).



The decition box represents the functionality of a component/system. The NO box represents failure to perform correctly, the probability of which is obtained via a fault tree or single component failure probability qi

Fault tree arrow represents the number of the fault tree structure which corresponds to the decition box

The initiator triangle represents the initiating event for a sequence where λ indicates the rate of occurrence

Time delay 1 indicates that the time starts from the time at which the delay symbol is entered and continues up to the end of the time interval in the delay symbol

OR gate symbol: used to simplify the cause–consequence diagram when more than one decision box enters the same decision box or consequence box

Consequence box represents the outcome event due to a particular sequence of events

Figure 5.7 Symbols used in a cause–consequence diagram

Disadvantages: Hard to use—requires very skilled analyst(s). Difficulty of modelling increases very rapidly with system complexity. Has not been widely adopted, perhaps because of difficulty of use.

5.13 Dow Fire and Explosion Index

The fire and explosion index (F & EI) calculation method is a tool to help determine the areas of greatest loss potential in a particular process. It also enables one to predict the physical damage that would occur in the event of an incident. The hazard classifcation guide developed by the Dow Chemical Company and published by the American Institute of Chemical Engineers, gives a method of evaluating the potential risk from a process, and assessing the potential loss. It is a ranking system that gives a relative index to the risk of individual process units due to potential fires and explosions. It serves as a guide for the selection of fire and explosion protection methods, assists in determining the spacing between adjacent process units, ranks individual process units where special safety attention can be focused, and serves as a guide for insurance agencies to set insurance rates. It ranks individual process units where special safety attention can be focused. A numerical fire and explosion index (F & EI) is calculated, based on the nature of the process and the properties of the process materials. The larger the value of the F & EI, the more hazardous the process. Primarily, Dow method calculates the fire and explosion index for a process unit, taking into consideration the flammability and reactivity of the material handled in the process units under the general and special process conditions.

Strengths of the method:

Methodology is easy to duplicate. Uses material factors that relate to reactivity and flammability. Identifies equipment that can present a flammable or explosive hazard. It suggests approaches to control a hazard. Methodology forces the user to evaluate the different aspects of a process unit that increase the severity of a fire or explosion. Relatively easy to learn how to use the methodology. It is based on actual loss experience, but is still fairly conservative. Industry recognized the methodology for risk ranking a chemical process.

Limitations of the method:

- It is not a perfect tool but a useful tool.
- Intended to be used during design stage of a project. Can also be used on an existing plant, but is harder to apply.
- Calculates maximum probable property damage (MPPD), but is not a good tool for demonstrating normal expected loss.
- Loss control credit factors do not change the F & EI, they only affect the maximum probable property damage.

The method involves material factor (MF), which is a measure of reactivity and flammability, and general process hazards (GPH), which play a primary role in determining the magnitude of a loss incident. General process hazards considered include exothermic and endothermic reactions, material handling and transfer, enclosed or indoor process units, access, and drainage and spill control. Special process hazards (SPH), contribute to the probability of a loss incident. Special process

Table 5.10 gives the degree of hazard in terms of the numerical value of F & EI.

Table 5.10 Assessment of hazard in terms of F & EI

F & EI range	*Degree of hazard*
1–60	Light
61–96	Moderate
97–127	Intermediate
128–158	Heavy
≥159	Severe

hazards include toxic materials, subatmospheric pressure (< 500 mm Hg), operating in or near flammable range, tank farm storage of flammable liquids, always in flammable range, quantity of flammable/unstable material, process upset or purge failure, dust explosion, liquids or gases in process and in storage, combustible solids in storage, pressure, low temperature, leakage—joints and packing, use of fired equipment, hot oil heat exchanger system, rotating equipment, and corrosion and erosion.

Figure 5.8 gives the procedure for calculating F & EI.

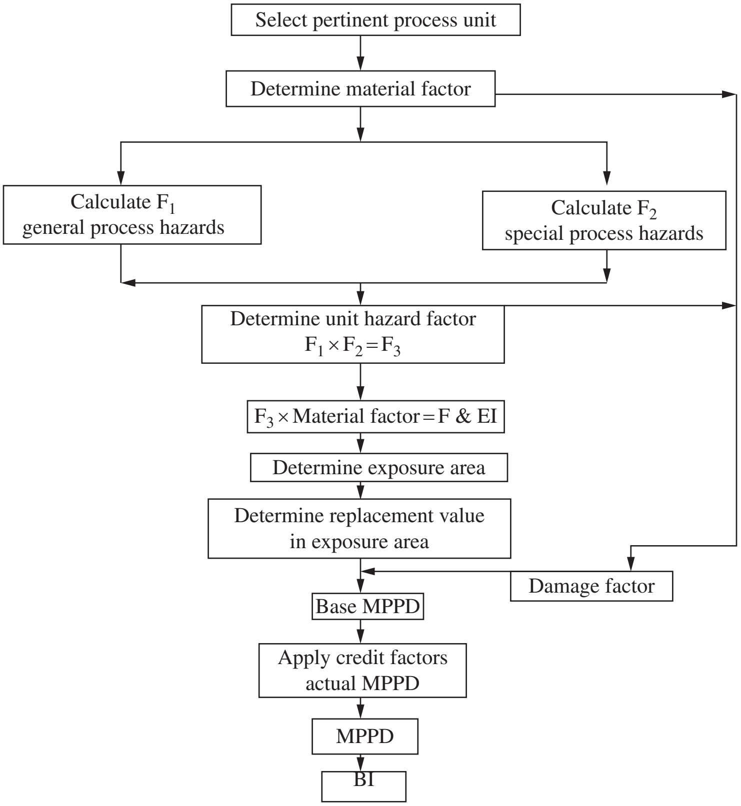


Figure 5.8 Procedure for calculating fire and explosion index

Steps involved in the calculation of F & EI are given in the Dow Guide and Figure 5.8

The first step is to prepare the plot plan, process flow sheet, and identifying the units that would have the greatest impact on the magnitude of any fire or explosion. The index is calculated for each of these units.

Fire & Explosion Index (F & EI), is a measure of the relative hazard and relates to an exposure radius. A numerical index (F & EI) is calculated, based on the nature of the process and the properties of the process materials. The larger the value of the F & EI, the more hazardous the process is.

The basis of F & EI is a *material factor* (MF). Material factor is the intrinsic rate of potential energy release caused by fire or explosion produced by combustion or chemical reaction. The MF is then multiplied by a *unit hazard factor*, F_3, to determine the F & EI for the process unit. The unit hazard factor is the product of two factors which take into account of the hazards inherent in the operation of the particular process unit: the general and special process hazards, $F_1 \text{x} F_2$.

The material factor is a number ranging from 1–40 and is a measure of the intrinsic rate of energy release from the burning, explosion, or other chemical reaction of the material. Measure of the flammability (N_f) and reactivity (N_r) of a material. Values for the MF for over 300 of the most commonly used substances are given in the Dow guide. The guide also includes a procedure for calculating the MF for substances not listed from knowledge of the flash points, flammability and reactivity ratings, N_f and N_r, and for dusts–dust explosion test data, in terms of S_t. Some typical material factors are given in Table 5.11.

Table 5.11 Some typical material factors

Material	*MF*	*Flash point(°C)*	*Heat of combustion(MJ/kg)*
Acetaldehyde	24	−39	24.4
Acetone	16	−20	28.6
Acetylene	40	Gas	48.2
Ethylene	24	Gas	47.195
Propylene	21	Gas	45.799
Ammonia	4	Gas	18.6
Benzene	16	−11	40.2
Butane	21	Gas	45.8
Chlorine	1	–	0.0
Cyclohexane	16	−20	43.5
Ethyl alcohol	16	13	26.8
Hydrogen	21	Gas	120.0
Nitroglycerine	40	–	18.2
Sulphur	4	–	9.3
Toluene	16	40	31.3
Vinyl chloride	21	Gas	18.6

Table 5.12 gives material factor determination guide.

Table 5.12 Material factor determination guide

Liquids and gases flammability or combustibility1	***NFPA 325 or 49***	$N_r = 0$	$N_r = 1$	$N_r = 2$	$N_r = 3$	$N_r = 4$
Non-combustible[2]	$N_f = 0$	1	14	24	29	40
F. P > 93°C	$N_f = 1$	4	14	24	29	40
38°C< F.P. < 93°C	$N_f = 2$	10	14	24	29	40
−5°C < F.P. > 38°C or						
F. P. < − 5°C and						
B P. ≥38°C	$N_f = 3$	16	16	24	29	40
F. P. < −5°C and						
B. P. ≥38°C	$N_f = 4$	21	21	24	29	40
Combustible dust or mist[3]				24	29	40
S_t–1 ($K_{st} \leq 200$ bar.m./s)		16	16	24	29	40
S_t–2 ($K_{st} = 201–300$ bar.m./s)		21	21	24	29	40
S_t–3 ($K_{st} < 300$ bar.m./s)		24	24	24	29	40
Combustible solids				24	29	40
Dense > 40 mm thick[4]	$N_f = 0$	4	14	24	29	40
Open < 40 mm thick[5]	$N_f = 1$	10	14	24	29	40
Foam, fiber, powder, etc.[6]	$N_f = 2$	16	16	24	29	40

*F.P. = Flash point, closed cup. B.P. Boiling point at standard conditions of temperatures and pressure

*Notes:

(i) Includes volatile solids. Will not burn in air when exposed to temperatures of 438°C for a period of 5 min.
(ii) K_{St} values are for a 16 L or larger closed vessel with strong ignition source.
(iii) Includes wood (5 cm nominal thickness), magnesium ingot, tight stacks of solids, and tight rolls of paper or plastic film. Includes coarse granular material, such as plastic pellets, rack storage, wood pellets, and non-dusting ground material such as polystyrene. Includes rubber goods such as tyres and boots, STYROFOAM brand plastic foam and fine material such as METHOCEL cellulose ethers in dust/leak-free packages, etc.

Temperature adjustment of material factor: It is important to recognize that the MF represents the hazard of the selected material at *ambient temperature* and *pressure*. Reactivity of materials increase with increased temperatures. Hazardous situations with materials get enhanced with temperature, apart from weakening of materials of construction used for reactors and other equipment. If the process unit temperature is above 60°C, the MF requires adjustment. No adjustment is required for material that exhibits reactivity at temperatures less than 60°C, has flash point less than 60°C, and is handled at above its flash point at ambient temperature. Temperature adjustment is determined using Table 5.13 effects of pressure are discussed under *Special Process Hazards*.

Exothermic start is the temperature when heat generating chemical reaction temperature is detected in accelerating rate calorimeter or similar calorimeter. In calculating the F & EI for a unit the value for the material with the highest MF, which is present in significant quantities, is used. General Process Hazards (F_1): The general process hazards are factors, given below (From A to F), that play a primary role in determining the magnitude of the loss following an incident.

Exothermic chemical reactions: The penalties are 0.30 for a mild exotherm, (such as hydrogenation, hydrolysis, isomerization, sulfonation, and neutralization), 0.50 for a moderately exothermic reactions (such as alkylation, esterification, addition reactions, oxidation, polymerization, and condensation), 1.00 for a critical-to control exothermic reaction (such as halogenation), and 1.25 particularly sensitive exothermic reaction (such as nitration)

Table 5.13 Material factor temperature adjustment

Material factor temperature adjustment N_f S_t N_r
Enter N_f (S_t for dusts) and N_r
If temperature is < 60°C, go to *e*
If temperature > flash point, and > 60°C, enter 1 under N_f ----
If temperature is above exothermic start or S.I.T., enter *1* under N_r ----
Add each column, but enter 4 when total is 5
Using e and table, determine MF and enter on F & EI form

*Note: 60°C can be reached in storage due to layering and solar heat.

Endothermic processes: A penalty of 0.20 is applied to reactors, unless the energy is contributed by the combustion of a fuel for which it should be 0.40. For example, calcination has a penalty of 0.40, electrolysis has a penalty of 0.20, and pyrolysis or cracking has a penalty of 0.20, if electricity is used as energy source, and 0.40 if direct fired heat is used.

Materials handling and transfer: This penalty takes into account of the hazard involved in the handling, transfer and warehousing of the material. The loading or unloading process for Class I flammables or LPG type chemicals with the lines that can be connected or disconnected requires a penalty of 0.50. Air present in centrifuges, batch reactors, or mixers (inerted or not) that might initiate fires or reactivity hazards requires a penalty of 0.50. Warehouse or yard storages (not storage tanks) involving chemicals with potential fire hazards requires a penalty of 0.85, 0.65, 0.40, and 0.25, depend on the flammability of the chemicals handled. Using racks without rack sprinklers, will attract an additional penalty of 0.20.

Enclosed or indoor process units: Enclosed area is defined as any roofed area with three or more sides or an area enclosed by a roofless structure with walls on all sides. Accounts for the additional hazard where ventilation is restricted. Penalties applicable depend on the following categories of enclosures:
Dust collectors located inside enclosures a penalty of 0.50. Handling flammable fluids at a temperature above their flash points in an enclosed area requires a penalty of 0.45. LPG or any flammable fluids handled above their boiling points in an enclosed area require a penalty of 0.60. However, if more than 4,536 kg (10,000 lb) of flammables are handled, the penalty will be 0.90. All the above penalties will be reduced by 50 percent if properly designed mechanical ventilation is in place.

Access of emergency equipment: Access should be at least from two sides, with one access should be from a roadway and accessible monitor nozzle during operation. Process areas over 930 m^2 (10,000 ft^2) or 2,323 m^2 (25,000 ft^2) with inadequate accesses will have a penalty of 0.35.

Drainage and spill control: penalizes design conditions that would cause large spills of flammable material adjacent to process equipment, such as inadequate design of drainage. This penalty is given only for material with flash point is below 60^{o}C or material is handled above its flash point. The main factors of the penalty arethe total volume of flammables and fire fighting water that are safe enough to handle such amounts. The drainage is calculated as the combined volume of the following:

Special process hazards (F_2): Contribute primarily to the probability of a loss incident. Some contributing factors are type of reaction, process temperatures, process pressure and quantities of fuel. The special process hazards are the following factors that are known from experience to contribute to the probability of an incident involving loss.

(i) **Toxic materials:** The presence of toxic substances after an incident will make the task of the emergency personnel more difficult. The factor applied ranges from 0 for non-toxic materials, to 0.8 for substances that can cause death after short exposure. This penalty depends on health factor, N_h, of the material and given by Penalty = 0.20 × N_h.

(ii) **Sub-atmospheric pressure:** Allows for the hazard of air leakage into equipment, which might result in fires or explosions. It is only applied for pressures less than 9.5 bara (500 mm Hg).

(iii) **Operation in or near flammable range:** Covers for the possibility of air mixing with material in equipment or storage tanks, under conditions where the mixture will be within the explosive range. The more hazardous the materials or process conditions are, the higher the penalty used. However, no penalty is used if penalty is already applied under (ii). The following conditions are considered:

Tank storage handling flammable liquids with N_f 3 or 4 with a possibility of air ingress during pump-out or sudden cooling of the tank, non-inerted storage handling combustible liquids at temperatures above their flash points, or open vent or non-inert gas padded operating pressure-vacuum relief requires a penalty of 0.50.

Process equipment operating near flammable range of some material upon instrument failure, or any process that depends in inert purge to make it out of flammable range, or barges or tank cars requires a penalty of 0.30. Process or operation always in flammable range of the material(s) requires a penalty of 0.80.

(iv) **Dust explosion:** Covers for the possibility of a dust explosion. The degree of risk is largely determined by the particle size. The penalty is applied to any process handling combustible dusts such as transferring, blending, grinding, conveying or bagging, etc. The finer the dust the higher the maximum pressure rise and also the maximum pressure generated and hence the higher the hazard. The penalty factor varies from 0.25 for particles above 175μm to 2.0 for particles below 75μm. Table 5.14 gives penalties for different size ranges of dusts.

Table 5.14 Dust explosion penalties

Particle size (μ m)	*Tayler mesh size*	*Penalty*
+ 175	60–80	0.25
150–175	80–100	0.50
100–150	10–150	0.75
75–100	150–200	1.25
< 75	> 200	2.00

**Note:* The penalty is reduced if inert gas atmosphere is used. Source: AIChE

Table 5.15 High pressure penalty for flammable and combustible liquids

	Pressure	
Psig	***kPag***	***Penalty***
1,000	6,895	0.86
1,500	10,343	0.92
2,000	13,790	0.96
2,500	17,238	0.98
3,000–10,000	20,685–69,950	1.00
> 10,000	> 20,685	1.50

**Source:* AIChE

(v) Relief pressure: This penalty accounts for the effect of pressure on the rate of leakage, should a leak occur. Equipment design and operation becomes more critical as the operating pressure is increased. The factor to apply depends on the relief device setting and the physical nature of the process material. Operating pressure above atmospheric pressure might result in leakage of flammables, with leakage increasing with increase on pressure. The penalties above 1,000 psig operating pressures are given in Table 5.15

(vi) Low temperature: This factor allows for the possibility of brittle fracture occurring in carbon steel, or other metals, at low temperatures, at/or below their ductile/brittle transition temperatures. If the process utilizes carbon steel construction and operates at or below its ductile/brittle transition temperature, the penalty is 0.30. For other materials the penalty is 0.20.

(vii) Quantity of flammable material: The potential loss will be greater, the greater the quantity of hazardous material in the process or in storage. The factor to apply depends on the physical state and hazardous nature of the process material, and the quantity of material. It varies from 0.10 to 3.0. There are three categories, calculated separately by considering only one applicable category based on the material selected for MF.

***Liquids or gases in process*:** Considers the quantity of the spilled material that creates fire, explosion or reaction hazard. The penalty is based on the flow rate of the material for 10 minutes, where the larger value between the process unit and the largest quantity in the connected unit is applied.

Table 5.16 gives process unit risk analysis summary.

Table 5.16 Process unit risk analysis summary

1. Fire & explosion index (F & EI)	
2. Radius of exposure	m
3. Area of exposure	m^2
4. Value of area of exposure	$

(Continued)

Table 5.17 (Continued)

5. Damage factor	
6. Base maximum probable property damage (base MPPD) [4 × 5]	$
7. Loss control credit factor	
8. Actual maximum probable property damage (actual MPPD) [6 × 7]	$
9. Maximum probable days outage (MPDO)	Days
10. Business interruption (BI)	$

*Refer to *Fire & Explosion Index Hazard Classification Guide* for details.

Table 5.17 gives summary of fire and explosion index calculation form

Table 5.17 Fire and explosion index estimation form

Area/country:
Company:
Location:
Date:
Plant:
Process unit:
Prepared/Evaluated by:
Reviewed by:
Approved by:
Materials in process unit:
Design, start-up, normal operation, and shut-down details:
Basic material(s) for material factor:

Note: Adjusted material factor for temperature effect (See Table 5.13)

1. General process hazards		
	Penalty factor	***Penalty factor***
	range	***used***
Base factor	1.00	1.00
A. Exothermic chemical reactions	0.3–1.25	
B. Endothermic processes	0.2–0.4	
C. Material handling and transfer	0.25–1.05	
D. Enclosed/indoor process units	0.25–0.90	
E. Access	0.2–0.35	
F. Drainage and spill control m^3	0.25–0.50	
General process hazard factor, F_1		

(Continued)

Table 5.17 (Continued)

2. Special process hazards		
Base factor	1.00	1.00
A. Toxic material(s)	0.20–0.80	
B. Sub-atmospheric pressure (< 500 mm Hg)	0.50	
C. Operation in or near flammable range --- inerted --- not inerted		
1. Tank farm storage for flammable liquids	0.50	
2. Process upset or purge failure	0.30	
3. Always in flammable range	0.80	
D. Dust explosion	0.25–2.00	
E. Operating pressure, kPag	---	
Relief valve setting, kPag	---	
F. Low temperature	0.20–0.30	
G. Quantity of flammable/unstable material	----- kg	
H_c ---- kcal/kg		
1. Liquids or gases in process	---------	
2. Liquids or gases in storage	---------	
3. Combustible solids in storage, dust in process	---------	
H. Corrosion and erosion	0.10–0.75	
I. Leakage—Joints and packing	0.10–1.50	
J. Use of fired equipment	----------	
K. Hot oil heat exchange system	0.15–1.15	
L. Rotating equipment	0.50	
Special process hazards, F_2	---------	
Process unit hazards factor, $F_1 \times F_2 = F_3$	---------	
Fire and explosion index, $F_3 \times MF$	**-------**	

Mond Index, developed by ICI, uses specifically the material toxicity in addition to the other aspects discussed under Dow analysis.

5.14 Security Vulnerability Analysis

Security vulnerability analysis (SVA) is a process in identifying and then preventing potential security weaknesses in a facility—weaknesses that an adversary could exploit to gain access to a facility, cause intentional damage or a hazardous release, and inflict fear in a community. It is presumed that an adversary will look for targets with the greatest community impact, that is, the highest consequences and the fewest countermeasures/safeguards to circumvent. SVA is a qualitative rather than a quantitative process that allows the ranking and comparison of security risks from facility to facility or from company to company.

Similarities between PHAs and SVAs: These measures have a common goal to prevent a hazard from developing into an unwanted consequence. In PHA, failures are caused by *unintentional* situations or events. The resulting consequence and the probability that the consequence will actually occur are *independent*. The consequence does not affect the probability and the probability does not affect the consequence after it occurs.

SVAs differ from PHAs in that SVAs address *intentional* situations or events, and probability and consequence are inter-dependent. This inter-dependence is key to development of security-related risk management efforts.

5.15 Annexure

Table 5.18 gives a typical *work place check list*.

Table 5.18 Work place hazard checklist

Item	*Yes*	*No*	*Action required*
WORK ENVIRONMENT			
Ventilation			
Removal of fumes and dust			
Temperature and humidity control			
Noise levels			
Vibration			
Lighting—general purpose			
- for a particular task			
- absence of glare			
- work area			
- corridors			
- exterior			
Ergonomics—layout of work area			
Furniture			
HYGIENE			
Separate work and eating areas			
Drinking water			
Washing facilities			
Toilets			
Work clothes lockers and hanging areas			
Regularly cleaned area			
HOUSEKEEPING			
Storage—racks, bins, shelves			

(Continued)

Table 5.18 (Continued)

- aisles and walkways kept clear
- neat and orderly
- not too high
- heavy items kept at low level
- sufficient space to access items
Removal of combustibles
Rubbish—regularly removed
- sufficient bins
- separation of wastes
TRAINING
Induction
Task specific
Process specific
Management
Refresher courses
EMERGENCY EQUIPMENT
Procedures
Contact telephone numbers
Safety showers
Eye wash units
Breathing apparatus and/or respirators
First-aid kit
First-aid officers—name
- location
Antidotes where applicable
Torches
Loud hailer
Emergency lighting
FIRE PROTECTION
Fire separation—walls and floors
- doors and windows
- ceilings and ducts
- vertical shafts
Isolation of risk areas
Fire detection system
Alarm and emergency evacuation system

(Continued)

Table 5.18 (Continued)

Are alarms audible in all areas
Fire extinguisher type
- location
- serviced
- operator training
Fire hose reels
Fire hydrants
Automatic fire fighting system
Access for fire brigade
EVACUATION
Procedures established
Wardens appointed
Display of floor plans and escape routes
Practiced regularly (twice yearly)
Communication system
Exits - unobstructed and open from inside
PERSONNEL PROTECTION
(consider correct selection, location, information and warning signs and maintenance)
Coats/overalls
Eye protection
Gloves
Footwear
Respirators
Helmets
Hearing protection
MANAGEMENT
Policy displayed
Committee—employee representative
- regular meetings
Responsibilities defined
Departmental safety officer (DSO)
Employee representatives
Safety manual
Qualifications and training of operators
Review of research projects

(Continued)

Table 5.18 (Continued)

Accident and incident reporting
Hazard reporting and follow up
Provision for visitors
Provision for disabled
Monitoring effectiveness of OS & H program
WORK PRACTICES
Avoid manual handling
Use mechanical handling equipment
Confined space procedures
Permits—68 contractors
- hot work
- fire detection isolation
Advice to cleaners and maintenance personnel
Not working alone
Fail-safe protection
Fall protection
FLAMMABLE LIQUIDS
Stored in a flammable liquids cabinet
Quantities are not excessive
Suitable containers
Spark proof electrics
Static energy control
Class-B fire extinguisher near by
Correct signage
Bunding
COMPRESSED GASES
Reticulated from outside the building
Number of cylinders inside rooms
Cylinders secured
Segregation of incompatible gases
Transported on appropriate trolley
Serviced regularly
Tamper proof
Correct signage
Check lines carrying gas

(Continued)

Table 5.18 (Continued)

ACIDS AND POISONS
Separate storage
Corrosive/acids cabinet
Not excessive quantities
Correctly signed
Neutralizing agents
Decant in fume hood
HIGH HAZARD PROCESSES
Detailed preliminary studies
Special protective equipment
Independent assessment
PRESSURE EQUIPMENT
Legislation and code compliant
Safety devices
Regularly maintained
Correct signage
Qualified electrician used to install
Regular maintenance
ELECTRICAL EQUIPMENT
Sufficient circuits
Protection of fittings against external damage
Condition of plugs and leads
Trailing leads
CHEMICALS
Material safety data sheets (MSDS)
Register of chemicals
Containers—suitable type
- condition
Correct labeling
Only sufficient stock
Storage—suitable
- sufficient
- location
Segregation into classes
Carriers for large bottles

(Continued)

Table 5.18 (Continued)

Fume cupboards—AS/NZS 2243(8) compliant
- regularly tested
- not used for storage of
chemicals
- condition
Waste collection and disposal spill kit
- location
- appropriate
- easy access
MECHANICAL AND HEAT HAZARDS
Guarding of machines
Maintenance of machines
Emergency isolation switches
Cranes and hoists—serviced
- marked
Guard rails
Ladders and steps
Scaffolds
Bays and screens for welding and grinding
Ovens and furnaces
Heating equipment

Review Questions

1. (a) For a chemical process, give a typical methodology used in order to identify the hazards involved in the process.
   (b) What type of questions that must be generated to facilitate identification of hazards involved in the process?
2. Illustrate, by means of a suitable diagram, hazard identification and risk assessment procedure for a chemical process.
3. (a) What are hazard and operability studies?
   (b) What are check lists? How are they useful in identifying hazards?
4. What is meant by risk assessment? What are the steps involved in risk assessment procedures?
5. (a) What is the difference between probabilistic risk assessment (PRA) and quantitative risk analysis (QRA)?
   (b) What types of data are required for carrying out quantitative risk analysis (QRA)?
6. What are the important hazard identification methods? List them.
7. Give a typical check list for possible release of hazardous materials and energy from equipment and piping in a process plant. Include all possible events that can involve such releases.

8. What are the different types of hazards involved in an ammonia manufacturing facility with natural gas as the raw material? List them.
9. What are the types of hazards involved in a petroleum refinery, especially distillation and catalytic conversion units? Include all possible hazards.
10. (a) What is the usefulness of Dow fire and explosion index calculations?
    (b) Briefly describe the procedure involved in the calculation of fire and explosion index.
11. (a) What is HAZOP study?
    (b) What are the procedural steps involved in a HAZOP study?
12. What are the guide words used in a HAZOP study? Give their meanings and comment on them.
13. Describe a safety review process for using a cylinder of phosgene to charge gaseous phosgene to a reactor. Review up to the reactor only.
14. Liquid levels in storage tanks are frequently determined by measuring the pressure at the bottom of the tank. In one such tank the *material stored in the tank was replaced by a different material* and an overflow resulted. Why? Give reasons.
15. What is an event tree? Explain its utility.
16. What are the different types of hazards associated with chemical process plants? Give brief description of each of such hazards.
17. (a) How are hazard severity, probability of occurrence and risk related? Give the equation.
    (b) What are the benefits of a HAZOP study?
18. Name the important events that can lead to emergency situations in plant operations.
19. Give examples of possible causes with respect to the following guide words for **flow** in a HAZOP study.
    (i) HIGH
    (ii) LESS
    (iii) NONE
    (iv) REVERSE
20. Give examples of possible causes with respect to the following guide words for **pressure** in a HAZOP study.
    (v) HIGH
    (vi) LOW
21. (a) Name different methods used to determine and evaluate the hazards of the process being analyzed?
    (b) Describe any one of the methods named in part (a) of the question.
22. (a) What are the elements common to all process hazard analyses.
    (b) Give a list of hazards commonly found in process operations, grouped according to how thermal and chemical energy are stored. Construct a fault tree for the top event of fire/explosion.
23. (a) What are the different symbols used in the construction of fault trees.
    (b) What is cause–consequence analysis? Describe through an example.
24. (a) In Dow Fire and Explosion Index estimations, what is the role of *Material Factor*?
    (b) What is the highest value of material factor? Give example of a material that has the highest value of material factor.
25. Discuss the process of HAZOP safety reviews.

26. How are hazard surveys carried out? Explain.
27. (a) What is the utility of process hazard checklists?
    (b) Give a typical checklist illustrating how hazards can be pin-pointed and highlighted.
28. Discuss and explain plant layout issues that are to be included in a hazard survey.
29. (a) How is degree of hazard classified based on Fire and Explosion Index?
    (b) How is degree of hazard, determined by Dow Fire and Explosion Index?

    Index procedure for a plant or unit of a plant, is useful in determining safety measures to be incorporated for the plant or unit. Give examples of such measures.
30. What are the types of general and special process hazard categories that are included in Dow Fire and Explosion Index estimations?
31. Which of the following are more hazardous?
    (i) Materials in storage or in process
    (ii) Exothermic reactions or endothermic reactions
    (iii) Acetylene or ethylene
    (iv) Fuel oil or butane
32. List out the factors that can be considered as general process hazards.
33. Compare HAZOP and what-if analyses in safety studies.
34. What is safety audit for a chemical plant? What are the main elements involved in such an audit?
35. List down the hazards involved in the manufacture of polyethylene, starting from the raw materials stage to the packaging stage of the finished product.
36. What is the utility of check lists in inventory control in a large chemical manufacturing facility? Explain.
37. What are the preventive and protective measures used in process industry followed by a hazard survey?
38. Why, despite formal mandatory hazard analyses carried out by the industry, accidents continue to take place? Give reasons for such situations, which, many times, are repetitions of past incidents.
39. Suggest measures to be considered with respect to education, training, retraining, and motivation that are to be adopted to improve process safety.
40. What are the plus and minus points in different hazard analysis methods?
41. What is ALARP? In what way is it useful?
42. What is PSM? What is PHA? What is SVA? Briefly discuss these.

Key words for Internet searches

AIChE, DOE, AS/NZS 2243(8)

*Note: *Vast number of sites is given in Appendix A of the book for the purpose of use in internet searches for key words by enterprising teachers, students, industry professionals, and managements*.

Chapter 6

Preventive and Protective Measures

Learning Objectives

6.1 Safety Options

Prevent by using inherently safe design methods.
Control by including primary response systems.
Mitigate by using secondary response systems to limit impact.
Buffer by isolating facilities away from populations.

6.2 Process Safety Approaches

Safety approaches can be categorized as inherent, passive, active, and procedure-based. These approaches are of use in a comprehensive safety management, of both hazards as well as plant in which such hazards are likely to be present. These approaches are not new, but evolved over periods of time, mostly based on experiences while designing and running the plants.

Inherent Safety

The wording of this concept was coined by T. A. Kletz of U.K. based Imperial Chemical Industries (ICI). This was based on the *green chemistry* approach towards safety. Nonhazardous or low hazardous processes and materials are substituted in place of hazardous processes and process materials. For example, ammonia manufacture in the past was based on high pressures of the order of 1,000 atm, but the use of catalysts reduced the operating pressures to around 300 atm. At the same time instead of thicker monolithic construction of reactors, multilayer reactors with better materials of construction came into existence, reducing failures. In those periods, the words *inherent* or *green chemistry* were not in use. Environment-friendly processes and materials are coming into existence. Applications of highly hazardous materials are being replaced by less or no hazardous materials came into use. Water replaced hydrocarbon liquids as solvents, thereby reducing fire or toxic risk to plants and people. Less hazardous pesticides came into existence in place of high-risk pesticides.

Passive

Consequences and frequency of incidents are reduced without use of safety devices by reducing reaction pressures as mentioned in ammonia example, and design of equipment to withstand higher pressures to contain explosions or runaways. Operation, inspection, and maintenance of equipment become important to reduce failure possibilities.

Active

Use of controls, interlocks and sprinklers over reactors that are prone to fire risks, are examples of active systems, which detect and take action while hazardous conditions develop.

Procedural

Procedural safety features include standard operating procedures, safety rules and procedures, operator training, emergency response procedures, and management systems. For example, an operator may be trained to observe the temperature in a reactor and apply emergency cooling if it exceeds a specified critical value. In general, for a high hazard system, procedural risk management systems do not, by themselves, provide adequate risk management. Human reliability is not high enough, and people often cannot diagnose a problem, determine the appropriate action, and take that action quickly enough. However, procedural safety systems will always be a part of a comprehensive risk management program—at a minimum they will be required to ensure ongoing maintenance and management of active and passive safety systems.

Table 6.1 gives a brief summary of the strategies involved in active, passive, and inherent safety measures to reduce or prevent hazardous situations in plant operations. In general, the preferred ranking of methods to control process risks is—inherent > passive > active > procedural or administrative.

Table 6.1 Approaches involving active, passive, and inherently safer methods to minimize or prevent plant hazards

Method	*Description*
Active	Controls, safety interlocks, automatic shut-down systems. Multiple active elements. Sensor—detect hazardous condition. Logic device—decide what to do. Control element—implement action. Prevent incidents, or mitigate the consequences of incidents. Examples of active systems: high-level alarm in a tank shuts down an automatic feed valve. A reaction capable of generating 10 barg (150 psig) pressure in case of a runaway in a 1 barg (15 psig) reactor with a 0.35 barg (5 psig) interlock that stops feeds and a rupture disk to reduce pressure directing contents to effluent treatment (what could happen?).

(Continued)

Table 6.1 (Continued)

Passive	Minimize hazard using process or equipment design features which reduce frequency or consequence without the active functioning of any device. Examples of passive systems: containment dike around a hazardous material storage tank. A reaction capable of generating 10 barg (150 psig) pressure in case of a runaway in a vessel designed for 17 barg (250 psig). (The reactor can contain the accident unless e.g. damage). Inherent safety: Eliminate or reduce the hazard by changing the process or materials which are non-hazardous or less hazardous. Integral to the product, process, or plant—cannot be easily defeated or changed without fundamentally altering the process or plant design. Examples of inherently safer system: substitution of water for a flammable solvent in a process. An atmospheric pressure reaction using nonvolatile solvents (no potential for overpressure).
Procedural	Standard operating procedures, safety rules, emergency response procedures, training. Examples: confined space entry procedures. The same reactor under reference without the interlock. The operator is instructed to monitor the pressure and shut-down feed (human error).

6.3 Inherent Safety and Design

Strategies for designing inherently safer processes can be divided into four groups:
Minimize – use small quantities of hazardous materials, reduce the size of equipment operating under hazardous condition such as high temperature or pressure. Process intensification can reduce inventory of hazardous materials.
Substitute – use less hazardous materials, chemistry, and processes. Use of alternative reaction routes or process conditions in order to reduce the risk of runaway exothermic reactions, fires, explosions and/or the generation or release of toxic materials. It should be noted that in some cases changes made to improve the environment have resulted in inherently less safe designs. For example, the collection of vent discharge gases for incineration or for absorption on to carbon beds has resulted in explosions when the composition of the gases in the vent system has entered the flammable range. Examples include use of water-based solvents in place of organic solvents, elimination of CFC refrigerants, use of cyclohexane in place of benzene, supercritical CO_2 in place of methylene chloride, use of membrane process to produce Cl_2 which eliminates need for Hg, and change sequence of steps for reaction to avoid toxic intermediates.
Moderate – reduce hazards by dilution, refrigeration, process alternatives that operate at less hazardous conditions.
Simplify – eliminate unnecessary complexity, design *user friendly* plants.

Inherent safety is a concept particularly used in the chemical and process industries. An inherently safe process has a low level of danger even if things go wrong. It is used in contrast to safe systems where a high degree of hazard is controlled by protective systems. It should not be confused with intrinsic safety that is a particular technology for electrical systems in potentially flammable atmospheres. Inherently, safer chemical processes involve the use of smaller quantities of hazardous materials, the use of less hazardous materials, the use of alternative reaction routes or process conditions in order to reduce the risk of runaway exothermic reactions, fires, explosions and/or the generation or release of toxic materials. An inherently safer design is one that avoids hazards to people and environment instead of controlling them, particularly by reducing the inventories of hazardous material at any time and the number of hazardous operations in the plant. Traditional safety practices typically reduce risk by lowering the probability of an incident and/or mitigating the consequences of an incident. This approach alone, although extremely important and generally effective, does not reduce the hazards of serious chemical incidents because it attempts to control hazards rather than eliminate them. Inherent safety is especially important in present-day world where terrorists may cause a chemical release by methods that bypass or defeat normal safety systems. Example of change over from batch to continuous process: The old batch process for the manufacture of nitroglycerin, the reaction was carried out using one tons of material, the reason is because the time scale was long, 92 hr. The mixing process in the batch reactor was not good. The problem was solved by the design of a small, continuous flow, well-mixed reactor with residence time reduced from 2 hr to 2 min. Continuous processes can be designed with more *error tolerance* than batch processes. A very simple example is making piping and joints capable of withstanding the maximum possible pressure if outlets are closed. The Dow fire and explosion index is essentially a measure of inherent danger and is the most widely used quantification of inherent safety.

It uses less hazardous materials, alternative reaction routes or process conditions in order to reduce risk of runaway exothermic reactions, fires, explosions, toxic release, and so on. It includes consideration of chemistry as well as engineering issues such as plant siting and layout, transportation, and detailed equipment design. Applicable at all levels of design and operation from conceptual design to plant operations. The important principle in inherent safety is to eliminate the hazard itself. To eliminate hazards, change the process or change the materials to nonhazardous or less hazardous ones, or change the conditions of use. The best method to achieve this is to reduce the inventory of hazardous substances such that a major hazard is no longer presented. However, this is not often readily achievable. Other possible methods to achieve an inherently safer design are as follows:

Intensification to reduce inventories: This is the most widely used method of inherently safer design. Intensification should attempt to reduce quantities of material in the process reactors, distillation and other separation equipment, storage vessels, material transport systems, and energy systems. For example, hazardous reactants, such as phosgene, are often generated as required in adjacent plant so that the actual amount in the pipeline is kept to an absolute minimum. Plug flow/tubular reactors with static mixing elements, centrifugal distillation techniques, or innovative, high surface area heat exchangers, which involve less inventories than batch reactors should be preferred. Cyclone-type reactors involve smallest possible inventories. Other intensification methods include use of smaller quantities in sumps, using pipeline transport in place of tanker transport, and layout to minimize piping.

Substitution of hazardous substances by less hazardous alternatives. If intensification cannot be achieved an alternative is substitution, the use of safer, nonflammable or less flammable, less toxic solvents, refrigerants or heat transfer materials, like water should be used. For example, some ethylene oxide plants use hundreds of tons of boiling paraffin to cool reaction tubes and this presents a bigger hazard than the mixture of ethylene and oxygen in the tubes. Modern plants now use water for cooling instead of paraffin. Other examples of substitution include use of cyclohexane in place of benzene, use of supercritical solvents, elimination of CFCs as refrigerants, use of catalysts to enhance reaction selectivity, or to allow desired reactions to be carried out at a lower temperature or pressure, and replacing membrane cells in place of mercury cells for caustic soda and chlorine manufacture. Another example is use of solid super-acid catalysts, proposed as replacements for catalysts such as hydrogen fluoride and aluminum chloride for processes such as alkylation and acylation. Release of hydrogen fluoride from alkylation plants results in the formation of denser-than-air clouds that descend to ground levels, causing health hazards to people. Replacement by sulfuric acid gives rise to liquid spills, which are much easier to handle and treat. Other new chemical synthesis technologies such as electrochemical techniques, enzymatic synthesis, bio catalysis, domino reactions, and laser light *micromanaged* reactions are being investigated in the laboratory and offer potential future inherently safer industrial processes. There are many examples of hazardous chemicals, such as benzene and other known carcinogens, which have been replaced by other chemicals that either have a reduced risk potential or have no known risks associated with them. The replacement of solvent-based paints and inks by water-based materials in the engineering and printing industries has not only reduced health risks, but has eliminated fire risks and led to environmental benefits by reducing the potential for pollution. In addition to using safer chemicals, it is possible to reduce the risks associated with manufacture by making changes in the reaction routes. The most widely quoted alternative route is for the product made at Bhopal, the insecticide carbaryl. The reaction pathway involved reacting methylamine and phosgene to generate methyl isocyanate which in turn was reacted with α-naphthol to form carbaryl. It was the release of the intermediate methyl isocyanate which caused the disaster at Bhopal. The alternative reaction route is to use the same raw materials but in a different order. Phosgene and α-naphthol can be reacted together to give naphthyl chloroformate. No methyl isocyanate is produced in this alternative reaction route. When considering alternative reaction routes it is important to consider, in turn, the reactants, the catalysts, the solvents, the intermediates and the compatibility of all materials used. For example, in a particular process, acetone was used as a solvent. However, it was realized because of the heat of reaction that the uncontrolled addition of one of the reactants or the loss of cooling would have led to a vigorous boiling of the mixture and result in the possible over pressurization of the reactor and loss of containment. The simple replacement of acetone with toluene, which has a higher boiling point, eliminated this hazard. An understanding of the relationship between chemical structure and hazardous properties of materials is valuable in identifying inherently safer material substitutions. For example, hydrocarbons of higher molecular weight are generally less of a fire hazard than lower molecular weight materials of a similar structure. Benzene is a greater fire hazard than toluene, and toluene is more of a fire hazard than xylene. Similarly, longer chain aliphatic hydrocarbons are less of a fire hazard than shorter chain materials.

Attenuation or moderation: To reduce hazardous process conditions, that is, temperature and pressure. Moderation of conditions can be accomplished by physical means such as lower temperature or dilution, and by chemical means such as using a different reaction chemistry that requires less severe conditions.

Limitation of effects: By changing designs or process conditions rather than by adding on protective equipment that may fail. For example, it is better to prevent overheating by using a fluid at a lower temperature rather than use a hotter fluid and relying on a control system. Minimizing diked areas around storage tanks, avoiding having multiple stage reactions in a single vessel, keeping conditions below decomposition levels, using submersible pumps, minimizing equipment with moving parts, isolating reactive chemical storage, and using safe locations for operating facilities are some other examples of limiting effects.

Dilution: Dilution reduces the hazards associated with the storage and use of a low boiling hazardous material in two ways, namely, by reducing the storage pressure, and by reducing the initial atmospheric concentration if a release occurs. Materials which boil below ambient temperature are often stored in pressurized systems. The pressure in the storage system can be lowered by diluting the material with a higher boiling solvent. This reduces the pressure difference between the storage system and the outside environment, reducing the rate of release in case of a leak in the system. If there is a leak, the atmospheric concentration of the hazardous material at the spill location is reduced. The reduced atmospheric concentration at the source results in a smaller hazard zone downwind of the spill. Examples of materials which have been handled in a dilute form to reduce the risk of handling and storage include aqueous ammonia or methylamine in place anhydrous, muriatic acid in place of anhydrous HCl, and sulfuric acid in place of oleum (SO_3 solution in sulfuric acid). The area impacted by a leak of hazardous material can be reduced significantly by dilution.

Simplicity: Simpler plants are safer than complex plants as they provide fewer opportunities for error and contain less equipment that can fail and fewer opportunities for human error. Simpler systems/processes should be used to reduce potential loss of containment or possibility of errors causing a hazardous event.

Containment: In many cases, it is possible to design process equipment strong enough to contain the maximum or minimum pressure resulting from a process incident. Containment within the process vessel simplifies the design by eliminating high pressure interlock systems. Emergency relief devices such as rupture discs or relief valves may still be required by regulations and codes but the size may be reduced and the hazards associated with opening of the relief devices may be considered to be eliminated. Catch tanks, scrubbers, flare stacks, or other devices to dispose of the effluent from emergency relief systems safely may also be eliminated. Increasing vessel strength to avoid the need for relief valves, using materials that can function over the range of process conditions, elimination of opportunities for human error through simple instructions, elimination of extra equipment, and minimization of numbers of control loops are some examples of simplicity. The maximum pressure resulting from a deflagration of a combustible dust or flammable vapor in air initially at atmospheric pressure is often less than 10 bar. It may be feasible to build equipment strong enough to contain this type of event. Designing vessels for full vacuum eliminates the risk of vessel collapse due to vacuum. Many, storage and transport vessels have collapsed by pumping material out with the vents closed.

Modified storage arrangements: If the above alternatives to achieve inherently safer processes cannot be applied and large quantities of hazardous materials are still needed, then it should be handled in the least hazardous form or in minimum quantities. Consequently, large quantities of ammonia, chlorine, and liquefied petroleum gas are now usually stored as refrigerated liquids, at low pressure below their boiling point rather than under pressure at atmospheric temperature.

Refrigerated storage reduces the magnitude of the consequences of a release from a hazardous material storage facility in three ways: lower storage pressure, reduced immediate vaporization of leaking material, subsequent evolution of vapors from the spilled pool of liquid, and reduced or no liquid aerosol formation. The lower pressure results in lower leak rates and the lower temperature lowers the vaporization rate. The inventories of toxic or flammable materials that are not manufactured on site can be reduced significantly from hundreds of tons to tens of tons if reliable and regular supplies can be delivered, perhaps on a daily basis or on a just-in-time basis. In such circumstances, a release of such materials, although still involving a comparatively large quantity, reduces the potential to cause injury or damage.

This approach does not necessarily involve the modifications of existing plant, though smaller storage tanks would prevent inadvertent increases in the inventories in the future.

Energy limitation: Consideration should also be given to limiting the amount of energy available in the manufacturing process. For example, it is better to prevent overheating by limiting the temperature of the heat transfer fluid than to rely on interlocks which may fail or be disconnected. Semibatch or gradual addition batch processes limit the supply of one or more reactants, and increase safety when compared to batch processes in which all reactants are included in the initial batch charges. For an exothermic reaction, the total energy of reaction available in the reactor at any time is minimized.

Safer products: Examples include the substituting of asbestos by less hazardous alternatives in the manufacture of both insulation material and friction linings used in the braking and clutch systems of motor vehicles. Another example is use of latex paints rather than oil-based paints.

Other means: The use of designs that include avoiding potential domino effects, making incorrect assemblies impossible, tolerating misuse, keeping computer software and controls easy to understand and use, keeping process status clear, having well-defined instructions and procedures, employing passive safety, and minimization hazards throughout life cycle of the materials. Rigorously following tag-out procedures, avoiding reverse flow designs, keeping processes separated, and having reviews before the design becomes finalized fall under other means.

Fail-safe or fail-secure describes a device or feature which, in the event of failure, responds in a way that will cause no harm, or at least a minimum of harm, to other devices or danger to personnel. Fail-safe components of a system are distinguished from fail-secure components in that, in the former, component failure allows, but does not cause or invite, a certain improper system behavior. In the latter, component failure does not allow a certain improper system behavior, although some proper behaviors are impeded. For example, a lock that unlocks at the wrong time has failed, but it may be considered fail-safe if its failure does not send the door flying open or attract undue attention to the unlocked state of the door. In contrast, a fail-secure lock will remain locked during a failure, but cannot be unlocked even with the correct key. Significantly, despite popular belief to the contrary, *fail safe* does not mean that the device or system is designed so that failure is impossible; it simply means that when failure does occur, it should occur in the safest fashion. Inherently safe design (ISD) is supplemented by control systems, alarms and interlocks, shut-down systems, protection systems and devices and response plans.

Categories of Inherently Safer Design

Intensification: It minimizes inventories of hazardous materials. Examples include use of plug flow reactors in place of batch reactors which use smaller quantities and may have better heat transfer. Eductor or cyclone reactors have the smallest practical volume for oxidations and explosive mixtures. Other intensification options include reduction of inventories and quantities in sumps, use of centrifugal mixers for reactors, use of plant layout to minimize piping.

Attenuation: It uses hazardous materials under the least hazardous conditions. Examples include reduction of temperatures in reactors, use of dilute reactants in solvents, use of gravity or gas pressure to transport unstable liquids, and use of refrigerated storage instead of pressurized storage.

Limitation: It changes designs or conditions to reduce potential effects. Examples include minimization of diked areas around storage tanks, avoiding having multiple stage reactions in a single vessel, keeping conditions below decomposition levels, using submerged pumps, minimizing equipment with moving parts, isolation of reactive chemical storage, and using safe locations for operating facilities.

Simplification: It reduces complexity to reduce the opportunity for error. Examples include increasing vessel strength to avoid the need for relief valves, use of materials that can function over the range of process conditions, elimination of opportunities for human error through simple instructions, elimination of extra equipment, and minimization of numbers of control loops.

Other means: These include using designs that avoid potential *domino* effects, making incorrect assembly impossible, tolerating misuse, keeping controls and computer software easy to understand, keeping processes separated, rigorously following tag-out procedures, avoiding reverse flow designs, having reviews before the design becomes finalized, keeping process status clear, having well-defined instructions and procedures, using passive safety, and minimize hazards throughout the life cycle of the material.

6.4 Plant Layout

General: The plant layout shall be arranged to maximize safety, prevent spread of fire, facilitate easy operation and maintenance, consider future expansion, and economize the project. Plant design, siting, and layout has an important bearing in the safety of a process plant. Overall plant layout should involve considerations such as wind direction, soil condition, and product flow. The plant should be located downwind of public roads. No traffic should be permitted through plant area. Utilities, furnaces and fired heaters, flares, workshops, and other units with likely ignition sources should be downwind of process and storage areas, separated from potentially hazardous areas, preferably on the periphery of process areas, with a minimum distance of 15 m (30 m for LPG/LNG facility). Distance between flares and flammable storage area should be a minimum of 60 m. Filling stations should be located near the entrance areas. Parking areas should preferably be located outside the main gate with a minimum distance of 30 m.

Security and firefighting services should be located near the fence with minimum number of entrances and straight roads. Flood lights should be provided pointing outside. There should be no crossing of road/rail traffic and one way traffic should be ensured in these areas. Provision should be made for expansion of tankage for crude and products in a refinery. Control rooms, switch houses, and transformers are critical items and located in *safe* areas as per codes. Control rooms should be located upwind of units with flammable/toxics. Noise producing equipment such as compressors, heavy duty pumps, steam vents, etc., should be avoided near control rooms.

Holding basins/oil-water separators and treatment plants should be located away from plant and storage areas with levels facilitating easy drainage.

A major objective behind optimized plant layout is to avoid escalation of fires and explosions to protect people, assets and reputation, using the principle of inherent safety. Some examples are good separation between hazardous and vulnerable areas, and minimize equipment, liquid hydrocarbon inventory in process equipment, vulnerability through selection of equipment type, and exposure to people through reduced process complexity and maintenance.

Plant layout is often a compromise between a number of factors such as the following:

The need to keep distances for transfer of materials between plant/storage units to a minimum to reduce costs and risks, the geographical limitations of the site, interaction with existing or planned facilities on site such as existing roadways, drainage, and utilities routings, interaction with other plants on site, the need for plant operability and maintainability, the need to locate facilities for hazardous materials as far as possible from site boundaries and people living in the local neighborhood proximity of the site close to populated areas and other "no activity" zones should be avoided. Bhopal disaster, which cased over 2,000 deaths, and its continued effects on the population around, is a point to be reckoned with, location near *growing* cities is risky in terms of exposures of populations to hazardous releases. Blast walls may be needed to isolate potentially hazardous equipment, and confine the effects of an explosion. At least two escape routes for operators must be provided from each level in the process building. An example is location of a chemical plant on the outskirts of Delhi, with the city growing around the plant, caused frequent exposures of the population to chlorine releases. Ultimately, the plant operations were to be shifted away from the area, with considerable expense.

The need to prevent confinement where release of flammable substances may occur. The need to provide emergency escape routes for on-site personnel. The need to provide access for emergency services. To ensure safe emergency evacuation of occupants. To allow for quick emergency response, and the need to provide acceptable working conditions for operators. The most important factors of plant layout as far as safety aspects are concerned are those to prevent, limit and/or mitigate escalation of adjacent events (domino), ensure safety within onsite occupied buildings, control access of unauthorized personnel, facilitate access for emergency services.

Layout piping and equipment diagram(s) should indicate all equipment, ladders, structure, trolley beams, all instruments, valving and hand-wheel orientation, drip funnel locations for underground drains, all electrical switch gear, lighting panels, and sampling systems shall be indicated.

Examples of Specific Safety Aspects in Plant Layout

Separation and isolation: Chemicals which may react with one another are to be physically separated; oxidizers are to be stored in areas remote from fuel storage.

Areas of potential explosions: Storage of explosives, reaction vessels are to be isolated so if there is an explosion, the damage and risk to employees is minimized. Locating all high volume storage of flammable/toxic material well outside process areas. High-pressure gas lines shall not pass through a process area or run within 30 m of important structures or equipment without shut-down valve to ensure that portions of piping within the process area can be isolated from the main gas line and depressurized in the event of an emergency. However, extensive use of shut-down valves may not be needed, since; the increased complexity of the system will require a greater degree of preventive maintenance if unwarranted shut-downs are to be avoided. Shut-off valves shall be provided on all gas and product pipelines into and out of the plant.

The importance of location of occupied buildings, both permanent and temporary, relative to highly hazardous processing facilities is highlighted by several accidents involving deaths of employees. Location and blast resistant design of control rooms received attention after Flixborough disaster, which resulted in large number of deaths of occupants of control room, and in recent times Texas refinery accident involving several deaths. The distance between occupied buildings and plant buildings will be governed by the need to reduce the dangers of explosion, fire and toxicity. In particular, evacuation routes should not be blocked by poor plant layout, and personnel with more general site responsibilities should usually be housed in buildings sited in a nonhazard area near the main entrance. Consideration should be given to siting of occupied buildings outside the main fence. In all cases, occupied buildings should not be sited downwind of hazardous plant areas. Buildings should be designed so that all parts of the building are well ventilated by natural or forced ventilation.

Equipment spacing: It is covered by various codes and standards. These minimum distances are intended only to prevent minor fires from spreading to adjacent equipment. In addition, these distances have been selected to minimize the probability that minor fires will escalate to involve the complete unit. In the case of BLEVEs, it is impractical to provide enough spacing between equipment to prevent a BLEVE at one vessel from spreading to other equipment.

Pumps for high hazard/high temperature fluids should have adequate distances (≥ 3 m between pump bodies). Large compressors should be grouped in one area. Tank farms should preferably *not* be located at higher levels than process units in the same catchment area. Provisions to be made for distances between tanks in a facility and between the facility and adjacent buildings. The separation distance is dependent on the particular type and amount of fuel product. Individual secondary containment for tanks is used to further minimize the risk of heating adjacent tanks in the event of a fire. API gives guidelines and recommendations for separation distances for petroleum storage tanks. These distances depend on the nature of hazards involved. For example, the distances are less for liquids with low vapor pressures, such as petroleum products than those having high vapor pressures, such as LPG and LNG. Not more than two rows of tanks for products should be allowed to facilitate fire tender entry on both sides. Soil condition and drainage should be given due consideration.

Generally, a distance of 15 m is specified by codes for petroleum products and larger distances (30 m) for LPG and LNG. Distance between LPG pressure storage tanks should be *one-quarter of the sum of the diameters of two adjacent tanks*. Distance between low-pressure refrigerated LPG tanks should be one diameter of the largest low pressure refrigerated storage tanks but not less than 30 m. One code gives a distance of 60 m for pressure storage and 90 m for refrigerated storage of ethylene. The implication is that the risk of failure is more for refrigerated storage tank than for a pressure storage vessel. The distances can be reduced if suitable fire/blast walls are constructed between units. Because BLEVEs are so large, it is impractical to provide enough spacing between equipment to prevent a BLEVE at one vessel from spreading to other equipment as stated earlier. Thus, while proper equipment spacing is important, it cannot be relied upon to prevent BLEVEs.

Minimum widths of access way shall be for vehicular access ways within units 4.0 m, pedestrian access ways and elevated walkway1.2 m, stairways and platforms 0.8 m, foot paths in tanks areas 0.6 m, maintenance access around equipment one m, and fire truck access way 6 m.

Minimum headroom clearance for access ways shall be for over railways or main road 6.8 m, over access roads for heavy trucks 6 m, for passage of truck 4 m, for passage of personnel 2.1 m, and over fork-lift truck access 2.7 m.

Remote isolation facilities minimize the quantity of material that is released in the event of a spill or other undesirable incident. Because of the hazards associated with materials that might experience BLEVEs, and the volumes of the vessels in which such materials are stored, emergency isolation of these vessels should be accomplished by remotely operated emergency isolation block valves (EBVs) located in all main process piping below the high liquid level of the vessel. Since, these EBVs would be within the presumed fire zone, their actuators and power supplies need to be fireproofed. In addition, the actuation buttons must be at a safe location outside the spill-containment area for the vessel.

Crude oil and petroleum product terminals generally use the above ground piping systems, consisting of pipelines, hoses/loading arms, valves, instrumentation connections, meters, and pump stations, to transfer the product between tanks and transport links. Elevation of tank farms and impounding basins should not be above process areas. Other equipment includes vapor recovery systems and components of secondary containment zones in the loading bays for rail/tank trucks. Depending on the product, handling systems involving gravity, pump, compressor, and inert gas techniques are employed to move the product in and out of tanks. The design, construction, and operation of these systems are subject to codes and international standards.

No ignition sources should be permitted inside bunds. Pumps, pipe tracks, and fire hydrants should be located outside dike/bund areas. The pumps should be grouped into bays. The suction lines should be kept as short as practical. Furnaces and boiler plant should be located downwind to prevent them from becoming sources of process area fires and explosions. Flare systems (given at the end of the chapter may involve some repetition) should be located far away from process and storage areas, with provision of large vacant plot areas around the flare stack. An area of 60 m around a flare stack, free from grass or other combustible material, is provided. Layout should consider thermal radiation effects of the flames from a flare system on personnel and equipment. Flare height should be designed with consideration to potential radiation levels around the flare. These levels should not exceed allowable radiation levels on the ground. When flashback occurs, gases will burn inside the flare stack, gas collection header or plant piping. To prevent this, and minimize the risk of explosion, flares must be equipped with flashback protection. One such approach involves the use of liquid seals in the flare system, which keeps the flame front from propagating back into the plant piping. In case of liquid carryover due to maloperation or failure of knockout drum before the flare stack burning liquid droplets may rain around and become possible ignition sources leading to large fires. The area should be kept clean avoiding any debris and dry grass around.

Storage tanks should not become obstructions for entry of firefighting vehicles to process areas. There have been instances of blockages for entry of fire engines to process areas under emergency due to tank fires obstructing their way to plant areas. Provision for additional cooling water capacity for adjacent tanks, for use during fires be made.

Drainage: Where hazardous liquids may leak or spill from piping or vessels, provisions are to be made to prevent their spread to areas where employees may be exposed to the hazard. Examples of possible methods include diking around storage tanks, and groups of storage tanks with pumping facilities to permit flow of spilled flammable liquids away into segregated drains leading to oil separation and recovery units. Drainage should have provision for fire water. Proper sloping and paving of the ground surface areas to prevent accumulation of spills is an essential element for spill control and drainage. Storage tanks holding flammable liquids should be installed in such a way that any spill will not flow towards a process area or any other source of ignition. Precautions are taken to minimize spills when connections are broken. The area should be well-ventilated with provision to treat ventilated air. All spills such as grease, oil, or water should be cleaned up immediately, as delays could result in accidents. Sloped containment pads for pumps, process buildings and structures and other potential spill areas, prevention of soil and surface water contamination. These provisions will also prevent spread of a fire in the event of ignition of a flammable material spill, undesirable effects of contact with incompatible and corrosive materials. Segregation of hazardous waste water drains from storm water drains with treatment facilities. Provisions should include control of unexpected hazardous vapor or gas releases within the drain lines.

Housekeeping: Effective maintenance and cleanliness of work areas should be ensured. Repairs and maintenance should be followed by removal of any waste materials like rags, oily surfaces and obstructions.

Enclosed spaces: Some processes that are safe in open air may become hazardous if enclosed. If areas of potential or frequent leaks or spills are enclosed to prevent environmental contamination or the spread of the chemicals, adequate precautions to prevent formation of flammable and toxic concentrations within the enclosures and protection of employees should be ensured through good ventilation, without releasing such hazardous materials to the environment. Automatically, sampling of the air in the enclosures should be provided.

Emergency relief vents are piped and discharged to scrubbers, neutralizers, flares, incinerators, precipitators, etc., to remove hazardous materials. Explosion relief vents should be directed away from vulnerable areas such as other plants or buildings, roadways near site boundaries.

Incompatible materials: Avoidance and segregation of incompatible materials, including materials of construction for vessels, storage, piping, valves, pumps, flanges, packing, gaskets, sealing compounds, sampling systems, etc, should be ensured. Potentially reactive chemicals may have their reactions catalyzed by common materials which easily enter systems whenever seals are opened. Examples include water or rust which may easily enter a system during transfer from one vessel to another, either during hookup or disconnect, or during pressurizing or venting of tanks. If vessels are pressurized by inert gases, filters should be used in the gas lines to remove solid particles. If vacuum relief or pressure relief valves are on the vessels, they should be protected so that entry of potentially hazardous contaminants through them when open.

To eliminate/minimize dust toxicity or explosion hazards in solids handling, the use of pellets or granules in place of fine dusts is safer. Care should be exercised while inerting the atmospheres to eliminate explosion hazards, not to introduce asphyxiation hazards. Environmental issues should be addressed while using explosion-suppression agents such as CFCs.

Suitable controls and instruments for measurements such as temperature, pressure, flow, liquid level, and analysis should be provided for both normal conditions of operation and for emergencies.

Physical facilities: Provision of fixed and portable firefighting systems and eye wash fountains, water deluge and sprinkler systems at strategic locations should be included in the layout.

Provision of barriers such as blast walls, fire doors, water or steam curtains, deluge and sprinkler systems may be needed to isolate potentially hazardous equipment, and confine the effects of an explosion. Location of hazardous parts of the plant in strong buildings and strong construction of vessels will be helpful to contain explosions and minimize damage.

Emergency planning: In addition to a good design, a facility needs a plan to guide the emergency response team and plant personnel in the event of an accident. With such a plan, personnel waste little or no time determining the best course of action. It is vitally important that flexible emergency plans be developed in advance and that sufficient analysis be done to identify all likely impacts and complications that may arise. The emergency plan must take into account the severest impact any accident might have and direct the actions of the emergency response team in preventing that impact. Plans should be developed for each potential accident and area. The plan should include a summary of key actions and more detailed descriptions of each action. In an emergency, rapid isolation of vessels or process plant is one of the most effective means of preventing loss of containment or limiting its size. Emergency isolation facilities and procedures for all significant inventories should be included in emergency plans. Giving information and training to operators and maintenance staff is important. Site personnel should know the contents of the plan, including specific action they should take in an emergency. Risks from a major accident hazard can be reduced effectively by fitting pipe work with remotely operated shut-off valves, which can be closed quickly in an emergency. They should be installed if a foreseeable release of a dangerous substance from a section of pipe work or associated plant could cause a major accident and the consequences could be significantly reduced by rapid isolation. Important factors to be considered in plant layout are summarized in Table 6.2.

Table 6.2 Summary of important factors to be considered in plant layout

Segregation of hazardous and nonhazardous areas
Area classification of electrical equipment
Use of codes of practice recommending minimum safe separation distances for bulk storage of petroleum liquids:
Recommended separation distances and isolation should be followed
Chemicals which may react with one another are to be physically separated; oxidizers are to be stored in areas remote from fuel storage
Areas of potential explosions, storage of explosives, reaction vessels are to be isolated so if there is an explosion, the damage and risk to employees is minimized
Handling of H_2S and chemicals with high toxicity should be located far away from control rooms
No storage of flammables within battery limits of any process plant
Number and size of vessels with flammable liquids within process units be kept to minimum and should be as close to ground as possible
Pumps/compressors for flammables are located in the open with smallest possible weather shield
Plant buildings and interiors are constructed by noncombustible materials
Workshops/stores/administrative buildings are located well away from process area
Furnaces should be away from distillation columns, compressors, pumps, etc.
Cable trenches and instrument cabling should be protected from accidental damage and seepage
Fire-proofing structures, vessels, columns, skirts/supports should be more than or equal to 3 m height
3 hr fire rating should be provided for vertical and horizontal supports of major pipe racks in heart of process area
Supports of fan coolers located over pipe racks should have 1 hr fire rating with water sprays and 2 hr without water sprays
Firefighting requirements.
Prevention of services from being put out of action by fire/explosion/flooding
Fire breaks between units to confine fires to one location
Discharge of burning gases/droplets from tall stacks/flares (free space without any combustibles, like dry grass, to be provided around)
Drainage:
Where hazardous liquids may leak or spill from piping or vessels, provisions are to be made to prevent their spread to areas where employees may be exposed to the hazard. Examples of possible methods include diking and grading

(Continued)

Table 6.2 (Continued)

Provisions should be made to control unexpected hazardous vapor or gas releases within the drain lines. Segregation of drainage to avoid fires/explosions in sewers
Sizing drains in each area of plant (with e.g. one acre size) with adequate capacity for plant spills, fire water and storm water for example 9 m^3/min (2,400 gpm) each area
Twice for example 18 m^3/min (4,800 gpm) for plant main drainage
Providing for portable pumps for excess capacity requirements under large fire conditions > 38 m^3/min (10,000 gpm) to avoid pools in process areas
Provision of traps or other means to keep drains fully flooded to avoid vapor space (explosion chances)
Paving under equipment with likely leaks/spills with slopes towards drains to avoid liquid pools
Access: emergency shut-down switches/isolation valves should be easily accessible
Ventilation and housekeeping: work areas should be well ventilated and properly maintained
Open construction should be preferred wherever possible or otherwise provided with fail-safe exhaust systems. Flammable storages should be sited in the open air so that minor leaks or thermal out breathing can be dissipated by natural ventilation
Dominant wind direction should be considered
Some processes which are safe in open air may become hazardous if enclosed. If areas of potential or frequent leaks or spills are enclosed to prevent environmental contamination or the spread of the chemicals, adequate precautions to protect employees should be taken
Examples include ventilating the confined space/room and treating the exhaust; automatically sampling the air in the confined space; having employees sample before entering the confined space
Building locations (control rooms): location of control rooms assumed prominence after Flixborough accident which killed 23 people. There should be minimum occupancy
Emergency routes: emergency routes should be provided, which should be well labeled/displayed prominently

Plant layout applicable to the reduction of the risks from release of flammable or toxic materials should include locating all high volume storage of flammable/toxic material outside process areas. Locating hazardous plant away from main roadways through the site. Fitting remote-actuated isolation valves where high inventories of hazardous materials may be released into vulnerable areas. Provision of ditches, dykes, embankments, sloping terrain to contain and control releases, and limit the safety and environmental effects. Siting of plants within buildings as secondary containment. Siting of plants in the open air to ensure rapid dispersion of minor releases of flammable gases and vapors and thus prevent concentrations building up which may lead to flash fires and explosions.

Wind shielding should be provided by growing trees around the plant to reduce wind velocities and prevent dust entry and deposits within pipe trenches and plant equipment. Providing green belt around plant site reduces pollution effects to the community around.

Hazardous area classification for flammable gases, vapors, and dusts to designated areas where there are ignition sources should be eliminated. A typical site layout is given in Figure 6.1.

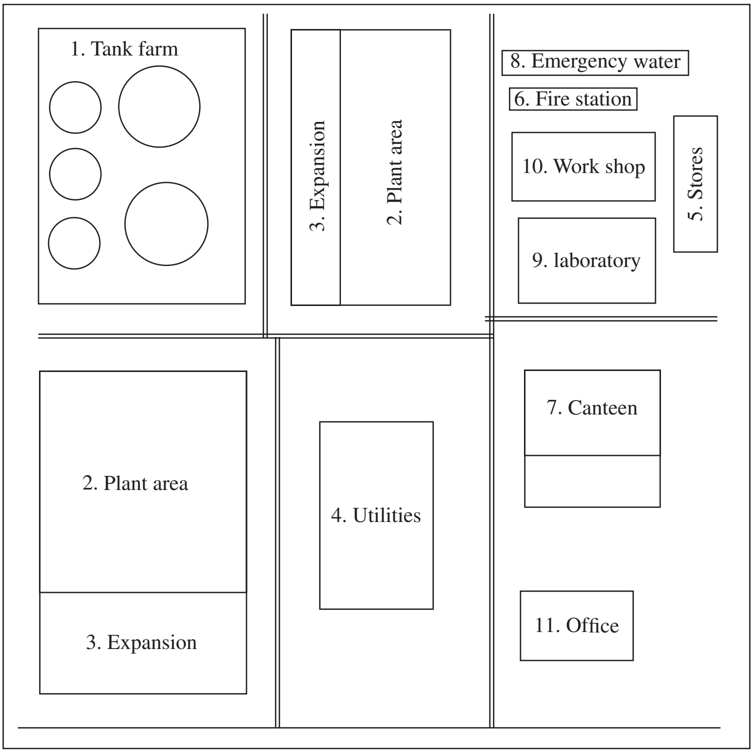


Figure 6.1 Typical plant site layout

Provision for future expansion: Many times, though provisions are made for expansions, these become inadequate with constraints of land availability, often leading to compromises, making the intent of original provisions defeated. An example is locating additional storage facilities coming in the way of plant accessibility to fire tenders reaching burning process areas with the burning contents of the storage tanks preventing such fire tenders reaching the burning process areas.

An observation on plant location: Locations should be away from populated areas/cities. Once a plant is located in a "no-activity" zone, population build-up around the plant areas start increasing for different reasons such as finding employment opportunities or growth of cities around. Bhopal is one instance involving large population strength around Union Carbide pesticides plant. Another instance is growth of populations in the vicinity of DCM chemical works in Delhi. Chlorine leaks became intolerable to the populations around, leading to re-location of the industry, rather than re-location of populations.

6.5 Inherent Security

Hazardous releases can result from extraordinary events such as accidents, natural events, or deliberate acts. Accidents occur due to human error or malfunctioning of equipment. Natural events are phenomena such as floods, earthquakes, and lightning. Deliberate acts are performed with the intention of causing harm and include terrorism, sabotage, vandalism, and theft. Both safety and security programs typically use defense in depth to protect against accidents and deliberate acts toward destruction. This is called *layers of protection* in safety and *rings of protection* in deliberate acts of destruction. Generally, safety protection aims at preventing release and security protection aims at preventing access. In modern plants, process safety relies on the principle of *multiple protection layers* (see Figure 6.2). Each layer of protection consists of a grouping of equipment and/or human actions, shown in the order of activation. The classical onion diagram (Figure 6.2) illustrates the safety layers that are used to prevent process plant incidents. This diagram helps to explain the following four basic process risk management strategies: Inherent, passive, active, and procedural or administrative. Inherent safety is at the core of the onion, namely, the process design. A process that cannot have a major fire, explosion or toxic release is inherently safer than one that could if one or more layers of protection were to fail.

*Source of the concept: CCPS, 1996

For security to be effective, it has to be deployed in a coordinated fashion across the whole plant or organization. Good security starts with ensuring that staff, management and contractors understand and follow appropriate practices. As for inherent safety, there are some inherent security measures, as in the case of safety, that can be applied towards security management. They include:

Perception: Plants should control how much attention they attract. Locations close to population centers, close to highways, prominent signage, and transportation are more likely to be attacked. Facilities that avoid publicity also avoid attention of adversities.

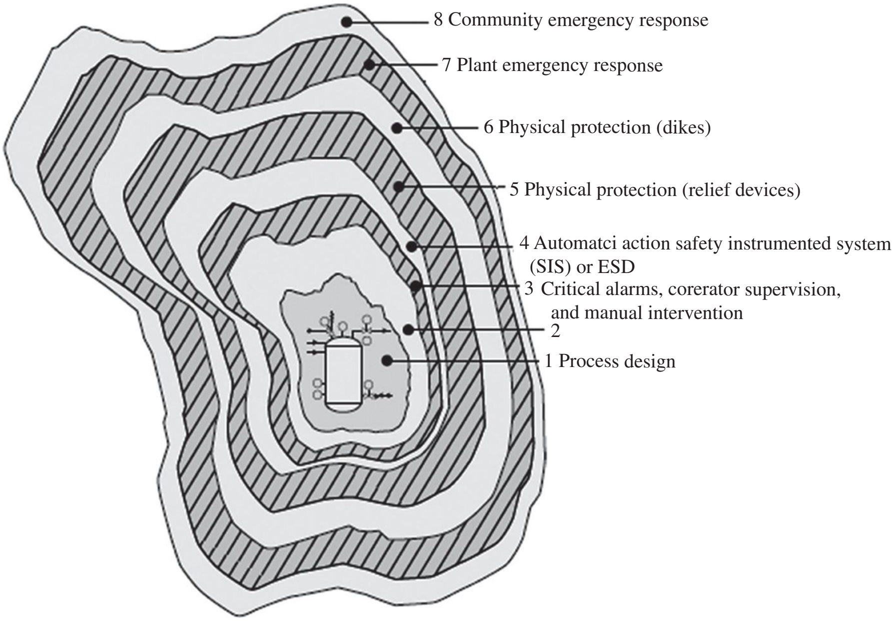


Figure 6.2 Typical layers of protection in a modern chemical plant

Information: The less information available on a facility, the more secure it will be, as information available on hazardous materials is needed by adversaries to plan for an attack. Information on chemicals handled, inventories, capacities of tanks and vessels, and locations should be controlled. Right to know should be balanced with need to know by local communities and media. In-plant signs make it easier for intruders to identify specific targets.

Layout: Sensitive areas should be located in central areas of the plant, where they will be less vulnerable. Hazardous material sites and signs should be kept free from obstructions that facilitate detection by unauthorized personnel. As disabling control systems and utilities may cause releases, they should be kept in difficult locations to prevent detection and access by intruders. Buffer zones provide good separation spaces from populated areas and boundaries.

Design: Protection of tanks and vessels should receive consideration for protection from air borne and propelled missiles and projectiles. Robust designs, thick-walled vessels, double-walled construction, use of internal baffles, mounding, underground installations, avoidance of flexible hoses, and sight glasses are some of the considerations for the design.

Safeguards: Attacks may involve disabling safeguards immediately prior to causing a hazardous material release. Some safeguards are more easily disabled than others. For example, fire water tanks are less secure than lagoons and below-grade dikes.

Computers: One should be careful with the use of Internet connections to process control networks. They should be protected from cyber-attacks. Allowing remote access to the control system without creating and enforcing an appropriate access control system is a blunder as far as security is concerned. *Balanced approach* toward safety, security, and operability may have to be adopted as these might be of conflicting in nature.

Elements of Process Security Program

Management systems: Policies, procedures, instructions, and documentation must be developed to manage implementation of process security within an organization.

Coordination with other organizations: Process security management requires involvement of outside organizations. Relationships must be established to share information and facilitate emergency response.

Employee involvement and security awareness: Employee involvement improves design and implementation of process security management program.

Process security information: This includes, for example, specifications for acceptable devices such as closed-circuit television cameras to operate in electrically classified areas.

Risk assessment: Risk assessment for deliberate acts involves performing a *threat analysis* to identify the type of event and source, and conducting a *vulnerability analysis* to determine how it might happen and its likelihood, and considering what can be done to lower the risk in the form of *security measures* and *safeguards*.

Security procedures: When coupled with policies and documentation requirements, they help ensure that tasks are not only performed but also carried out correctly. Written procedures should be developed for different security activities.

Training: Failure to train personnel to address terrorism and criminal acts increases vulnerability of facilities.

Contractors: Contractors often perform maintenance and other work at process plants. A process security management program must address the possible impact of contractors on security.

Security systems integrity: Security systems work correctly only if they are properly designed, fabricated, installed, maintained, inspected, and tested.

Management of change: Conditions at many plants change continuously with managements changing, processes and threat perceptions changing, and employees coming and going.

Incident reporting and investigation: Incidents include suspicious events, breaches in security program, which might be a precursor to an attack. Actual attacks might be forestalled by proper incident reporting and investigations.

Emergency response and crisis management: Plans must be made to respond to attacks, and they must be reviewed based on new information inputs.

Reviews, audits, and inspections: Various types of reviews, audits, and inspections must be carried out regularly as part of a security program. See details about safety audits at end of this chapter.

6.6 Explosion Prevention and Protection

Explosion prevention techniques attempt to minimize or eliminate the occurrence of explosions, whereas explosion protection techniques control the effects of the explosion in such a way as to minimize or eliminate the damage that could occur due to an explosion.

Explosion prevention options:

Design: Designing equipment and piping to withstand explosion pressures.

Oxygen reduction: As the oxygen content in the atmosphere is reduced, there is a decrease of both ignition sensitivity and combustion rate of combustibles. In many cases the explosion hazard may be reduced markedly by only a moderate reduction of the oxygen content.

Inerting by dry nitrogen gas to lower oxygen levels to below those which support combustion. For example, minimum safe oxygen concentrations to be maintained to prevent fires and explosions are for combustible dusts about 9–16 percent, for propane 11 percent, and hydrogen 5 percent.

Inerting

The partial or complete substitution of the air or flammable atmosphere by an inert gas is a very effective method of explosion prevention. As increasing amounts of inert gas or vapor are added to a flammable atmosphere, the flammability limits of the fuel approach each other and finally merges. Inerting is normally considered when the flammable or explosive hazard cannot be eliminated by other means that is, substitution of flammable material with nonflammable, adjustment of process conditions to ensure that the substances are below their flammability limits. Typical uses are within storage tanks where a material may be *above its flashpoint* and within reactor systems when flammable atmospheres may be possible. Inert gases are also used to transfer flammable liquids under pressure. Inerting is applicable to enclosed plant, since, plant that is substantially open to atmosphere cannot be effectively inerted because the prevailing oxygen concentration is likely to vary.

Purging ***and*** *inerting* ***(or blanketing)*** These process vessels and equipment are two common, yet distinctive, practices to control the concentration of oxygen, thereby reducing fire and explosion hazards. Purging usually refers to the short term addition of an inert gas (e.g. nitrogen or carbon dioxide) to a tank, process vessel, or other piece of process equipment that contains flammable vapors or gases to render the space nonignitable for a specific timeperiod (say, during a maintenance outage). By contrast, inerting (or blanketing) is the long-term maintenance of an inert atmosphere in the vapor space of a container or vessel during operation. A major risk associated with use of inerting is that of asphyxiation, particularly in confined spaces. In those events where people are required to enter a confined space, a formal management control system in the form of *a permit to work* should be in place so that appropriate precautions and control measures can be implemented. The practice of inerting is also employed in explosion suppression systems, where typically a quick acting pressure switch responds to the initial comparatively slow increase in pressure due to initiation of explosion conditions. This, in turn, triggers injection of an explosion suppressant such as chlorobromomethane or carbon dioxide into the path of the advancing flame front. This technique can also be used to provide protection to interconnected plant by inerting plant items downstream of the explosion. In most inerting systems, a slight positive pressure should be maintained within the enclosed plant to reduce the possibility of air ingress. Inert gases may be generated on site, or via bulk storage of cylinder facilities.

Gases that can be used for inerting include nitrogen, carbon dioxide, argon, helium, and flue gases. Although nitrogen or carbon dioxide is the most common inerting gases, steam is sometimes used. If so, it must be supplied at a rate sufficient to maintain the vessel temperature so that condensation by cooling does not draw in atmospheric air or collapse the vessel by implosion.

Table 3.31 illustrates that carbon dioxide is a better flame suppressant than nitrogen. However, the major disadvantage for carbon dioxide is its corrosiveness in the presence of moisture, which makes it to be unattractive compared to nitrogen as an inerting gas. Also nitrogen is less reactive than carbon dioxide. Carbon dioxide on expansion forms solid particles (dry ice) due to cooling effect, giving rise to static electricity problems. Low temperatures resulting due to cooling effect of carbon dioxide can cause burns to personnel on contact and low-temperature embrittlement of steel. Possible sources of purge or inerting gases include commercially available gases supplied from high-pressure cryogenic tanks or standard cylinders, or on site air separation plants that remove oxygen from the air and recover nitrogen by liquefaction followed by absorption, chemical reaction, or membrane permeation. Continuous inerting methods involve fixed and variable rate. *Fixed rate application* involves continuous feeding of inert gas into an enclosure (e.g. vessel) at a constant rate and the corresponding release of a mixture of inert gas and flammable vapor that has been picked up in the vessel's head space. To ensure that the vessel is completely protected, the rate must be sufficient to satisfy peak demand requirements. The peak demand for continuous inerting is typically controlled by the maximum liquid withdrawal rate coupled with potential temperature changes. For a vessel containing a flammable liquid, the inert gas demand based on liquid withdrawal is the capacity of the largest pump used to withdraw liquid or the maximum possible gravity outflow rate, whichever is greater. The maximum demand from a temperature change will occur in outdoor tanks operating at or near atmospheric pressure as a result of the sudden cooling from a summer thunderstorm. *Variable rate* or demand inerting involves feeding inert gas into the vessel at a rate that is a function of demand. Demand is based on maintaining a pressure within the vessel that is slightly above that of the surroundings. Variable application offers an obvious advantage over continuous in that inert gas is supplied only when it is actually needed, thereby reducing the total quantity of inert gas required; product loss; and disposal problems. A disadvantage is the dependence upon flow control devices actuated by very low-pressure devices actuated by very low-pressure differentials that are sometimes difficult to maintain.

Batch purging: The common batch purging methods are siphon, vacuum, pressure, and sweep-through. *Siphon purging* involves filling the vessel to be purged with liquid (i.e. product or water) followed by introducing the purge gas, typically nitrogen, into the vapor space as the liquid is drained. Purging or air freeing is the first step in putting an equipment into operation. Water freeing should be after this step. Steam or nitrogen purging or less commonly filling with water is practiced. Steam is usually cheaper and quicker than nitrogen for purging. Steam cannot be used for plant/equipment designed for refrigeration/cryogenic service as the insulation may not be able to withstand the steam temperatures. Also moisture can degrade materials, for example, acid-based catalysts in reactors. KOH pellets in vessels, etc. Use of nitrogen is a solution for such equipment. The required purge gas volume equals the volume of the vessel. The rate of application corresponds to the volumetric rate of liquid discharge. Siphon purging may not be appropriate if the liquid is above its flashpoint due to evaporation into the space. Criteria for sizing purge lines involve calculation of volume of equipment to be purged and multiplication of this value by 4.0. It is usually assumed to be 10-hr purge period. High point pockets in vessels should be avoided, as these vents are often difficult to climb to and operators usually forget to close them. In one instance, 10 percent of propylene overhead product was lost for a week before the vent valve was closed, creating hazardous atmospheres in the vicinity of the vent. Purge lines should not be designed to be permanently connected to high pressure vessels to prevent high pressure process fluids entering with purge systems. In one instance propane at 20 bar, leaked past a steam purge connection into a 10 bar steam system. The problem was finally detected when an operator observed propane vapors, instead of steam, being emitted from a fire suppressant steam nozzle. V*acuum purging* is one of the most common vessel inerting procedures provided that the vessel is designed for the maximum vacuum that can be developed by the source (e.g. a vacuum pump). The steps in a vacuum purge are (i) drawing a vacuum on the vessel until the desired level is achieved; (ii) relieving the vacuum with an inert gas such as nitrogen to atmospheric pressure; and (iii) repeating steps (i) and (ii) until the desired oxygen concentration is reached. The amount of purge gas required depends on the number of evacuations needed to develop the desired oxygen concentration.

Pressure purging: Vessels may also be purged by adding inert gas under pressure and, after the gas has sufficiently diffused, venting to atmosphere. As with vacuum purging, more than one pressure cycle may be necessary to reduce the concentration of oxygen to the desired level.

Sweep-through purging: This method introduces a purge gas into a vessel at one opening and withdraws the mixed gas at another opening and vents it to the atmosphere (or an air pollution-control device), thus, sweeping out residual flammable vapor. The quantity of purge gas required depends on the physical arrangement. Sweep-through purging is commonly used when the vessel is not rated for pressure or vacuum. The purge gas is introduced and withdrawn at atmospheric pressure.

Where flammable dusts are handled in an atmosphere containing flammable gas or vapor, determination of flammable limits is difficult and use of inerting should be considered wherever possible. Reliability of the supply of inert gas is of vital importance, and the system should be regularly inspected and maintained. One of the causes for Flixborough explosion was unreliable supply of nitrogen which depended on supplies from outside.

Inert gases are often used to purge tanks and vessels that normally contain flammable substances prior to maintenance, commissioning or decommissioning. The presence of inert atmospheres should always be taken into consideration during operational or maintenance activities since potential hazards could arise from asphyxiation and loss of inert atmosphere. Many chemicals, polymers, and food products degrade through reactions with oxygen or moisture in the air. Purging, pressure transferring, and blanketing with nitrogen protects against material degradation. During blanketing, dry nitrogen is used to replace the atmospheric air inside a storage tank or reactor to minimize contamination and reduce the formation of undesirable and potentially hazardous reaction byproducts. By creating a slightly positive tank pressure, blanketing also minimizes air infiltration. The risk of corrosion can also be reduced by using an inert atmosphere to exclude moisture. The use of a nitrogen blanket in the space of a vessel reduces vapor and product losses. In blanketed storage tanks, vapors are vented only when a pressure-relief valve opens up, whereas in non-blanketed storage tanks, potentially hazardous vapors may escape continuously through evaporation. Very often, product streams reaching a reactor vessel or storage tank contain considerable quantities of dissolved oxygen, which can be more detrimental to product quality than oxygen in the space of a vessel. Sparing systems dissolve nitrogen into liquids and strip dissolved oxygen. When supplied in cryogenic form, nitrogen is also useful as a refrigerant to condense and recover chemical vapors for either environmental or economic reasons. Such systems use cryogenic nitrogen to recover chemical vapors as they too recover chemical vapors as they are vented from trucks, rail cars or other vessels By definition, an inert gas is nonflammable, chemically nonreactive and. noncontaminating. For most industrial uses, the inert gas must also be nontoxic and free of moisture. Relative advantages of different inert gases are as follows:

Flue gases: These inert gases have several disadvantages. Although they have theoretically 79 percent nitrogen and 21 percent carbon dioxide, other byproducts, including oxygen, carbon monoxide, water vapor, and soot particles are always present. Accordingly, filtration and drying are usually required prior to use.

Carbon dioxide: Because CO_2 is soluble in many liquids, it may react with moisture to form carbonic acid, which can react with the products being blanketed or cause equipment corrosion.

Nitrogen: Nitrogen is the most commonly used blanketing gas. It is considered nonreactive except under extreme temperatures and pressures, and its low solubility keeps it from contaminating most liquids. In addition to being colorless, odorless, tasteless, and nontoxic, nitrogen has a very low dew point and is a poor conductor of heat and electricity. Nitrogen can be delivered continuously through rail cars, trucks, pipelines, and produced onsite.

Ignition control: Ignition prevention and control measures such as ignition sources and electrical equipment in hazardous areas, including electrical area classification are already discussed.

Permit to work system: In an effort to establish some control over operations using flames or producing sparks, many industrial firms have instituted hot work permit programs. Important features of a hot work permit program include the following:

(i) Inspection of the area where work is to be done and seeing how close combustible materials are to the work area.
(ii) Establishment of fire watches if hazards warrant them. A fire watch should stay on duty for 30 min after all spark producing equipment has been shut-down.
(iii) Providing fire extinguishing equipment, usually manned by a standby employee.
(iv) Communicating with, and coordinating the activities of all departments concerned with fire protection.
(v) Isolation of flammable and combustible materials from sources of ignition.
(vi) Limiting unauthorized use of flame or spark producing equipment.

Explosion Protection

Explosion protection techniques include containment, detection, control, use of fail-safe devices, venting, inclusive of flameless venting, isolation, suppression, and fire protection measures.

Primary explosion protection: Primary explosion protection aims at preventing the formation of an explosive atmosphere that can be achieved by avoidance or restriction of release of any flammable material, increasing air circulation by natural or artificial ventilation to flammable concentrations to below LFL, inerting by adding N_2 or CO_2 and monitoring concentration of the flammables through gas detection systems. For explosible dusts, inerting through mixing of noncombustible dusts is one means of reducing explosion severity of explosible dusts. Calcium sulfate, calcium carbonate, and sodium bicarbonate are some inerting solids used.

Secondary explosion protection: As releases cannot be eliminated completely in many process areas and inerting in working areas is not always feasible, primary protective measures alone are not sufficient, secondary measures will be necessary for safe operation which include avoidance of ignition sources, limiting surface temperatures of equipment to below SITs of the flammables, limiting energy levels through intrinsic safety levels in electrical equipment, limiting explosion damage through the use of flameproof enclosures, limiting arcs and sparks by encapsulation, oil immersion or powder filling in electrical enclosures, and using other means such as explosion venting, explosion suppression, and explosion containment.

The basic measures for protection against ignition leading to fires and explosions from electrical systems can be categorized into explosion *containment, segregation*, and *prevention*. Explosion-proof enclosures are based on the principle of containment. Method of segregation attempts to physically separate or isolate the electrical parts or hot surfaces from an explosive mixture. This method includes different techniques, such as pressurization, encapsulation, etc. Preventive measures limit the energy, both electrical and thermal, to safe levels under both normal operation and fault conditions. *Intrinsic safety* is the most representative technique of this method.

Containment of Explosion

This method of protection relies on the ability of equipment as well as all interconnected pipe work, flanges, manhole covers, instrumentation mountings etc., to withstand the maximum explosion pressure. The containment of the explosion pressures developed by a dust explosion requires powder handling equipment of high strength, possibly capable of withstanding pressures in the range 7–10 barg. Containment includes overpressure protection, overfill and spill protection, and protection from leakages.

Overpressure protection: All vessels are required to have overpressure protection. Overpressure protection, incorporating pressure relief valves (PRVs), must be provided for vessels that store materials subject to a BLEVE. The relief device can be located directly on the vessel or installed within a process or utility pipeline connected to the vessel. As a minimum, PRVs are sized to prevent overpressure in the case of fire exposure, as long as such exposure does not lead to overheating of the vessel wall, which results weakening of the metal and causing failure even at working pressure of the vessel. Equipment can be protected from overpressure by using blinds or by physically disconnecting piping, rather than using valves to isolate equipment from pressure.

Overfill protection: Overfill protection for a pressure vessel should incorporate redundant instrumentation with two level measuring devices that are independent of each other and that can be repaired without removing the vessel from service. In addition, the vessel must be provided with a high level alarm independent of the other level instruments. *Spill containment* consists of diking to prevent the uncontrolled dispersal of flammable liquids. Spills are confined inside diked area and diverted from the vessel, to prevent accumulations near the vessel, with the ground graded and sloped away from it. The areas where material collects should have sealed, valved connections to the plant sewer or drainage systems.

Detection

The first step in any active explosion protection system is detection. A developing deflagration generates pressure and radiation and the detection of either can be used as the indication of an impending explosion. Pressure detection has been used almost predominately although the use of optical detection is increasing. The use of mechanical switch-type devices for pressure detection has many problems, such as slow and variable response, no output signal other than activation, limited application to static activation, no supervision of contact integrity, frequent recalibration of spring-based mechanism and sensitivity to orientation, vibration, and shock. In short, they lack speed, provide no information, are not highly reliable and unstable. In modern systems, mechanical switches are replaced by transducers, which continuously convert pressure energy into an electrical output signal. Optical detection in conjunction with pressure detection provides several advantages in protection design. The radiation of a spark at one extreme or a flame front at the other extreme allows detection that often would not be possible with pressure detection. Key advantages are the ability to respond to very low levels of radiation, for example, sparks and the ability to detect a flame front faster than a pressure detector. Spark or flammable gas detection systems use infrared detection of a spark traveling through duct work.

Control

The modern controllers are based on high-speed microcontrollers and have the capability to capture and analyze the data before making an activation decision. This has the advantage that it is not only in sensing an actual explosion, but in discriminating against nonexplosions and preventing unintended activations. False signals can result from electrical spikes, particle impacts on the detector face, process pressure changes, etc. Signals can be filtered and compared in order to make a decision. A continuous pressure signal can also be used for warning purposes. Warning signals result when the pressure exceeds a preset level, lower than the activation pressure.

Safe design for primary control systems:

Intensification: Minimum number of loops should be used for process control. One should determine which variables that needs to be controlled and which variables are used to make adjustments.

(i) Independent sensors should be used for alarmed variables and feed forward and cascade control opportunities should be considered.

(ii) Specialized controls should be used for start-up, partial shut-down and controlled shut-down. Start-up should be based on standard times as well as achieving conditions. Partial shut-down needs to consider all upstream and downstream unit operations. Complete shut-down should be tested during turnarounds. Emergency shut-downs should have backup.

(iii) All interactions between interconnected unit operations should be considered. Reverse flows should be avoided. Overpressurization due to loss of flows and impact of materials that are not at design temperatures should be taken into consideration.

Alarms

Ineffective alarm systems pose a serious risk to safety. Too often, alarm system effectiveness is unknowingly undermined by poorly configured alarms.

Poorly configured and performing alarm systems in processing plants can actually hinder the operator's ability to effectively manage abnormal situations. This is a common problem throughout the industry and has resulted in unplanned outages and decreased profitability. An effective alarm system is a key element for reliable operations.

Increasingly, it is found that alarm system failures are a contributing factor to several industry incidents and accidents.

The widespread use of modern distributed control systems (DCSs) is the catalyst for present-day alarm system problems. Best practices in effective alarm system design evolved after many of these systems were installed, resulting in inconsistent application and a near exponential growth in the number of configured alarms. In process industry, the alarm systems are often improperly configured by system integrators, without much involvement from the end user of the system. Poor initial alarm configurations can result from integrators reusing engineering from other projects or by applying rules of thumb that are not directly relevant to the specific operator's needs. Alarms are not correctly prioritized, mixing trivial and important alarms in an inconsistent manner. Another problem is that data necessarily logged for predictive maintenance purposes are often mistakenly routed to the alarm system, distracting the operator from genuine alarms. Some of the most prevalent alarm system problems include the following:

High continuous alarm rates: Alarm rates are often far above the ability of an operator to handle. Thousands of alarms must be ignored each week in such a system, with no guarantee that the right ones are always acted upon.

Alarm floods: an operator may experience hundreds of alarms within a few minutes of a minor upset, which may mask critical alarms and prevent timely corrective action.

Improperly suppressed alarms: Without records or notifications, improperly suppressed alarms can obscure visibility to critical alarms.

Chattering and nuisance alarms: These contribute to operator fatigue and make detection of valid alarms more difficult.

Stale or long-standing alarms: These clutter the alarm system, also making detection of valid alarms difficult.

Some basic principles for proper alarming that are generally not followed in the process industry include the following:

- Alarms must only be used for situations requiring operator action.
- Alarms are not used to indicate normal status changes.
- Alarm prioritization must be meaningful and consistent.

Some guidance on alarm settings, human interface (alarm presentation), alarm processing, and system management controls for both safety related and other alarm systems include the following:

The alarm system should be designed to appropriate safety integrity level (1 or 2) with the designated reliability. The alarm system should be independent from the process control system and other alarms unless it has also been designated safety related. The operator should have a clear written alarm response procedure for each alarm which his simple, obvious and invariant, and in which he is trained. Alarm documentation and rationalization (D & R) is a consistent methodology for rationalizing, prioritizing, documenting, and revising alarms. D & R involves a thorough re-examination of an existing alarm system to ensure it complies with the alarm philosophy. During D & R, a team of knowledgeable people discuss each configured and possible alarm to verify it represents an abnormal situation requiring operator action. Alarms failing this test are de-configured. The remaining alarms are properly prioritized, and the alarm causes, consequences, proper operator responses, and any special alarm handling are documented. Performing a D & R creates a Master Alarm Database, which is the collection of proper settings and information for each alarm. This document will be used in the rest of the process for state-based alarm management, flood suppression, audit and enforcement mechanisms, management of change, and operator information. The alarms should be presented in an obvious manner, distinguishable from other alarms, have the highest priority, and remain on view at all times when it is active. The claimed operator workload and performance should be stated and verified. Alarms that are not designated as safety alarms should be carefully designed to ensure that they fulfill their role in reducing demands on safety-related systems. For all alarms, regardless of their safety designation, attention is required to ensure that under abnormal condition such as severe disturbance, onset of hazard, or emergency situations, the alarm system remains effective, given the limitations of human response. The extent to which the alarm system survives common cause failures, such as a power loss, should also be adequately defined. Processes and sensors change over time, and alarm behavior will change with them. Alarms working correctly now may become nuisances or malfunction in the future. Therefore, alarm system key performance indicators (KPIs) should be developed and routinely reported to appropriate personnel. Additionally, effective management of change methodologies, as well as an ongoing program of system analysis and correction of problems as they occur, is needed to maintain an effective alarm system. Modern alarm management software is an essential element to monitoring and maintaining alarm system performance.

Alarm displays may be color-coded according to their function. An example can be as follows:

- Alarms → Yellow
- Pre-alarms → Orange
- Shut-down → Red
- Bypass → Red

Table 6.3 gives a summary of types of alarms used in process industry.

Table 6.3 Types of alarms and their applications

Type	*Applications*
Process alarms	May be related to efficiency of the process or indicate defects in the equipment. This type of alarm is normally incorporated into the plant control system and shares the same sensors as the control system
Equipment alarms	These alarms assist with detection of problems with equipment and do not directly affect the operation of the process. An example of equipment status alarm is whether a pump is on or off, or motor is running or stopped
Safety related alarms	These alarms are used to alert operators to a condition that may be potentially dangerous or damaging for the plant. Such alarms should normally have a high priority and where they are involved in protecting against maloperation by the control system they should be independent of the devices they are monitoring. In many cases these alarms are generated by the safety shut-down system itself

(Continued)

Table 6.3 (Continued)

Shut-down or start-up	This type of alarm tells the operator that an automatic alarms shut-down event has been reached and has been initiated by the safety interlock system (SIS). Not all alarm systems will result in shut-downs. There are cases whereby such alarms are the result of automatic start-up. For example, in the case of power failure, the system will cause the stand-by generator to power. Another example is the auto-start of the stand-by pump when the regular unit goes down
Pre-alarms	Warn the operating personnel to the fact that there is a potentially dangerous trend is developing and to give the operating personnel some time to take action to correct the problem before matters reach the point where the emergency shut-down is activated
Other alarm systems	In addition to critical process safety alarms, separate system could incorporate the following alarms: fire, spill or toxic release, safety shower, power system fault, electrical room or substation smoke detector, ventilation failure, abnormal measurement alarm functions whether measurement is outside of specified limits, an alarm switch without its own sensor. when it is not necessary to know the actual value of the process variable, only whether it is above (or below) a specified limit, an alarm switch with its own sensor serves as a back-up in case the regular sensor fails, etc.

Trips and Interlock Systems

A system or device is deemed to be safety-related if it provides functions which significantly reduce the risk of a hazard, and in combination with other risk reduction measures, reduces the overall risk to a tolerable level, or if it is required to function to maintain or achieve a safe state for the equipment under control. A typical example of a safety-related system (SRS) is the safety instrumented system (SIS), which is also referred as safety interlock system, emergency shut-down system (ESD), or safety shut-down systems (SSS). Protective tripping systems provide a defense against excursions beyond the safe operating limits by detecting an excursion beyond set points related to the safe operating limits (i.e. the onset of a hazard) and taking timely action to maintain or restore the equipment under control to a safe state. Trip systems are provided to protect the plant from hazardous situations by shutting down the plant if certain parameters go outside the specified limits. A trip system may be very straight forward, involving a simple actuation of a final control element when the sensor detected a deviation from a safe operating limit. Often, the trip system is more complicated, with interlocks sequence involving several pieces of equipment. Disarming trips is a permissible practice, provided it is done in accordance with the design intent and with proper procedures and restoration practices. Methods used to disarm trips safely include both key interlocks and permit systems. Interlocks are used to control operations which must take place in a specified sequence and equipment's which must have specified relations between their states. Some literature uses the word interlock, which includes both trip and interlock functions. An interlock is often used to prevent access during the operation of equipment. An example is installing electrical switchgear in a room where an interlock prevents the door opening until there is electrical isolation. Interlocks are used in plant start-up operations to ensure that all the pre-start-up conditions are met.

Use of fail-safe device/operational arrangements: Fail-safe devices are of three types, namely, *fail-passive, fail-active*, and *fail-operational systems*.

Fail-passive systems: These systems involve reduction of energy levels to their lowest levels. The system will not operate until corrective action is taken, but no further damage will result from the hazard causing inactivation. Examples include use of circuit breakers and fuses for protection of electrical devices/circuits. *Fail-active* systems involve maintaining the system in energized condition in a safe mode until corrective or over-riding action occurs or that activates an alternative system to eliminate possibility of an accident. An example is a battery-operated smoke detector. When battery reaches a point where it requires replacement, it emits a different signal from the alarm signal.

Fail-operational arrangements: These allow the system functions to continue safely until corrective action is taken. Other examples of fail-safe devices are control rods on nuclear reactors, which drop automatically into place to reduce reaction rate if it exceeds limits and self-sealing breakaway fuel line connections.

Venting

Another protection option is venting, the control of pressure, by release of a deflagration through an opening of the appropriate size. Explosion venting devices are designed to open at the incipient stages of an explosion event and are sized to ensure that the rising pressure does not exceed that of the pressure shock resistance of the vessel. In its simplest form, a vent is an aperture in the top or side of a vessel to provide a means of pressure relief during an explosion. The closure, vent panel, door, etc., opens at predetermined pressure to prevent damage to the enclosure. In order to protect people close to a vented vessel located indoors the vent discharge must be directed outside the building with suitable ducting. This ducting has a substantial effect on the pressure experienced inside the vessel during the venting process and this must be allowed for in the vent area calculations. In some cases, the increase in pressure can be so great that an alternative protection method is required. In explosive venting, an explosive charge is used to ensure complete opening of the vent within 5–10 ms after receipt of the signal. Type of sensor used is extremely important. For example, choice of a pressure switch itself in determining the opening time of the vent. Upon receipt of the signal from the sensor, detonation of the explosive actuator within the liquid used to transmit the explosion through to ensure vent opening within the above mentioned time. Although rupture discs are used for opening vent systems, they have inertia to increase time of opening the vent, fast pressure rises due to, for example, in the case of systems involving high burning rates require explosive vent systems, even though they are expensive. Care must be exercised to see that both vent and detector must be compatible with each other.

In order to protect people close to a vented vessel located indoors and to prevent external dust deposits from becoming involved in a secondary dust explosion, the vent discharge must be directed outside the building with suitable ducting. This ducting has a substantial effect on the pressure experienced inside the vessel during the venting process and this must be allowed for in the vent area calculation. In some cases, the increase in pressure can be so great that an alternative protection method is required. The Dangerous Substances and Explosive Atmosphere Regulations (DSEAR) require industry to critically review the explosion prevention/protection methods used with all equipment handling dangerous substances. It is not uncommon for powder manufacturers/processors, particularly in the traditional industries, to find that their current level/type of explosion protection does not satisfy the requirements of DSEAR and that additional protection is required to meet the health and safety requirements.

Flameless venting is a passive protection means and an attractive alternative to normal venting and suppression. *Flameless venting devices* combine the techniques of explosion venting and flame arresting (flame arresters are described in later paragraphs). Flameless venting devices typically comprise a vent panel, flanged housing, and a flame arrester element. The flame exiting through the vent opening is required to pass through flame arresting elements. Flame propagation beyond the arrester is prevented by heat dissipation in the element, reducing the burning fuel below its ignition temperature. The surfaces of the arrester are fabricated from various layers of high temperature stainless steel mesh. Layers of stainless steel mesh absorb heat generated by combustion. The device is bolted onto the explosion vent on the vessel with its open end overlapping the vent aperture. There are several types of flameless venting devices. They are passive devices that consist essentially of a cylinder closed at one end and open at the other. Common designs of explosion vents are as follows:

Membrane: A membrane that breaks at a preset pressure on the explosion vent to allow the flame front to exit from the vent in high-pressure situations (explosion).

Hinged/restrained panels: By installing hinged or restrained panels with springs that open at preset pressure, the flame front is allowed to exit the system.

Explosion venting has the advantage of being relatively inexpensive compared to other explosion protection options and in many cases simple to install. However, it is not suitable to toxic materials, some of which may be released to the atmosphere in the event of an explosion. Also release of combustion products inside a building is usually not acceptable. While venting is a reliable, cost effective method of preventing damage from pressure, it does not affect flame. Often vessels are equipped with a fire extinguishing system utilizing inert gases such as CO_2 or N_2. Re-closing vents are used to prevent escape of exiting gases and entry of air into the system. Figure 6.3 illustrates effectiveness of venting.

NFPA guidelines for venting: Multiple vent locations can be provided along the length of a pipe or duct to reduce the maximum pressure generated during a deflagration.

Deflagration vents should be located as close as possible to ignition sources where these sources can be identified. Pipes or ducts connected to a vessel in which a deflagration can occur also need deflagration protection. Such protection can be accomplished by installing a vent on the pipe with an area equal to the cross-sectional area of the pipe or duct. It should be located on the pipe or duct no more than two pipe or duct diameters from the point of connection to the process vessel or equipment. For systems that handle gases, vents should be provided on each side of turbulence-producing devices (e.g. elbows) at a distance of no more than three diameters of the pipe or duct. In order to use the correlations presented

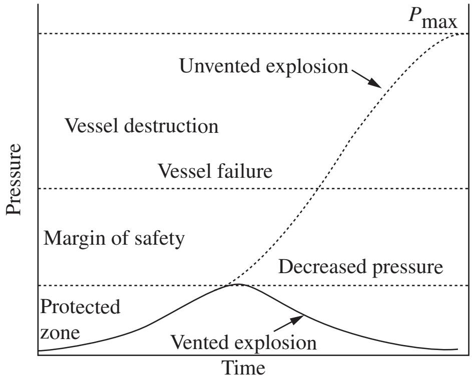


Figure 6.3 Illustration of vented and unvented explosion pressures

later in the guide, the weight of the deflagration vent closures should not exceed 12.2 kg/m^2 of free vent area. The static burst pressure of the vent closures should be as far below the maximum pressure generated in the pipe or duct by the deflagration that one wishes to allow during venting as practical and should be consistent with operating pressures. Deflagration vents should discharge to a location that cannot endanger personnel. Consideration should be given to reaction forces that develop during venting. Although direct venting to atmosphere involves environmental issues, atmospheric dispersion through tall stacks or shorter stacks with steam injection for dispersion is used several times. Whenever atmospheric venting is used for hazardous gases, a simplified quantitative consequence analysis should be performed. This analysis should evaluate the potential effects, where applicable, of vapor cloud explosion, thermal radiation from continuous burning of the vented vapors, impingement on nearby equipment by a jet flame, a flash fire, and toxic gas exposure.

Because the concentration of heavy and hazardous organics may be high in relieved fluids, safe venting may require tall stacks, as the heavy gases are denser than air. By the use of steam injection, the released gas can be much more buoyant and less concentrated, and the gases may be vented at a higher velocity, favoring better dispersion. Steam injection systems cost much less than other treatment methods such as use of flares or scrubbers. However, the drawbacks include additional steam demand with lifting more of relief systems and possible steam condensation, particularly during humid weather.

If changes in outlet piping tip size and the tip elevation do not mitigate pressure relief discharges adequately, steam injection should be considered. Steam injection has the following advantages.

Dilution of the vented organics usually decreases average molecular weight and density of the vented stream further, and it the tip velocity in the outlet of the relief piping, and thereby increases in the plume rise.

Explosion Suppression

Explosion suppression systems are designed to prevent the generation of high pressures by fuel–air explosions in vessels. Essentially, explosion suppression relies on detecting an explosion in the early stages by monitoring internal pressure or UV/

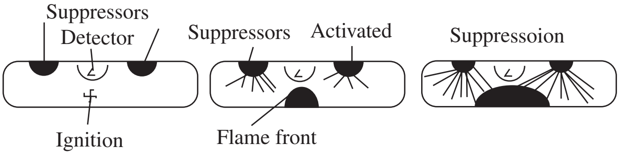


Figure 6.4 Automatic explosion suppression system

IR radiation and then injecting an extinguishing agent into the growing fireball. This maintains the *explosion pressure* to an acceptable level and prevents an explosion from developing.

With explosion suppression systems, the explosion within the plant is contained, even in cases where the plant may be lightly constructed. This makes suppression systems particularly suitable where the discharge of a toxic dust would give rise to environmental pollution, or where the relative position of the vessel with respect to any outside wall is such that the resulting back pressures are unacceptable explosion suppression systems do not prevent an explosion from occurring but mitigate its effects on the protected equipment. The flame front is extinguished at the early stages of the explosion development, considerably reducing the risk of post explosion fires and secondary explosions events.

Suppression is based on extinguishing the propagating flame front by physical (heat absorption) or chemical methods. The mechanism of suppression is related to the type of agent used; dry powder such as sodium bicarbonate, clean agents such as HFC 227, or the early agent of choice, Halon 1011. Regardless of the agent, the key to successful suppression is the rapid delivery of sufficient agent to terminate the combustion process. The overall delivery of agent to the flame front is affected by how quickly the dispersion begins, how fast the delivery is, and the quantity of agent delivered. Explosion suppression systems must detect the combustion event and inject a chemical suppressant in a matter of milliseconds. From the time of detection to full release of the suppressant happens typically in less than 50 ms.

Figure 6.4 illustrates working of an explosion suppression system.

Common extinguishing agents are water, Halon substitutes, and dry chemical formulations typically based on sodium bicarbonate or ammonium dihydrogen phosphate. The extinguishing mechanism of each agent is often a combination of thermal quenching and chemical inhibition. The selection of the appropriate agent is usually based on several considerations such as effectiveness, toxicity, cost, product compatibility, and volatility.

Water is often a very effective suppressant, and should be used whenever possible since, it is not toxic and is easier to clean up in comparison to the other types of suppressants.

Explosion Isolation

In the chemical industry there have been a number of major incidents in which loss of containment of a hazardous substance was one of the main factors. These losses occurred because vessels or process plant containing large quantities of hazardous substances could not be isolated quickly enough. Installations that can cause this type of major incident should have emergency arrangements for the safe and effective shut-down of plant and equipment in a controlled manner.

Isolation of hazardous inventories: In an emergency, rapid isolation of vessels or process plant is one of the most effective means of preventing loss of containment or limiting its size. The extent of isolation provision should be designed to ensure a safe process state and minimize loss of containment. Emergency isolation facilities and procedures for all significant inventories should be included in emergency plans.

Isolation is used to separate incompatible materials/conditions that together would constitute a hazard. For example, a fire hazard is eliminated if fuel, or oxygen or source of ignition is eliminated. Other examples include use of thermal insulation on hot or cold surfaces to prevent injury to personnel on contact with such surfaces, use of explosion-proof equipment in flammable atmospheres, keeping corrosives from incompatible materials, and use of protective devices to prevent exposure to hazards. Isolation is being recognized increasingly as a protective measure in conjunction with suppression, venting, or even containment. A process without interconnections is rare and any process with interconnections is subject to flame propagation through the ductwork. Measures will be needed to prevent an explosion initiated in one plant item from propagating along pipes, ductwork, chutes or conveyors, and starting a subsequent explosion in other plant items or outside the equipment. Measures should therefore be taken to create barriers to avoid propagation of an explosion. There are basically two types of isolation barriers available: mechanical barriers include rotary valves, screw feeders, and quick acting valves, whereas chemical barriers rely on the detection of the flame front or the pressure wave an activation of suppressors located downstream of the detector.

Manual valve isolation may be acceptable in some cases where more rapid emergency isolation is not necessary for preventing a major accident.

Manually operated valves should be readily accessible and clearly marked, considering the difficult and confusing circumstances in which emergency shut-down will probably takes place. Manual valves often have been fitted mainly for maintenance work and might not provide the safest or most effective way of achieving emergency isolation. One should not use them in situations where the operator effecting the isolation would be placed in any danger.

Where an explosion hazard exists, mechanical isolation devices such as quick sliding gate valves, shall be provided to prevent explosion propagation between pieces of equipment connected by ductwork. *Explosion diverter valves* are used to divert advancement of a flame front from other equipment in process piping.

Valves that are activated by process measurement sensor and close automatically on detection of abnormal process or equipment conditions, such as increased pressure or temperature, normally function as part of a trip or shut-down system. They can be designed for emergency isolation. Fireproofing may also be necessary to ensure they continue to function in emergency situations.

Remote isolation: Risks from a major accident hazard can be reduced effectively by fitting pipe work with remotely operated shut-off valves (ROSOVs) which can be closed quickly in an emergency. ROSOVs may be *manually activated* through push buttons located at some distance from the valve. Leak detection may trigger an alarm, usually both on the plant and in the control room, to which the operator can respond by operating the ROSOVs and other systems as necessary.

Emergency isolation systems should be planned to suit the plant system design and operating practices. ROSOVs may be needed at process vessels, pumps and other ancillary equipment and pipe work, taking into account likely points of release such as equipment joints and fittings and rotating equipment, for example pump seals. They should be installed as close as possible to the vessel or plant and be accessible for routine testing and maintenance. Generally, valve closure should be as quick as is possible.

Remote isolation facilities minimize the quantity of material that is released in the event of a spill or other undesirable incident. Because of the hazards associated with materials that might experience BLEVEs and the volumes of the vessels in which such materials are stored, emergency isolation of these vessels should be accomplished by remotely operated emergency isolation block valves (EBVs) located in all main process piping below the high liquid level of the vessel. Since, these EBVs would be within the presumed fire zone, their actuators and power supplies need to be fireproofed. In addition, the actuation buttons must be at a safe location outside the spill containment area for the vessel.

ROSOV selection features: There are some important features to be considered in selecting an appropriate ROSOV. The valves should be classified as *safety critical* valves and be subject to appropriate inspection and maintenance requirements. Regular testing is required, especially where valve operation is infrequent. Companies should determine the frequency and nature of testing based on design and use. In the absence of this assessment, a minimum of 3 monthly intervals is recommended. Only perform a dual function (i.e. control and emergency isolation) in special circumstances and their role in emergency isolation of inventories must be recognized and justified by design.

Employ fail-safe principles. ROSOVs are generally configured to fail closed. Back-up power/air supplies should be provided if closure on failure of plant systems is not acceptable. Remain in the fail-safe position once operated until manually reset. Provide effective leak tightness throughout the emergency. Be protected against external hazards such as fires or explosions, where the major accident hazard is a fire or explosion risk, for example where the valve could be subject to flame impingement.

Chemical isolation barriers are other options for isolation. Suppressant barriers are rapidly established (even on very large ducts) and effectively extinguishing the propagating flame front.

Automatic explosion isolation system is illustrated in Figure 6.5.

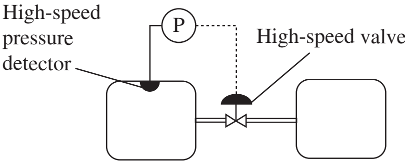


Figure 6.5 Automatic high-speed isolation system

An emergency shut-off valve is fitted to all liquid and vapor connections, which are larger than 3 mm for liquids and 8 mm for vapor, other than for relief valves, level gauges and drainage connections. The emergency shut-off valve should be installed in addition to manual shut-off valves. Where the shut-off valve is actuated, can be operated from a safe area and is of the fail-safe type, then an additional emergency isolation valve is not deemed necessary. The shut-off valve should be located as close to the vessel connection as practicable. The rate of closure of an emergency isolation valve should not be so rapid that it causes undue pressure surges. Long runs of larger diameter pipework may require lower rates of closure to prevent liquid hammer.

Fire Protection

Adequate *fire protection equipment* is necessary so that plant personnel can quickly extinguish small fires, quickly bring larger fires under control, and cool exposed equipment to prevent propagation of any fire. In all cases, it is extremely important to limit the amount of heat absorbed by the vessel as much as possible to avoid overheating of the vessel. Three approaches are widely used to limit heat input, namely, fireproofing of horizontal drums, water deluge systems on spheres and water spray systems.

Fireproofing

Fireproofing, a passive fire protection technique, is probably the most effective way to minimize heat input. Typically, fireproofing is designed to protect the structural steel which supports high risk or valuable equipment. The failure point is generally considered to be about 600°C, as this is the point where steel loses approximately 50 percent of its structural strength.

Tanks, pressure vessels, and heat exchangers may experience a significant cooling effect from liquid contents and so, less fireproofing protection is generally required.

Plate heat exchangers are a special concern because of the gasketing material between plates. These exchangers are provided with a protective enclosure designed to prevent the exchanger from exceeding its maximum operating temperature, which is about 150^{o}C, for about an hour. Electrical components required for emergency isolation, depressurization and plant shut-down are fireproofed with about 15–20 min rating.

The barrier material, usually light-weight concrete, gunite, vermiculite, perlite, or fiber-type insulation, has a low thermal conductivity and is noncombustible. Critical structures in a process plant are fire protected up to 10 m above grade. The structures typically include primary steel work with the potential for pool fires and pipe tracks.

Board systems and applied coatings, such as epoxy-based intumescent resins are also used. Intumescent epoxies are complex proprietary materials.

Intumescent materials, when exposed to heat or flames, undergo a chemical change becoming viscous then forming expanding bubbles that harden into a dense, heat insulating multicellular char. Board systems are used for structural members and protective enclosures, for example, cable systems. These are applied to structures including vessel supports and equipment. As a coating for steel, fireproofing may provide a good measure of corrosion protection.

Some thermal insulation systems, such as cellular glass, may serve a dual role as fireproofing. The fireproofing should be thick enough to maintain the vessel temperature below the failure point for *at least 2 hr*. During this time, firefighters will presumably bring the fire under control and personnel can evacuate from risky areas. To improve fire resistance, polyurethane foam insulation is commonly formulated with flame retardant additives, such as organophosphorus compounds and/or halogenated organics.

In the absence of fireproofing, failure of equipment supports and piping can break piping and equipment supports, causing failure of vessels and equipment, releasing contents, which may be flammables or toxics, increasing fire or toxic risks. The main advantage of fireproofing is that it is a passive means of protection. However, adequate maintenance is needed to ensure that it is in good condition.

The major disadvantage of fireproofing is that it provides protection for a limited time. In addition, if the fireproofing is not properly maintained, accelerated corrosion of the metal under it may occur.

Fireproofing is the preferred method of protecting horizontal vessels. Tanks, pressure vessels and heat exchangers may experience a significant cooling effect from liquid contents and so require less fireproofing protection.

It should be noted that damaged fireproofing can lead to entry of moisture into the structures and increase corrosion to the steel supports, in addition to further damage to fireproofing material.

Water Deluge and Spray Systems

Water deluge system, an active method for fire protection, is another way to protect a vessel against fire exposure. The purpose of most deluge systems is to control heat input to vulnerable equipment or structures. This method uses one or two large deluge heads and weirs to evenly distribute water over the vessel surface. The functions of a deluge system include extinguishment of fire, control of burning, exposure protection, and prevention of fire. For vessels protected by deluge systems the most important points are the vessel ends, the portion of the vessel that contains a vapor space (i.e. the unwetted portion), flange connections that can leak and if the vessel is located close to the ground without good surface drainage, the immediate underneath surface of the vessel that would expose to the flames. A deluge system will generally be controlled by an automatic detection system that trips the deluge when there is a confirmed fire in the protected area. Tradition is to use pilot head detection of fusible elements on a pressurized air line that is linked back to the deluge control valve. This approach is not ideal because of potentially long response times. The fusible element is normally a sprinkler that is designed to respond to hot air rising from a fire and collecting under a ceiling. In the open, hot air will not collect, so the heads take longer to respond. That means they require a large fire to operate them. In addition, pilot heads mean another system of small bore pipe work wrapped round the process plant. In general, a flame detection system is much more sensitive.

The main advantage of deluge systems is that the water can keep the vessel wall cool enough to prevent failure caused by overheating indefinitely. Another advantage is the size of the piping and deluge heads, because of their large diameters; the system is not prone to plugging and is likely to survive any initial explosion prior to system activation.

The main disadvantage of water deluge systems is that they must be carefully designed to ensure that the water is distributed evenly over the vessel surface. Any dry areas, especially in the vapor space, can leave the exposed metal unprotected. Because of this difficulty, deluge systems are used almost exclusively on spheres and on dome roof tanks. Even there, some areas, such as the underside of a sphere, may not receive sufficient water during a fire. Protection of these areas requires additional water from fixed fire monitors or from hoses. Under fire conditions, and especially if the fire is under a sphere, thermal updrafts tend to pull the water away from the vessel surface in areas below the horizontal equator of the sphere. In addition, soot formed in the fire and deposited on the sphere will decrease the adhesion of the water film, and also lead to the film not adequately covering these surfaces. In dome-roof tanks, similar effects happen in the lower portions of the vessel walls. Another disadvantage is that the system must be activated when the fire occurs. Typically, activation is manual, but some sites have reduced response time by installing valves that are remotely activated from a permanently staffed location. It is also possible to use various fusible systems, which will activate the deluge system if fire occurs close to a protected vessel.

Where active fire protection in process units is found to be necessary, the standard approach is to use water spray deluge, usually based on NFPA 15. The purpose of most deluge systems is to control heat input to vulnerable equipment or structures. NFPA 15 lists the following functions:

(i) Extinguishment of fire
(ii) Control of burning
(iii) Exposure protection
(iv) Prevention of fire

Water spray can extinguish certain types of fire, but is primarily used to control burning and limit the severity and for exposure protection. These in turn serve to limit further failures that could lead to additional releases. The most common application of water sprays is the use for cooling process vessels. The important surfaces for process vessels to be protected are the vapor spaces and hemispherical ends. Electrical transformers are provided with water spray coverage where their value or criticality is considered high.

The classical water spray system uses open nozzles spraying water from about 0.5 to 1.5 m off the protected equipment or structures. Pipe work is arranged in a tree or grid. Each system served by a master control valve.

Water spray systems use a number of small spray nozzles that produce cone shaped sprays of fine mist. Water is sprayed usually from about 0.5 to 1.5 m distance from the protected structure or equipment. They are generally used where the other approaches are impractical due to, for example, high wind conditions that prevent the deluge system from evenly distributing the water.

The main advantage of a water spray system is that it can be adapted to any vessel or equipment. In addition, like the water deluge system, it can provide protection indefinitely.

However, water spray systems have several drawbacks. The water rates required may need to be higher than for deluge systems (4–20 L/min/m^2.)

A water spray system usually consists of small diameter piping. This size is more vulnerable to any initial explosion than the deluge system.

Because the spray nozzles used are small, they are prone to plugging, which can be minimized/eliminated by using alloy piping or strainers. Larger nozzles are impractical, as they would require higher water rates and higher pressures to achieve similar coverage. They require operator intervention. Moreover, they are more expensive systems, but that would require additional maintenance.

Water flooding is the principle to inject water into the interior of a storage tank for the purposes of preventing flammable or combustible liquids from being released from a leakage point or to extinguish a fire.

Steam is most effective in smothering fires when they are located in relatively small confined areas. Steam extinguishes fire by the exclusion of free air and the reduction of available oxygen content to the immediate area, similar to other gaseous suppression agents. Steam curtains and barrier walls are used in very hazardous locations to prevent fires.

Emergency Scrubbing

Many operations require standby emergency scrubbers for potential release of toxic gases or vapors. Facilities involving hazardous quantities of chlorine, sulfur dioxide, toxic gases, and the like, must invest in emergency stand-by equipment to prevent accidental chemical releases.

The famous example of highly toxic methyl isocyanate (MIC) at Bhopal triggered one of the worst accidents in the history of chemical industry accidents, which was triggered failure in the activation of an emergency scrubber, which was in place but under shut-down mode.

Emergency scrubber systems include conventional absorption columns, venturi scrubbers, which operate on wet mode, and dry scrubbing systems that do not create liquid waste treatment problems. Wet scrubbing media include sodium hydroxide, calcium hydroxide, phosphoric acid, potassium permanganate, and other specific liquid solutions, depending on the nature of gases, or vapors. Dry systems involve lime, active carbon, and other adsorbents.

Dry scrubbers have several advantages over conventional wet scrubbers. For instance, dry scrubbers require significantly less maintenance than wet scrubbers. They have just one moving part: a blower. Dry scrubbers are much safer, too. For example, instead of using toxic liquid caustic, they neutralize chlorine with nontoxic dry-scrubbing adsorption media in pellet form. Hazards associated with emergency response to an unsecured scene are multiplied when materials to be managed are shock sensitive, air/moisture sensitive, high energy compounds, unknowns, or compressed gas cylinders. Figure 6.6 gives summary of prevention and mitigation options in hazard management.

Choice of technology was already discussed under inherent safety. Steps to prevent accident initiating events involve options such as maintenance, inspection, testing, worker training, operating procedures, and safeguards against process deviations. Releases are minimized through safety options to suppress a hazard in initiating stage by early detection, flow restricting and isolating valves, cooling systems, double-wall storage tanks, and double coaxial distribution lines and raceways for containment,

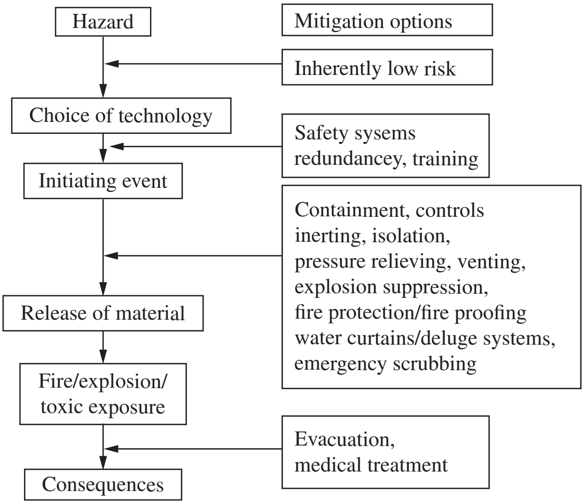


Figure 6.6 Prevention and mitigation options for hazard management

and adequate ventilation. Double wall shells are used for ammonia storage tanks and to prevent radioactive releases from nuclear power plants are common examples. Earlier paragraphs and Figure 6.6 give some of the measures.

Prevention/minimization of human exposures include remote location of gas storage, exclusion zones adjacent to plant boundaries, early warning systems, emergency preparedness, response, and evacuation plans. It is essential that such plans be regularly rehearsed and practiced under simulated emergency conditions to test the response of personnel, increase their experience, and evaluate the effectiveness of equipment. Quick response and medical preparedness is essential to reduce consequences if exposures occur.

Occupational hazard prevention meters are used for professionals in workshops and outside. An example of these occupational hazard meters are the radiation dosimeters. These occupational hazard meters determine if the maximum radiation is exceeded by means of diverse sensors and calculations based on a microchip. Other dose meter types are noise dosimeters to prevent auditory hazards in the working place. Occupational hazard meters belong to any set of instruments to prevent occupational hazards to avoid long-term diseases and offer security in the working area. Gas meters are other important instruments to prevent occupational hazards. Both portable and fixed gas meters, continuously measure the amount of gas (such as ozone, oxygen, carbon monoxide, hydrogen supplied, or flammable gas among others) in the atmosphere and they warn us when limit values are exceeded. Workers can be safe in dangerous area with gas meters.

6.7 Storage Containers for Cryogenic Fluids

The containers should be of double-wall construction with an insulating vacuum space and insulation between the innervessel and the outer vessel. The vessel used for storing cryogenic liquids should be equipped with pressure relief devices for the inner vessel. The vessel used for storing cryogenic liquids should also be equipped with pressure relief devices for annular vessel.

Problems related to storage of cryogenic liquids: Reduced ductility of most metals causes embrittlement. There is a transition between ductile and brittle behavior. Only containers that have been specially designed for storing cryogenic liquids should be used. All system components, piping, valves, etc., must be of appropriate material to withstand the extreme temperatures and the likelihood of pressure build up on temperature increases and thermal contraction inducing stresses.

6.8 Electrical Area Classification

Hazardous areas, in which potentially explosive atmospheres exist, are encountered in a wide variety of industries. Particular care has to be taken with electrical systems and equipment because of their potential for creating sparks and hot spots that could ignite a gas, vapor, mist, or dusty atmosphere. Such environments are encountered almost everywhere, in industry and normal activity-related areas in which flammable and explosive materials are stored or handled. Industries such as refineries and gas processing and handling areas, petrochemical plants, chemical, and pharmaceutical processing, mining.

Flour mills, bakeries, sugar, wood processing, coal handling plants, paper mills and metal industries such as aluminum and magnesium, for example, can all have areas where dust-laden atmospheres are potentially explosive. Listing hazardous areas become exhaustive as electrical equipment is involved everywhere.

Electrical codes and practices are formulated by many countries for enhanced safety in industrial units. U.S. National Electrical Code (NEC), CENELEC of Europe and codes of several countries are involved in providing guidance in safety of industries dealing with electrical equipment.

A large number of variables must be considered in order to correctly determine electrical area classified areas. These variables include properties and behaviors of materials, volumes, pressures, temperatures, flows, piping, and equipment construction, weather, building arrangements, adequacy of mechanical ventilation and gas detection systems, operator interfaces, and experience.

The NEC states that each room, section, or area shall be considered individually in determining its classification.

A plan drawing (three-dimensional) of the plant areas showing areas of different classifications for electrical equipment use will be most valuable to electrical/instrument engineers in equipment selection and to installation contractors and maintenance personnel involved in installation, replacements, and revisions. The extent of areas depends on flammability limits, quantities of vapors/gases likely to be released and their densities and obstructions to free movement of air/gases.

Classification of Hazardous Locations

Hazardous locations are classified depending on the properties of the flammable vapors, liquids, or gases or combustible dusts and ignitable fibers, that may be present and the likelihood that a flammable or combustible concentration is present.

Class I	Flammable gases or vapors
Class II	Combustible dusts
Class III	Combustible fibers or flying's

There are two codes of practice internationally followed, one is based on U.S. National Electrical Code (NEC) division classification system, followed in U.S. and Canada, and the other is International Electro-Technical Code (IEC) zone classification system, followed in Europe.

NEC Division Classification System

Article 500 of the NEC and Section 18 of the Canadian Electrical Code (CEC), classify hazardous locations according to the properties of the flammable vapors, liquids, or gases, or according to the combustible dusts or fibers that may be present and the likelihood that a flammable or combustible concentration or quantity is present.

Areas where fire or explosion hazards may exist due to flammable gases or vapors, flammable liquids, combustible dusts, or ignitable fibers or flying are defined by the NEC and the CEC as *hazardous locations*.

The class and division of an area are based on the type of hazard (Class) and the expected frequency of the hazard (Division).

Class: The class of a location defines the type of explosive danger that exists or may exist in the location.

Hazardous location classes (Figure 6.7):

Division: The *division* of a location defines the *frequency* that the hazard exists or may exist in a location.

Hazardous location divisions

- **Class I**
- *Division 1:* Areas where one or more of the following conditions exist:
  - (i) Ignitable concentrations of flammable gases or vapors can exist under *normal* operating conditions.

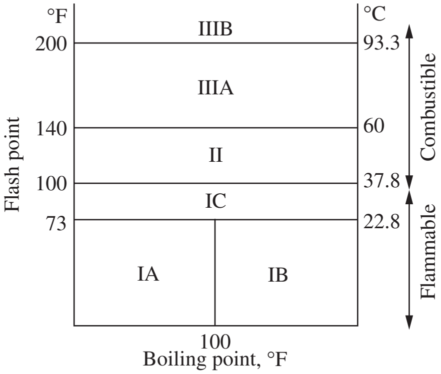


Figure 6.7 Classification of flammable and combustible liquids as defined by NFPA 30

(ii) Ignitable concentrations of such gases or vapors may exist frequently because of repair, maintenance operations, or leakage.
(iii) Break-down or faulty operation of equipment or processes might release ignitable concentrations of flammable gases or vapors and might also cause simultaneous failure of the electrical equipment in such a way as to directly cause the electrical equipment to become a source of ignition.

Typical locations include: Flammable storage areas where liquids and gases are transferred between containers/tank trucks, areas near open dome loading facilities or adjacent to relief valves in a petroleum refinery, because the hazardous material would be present during *normal* plant operations. LPG or natural gas storage and handling areas, aircraft hangars and fuel servicing areas, paint spraying operations using flammable paints and solvents, hot dip operations using flammable coatings, drying rooms/enclosures involving removal of flammable solvents from solids. Pump rooms containing flammables with poor ventilation, refrigeration chambers storing flammable liquids, areas between inner and outer roof sections of floating roof storage tanks for flammable volatile liquids, etc.

- *Division 2:* Areas where one or more of the following conditions exist:

(i) Volatile flammable liquids or flammable gases are handled, processed, or used, but in which the liquids, vapors, or gases will *normally* be confined within closed containers or closed systems from which they can escape only in case of accidental leak/rupture or breakdown of such containers or systems, or in case of *abnormal* operation of equipment. (When the hazardous material is expected to be confined within closed containers or closed systems and will be present only through accidental rupture, breakage or unusual faulty operation, the situation could be called *abnormal*).
(ii) Ignitable concentrations of gases or vapors are normally prevented by positive mechanical ventilation and which might become hazardous through failure or abnormal operations of the ventilating equipment.
(iii) Areas are adjacent to a Class I, Division 1 location and to which ignitable concentrations of gases or vapors might be communicated unless such communication is prevented by adequate positive pressure ventilation from a source of clean air and effective safeguards are provided against ventilation failure.
(iv) Electrical conduits and their associated enclosures separated from process fluids by a single seal or barrier are classified as a Class I, Division 2 location if the outside of the conduit and enclosures is a nonhazardous (unclassified) location.

Typical locations include: Propane cylinder storage areas, closed/sealed drum bulk storage and down draft paint booth control rooms. If one of the containers is leaking, abnormal condition occurs, making the location a Class 1, Division 2 area.

- **Class II:** A location that is hazardous because of the presence of combustible dust.
- *Division 1:* A location in which combustible dust is in the air under normal operating conditions in quantities sufficient to produce explosive or ignitable mixtures; in which mechanical failure or abnormal operation of machinery or equipment might cause such explosive or ignitable mixtures to be produced and might also

provide a source of ignition through simultaneous (the word *simultaneous* is not included in the Canadian definition) failure of electric equipment, operation of protection devices, or from other causes; or in which combustible dusts of an electrically conductive nature may be present in hazardous quantities.

Typical locations include grain mills/elevators, flour mills, starch or candies manufacturing plants, plastics, medicines and fireworks manufacturing areas, wood processing operations (i.e. sanding), or combustible dusts of an electrically conductive nature such as ones that contain magnesium, aluminum, collectors for combustible dusts, areas where mechanical failure or abnormal operation might cause ignitable or explosive mixtures to be produced, open conveyor belts or open top bins where dust is released into the air during *normal* operation, coal handling, etc. Finely pulverized material, suspended in the atmosphere, can cause as powerful an explosion as one occurring at a petroleum refinery.

- *Division 2 (U.S.):* A location in which combustible dust is not normally in the air in quantities sufficient to produce explosive or ignitable mixtures and dust accumulations are normally insufficient to interfere with the normal operation of electrical equipment or other apparatus, but combustible dust may be in suspension in the air as a result of infrequent malfunctioning of handling or processing equipment and where combustible dust accumulations on, in, or in the vicinity of the electrical equipment or may be ignitable by abnormal operation or failure of electrical equipment.
- *Division 2 (Canada):* A location in which combustible dusts are not normally in suspension in air likely to be thrown into suspension by the normal or abnormal operation or the failure of equipment or apparatus in quantities sufficient to produce explosive or ignitable mixtures, but in which

    (i) deposits or accumulations of dust may be sufficient to interfere with the safe dissipation of heat from electrical equipment or apparatus.
    (ii) deposits or accumulations of dust on, in, or near electrical equipment may be ignited by arcs, sparks, or burning material from the electrical equipment.
    (iii) Typical locations include scrap paper baling, pit balers, and printing equipment. Areas or rooms adjacent to Division 1 areas are designated as Division 2, if gases or vapors could enter these areas *occasionally*.

- **Class III:** A location that is hazardous because of the presence of easily ignitable fibers or flying but in which such fibers or flying is not likely to be in suspension in the air in quantities sufficient to produce ignitable mixtures.
- *Division 1:* A location in which easily ignitable fibers or materials producing flying are handled, manufactured or used. The fibers and flying are not likely to be suspended in the air, but can collect around machinery or on lighting fixtures and where heat, a spark or hot metal can ignite them. Typical locations include clothing manufacture, wood working operations, and textile processing.
- *Division 2:* A location in which easily ignitable fibers are stored or handled (except in the process of manufacture). Typical locations include textile mills, cotton gins, garment packaging and distribution, book and periodical distribution, wood products storage, etc.

Classification of Materials

Materials are classified, for the purpose of selection of electrical equipment, as *groups*. The grouping designation is a breakdown of flammable gases and vapors or combustible dusts in groups that have similar characteristics. Groups not only have similar characteristics but also have rules that apply to each. The following classification is based on U.S. National Electric Code (NEC):

Class I has four Groupings: A, B, C, and D. Class II has three Groupings: E, F, and G.

The NEC group of a hazard is based on specific characteristics of the flammable and explosive hazard present. Different sealing techniques are required for the equipment, depending on the molecular size of the hazardous materials and other criteria.

Flammable gases and vapors are placed into NEC Groups based on a determination of explosion pressures and maximum safe clearance, maximum experimental safe gap—(MESG) between parts of a clamped joint under several conditions (details in NEC Article 500–505). The various groups A, B, C, and D for flammable gases and vapors, E, F, and G for combustible dusts, are described in Article 500 of the NEC.

The self-ignition temperatures and the NEC group of a large number of explosive gases, vapors and combustible dusts can be found in Article 500 of the NEC. The temperature identification number (often called T-rating) is based on the maximum operating temperature of the equipment.

*Marking: Approved equipment shall be marked to show the class, group, and operating temperature or temperature range referenced to a 40°C ambient. The temperature range, if provided, shall be indicated in identification numbers.

Table 6.4 gives groupings for selected chemicals.

Table 6.4 Group classification for selected chemicals

Gases/vapors
Group A
Acetylene
Group B
Acrolene, arsine, butadiene, ethylene oxide, propylene oxide, propyl nitrate, hydrogen, formaldehyde
Group C
Acetaldehyde, n-butaraldehyde, iso-butaraldehyde, crotonaldehyde, allyl alcohol, methyl mercaptan, butyl mercaptan, CO, cyclopropane, di-cyclopentadiene, di-ethyl ether, di-methyl amine, di-ethyl amine, di-isopropyl amine, di-n-propyl amine, 1,4-dioxane, epichlorohydrin, ethylene, ethyl mercaptan, n-ethyl morpholene, ethyl sulfide, hydrogen cyanide, hydrogen selenide, H_2S, methyl acetylene, methyl ether, mono-methyl hydrazine, morpholine, nitro-methane, nitro-ethane, n-propyl ether, tetra-hydrofuran, tri-ethyl amine, 1,1-dimethyl hydrazine, veleraldehyde

(Continued)

Table 6.4 (Continued)

Group D
Acetic acid (glacial), acetone, acetonitrile, acrylonitrile, allyl chloride, ammonia, benzene, butane, n-amyl acetate, sec-amyl acetate, butyl alcohol, sec- butyl alcohol, n-butyl acetate, sec-butyl acetate, butyl amine, butylene, chlorobenzene, chloroprene, cyclohexane, cyclohexene, cyclopropane, 1,1-dichloroethylene, 1,3-dichloropropene, di-isobutylene, ethane, ethanol, ethyl acetate, ethyl acrylate, ethyl amine, ethylbenzene, ethyl chloride, ethylene diamine (anhydrous), ethylene dichloride, gasoline, ethyl formate, ethylene glycol monomethyl ether, heptane, heptene, hexane, hexenes, 2-hexanone, isoamyl acetate, isobutyl acrylate, isoprene, isopropyl acetate, isopropyl amine, isopropyl ether, LPG, mesityl oxide, methane, methanol, methyl acetate, methyl acrylate, methyl amine, methyl cyclohexane, methyl ethyl ketone, methyl formate, methyl isobutyl ketone, methyl isocyanate, methyl methacrylate, isobutanol, tertiary butanol, nonane, natural gas, fuel oil, octane, octene, pentane, amyl alcohol, 2-pentanone, 1-pentene, naphtha, propane, propyl alcohol, iso-propyl alcohol, n-propyl acetate, propylene, propylene dichloride, propylene oxide, pyridine, styrene, toluene, tripropyl amine, turpentine, vinyl acetate, vinylidene chloride, xylenes
Dusts
Group E
Containing combustible metal dusts regardless of resistivity, or other combustible dusts of similar hazardous characteristics, having resistivity less than $10^{3/4}$ ohm-cm
Group F
Containing carbon black, charcoal, coal, or coke dust which have more than 9 percent total volatile matter or atmospheres these dusts sensitized by other materials so that they present an explosion hazard, and having resistivity more than 10 ohm-cm but equal or less than 10^8 ohm-cm
Group G
Flour, starch, plastic, etc., having resistivity of 10^5 ohm-cm or more

Notes:

1. Group D equipment shall be permitted if such equipment is isolated by sealing all conduit 12.7 mm (1/2 inch) or larger.
2. Group C equipment shall be permitted for this atmosphere if such equipment is isolated by sealing all conduits 12.7 mm (1/2 inch) or larger.
3. For classification of areas involving ammonia atmosphere, relevant codes for refrigeration, handling and storage of anhydrous ammonia may be consulted.

The only substance in Group A is acetylene. Acetylene makes up only a very small percentage of hazardous locations. Consequently, little equipment is available for this type of location. Acetylene is a gas with extremely high explosion pressures.

Group B is another relatively small segment of classified areas. This group includes hydrogen and other materials with similar characteristics. If one follows certain specific restrictions in the code, some of these Group B locations, other than hydrogen, can actually be satisfied with Groups C, D equipment.

Groups C, D are by far the most usual Class I groups. They comprise the largest percentage of all Class I hazardous locations. Found in Group D are many of the most common flammable substances such as butane, gasoline, natural gas, and propane.

In Class II dust locations one finds the hazardous materials in Groups E, F, and G. These groups are classified according to the ignition temperature and the conductivity of the hazardous substance. Conductivity is an important consideration in Class II locations, especially with metal dusts.

Certain chemicals may have characteristics that require safeguards beyond those required for any of the above groups. Carbon disulfide is one of the chemicals because of its low self-ignition temperature and the small joint clearance in equipment maximum experimental safe gap (MESG) to arrest its flame propagation.

Certain metal dusts may have characteristics that require safeguards beyond those required for atmospheres containing the dusts of aluminum, magnesium and their commercial alloys. For example, zirconium, thorium, and uranium dusts have extremely low ignition temperatures as low as 20°C and minimum ignition energies lower than any material classified in any of the Class I or Class II Groups. Certain dusts may require additional precautions due to chemical phenomena that can result in the generation of ignitable gases. Combustible dusts that are electrically nonconductive include dusts produced in the handling and processing of grain and grain products, pulverized sugar and cocoa, dried egg and milk powders, pulverized spices, starch and pastes, potato and wood flour, oil meal from beans and seed, dried hay, and other organic materials that may produce combustible dusts when processed or handled. Electrically conductive dusts are dusts with a resistivity less than 10^5 ohm-cm. Dusts containing magnesium or aluminum are particularly hazardous and the use of extreme caution will be necessary to avoid ignition and explosion.

Dust that is carbonized or excessively dry is highly susceptible to three spontaneous ignition. Equipment and wiring of the type defined as explosion-proof shall not be required and shall not be acceptable in Class II locations unless approved for such locations.

Where Class II, Group E dusts having a resistivity less than 10^5 ohm-cm are present in hazardous quantities, there are only Division 1 locations.

Table 6.5 summarizes different classified hazardous locations.

Table 6.5 Summary of Class I, II, and III hazardous locations

Classes 1	*Groups 2*	*Divisions*	
I Gases, vapors and liquids	A. Acetylene B. Hydrogen, etc. C. Ether, etc. D. Hydrocarbons, fuels, solvents, etc.	Normally explosive and hazardous	Not normally present in an explosive concentration, but may accidentally exist
II Dusts	E: Metal dusts (conductive,* and explosive) F: Carbon dusts (some are conductive,* and all are explosive) G: Flour, starch, grain, combustible plastic or	Ignitable quantities of dust normally are or may be in suspension, or conductive dust may be present. Dust layers are present	Dust not normally suspended in an ignitable concentration (but may accidentally exist)

(Continued)

Table 6.5 (Continued)

	chemical dust (explosive) may be in suspension, or conductive dust may be present		
III Fibers and flyings	Textiles, wood working, etc. (easily ignitable but not likely to be explosive)	Handled or used in manufacturing	Stored or handled in storage (exclusive of manufacturing)

*Electrically conductive dusts are dusts with a resistivity less than 10^5 ohm-cm

*Note: The type of hazard is defined as an *explosion hazard* in Class I and II locations, and a *fire hazard* in Class III locations.

Temperature Classification of Electrical Equipment

There is a classification used to indicate the maximum surface temperature that a piece of electrical equipment could reach when in service. The maximum surface temperature is generally based on a surrounding maximum ambient temperature of 40°C. The T-class of a piece of equipment can be compared to the self-ignition temperature of gases that may come into contact with it, and hence a decision can be made as to the suitability of the equipment to be used in that area.

Electrical equipment for use in hazardous locations are classified and labeled, indicating the maximum permissible surface temperatures and the chemical groups for which they are suitable. T-classes do not apply to Group I applications. Equipment for use in the mining industry has either a rigid 150°C or 450°C limit. Table 6.6 gives temperature identification numbers.

Table 6.6 Temperature identification numbers

Max. temperature (°C)	*Identification number(T-rating)*
450	T_1
300	T_2
280	T_2A
260	T_2B
230	T_2C
215	T_2D
200	T_3
180	T_3A
165	T_3B
160	T_3C
135	T_4
120	T_4A
100	T_5
85	T_6

Table 6.7 gives examples for the classification of gases and vapors into explosion groups and temperature classes.

Table 6.7 Examples for the classification of gases and vapors into explosion groups and temperature classes

Class	*Material in temperature class*					
	T_1	T_2	T_3	T_4	T_5	T_6
I	Methane					
IIA	Acetone	Ethanol	Benzene	Acetaldehyde		
	Ethane	i-Amyl acetate	Diesel oil	Ethyl ether		
	Ethyl ethanoate	n-Butane	Aircraft fuel			
	Ammonia	n-Butyl alcohol	Heating oils			
	Benzol		n-Hexane			
		Methanol				
		Propane				
		Toluene				
IIB	Coal gas	Ethylene				
IIC	Hydrogen	Acetylene				
						Carbon disulfide

For equipment to be used in a hazardous (classified) area, the equipment should be approved for *both* the *class* and *division* of the hazardous area and approved for the NEC Group of the hazard(s) present in the area. Also, the identification number of the equipment must be less than both the self-ignition temperature of the hazard(s) present in the area and less than the maximum allowed in the area.

IEC Zone Classification System

Zone: The International method of specifying the probability that a location is made hazardous by the presence, or potential presence, of flammable concentrations of gases and vapors. The term *division* is used in the United States and Canada and Zone is used in Europe. The purpose of *zoning* is to provide the basis for correct selection of a protection concept. Areas are classified depending on the properties of the flammable vapors, liquids, mists, gases, or combustible fibers/dusts that may be present in the environment and the likelihood that a combustible concentration of that gas or dust is present.
Table 6.8 gives IEC Zone classification system.

Table 6.8 IEC zone classification involving gases, vapors, and mists

Zone	*Definition*	*Example*
0	An area in which an explosive atmosphere consisting of a	Typically the space above the liquid in a storage vessel

(Continued)

Table 6.8 (Continued)

	mixture with air of flammable substances in the form of gas, vapor or mist, *is present continuously or for long periods* (> 1,000 h/year) *or frequently*. Equal to a Division 1 hazardous location in the United States and Canadian classifications.	
1	An area in which an explosive atmosphere consisting of a mixture with air of flammable substances in the form of gas, vapor or mist *is likely to occur in normal operation occasionally* (> 10 h/year and < 1,000 h/year). Equal to a Division 1 hazardous location in the United States and Canadian classifications.	The space immediately around vent pipe openings during filling
2	An area in which an explosive atmosphere consisting of a mixture with air of flammable substances in the form of gas, vapor or mist, *is NOT likely to occur in normal operation but, if it does occur, will persist for a short period only* (< 10 h/year). Equal to a Division 2 hazardous location in the United States and Canadian classifications.	Around Zone 1, it is usual to consider the surrounding space to be Zone 2

Table 6.9 gives IEC zone classification system for dusts.

Table 6.9 IEC zone classification involving dusts

Zone	*Definition*	*Example*
Zone 20	A place in which an explosive atmosphere in the form of a cloud of combustible dust in air is *present continuously, or for long periods or frequently*.	In general, these conditions when they occur, arise inside containers, pipes and vessels.
Zone 21	A place in which an explosive atmosphere in the form of a cloud of combustible dust in air is *likely to occur in normal operation occasionally*.	This zone can include, among others, areas in the immediate vicinity of, for example, powder filling and emptying points and areas where dust

(Continued)

Table 6.9 (Continued)

		layers occur and are likely in normal operation to give rise to an explosive concentration of combustible dust in mixture with air.
Zone 22	A place in which an explosive atmosphere in the form of a cloud of combustible dust in air is *not likely to occur in normal operation but, if it does occur, will persist for a short period only.*	This zone can include, among others, areas in the vicinity of equipment, protective systems and components containing dust, from which dust can escape from leaks and form dust deposits (e.g. milling rooms, in which dust escapes from the mills and then settles).

Differences between Divisions and Zones

Figure 6.8 illustrates the differences between divisions and zones.

Zone 2 is equivalent to Division 2. Division 1 is split between Zone 1 and Zone 0. It should be noted that heating cables can never be placed in Zone 0 areas. The use of the zone system requires that:

(i) Supervision of work: Classification of areas and selection of equipment and wiring methods shall be under the supervision of a qualified registered professional engineer.

(ii) Dual classification: In instances of areas within the same facility classified separately, Class I, Zone 2, locations shall be permitted to abut, but not overlap, Class I, Division 2 locations. Class I, Zone 0 or Zone 1 locations shall not abut Class I, Division 1 or Division 2 locations.

(iii) Re-classification permitted: A Class I, Division 1 or Division 2 location shall be permitted to be re-classified as a Class I, Zone 0, Zone 1, or Zone 2 location provided all of the space that is classified because of a single flammable gas or vapor source is re-classified.

The zone system approach will be most useful in new construction and significant upgrades.

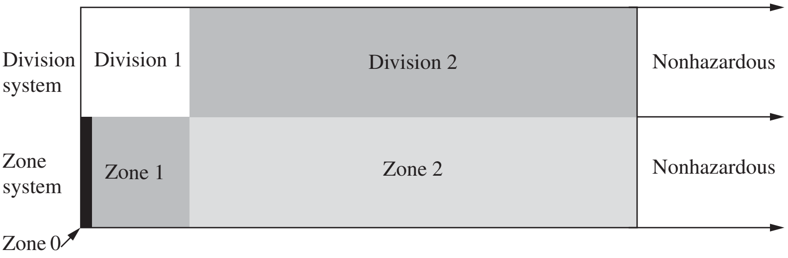


Figure 6.8 Differences between divisions and zones

6.8.7 Types of Electrical Protective Systems

Table 6.10 gives a summary of types of measures of protection and their applications.

Table 6.10 Types of electrical protective measures and their applications

Protective method	*Description*	*Application*
Flame/explosion proof	Parts that can ignite a potentially explosive atmosphere are surrounded by an enclosure capable of withstanding an explosion of a specified gas/vapor exploding inside the enclosure and prevents the propagation of the explosion to the outside flammable atmosphere	Class I Division 1 or 2. Switch-gear, control systems, motors, transformers, heating and lighting fixtures Relatively easy to be applied but with specific mechanical requirements. Difficulty in checks and maintenance
Increased safety	Additional measures are taken to increase safety, preventing possibility of unacceptably high temperatures and creation of sparks or arcs within the enclosure or on exposed parts of the electrical equipment where such ignition sources will not occur under *normal operation*	Division 1/Zones 1 and 2 areas. Terminal and connection boxes, small motors, use of high integrity insulation, protection against ingress of solids and liquids, control of maximum temperatures, Requires high impact strength for the enclosure
Intrinsic safety	Intrinsically safe equipment is defined as "*equipment and wiring which is incapable of releasing sufficient electrical or thermal energy under normal or abnormal conditions to cause ignition of a specific hazardous atmospheric mixture in its most easily ignited concentration*." Use of intrinsically safe circuits in which even under fault conditions, energy within the circuits is less than the minimum ignition energy of the flammable atmosphere in which it is to operate	Class I, Division 2 locations Instrumentation and control technology, communication technology, sensors, actuators. Economical and easy installation, checks and maintenance. Limited to low power circuits
Purged and pressurized enclosures	Purge/pressurization accessories are attached to an enclosure to prevent explosions in hazardous locations by purging combustible gases or dust and then maintaining a positive pressure with clean dry air or other inert gas to an enclosure to prevent explosions in hazardous locations by purging combustible gases or dust and then maintaining a positive pressure with clean dry air or other inert gas. Purging is defined as the	Class II, Division 1 Pressurized equipment, switch gear, control cabinets, computers, printers, instrumentation and electrical panels, large motors, analyzers. Suitable for large containers or for working area. Requires specific alarm systems. Pressurization is limited to protection of the apparatus that do not

(Continued)

Table 6.10 (Continued)

	process of supplying an enclosure with clean air or an inert gas, at sufficient flow and positive pressure to reduce to an acceptable safe level the concentrations of any flammable gases or vapors initially present and to maintain this safe level by positive pressure with or without continuous flow. Pressurizing is similar to purging except that pressurizing is used to prevent the entrance of hazardous dusts and cannot be used to clean out dust that already exists inside an enclosure. In the case of pressure loss, an automatic shutdown of the power supply can occur. The overpressure is maintained with or without constant flushing of the protective gas. The enclosure must withstand 1.5 times the overpressure experienced during normal operation	contain the source of a flammable mixture
Non-incendive equipment	Equipment having electrical/electronic circuitry that is incapable, under normal operating conditions, of causing ignition of a specified flammable gas-air, vapor–air, or dust–air mixture due to arcing or thermal means	Class I, Division 2, Class II, Division 2, Class III, Division 1 or 2
Non-incendive circuit	A circuit, other than field wiring, in which any arc or thermal effect produced under intended operating conditions of the equipment is not capable, under specified test conditions, of igniting the flammable gas-air, vapor-air, or dust-air mixture	Class I, Division 2, Class II, Division 2, Class III, Division 1 or 2
Non-incendive component	A component having contacts for making or breaking an incendive circuit; the contacting mechanism is constructed so that the component is incapable of igniting the specified flammable gas-air or vapor–air mixture. The housing of a nonincendive component is not intended to exclude the flammable atmosphere or contain an explosion	Class I, Division 2 Class II, Division 2 or Class III, Division 1 or 2
Hermitically sealed	Equipment sealed against entry of an external atmosphere where the seal is made by fusion, for example, soldering, brazing, welding or fusion of glass to metal	Class I, Division 2, Class II, Division 2 Class III, Division 1 or 2

(Continued)

Table 6.10 (Continued)

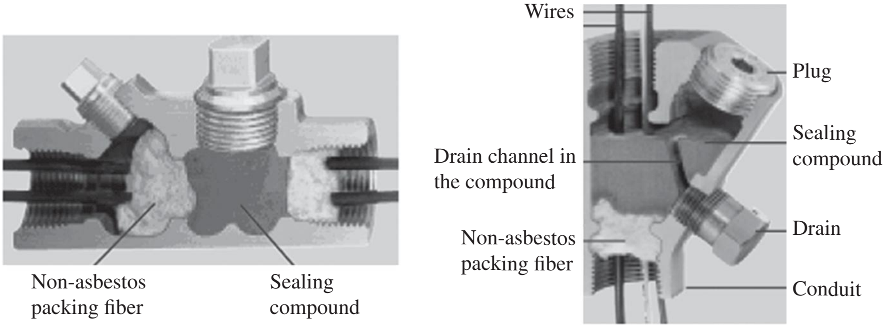
Oil immersion	All electrical parts are submerged in either nonflammable or low-flammability oil, which prevents the external atmosphere from contacting the electrical components. The oil often serves also as a coolant	Current interrupting contacts in Class I, Division 2 Suitable for transformers and where there are moving parts
Powder filled	Similar to the oil-immersion method of protection, except that the segregation is accomplished by filling the enclosure with powdered material so that an arc generated inside the enclosure will not result in the ignition of the hazardous atmosphere. The filling must be made in such a way as to prevent empty spaces in the mass. The filling material that is generally used is quartz powder and its granularity must comply with the standard	Suitable where there are nonmoving parts. Electronic devices, for example, fuses, capacitors. Difficulty in maintenance. Used in Zones 1 and 2
Encapsulation	Parts that may ignite a potentially explosive atmosphere are embedded in a sealing compound to prevent ignition of potentially explosive atmosphere. The encapsulating compound must be resistant to water absorption and other physical and chemical influences	Small capacity switch gear, control and signaling units, display units and sensors. Often used as a complement to other protection methods
Dust ignition-proof	Equipment enclosed to prevent dust ingress and does not permit arcs, sparks or heat generated/liberated inside the enclosure to cause ignition of the exterior accumulations or atmospheric suspensions of a specified dust on or in the vicinity of the enclosure	Class II, Division 1 or 2
Dust-tight	Enclosures constructed so that dust will not enter under specified test conditions	Class II, Division 2 or Class III, Division 1 or 2

*Notes: In the process instrumentation area, the most widely used methods of protection are *intrinsic safety*, use of explosion-proof enclosures and purging, or pressurization. Explosion proof method is the most widely known and has been used in applications for the longest period of time. However, it is generally agreed that the *intrinsic safety* protection method is safer, more flexible and costs less to install and maintain.

In the case of installations using conduits/tubes carrying the wiring, the tubes are connected to housings by means of unions and other fittings and are equipped with a seal at each entrance point and at specific intervals to prevent explosions that may occur inside the housing from traveling through the pipeline to other parts of the plant. Drains must be installed at low points at which condensate can accumulate.

Figure 6.9 illustrates sealing of conduits.

Figure 6.10 illustrates an explosion-proof enclosure with sealing fixture.



Seal for horizontal installation (without drain)

Seal for vertical installation (with drain)

Figure 6.9 Sealing of conduits

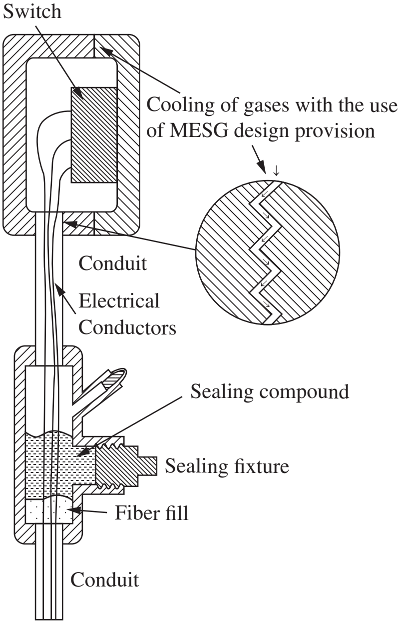


Figure 6.10 Explosion-proof electrical enclosures with sealing fixture

Source: R. Stahl Technology Group GMBH

6.9 Safety in Maintenance Operations

There are two different types of maintenance which can be distinguished:

Corrective maintenance: When actions are intended to restore a system from a failed state to a working state (e.g. repair or replacement of broken components). This type of maintenance is also known as *reactive maintenance* because the action is initiated when the unscheduled event of an equipment failure occurs.

Preventive maintenance: When actions are carried out at predetermined intervals or according to prescribed criteria intended to reduce the probability of failure or the degradation of the functioning of an item. In this case, actions are scheduled, proactive and intended to control the deterioration process leading to failure of a system (e.g. replacement, lubrication, cleaning, or inspection).

There is also a third type of maintenance which concerns large scale maintenance. This is carried out to allow an item to accomplish new or additional functions, or the same function in better conditions. It is frequently carried out during shut-down of the item.

Occupational safety and health risks related to maintenance: Because they carry out a wide range of activities, maintenance workers are exposed to many and varied hazards at work. There are physical hazards such as noise, vibrations, excessive heat and cold, radiation, high physical work load and strenuous movements and biological hazards. Maintenance workers are also at risk of all types of accidents.

Maintenance workers often have contact with vapor or gases, particles (dust, smoke), fibers and mists. Typical maintenance tasks during which workers come in contact with chemical substances include:

- Working in confined spaces with hazardous atmospheres
- Electrical arc welding
- Work in solid waste treatment plants
- Maintenance of industrial installations
- Work with asbestos

Major hazards related to maintenance: Lack of control of spares making use of incorrect materials or items outside specifications (e.g. non-flameproof equipment) are used as replacements for correct items leading to increased risk of loss of containment, fire or explosion.

Failure to drain and/or isolate plant prior to dismantling, causing release of flammable or toxic substances.

Maintenance being performed incompetently (particularly alarm/action set points on instruments incorrectly set, alignment of couplings on pumps and agitators causing overheating, motors running in wrong direction, safety features left disconnected/dismantled, gaskets left out, bolts torqued incorrectly or bolts missing, incorrect orientation of check valves, incorrect connections/installations of pipework/flexible, pipeline spades/orifice plates left in/removed, relief valve springs over tightened, incorrect assembly/installation of rupture discs.

Scheduled maintenance not being undertaken as required or break-down maintenance inadequate, leading to unrevealed failures of critical safety items.

Lack of knowledge by maintenance staff of the working environment where maintenance is being carried out (i.e. lack of risk assessments, warning signs, and emergency procedures), leading to ignition of flammable substances (e.g. heat sources such as cigarettes or welding, static and electrical discharge, use of non-sparking tools) or injury/fatality from incorrect personal protective equipment (e.g. respirators) being worn.

Unauthorized staff performing maintenance functions. Failure to re-commission plant correctly after maintenance to ensure that operations are not adversely affected in terms of safety considerations (e.g. contamination, flow rate changes, heat transfer rate changes, and mass transfer rate changes).

Confined Space Entry

A confined space has limited or restricted means of entry or exit, is large enough for a worker to enter and perform assigned work, and is not designed for continuous occupancy. Often the confined space will not *appear* to be hazardous; may have been entered on prior occasions without incident and may give no apparent sign of danger. At other times there may be ready indications of danger such as distinct odor of irritating or toxic gases, presence of arcing electrical equipment, continued mild shocks, or flowing grain or sand.

The main hazards involved in confined space entry include the following:

Oxygen deficiency, toxic contamination, flammable environment, possibility of electrocutions through electrical equipment, possibility of toxic gas generation during the work, lack of ventilation, difficulty in welfare monitoring, failure to escape on emergency, and combustible substances.

By their nature, confined spaces concentrate hazards of dangerous atmospheres, with certain gases that displace breathable air, or will allow the accumulation of toxic or flammable/explosive gases, and physical hazards, such as those which limit the ability to avoid contact with electricity, moving mechanical components or machinery, or unstable substances.

A confined space at any time contains, or is likely to contain an atmosphere that has potentially harmful levels of a contaminant, that does not have a safe oxygen level, and anything that could cause engulfment.

Examples of confined spaces include storage tanks, tank cars, cargo tanks, cellular double bottom tanks, ballast or oil tanks, septic tanks, sewage digesters, process vessels, pressure vessels, furnaces, boilers, silos, and other tank such as compartments, pits, pipes, sewers, sewer pump stations including wet and dry wells, tannery vats, shafts and ducts, and shipboard spaces entered through small hatchways or other access points, nitrogen purged pipe lines, and void spaces.

The presence of gases and toxic vapors in confined spaces makes the atmosphere very dangerous for the health of workers. Gases such as carbon disulphide, carbon monoxide, hydrogen cyanide, or hydrogen sulfide combined with lack of oxygen might be a cause of death. Recognition of confined space hazards, enable provisions for minimizing the need for entry and for use of appropriate work practices and equipment can be made.

Accidents in confined spaces are generally characterized by two factors, namely, an ignorance of the risks present in the workplace and during the accomplishment of the work by those in charge of the work, and a lack of communication between production and maintenance departments.

Summary of safety precautions while entry into confined spaces:

- Thorough cleaning and purging before hot work.
- Safety belt with one end outside.
- Life line to monitor welfare.
- On-going ventilation.
- A person to watch the welfare.
- Low voltage electrical appliances.

Table 6.11 gives the classification of confined spaces scheme.

Table 6.11 Confined space classification

	Class A	*Class B*	*Class C*
Characteristics	Immediately dangerous to life	Dangerous but not immediately life threatening	Potential hazard
Oxygen	≤16%* (122) or ≥ 25% (190)	16.1–19.4%* (122–147) or 21.5–25% (163–190)	19.5–21.4* (148–163)
Flammability	≥ 20% of LFL	10–19% of LFL	≤ 10% of LFL
Toxicity	IDLH**	≥ Contamination level, referenced in 29 CFR Part 1910, Subpart Z(IDLH**)	≤ Contamination level, referenced in 29 CFR Part 1910, Subpart Z

**Based upon a total atmospheric pressure of 760 mm Hg (sea level).

**Immediately Dangerous to Life or Health.

- Self-contained breathing apparatus. Breathing apparatus should be periodically checked, including to the fit to individuals who undertake entry and any deficiencies should be removed.
- Environmental monitoring for oxygen, toxic gases and flammable gases before entry.
- Pipeline isolation before entry.
- Electrical isolation before entry.
- Proper ladder for entry.

NIOSH developed a classification scheme for hazards in confined spaces, which is based on the oxygen content of the air, the flammability characteristics of gases or vapors, and the concentration of toxic substances that may be present.

Figures in brackets are in mm Hg.

Oxygen levels: Any atmosphere with less than 19.5 percent oxygen should not be entered without a NIOSH-approved self-contained breathing apparatus or a NIOSH-approved supplied air breathing apparatus.

*Source: NIOSH

The oxygen level in a confined space can decrease because of the type of work being done, such as welding, cutting or brazing, or it can be decreased by certain chemical reactions (rusting) or through bacterial action (fermentation). It can also decrease if oxygen is displaced by another gas, such as carbon dioxide, argon, helium, or nitrogen. Total displacement of oxygen by another gas, such as carbon dioxide, will result in unconsciousness, followed by death.

Flammable atmospheres: Flammable atmospheres generally result from evaporation of flammable liquids, byproducts of chemical reactions, enriched atmospheres or concentrations of combustible dusts.

Figure 6.11 illustrates oxygen levels and safety concerns.

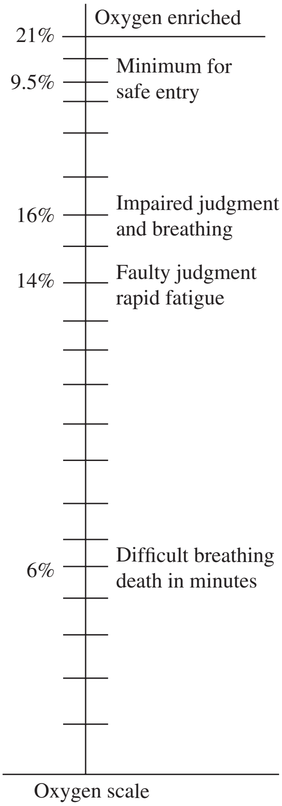


Figure 6.11 Scale of oxygen levels and breathing problems

An oxygen-enriched atmosphere (above 23.5 percent) will cause flammable materials, such as clothing and hair, to burn violently when ignited and may also cause some nonflammable materials to ignite. Therefore, pure oxygen *should never be used* to ventilate a confined space, which should be ventilated with normal air.

Because air cannot freely move in and out of confined spaces due to the design and configuration, the atmosphere inside a confined space can be very different from the atmosphere outside. Hazardous gases may be trapped inside, particularly if the space is used to store or process chemicals or organic substances that may decompose. There may not be enough oxygen inside the confined space to support life, or the air could be so oxygen-rich that it is likely to increase the chance of fire or explosion if a source of ignition is present.

Toxic atmospheres: The product stored in the space may contain a toxic component, which could be absorbed into the walls and have the potential for release depending on the use of the space. Toxic gases/vapors may be generated in confined spaces due to welding, cutting, brazing, painting, scraping, sanding, and degreasing with cleaning solvents/operations. The vapors from these solvents can build up to toxic levels in a confined space. Toxic fumes, mists, and dusts may be generated or present in confined spaces. Toxics produced by work near confined spaces can enter and accumulate in confined spaces. Activated carbon cloth, a material composed of fine carbon fibers, is claimed to be effective in the cleanup of toxic waste, by researchers at the University of Abertay, Dundee, Scotland.

General/Physical hazards: Temperature extremes, contact with hot objects, high humidity, noise, electric shock, ionizing radiation, engulfment of workers by solid materials such as coal, grain, and sand; wet and slippery surfaces; falling objects; and so on. Non-entry tank cleaning methods are increasingly used in present days.

Permit to Work System

Permit to work is required for entry into a confined space under the following circumstances:

The definition of a confined space is met.

Contains or has a potential to contain a hazardous atmosphere.

Contains a material that has the potential for engulfing an entrant.

Has an internal configuration such that an entrant could be trapped or asphyxiated by inwardly converging walls or by a floor which slopes downward and tapers to a smaller cross-section.

Contains any other recognized serious safety or health hazard immediately dangerous to life and health that prevents self-rescue.

A permit, signed by the entry supervisor verifying that pre-entry preparations have been completed and that the space is safe to enter, must be posted at entrances or otherwise made available to entrants before they enter a permit space. The duration of entry permits must not exceed the time required to complete an assignment. Also, the entry supervisor must terminate entry and cancel permits when an assignment has been completed or when conditions that are not allowed to arise. New conditions must be noted on the canceled permit and used in revising the permit space program. The standard also requires the employer to keep all canceled entry permits for at least one year.

Entry permits must include the following information:

Test results, initials/signature of the tester, name, and signature of supervisor who authorizes entry, name of permit space to be entered, authorized entrant(s), eligible attendants and individual(s), authorized to be entry supervisor(s), purpose of entry and known space hazards, measures to be taken to isolate permit spaces and to eliminate or control space hazards, that is, *locking out or tagging* of equipment and procedures for purging, making inert, ventilating and flushing permit spaces, name and telephone numbers of rescue and emergency services, date and authorized duration of entry, acceptable entry conditions, communication procedures and equipment to maintain contact during entry, additional permit(s), such as for hot work, that have been issued to authorize work in the permit space, special equipment and procedures, including personal protective equipment, alarm systems and rescue equipment, and any other information needed to ensure employee safety.

Table 6.12 illustrates a typical confined space entry permit.

Table 6.12 Typical confined space entry permit

Date and time issued:----
Date and time expires: ----
Job site/space I.D: ----
Job supervisor: ----
Equipment to be worked on: ----
Work to be performed: ----
Stand-by personnel: ----
1. Atmospheric checks: time---- oxygen ---- % explosive ---- % L.F.L. toxic ---- ppm
2. Signature of test person: ----
3. Source isolation (no entry): N/A Yes No pumps or lines blinded, ( ) ( ) ( ) disconnected, or blocked ( ) ( ) ( )
4. Ventilation modification: N/A Yes No mechanical ( ) ( ) ( ) natural ventilation only ( ) ( ) ( )
5. Atmospheric check after isolation and ventilation: oxygen ----% > 19.5% explosive ---- % L.F.L < 10% toxic ---- ppm < 10 ppm H_2S time ---- signature of test person: ----
6. Communication procedures: ----
7. Rescue procedures: ----
8. Entry, standby and back up persons: Yes/No
Successfully completed required training? ( ) ( ) Is it current? ( ) ( )
9. Equipment: N/A Yes No
Direct reading gas monitor tested ( ) ( ) ( )
Safety harnesses and lifelines for entry and standby persons ( ) ( ) ( )
Hoisting equipment ( ) ( ) ( )
Powered communications ( ) ( ) ( )
SABA or SCBA for entry and standby persons ( ) ( ) ( )
Protective clothing ( ) ( ) ( )
All electric equipment listed
Class I, Division I, Group D and nonsparking tools ( ) ( ) ( )
10. Periodic atmospheric tests: oxygen ----% time---- oxygen ---- % time ----
oxygen ----- % time ------- oxygen ------ % time ----
explosive ---- % time ---- explosive ---- % time ----
explosive ---- % time ---- explosive ---- % time ----
toxic ---- % time ---- toxic ---- % time ----
toxic ----% time ---- toxic ------- % time ----
Certified that we have reviewed the work authorized by this permit and the information contained herein. Written instructions and safety procedures have been received and are understood. Entry cannot be approved if any squares are marked in the “No” column. This permit is not valid unless all appropriate items are completed.

(Continued)

Table 6.12 (Continued)

Permit prepared by: (supervisor)	
Approved by: (unit supervisor)	
Reviewed by (Cs operations personnel):	
(printed name)	(signature)
This permit is to be kept at the job site. Return job site copy to safety office following job completion.	
Copies: white original (safety office)	
Yellow (unit supervisor)	
Hard (job site)	
Permit valid for 8 hr only. All copies of permit will remain at job site until job is completed	
Date:	
site location and description:	
Purpose of entry:	
Supervisor(s) in charge of crews type of crew phone #	
Communication procedures:	
Rescue procedures (phone numbers at bottom)	
Bold denotes minimum requirements to be completed and reviewed prior to entry	
Requirements completed date time:	
Lock out/de-energize/try-out:	
Line(s) broken-capped-blanked:	
Purge-flush and vent:	
Ventilation:	
Secure area (post and flag):	
Breathing apparatus:	
Resuscitator—inhalator:	
Standby safety personnel:	
Full body harness w/“D” ring:	
Emergency escape retrieval equipment:	
Lifelines:	
Fire extinguishers:	
Lighting (explosion proof):	
Protective clothing:	
Respirator(s) (air purifying):	
Burning and welding permit:	
Note: items that do not apply enter N/A in the blank.	
**Record continuous monitoring results every 2 hr	

(Continued)

Table 6.12 (Continued)

Continuous monitoring** permissible:
Test(s) to be taken entry level
Oxygen 19.5–23.5%
LFL under 10%
CO_2 + 35 ppm
Aromatic hydrocarbon + 1 ppm * 5 ppm
HCN (Skin) * 4 ppm
H_2S +10 ppm *15 ppm
SO_2 + 2 ppm * 5 ppm
NH_3 *35 ppm
*Short-term exposure limit: employee can work in the area up to 15 min.
TWA + 8 hr: employee can work in area for 8 hr (longer with appropriate respiratory protection).
Remarks:
Name of gas test person and check # instrument(s) used model and/or type serial and/or unit #
Safety stand-by person is required for all confined space work:
Safety stand-by confined space person(s) check:
Entrant(s) check:
Supervisor authorizing—all conditions satisfied:
Department:

Lockout/Tagout Procedures

The lockout/tagout policy establishes basic requirements involved in locking and/or tagging out equipment while installation, maintenance, testing, repair, or construction operations are in progress. The primary purpose is to prevent hazardous exposure to personnel and possible equipment damage. The procedures shall apply to the shutdown of all potential energy sources associated with the equipment. These could include pressures, flows of fluids and gases, electrical power, and radiation.

Lock-out means installing a locking device that keeps the switch, valve, or other mechanism from being turned on or opened. *Tag- out* means putting a tag on the locking device. The tag indicates DANGER or WARNING, along with a brief message. It has a place to include the date and name of the person who locked-out the equipment so that he or she may be easily found or notified. An example is locking a switch on an open circuit to prevent it from being energized.

Lock-in is to maintain an event/condition or to keep someone/some object/force/factor from leaving a safe restricted area. An example is to prevent a live circuit from being shut-off.

Lock out-tag out is a safety procedure which is used in industry to ensure that dangerous machines are properly shut-off and not started up again prior to the completion of maintenance or servicing work. It requires that hazardous power sources be *isolated and rendered inoperative* before any repair procedure is started. *Lock and tag* works in conjunction with a *lock* usually locking the device or the power source, and placing it in such a position that no hazardous power sources can be turned on. The procedure requires that a *tag* be affixed to the locked device indicating that it should not be turned on.

In lock-out and tag-out, maintenance employees work with production employees to positively prevent all forms of hazardous energy from causing harm. An example of use of lock-out and tag-out is while working on moving machinery. The push button station and starter shall be locked-out. A danger tag shall also be tied to the starter and push button station signed by the person working on the equipment. Any valve, for safety reasons should not be operated shall also be locked and tagged. Tags and locks shall be removed only by those who put them in place.

Major process safety incidents and individual injuries have been caused by failure of lock-out and tag-out. A prime example is the Bhopal catastrophe, one of the worst incidents ever to have occurred, which was caused in part by the failure of lock-out and tag-out process.

When two or more sub-contractors are working on different parts of a larger overall system, the locked-out device is first secured with a folding scissors clamp that has many padlock holes capable of holding it closed.

Each sub-contractor applies their own padlock to the clamp. The locked-out device cannot be activated until all workers have signed off on their portion of the project and removed their padlock from the clamp.

A lock selected by color, shape or size (e.g. red padlock) is used to designate a standard safety device, locking and securing hazardous energy. No two keys or locks should ever be the same. A lock of a person and tag must not be removed by anyone other than the individual who installed the lock and tag, unless removal is accomplished under the direction of the employer. The tag must have an identification showing the name of the person doing the lock and tag and a contact phone number. Procedures and training for the employer for such removal must have been developed, documented and incorporated into the energy control program of the employer.

The basis for use of lock-out and tag-out procedure is isolating a hazard, once it is recognized and preventing incompatible events from occurring, occurring at the wrong time and at the wrong sequence.

Examples of lock-outs or interlocks include the following:

To prevent pumping a highly flammable liquid into a tank or tank car unless the system is grounded.

To prevent personnel contacting moving parts of machinery by the use of guards.

Providing fenced enclosures for equipment such as high-voltage transformers

To provide interlocks for deactivation of hazardous electrical equipment/circuits when panels are opened or removed for maintenance/replacement.

Securing switch levers to prevent activation of electrical circuits/equipment on which work is accomplished.

Providing interlocking on devices which must be operated in specific sequence.

Shielding nuclear reactors to prevent exposure from radiation.

6.10 Personnel Protective Systems

Personal protective equipment (PPE) is designed to protect workers from serious workplace injuries or illnesses resulting from contact with chemical, radiological, physical, electrical, mechanical, or other workplace hazards. Besides face shields, safety glasses, hard hats, and safety shoes, protective equipment includes a variety of devices and garments such as goggles, protective clothing, gloves, vests, earplugs, and respirators.

The use of personal protective equipment is to reduce employee exposure to hazards when engineering and administrative controls are not feasible or effective to reduce these risks to acceptable levels.

Using personal protective equipment is often essential, but it is generally the last line of defense after engineering controls, work practices, and administrative controls. Engineering controls involve physically changing a machine or work environment. Administrative controls involve changing how or when workers do their jobs, such as scheduling work and rotating workers to reduce exposures. Work practices involve training workers how to perform tasks in ways that reduce their exposure to workplace hazards.

Protection from head injuries: Hard hats can protect workers from head impact, penetration injuries, and electrical injuries such as those caused by falling or flying objects, fixed objects, covering, and protection from long hair to prevent it from getting caught in machine parts, or contact with electrical conductors.

Protection from foot and leg injuries: In addition to foot guards and safety shoes, leggings (e.g. leather, aluminized rayon, or other appropriate material) can help prevent injuries by protecting workers from hazards such as falling or rolling objects, sharp objects, wet and slippery surfaces, molten metals, hot surfaces, and electrical hazards.

Protection from eye and face injuries: Besides spectacles and goggles, personal protective equipment such as special helmets or shields, spectacles with side shields, and face shields can protect workers from the hazards of flying fragments, large chips, hot sparks, optical radiation, splashes from molten metals, as well as objects, particles, sand, dirt, mists, dusts, and glare. Eye fountains and showers should be provided at strategic locations in plant premises and laboratory exits for emergency use to shield personnel as measures of first aid to prevent from injury for the eyes and skin.

Protection from hearing loss: Wearing earplugs or earmuffs can help prevent damage to hearing. Exposure to high noise levels can cause irreversible hearing loss or impairment as well as physical and psychological stress. Earplugs made from foam, waxed cotton, or fiberglass wool is self-forming and usually fit well. A professional should fit workers individually for molded or preformed earplugs. The earplugs must be cleaned regularly, or replaced.

Protection from hand injuries: Workers exposed to hazardous substances through skin absorption, severe cuts or lacerations, severe abrasions, chemical burns, thermal burns, and harmful temperature extremes will benefit from hand protection.

Protection from body injury: In some cases, workers must shield most or all of their bodies against hazards in the workplace, such as exposure to heat and radiation as well as hot metals, scalding liquids, body fluids, hazardous materials or waste, and other hazards. In addition to fire-retardant wool and fire-retardant cotton, materials used in body personal protective equipment include rubber, leather, synthetics, and plastic.

Respiratory protection: When engineering controls are not feasible, workers must use appropriate respirators to protect against adverse health effects caused by breathing air contaminated with harmful dusts, fogs, fumes, mists, gases, smokes, sprays, or vapors. Respirators generally cover the nose and mouth or the entire face or head and help prevent illness and injury. A proper fit is essential, however, for respirators to be effective. Medical evaluation and training must be provided before use of respirators.

6.11 Plant Modifications and Management Change

On several occasions, modifications made at design, commissioning, operational and maintenance stages contributed to disasters. One notion entertained in the design process is overdesign as a means of extra safety. This is not always true. For example, when considering pumps and control valves, which are common in any process plant, overdesign introduces several hazards. If a higher capacity or pressure pump is installed than is necessary, it might introduce a hazard in so far as the rest of the plant is not designed for these conditions. Similarly, an oversized control valve may also create hazardous situations, if reliance has been placed on a valve of a certain size to limit flow to a maximum value.

All modifications, whether involving procedures, plant and equipment, people, or substances—should be subject to formal management procedures.

Good industry practice requires that process and plant modifications should not be undertaken without having undertaken a safety, engineering, and technical review. This review should be traceable and identify changes proposed to the following factors:

Process conditions, operating methods, engineering methods, safety, environmental conditions, and engineering hardware and design

A form of risk assessment should then identify what hazards have been created by the change that may affect plant or personnel safety, and what action can be implemented to reduce or eliminate the risk. Additional hazards that may be introduced which need to be considered are fire, explosion and loss of containment.

Changes may affect other parts of the plant which may be quite remote from the source of the change. Therefore, all parts of the plant should be considered in undertaking hazard identification and risk assessments.

Factors that are crucial to the success and safe implementation of a plant modification procedure include the following:

Corporate history, communication between different departments, recognition of authorized personnel, accurate recording, and monitoring of changes to plant and process.

These are equally applicable to plant modifications as new plant. However, written procedures should be in place to determine what level of HAZOP (if any) should be applied. These procedures should take account of the degree of hazard and extent of the change, the worst case accident likely to arise as a result of the modification, previous HAZOPs relating to the item being changed, and the appointment of a competent person (excluding the HAZOP Chairman) to decide the requirements for HAZOP.

Poor management and control of changes to plant and process often results in increased risk to plant, people and environment. Consequently, control of operating procedures during change is a critical task. Only authorized personnel should amend existing operating procedures or issue temporary operating instructions during plant or process changes. It is good practice for the operating procedures to be authorized by representatives from several different departments. These may include operations, technical, health, safety and environmental, quality.

An assessment of change to risk should be an integral part of generation of procedures. The degree of control of change will depend upon whether the proposed change may be classed minor and major procedural changes.

The continued integrity of the plant during commissioning needs to be upheld by adequate maintenance, inspection and avoidance of unauthorized design or operational changes. To avoid hazards caused by modifications, it is necessary that any proposal for change be identified, and that the proposal is formally authorized after, after technical investigation, by competent personnel of senior status. Modifications should be designed, constructed, inspected, tested and proved to have achieved the design intent and should be maintained at least to the standard of the design criteria required by the process.

The requirements for decommissioning will vary depending upon the nature of the plant items to be decommissioned and the duty the plant items fulfilled. Operating procedures should be provided for decommissioning of hazardous plant in the same way as for commissioning. These procedures should be subject to hazard review and risk assessment. General measures that should be adopted for a common approach to decommissioning include communication with plant personnel to ensure surrounding plant areas are prepared for decommissioning activity, undertaking removal of hazardous substances via a cleaning procedure to ensure plant item is clean and empty with particular consideration where there may be dead legs where material may be trapped, consideration of the disposal of items that may be contaminated by absorption of hazardous substances and chemical change, mechanical isolation of the plant item from other surrounding plant items by physical disconnection or fitting of blanks, and electrical isolation of the plant item from power sources by physical disconnection.

Safety considerations involved in plant modifications received serious attention after failure of a temporary modification by the addition of a pipe section connecting two reactors due to removal of an intermediate reactor in a reactor train at Flixborough in 1974. Some examples involving lapses in plant modifications are illustrated below (Figure 6.12).

The following three phases in a production plant's life are potentially critical in regards to safety practices:

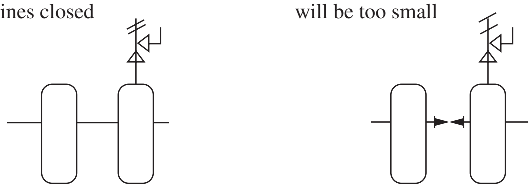
Transition: The first period deemed to be critical is the transition phase when a company acquires a production plant, petroleum refinery, or any other manufacturing facility. During this period, many experienced people leave the company while new management is learning the details of plant operations.

The relief valve was located on the inlet line

Relief moved to a new position leaving the relief valve on the dead leg

Relief valve was sized for inlet flow flow with all exit lines closed

Extra inlet line added and in case both lines together relief valve will be too small



A single relief valve was designed to protect two vessels connected together by piping without any valve or other restriction between them

Isolation valve was added between the two vessels, making it possible to isolate the first vessel from the relief valve

Figure 6.12 Modifications invalidating pressure relief arrangements

Restructuring: The second period is a phase of restructuring, when due to slow economic conditions, the demand for a product has slowed down. The company needs to save operating and maintenance costs. During this period some sections or the whole plant may be shut-down.

Routine: A third period is when the plant operation becomes routine and inexperienced people are allowed to take over and run the facility. The experienced staff relaxes and becomes less vigilant in reviewing plant safety on a regular basis.

During the periods mentioned above, it is particularly important for managers to include the following elements in their management of plant safety:

Review of technology: Whenever a plant is acquired, a thorough review of the acquired technologies must be made. Typically, companies feel confident in acquiring facilities when they are operating similar plants or manufacturing similar products. For example, a petroleum refining company taking over another refinery has good knowledge of refinery operations. However, there are several different process technologies available for the same operations or reactions. For example, there are many different alkylation processes in operation to produce motor and aviation fuels. Similarly in petrochemical production, such as for vinyl chloride, there are many routes for the same reactions and intermediate products. Some technologies employ fixed beds for oxychlorination, whereas others use fluidized bed reactors. A review of process technologies will reveal the differences in the technology and operating procedures. Once the differences have been identified, then all plant operators must be trained in all new technologies.

Plant operating procedures: Experience shows that the same plant can be started in a number of ways. All companies develop operating procedures to start-up and shut-down a plant. New procedures are certainly needed when the unit operations are different in plants where a different technology is employed. A wide variety of processes are available for ethylene, polyesters, vinyl chloride, and polyvinyl chloride (PVC). There are similar examples of various processes in petroleum refining. The operating procedures also differ depending on the complexity of the plant. Operating procedures should be updated on a regular basis.

Review of safety interlock and shut-down systems and procedures: The safety interlocks and shut-down systems are developed after comprehensive hazard and operability studies. Many are introduced after actual plant experience. These interlock systems must be reviewed and upgraded if required. All major companies control and operate their plants based on their in-house development. A thorough review will certainly improve the existing systems due to the combination of expertise from merged or acquired companies. Many times, safety interlocks are bypassed because new plant operators did not understand the rationale behind the safety interlocks.

Review of corrosion control systems: Control of corrosion in plant equipment is intricately linked with plant safety. There are many kinds of corrosion protection systems employed in chemical and petrochemical industries. These systems are developed after years of plant experience. This is an area that is often ignored when chemical plants or petroleum refineries are sold to new owners. Plants with near-perfect safety records lose that record within months of acquisition by new owners. Looking deeply into the reasons, it is observed that plant engineers and operators did not understand the function of various corrosion protection systems. In a vinyl chloride plant, for example, the overhead condenser for an ethylene dichloride distillation column was protected by the circulation of dilute caustic solution. After a new owner took over the facility, the circulation of caustic was stopped because the inexperienced engineers did not understand its role in preventing corrosion in the condenser and overhead piping.

Training of plant engineers and operators: This area also gets sidelined, particularly in old facilities. Experienced engineers take it for granted that young engineers will learn with hands-on experience. They can certainly learn the plant operation, but may not understand why the system was designed in a certain way. There should be an ongoing training program for new engineers and even experienced engineers if new technology is introduced in a plant. The review of various reactions and side reactions, optimum operating conditions, limits, and safety precautions should be essential for every person. In older facilities, there is a wealth of information available but only experienced people know how to access it. Training materials should be easily accessible to all new operators.

Review of past incidents and investigative reports: Experience shows that the same problems occur over and over again in the same facility. People are alert for a few years after an accident. Then, safety reports get filed away and forgotten. A new company taking over old facilities is busy with other priority items. Plant safety records and reports are reviewed at a much later stage. It is recommended that a thorough review of past safety history of a plant, followed by a plant safety audit that looks at the particular areas where accidents have occurred in the past.

Implementation of EPA and OSHA Standards: This should be given top priority during the plant shut-down period.

6.12 Industrial Hygiene

Hygiene is an important consideration to ensure health of people, whether in industry or in living areas. Good hygiene is one of the preventive measures for efficient operation of the plants. Industrial hygienists analyze, identify, and measure workplace hazards/stresses that can cause sickness, impair health, or significant discomfort in workers through chemical, physical, ergonomic, or biological exposures.

A work site analysis is a first step that helps an industrial hygienist determine what jobs and work stations are the sources of potential problems and addresses them how these affect the health of the worker and recommends to managements how to eliminate or minimize them through appropriate remedial actions.

Engineering controls, work practice controls, administrative controls, and when these are not feasible to implement, appropriate personnel protective equipment must be used.

It is worth reviewing different hazards as far as human exposures are concerned, while ensuring good hygiene in the industry. Chapter 3 presents hazards in greater detail.

- Air contaminants, dusts and fumes, mists, aerosols, fibers, gases, and vapors are some causes of health hazards.
- Harmful chemicals, toxic in nature, in the form of solids, liquids, or vapors can cause inhalation, skin absorption, and ingestion; corrosion to tissues can create health problems.
- Biological hazards include viruses and fungi that can cause acute or chronic infection to workers.
- Physical hazards include noise, radiation, vibration, temperature, illumination. These can cause health problems to workers.
- Ergonomic problems can also affect workers.

The above hazards are discussed in Chapter 3 and are important constituents of industrial hygiene.

Regular medical check-up is one of the primary necessities for the industrial managements to ensure health practices within the industry.

6.13 Relief Valves and Rupture Discs

Process equipment should be designed for pressures sufficiently higher than the actual working pressure to allow for pressure fluctuations and normal *operating pressure peaks*. In order that process equipment is not damaged or ruptured by pressures in excess of the design pressure, pressure relief valves are installed to protect the equipment. The design pressure of a pressure vessel is the value obtained after adding a *margin* to the most severe pressure expected during the normal operation at a coincident temperature. Depending on the situation, this margin might typically be the maximum of 10 percent. It should be noted that relief requirements for fire-induced runaway reactions are always more than pressure-induced runaways. A properly designed relief device protects a vessel against over-pressure but not necessarily over-temperature. Where ever fire exposure is possible, reactors should be protected by water deluge systems and/or fireproofing in addition to relief devices.

Relief devices are required to release vapors or gases into closed systems such as flare stacks or scrubbers to avoid environmental pollution.

Some practical applications of pressure relief valves:

For a pump discharging into a receiving vessel, the relief valve should be able to pass the volume of the fluid that the pump could deliver, if the feed valve is fully open and the vessel outlet is blocked.

Failure of a pressure reducing device can cause a sudden increase in downstream pressure. Therefore, consideration should always be given to making the downstream section capable of withstanding the upstream pressure.

On a distillation column overpressure may be created by an increase in heat input, loss of cooling in the condenser, increase in temperature difference in the reboiler, loss of subcooled feed, and loss of reflux.

Pressure relief should be provided between isolations, if the equipment is subjected to pressure from a high pressure source or of process heat or if the equipment is in a fire risk zone.

Low-pressure storage tanks are capable of withstanding only low pressures. Overfilling is one of the worst situations leading to overpressure development. The relief valve should be sized for flashing liquid, that is, the relief area calculated should be the sum of the areas required for liquid and vapor relief. As per codes, the relief should be enough to prevent the pressure rising above 110 percent of design pressure.

For the failure of a high-pressure tube in a heat exchanger, the relief valve on the low pressure side should be sized to handle the flow from twice the cross-sectional area of the tube.

Both safety relief valves and rupture discs are commonly used for relief from overpressurization and damage to equipment and piping and injury to personnel. Sometimes combination of a relief valve with a rupture disc can add service life to the relief valve and prevent process leakage, which is important from safety, conservation, and financial standpoints. They are used to prevent pressurization above a design pressure of a system, for venting during an unusual or emergency situation, and for normal depressurization during a shut-down, as examples. In some cases, such as when noncombustible gases including steam, air and nitrogen are used, venting into the atmosphere may be an option. In other cases, such as those typically encountered in the hydrocarbon industry, elaborate systems for the disposal of vented gases may be required. Verifying their capability to safeguard equipment integrity becomes important as process plants age, increase their capacities to adjust to new market requirements, undergo revamps or face new environmental regulations.

Capacity of relief devices: The volumetric capacity of the relief device must be equal or greater than the volumetric generation rate in the vessel. Vessel can be ruptured if the capacity is too low.

Safety relief valves are preferred over rupture discs when losing entire contents is unacceptable, fluids above normal boiling point, toxic fluids, need to avoid failing low, return to normal operations quickly, and withstand process pressure changes, including vacuum.

Rupture discs are preferred over relief valves when capital and maintenance savings are important, losing the contents is not an issue, benign service (nontoxic and nonhazardous), need for fast-acting device, potential for relief valve plugging, and for high viscosity liquids.

Both types are used in combination when a positive seal is required (toxic material, material balance requirements), to protect relief valve from corrosion, and system contains solids.

Relief Valves

Safety valve and safety relief valve are in use in industry for handling over pressurization. *Safety valve* is a device which pops up to fully open condition and remains in such a position till pressure is brought back to normal. A *safety relief valve* or simply a *relief valve* opens gradually as pressure develops and also closes gradually as pressure is brought back to normal.

A pressure relief valve is a safety device designed to protect a pressurized vessel or system during an overpressure event. An overpressure event refers to any condition which would cause pressure in a vessel or system to increase beyond the specified design pressure or maximum allowable working pressure (MAWP).

Since, pressure relief valves are safety devices, there are many codes and standards written to control their design and application. In many cases, discharges from pressure relief devices flow through a closed piping system to an elevated vent or flare. One primary function of an elevated vent or flare is to safely dispose of flammable and/or toxic gases discharged by the pressure relief devices, either by burning the gas to create less hazardous products of combustion, or by releasing it at an elevation that is sufficient to ensure that hazardous concentrations of the gas will not return to ground level.

Proper sizing, selection, manufacture, assembly, test, installation, and maintenance of a pressure relief valve are all critical to obtaining maximum protection.

Relieving pressure shall not exceed MAWP (accumulation) by more than 3 percent for fired and unfired steam boilers, 10 percent for vessels equipped with a single pressure relief device, 16 percent for vessels equipped with multiple pressure relief devices, and 21 percent for fire contingency.

Pressure reliefs should be provided on all vessels, blocked in sections of cool liquid lines that are exposed to heat, discharge sides of positive displacement pumps, compressors, and turbines, vessel steam jackets, and where process hazard analysis (PHA) indicates the need

A pressure relief valve must be capable of operating at all times, especially during a period of power failure when system controls are nonfunctional. The sole source of power for the pressure relief valve, therefore, is the process fluid.

Once a condition occurs that causes the pressure in a system or vessel to increase to a dangerous level, the pressure relief valve may be the only device remaining to prevent a catastrophic failure. Since, reliability is directly related to the complexity of the device, it is important that the design of the pressure relief valve be as simple as possible.

The pressure relief valve must open at a predetermined set pressure, flow at rated capacity at a specified overpressure, and close when the system pressure has returned to a safe level. Pressure relief valves must be designed with materials compatible with many process fluids from simple air and water to the most corrosive media. They must also be designed to operate in a consistently smooth and stable manner on a variety of fluids and fluid phases. These valves must start to open at or below the Maximum allowable working pressure (MAWP) of the equipment. When multiple pressure relief valves are used in parallel, one valve should be set at or below the MAWP and the remaining valve(s) may be set up to 5 percent over the MAWP. When sizing for multiple valve applications, the total required relief area is calculated on an overpressure of 16 percent or 27.6 kPa (4 psi), whichever is greater.

Relief systems with flaring have some limitations in their applications. There are many situations where it is not practical to connect pressure relief devices to a vent or flare header. For example, pressure safety relief valves on storage tanks for refrigerated liquefied gases relieve at low pressures, typically 13.8 kPag (2 psig) or less To safely dispose of this low pressure gas through an elevated flare or vent would require a very large diameter header system, otherwise the pressure drop in the header would create excessive back pressure on the relief valves. In other cases, such as mobile tank trucks, portable gas cylinders, and rail cars, the available pressure may be sufficient for disposal through a vent or flare system, but the mechanical configuration required to connect the relief device to a vent or flare system would be too expensive or too complex. In such cases, the common alternative is discharge directly to atmosphere via a short vertical tail pipe or stack. Figure 6.13 illustrates a typical conventional spring loaded pressure relief valve.

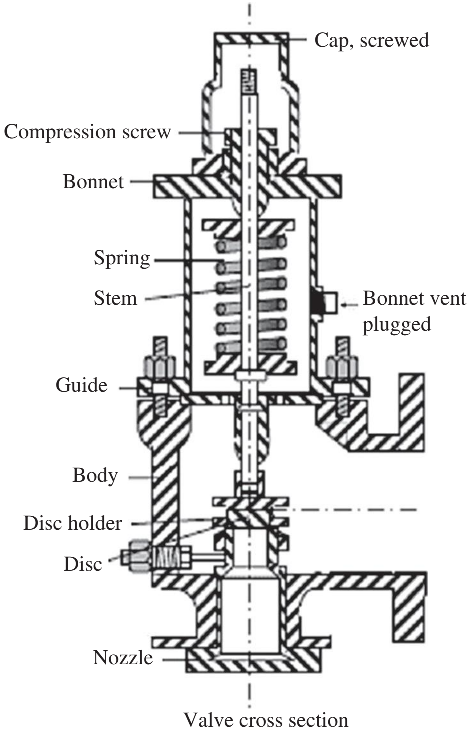


Figure 6.13 Conventional spring-loaded pressure relief valve

Conventional pressure relief valve: Conventional pressure relief valves are used when the back pressure is less than 10 percent. When it is known that the *superimposed back pressure* will be constant, a conventional valve may be used.

The type of pressure relief valves generally utilized in refinery and chemical processing plants are the spring-loaded, top-guided, high lift, nozzle-type pressure relief valve, which is classified as conventional relief valve.

Basic elements of spring-loaded pressure relief valve include an inlet nozzle connected to the vessel to be protected, movable disc which controls flow through the nozzle, and a spring that control the position of disc. The inlet pressure to the valve is directly opposed by the force of a spring. Spring tension is set to keep the valve closed at normal operating pressure.

At the set pressure the forces on the disc are balanced and the disc starts to lift and is fully lifted when the vessel pressure continues to rise above set pressure.

In spring operated pressure relief valves, leakage between the valve seat and disc or called *simmer*, which typically occurs at about 95 percent of set pressure. However, depending upon valve maintenance, seating type, and condition, simmer-free operation may be possible up to 98 percent of set pressure. *Simmer* normally occurs for gas or vapor service before it pops-up.

Spring-loaded relief valve is designed to pass its rated capacity at the maximum allowable accumulation. For conditions other than fire, the maximum allowable accumulation is 10 percent of the MAWP or 20 kPa (3 psi), whichever is greater if a single pressure relief valve is used. For fire, the maximum allowable accumulation is 21 percent of MAWP. For systems with multiple relief valves, the maximum allowable accumulation provided is 16 percent of MAWP or 28 kPa (4 psi), whichever is greater, as stated earlier.

Advantages: Most reliable type if properly sized and operated and versatile. Can be used in many services.

Disadvantages: Relieving pressure is affected by back pressure and susceptible to *chatter* if built-up back pressure is too high.

Spring relief devices require 25–30 percent of maximum flow capacity to maintain the valve seat in the open position. Lower flows result in *chattering*, caused by rapid opening and closing of the valve disc that can lead to destruction of the device and a dangerous situation. Oversized valves and valves handling widely differing rates can lead to chattering. Excessive inlet pressure drop and excessive built-up back pressure in relief systems can also lead to chattering.

Balance pressure relief valve: If the back pressure percentage is between 10–40, a balanced bellow safety valve is used.

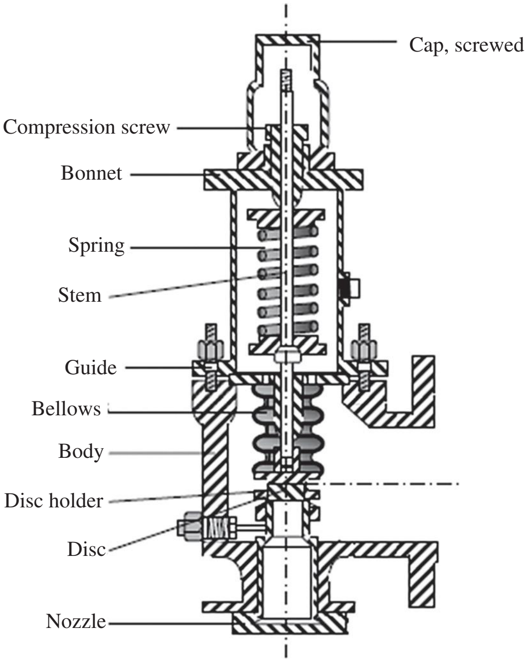
Balanced pressure relief valve is a spring-loaded pressure relief valve which consists of bellows or piston to balance the valve disc to minimize the back pressure effect on the performance of the relief valve. This type of valve is used when the built-up pressure (back pressure caused by flow through the downstream piping after the relief valve lifts) is too high for conventional relief valve or when the back pressure varies from time to time. It can typically be applied when the total back pressure (superimposed + build-up) does not exceed <50 percent of the set pressure. When superimposed back pressure is variable, a balanced bellows or balanced piston design is recommended.

The bellows or piston is designed with an effective pressure area equal to the seat area of the disc. The bonnet is vented to ensure that the pressure area of the bellows or piston will always be exposed to atmospheric pressure and to provide a telltale sign should the bellows or piston begin to leak. Variations in back pressure, therefore, will have no effect on set pressure. Back pressure may, however, affect flow. Back pressure, which may occur after the valve is open and flowing, is called *dynamic* or *built-up* back pressure. This type of back pressure is caused by fluid flowing from the relief valve through the downstream piping system. Built-up back pressure will not affect the valve opening pressure, but may have an effect on valve lift and flow. On applications of 10 percent overpressure, balanced bellows or balanced piston designs are recommended when built-up back pressure is expected to exceed 10 percent of the *cold differential test pressure* (CDTP). In addition to offsetting the effects of variable back pressure, the bellows or piston acts to seal process fluid from escaping to atmosphere and isolates the spring, bonnet and guiding surfaces from contacting the process fluid. This is especially important for corrosive services.

Advantages: Relieving pressure is not affected by back pressure, can handle higher built-up back pressure, and protects spring from corrosion.

Disadvantages: Bellows is susceptible to fatigue/rupture, may release flammables/toxics to atmosphere, and requires separate venting system.

Typical balanced pressure relief valve is showed in Figure 6.14.



Cross-section of bellows valve

Figure 6.14 Balanced pressure relief valve

Pilot-operated pressure relief valve: Pilot operated pressure relief valves are normally used when the back pressure is more than 40 percent of the set pressure or the operating pressure is close to the pressure relief valve set pressure. These valves consist of a main valve with piston or diaphragm-operated disc and a pilot. Under normal operating conditions the pilot allows system pressure into the piston chamber. Since, the piston area is greater than the disc seat area, the disc is held closed. When the set pressure is reached, the pilot actuates to shut-off system fluid to the piston chamber and simultaneously vents the piston chamber. This causes the disc to open.

The pilot operated pressure relief valve has several advantages. As the system pressure increases, the force holding the disc in the closed position increases. This allows the system operating pressure to be increased to values within 5 percent of set pressure without danger of increased seat leakage in the main valve. Another advantage of pilot operated pressure relief valves is the reduced cost of larger valve sizes. The large spring and associated envelope is replaced by a small pilot, thus reducing the mass and cost of the valve. These valves may be satisfactorily used in vapor or liquid services up to a maximum back pressure (superimposed plus built-up) of 90 percent of set pressure, provided that the back pressure is incorporated into the sizing calculation. They can be specified for blow-down as low as 2 percent. Pilots are generally designed with a separate control for set pressure and blow-down. Valves can be set to open fully at the set pressure and close with a very short blow-down. This type of valve is sufficiently positive in action to be used as a depressurization device.

Pilot-operated relief valves are commonly used in clean, low pressure services and in services where a large relieving area at high set pressures is required. The set pressure of this type of valve can be close to the operating pressure. These valves are frequently chosen when operating pressures are within 5 percent of set pressures and a close tolerance valve is required.

A properly selected and installed pilot operated pressure relief valve will operate effectively under all combinations of superimposed and built up back pressure, limited only by the valve pressure rating and practical considerations.

The disadvantages of pilot-operated pressure relief valves are the following:

Not recommended for dirty or fouling services, because of plugging of the pilot valve and small bore pressure sensing lines. If the pilot valve or pilot connections become fouled, the valve will not open. A piston O-ring seal is limited to a maximum inlet temperature of 230°C (450°F) and the newer designs are available for a maximum inlet temperature of about 540°C (1,000°F) in a limited number of valve sizes and for a limited range of set pressures. Vapor condensation and liquid accumulation above the piston may cause the valve to malfunction. Back pressure, if it exceeds the process pressure under any circumstance (such as during start-up or shut-down), would result in the main valve opening (due to exerting pressure on the underside of the piston that protrudes beyond the seat) and flow of material from the discharge backwards through the valve and into the process vessel. To prevent this back-flow preventer must be installed in the pilot operated relief valve. For smaller sizes it is more expensive than spring-loaded relief valve.

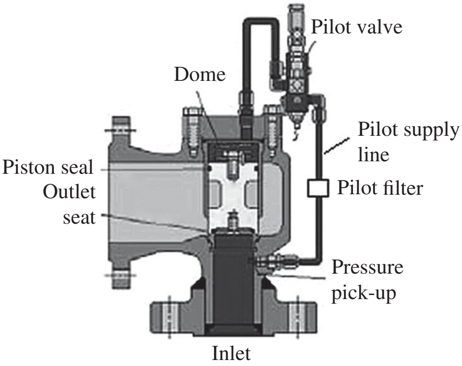


Figure 6.15 Pilot-operated relief valve

Figure 6.15 illustrates a typical pilot-operated pressure relief valve.

Temperature activated relief valve system: A temperature activated relief valve system can be set to open or closed a relief valve at given temperatures. This opening and closing is achieved by using an actuator (attached to the valve) and a control system. The use of a temperature activated relief valve system allows control of the process variable (i.e. temperature) that directly affects the rate of reaction.

The relief valve can be opened either at a specified temperature above the operating temperature, or when the rate of temperature rise meets a specified value. This enables the onset of an exothermic reaction to be detected and action taken at an earlier stage than would be possible using conventional pressure activated relief valves. By keeping the relief valves open until the temperature of the system has reached a level where the rate of reaction is essentially zero, the system can be brought to a safe condition, while venting the least amount of material. The lower the opening set point temperature and the higher the closing set point temperature, the smaller the amount of material that is vented from the system. An additional advantage to using temperature as the basis for opening the relief valve is that the lower the temperature, the lower the reaction rate and the lower the potential for two phase flow effects in the inlet and outlet piping. Holding the valve open may also minimize issues concerning two phase flow through the relief valve itself. While the use of a temperature activated system can be highly effective, care must be taken in its design and installation so that the required availability is achieved. This usually requires the use of redundant components (sensors, processors, and valving), plus the ability to functionally test the system online.

Thermal relief valves are provided on cooling services where a system can be locked in by isolating valves. The discharge from the relief valve should be piped to grade in offsite areas, to the nearest drain in process areas.

Table 6.13 gives individual relief rates to be used in the design of relief systems.

Table 6.13 Relief rates to be employed in the design of relief systems

Condition	*Relief device for vapor*	*Relief device for liquid*
1. Closed outlet on vessels	Total incoming steam and vapor plus pump-in that generated therein at relieving conditions	Maximum liquid rate
2. Cooling water failure to condenser	Total vapor to condenser at relieving condition	------
3. Column reflux failure at top	Total incoming steam and vapor plus that generated therein at relieving condition less vapor condensed by side stream reflux	------
4. Side stream reflux failure	Difference between vapor entering and leaving section at relieving conditions	------
5. Lean oil failure to absorber	None, normally	------
6. Accumulation of non-condensable	Same effect in columns as found for Item 2; in other vessels, same effect as found for Item 1	-----
7. Entry of highly volatile material	-------	------
Water into hot oil Light hydrocarbons into hot oil	Usually not predictable for columns twice the internal cross-sectional area of one tube to provide for the vapor generated by the entrance of the volatile fluid due to tube rupture	------
8. Overfilling storage or surge vessel	-----	Maximum liquid pump-in rate
9. Failure of automatic control	Must be analyzed on a case-by case basis	-----
10. Abnormal heat or vapor input	Estimated maximum vapor generation including noncondensable from overheating	-----

(Continued)

Table 6.13 (Continued)

11. Split exchanger tube	Steam or vapor entering from twice the cross-sectional area of one tube; also same effects found in item 7 for exchangers	-----
12. Internal explosions	Not controlled by conventional relief devices but by avoidance of the circumstances	-----
13. Chemical reaction	Estimated vapor generation from both normal and uncontrolled conditions	-----
14. Power failure (steam, electrical, or other)	Study the installation to determine the effect of power failure; size the relief valve for the worst condition that can occur	-----
15. Distillation columns	All pumps could be down, with the result that reflux and cooling water would fail	------
16. Reactors	Consider failure of agitation, quench or retarding steam; size the valves for vapor generation from a runaway reaction	------
17. Air-cooled exchangers	Fans would fail; size valves for the difference between normal and emergency duty	-------
18. Surge vessels	------	Maximum liquid inlet rate

*Note: These design guidelines are very general and not intended for specific design cases.

Inlet and outlet piping considerations: Satisfactory operation of a pressure relief valve requires that it be mounted *vertically*, preferably on a nozzle at the top of a vessel or on a tee connection on top of a pipeline. The minimum inlet piping size should be equal in size to the pressure relief valve; the length should be minimized to reduce pressure drop and bending moments resulting from the reaction thrust developed from the discharging fluid.

A rule of thumb is to design the inlet piping such that the total pressure drop in the inlet piping does not exceed 3 percent of the valve set pressure. When a single pressure relief valve is installed to protect several vessels, the connecting piping between these vessels should be adequate in size to keep the pressure drop within these limits.

A rule of thumb is to design the discharge piping such that the total pressure drop in the outlet piping does not exceed 10 percent of the valve set pressure. The type of discharge piping selected will depend largely on the hazardous nature of the service and on the value of the material that might be lost through a discharge event. For air or nonhazardous gas service, the discharge piping is normally directed vertically and extended such that it does not present a safety concern.

Discharge elbows fitted with drain lines are normally used on steam and vapor services. The vapor discharge from these elbows is directed into a larger diameter riser pipe that is independently supported.

The discharge piping should be extended vertically downward to a suitable drain for nonhazardous liquid service. A closed discharge piping system is required for hazardous services, or for services involving expensive chemicals. Collection systems for these categories of fluids may consist of considerable piping with numerous pressure relief valves discharging into a common manifold. The pressure drop through this type of piping system must be calculated accurately, taking into consideration the fact that simultaneous discharge events may occur.

The classical methods for pressure drop determination can be employed for both inlet and outlet piping arrangements. Values for the density, velocity, and viscosity of the discharging fluid should be based on the average pressure and temperature of the respective pipe component. The formation of hydrates, polymerization, and fluid solidification in pressure relief valve piping might be an additional concern.

Supports for pressure relief valve piping should be designed to minimize the transfer of pipe loads to the valve body.

Allowance shall be made for piping expansion in cases of high temperature service; valve displacement due to thermal expansion may cause valve leakage or faulty operation.

The internal pressure, dead loads, thermal expansions, reaction thrust, resulting dynamic forces, and resulting bending stresses due to discharging fluid will be exerted on the pressure relief valve inlet and outlet bends and elbows.

Additional considerations are as follows:

- Design discharge piping with clean-outs to preclude internal obstructions.
- Test the piping hydrostatically to 150 percent of the maximum anticipated pressure of the discharge system.
- Provide covers or caps to prevent the intrusion and accumulation of rain or the entrance of birds or rodents.
- Design piping to be self-draining.

Summary of causes of malfunction of relief valves is given in Table 6.14.

Table 6.14 Symptoms, causes, and remedies

Symptoms	*Causes*	*Remedies*
Leakage	Operating pressures may increase until they crowd the valve setting vessel code recommendations or the maximum allowable working pressure of the vessel corrosion or erosion. Sand in high pressure gas lines erodes softer seat and disc materials When operating pressure is fairly high pressure surge can unseat the disc and cause leakage	One remedy is to observe pressure Another remedy may be to replace metal-to-metal seats with ones using O-ring pressure seals. Seats made of hard materials may be used in valves used in such service It should be checked whether the popping pressure tolerance is within limits manufacturer's recommendations should be observed

(Continued)

Table 6.14 (Continued)

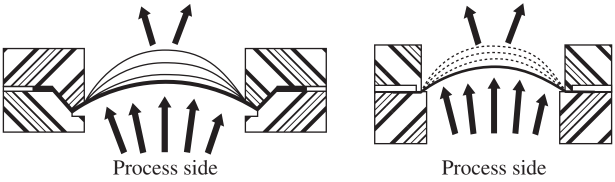
	Incorrect compensation of the spring setting for high temperature applications when the spring is "cold set"	
	Solid particles between seat and disc	One remedy is to use special knife edge seat arrangement which might cut through deposits or using a resilient O- ring seat
	Unsupported outlet piping	Outlet piping should always be supported
	Thermal stress on the outlet piping	Use of flexible supports or expansion loops/joints
	Vibration of piping/vessel	Use of conventional methods to reduce vibrations
	Valve installation should be checked for upright/vertical position	Valves should be installed vertically
	Incorrect assembly	To ensure correct assembly
	The nature of the fluid handled	Metal-to-metal seats are not suitable for H_2-like fluids. Proper MESG should be ensured

Rupture Discs

Rupture discs are non-closing devices, once opens on increased pressures in a vessel, piping or other equipment. When pressures inside equipment increase over design and operating pressures, the disc fails by rupture, releasing the contents of reactors or other equipment to the atmosphere or to a manifold leading to containment or treatment vessels. The difference between rupture discs and relief valves is that the later get back to their seats, re-closing the container, stopping out-flows of the contents. The rupture disc is a thin metal disc backed by a membrane. It provides a leak-proof seal by the use of flanged joints.

According ASME code "a *rupture disc device* is a non-reclosing pressure relief device actuated by inlet static pressure and designed to function by the bursting of a pressure containing disc and a *rupture disc* is the pressure containing and pressure sensitive element of a rupture disc device." "The *manufacturing design range* is a range of pressure within which the marked burst pressure must fall to be acceptable for a particular requirement as agreed upon between the rupture disc manufacturer and the user or his agent." If the internal pressure of the vessel rises to a predetermined level, the rupture disc bursts, providing an instantaneous, unobstructed full relief, preventing overpressure disasters and damaged equipment. A wide range of materials are used in making the discs, which include, nickel, copper, stainless steel, aluminum, silver which are expected to offer more resistance to corrosion than the vessel to which it is fitted. The discs are often are made of composite materials and with linings or coatings.

Figure 6.16 illustrates tension type rupture discs.



(a) With 30° seat (b) With flat seat

Figure 6.16 Tension-type rupture discs

Types of rupture discs: Different types of rupture discs are forward acting solid metal discs, reverse acting discs, composite discs, scored metal discs, and graphite discs. The forward-acting disc is generally less expensive than the reverse acting disc.

Tension-type rupture discs are oriented in a system with the process media pressure against the concave side of the rupture disc (Figure 6.16(a), 30° Seat; Figure 6.16(b), Flat Seat). As the process pressure increases beyond the allowable operating pressure, the rupture disc starts to grow. This growth will continue as the pressure increases, until the tensile strength of the material is reached and rupture occurs.

Conventional prebulged design: Standard rupture discs are made of thin metal foils which are domed. The discs are installed with the inside of the dome (concave side) exposed to the pressure. Their maximum operating pressure should not exceed 90 percent of their design burst pressure (*operating ratio*). This guidance was developed to protect these discs from the effects of repeated pressure pulsing. At 90 percent of design, the service life might be more like 5,000 cycles. They are usually designed to act in tension. It has a random bursting pattern which means it can be fragmenting (loose material) and thus cannot be used in combination with relief valves. This

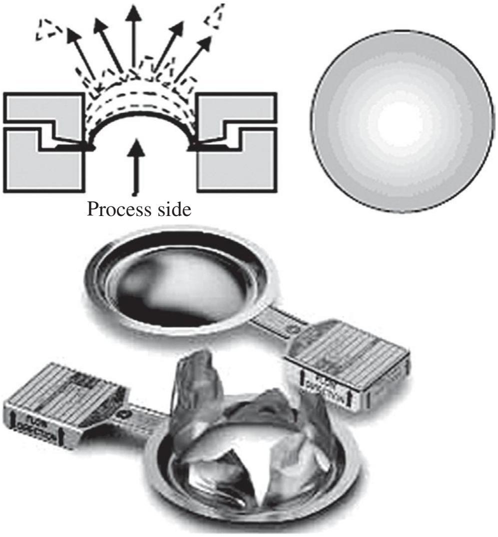


Figure 6.17 Forward acting conventional solid metal rupture disc

type of rupture disc can be used in vacuum or larger back-pressure services but will require special supports to prevent reverse flexing. Its main advantage is that it is cheap. Figure 6.17 illustrates this type of disc.

These discs are formed from flat discs by application of a pressure, normally above 70 percent of bursting pressure, to the underside of the disc. When the operating pressure grows beyond prebulging pressure, dome of the disc starts to grow and as operating pressure approaches 95 percent of bursting pressure, localized thinning in the region of the dome center occurs, leading to failure. To avoid early failure due to creep, normal operating pressure should not exceed 70 percent of bursting pressure. This value should be still less where the operating pressure pulsates. These discs are not generally well suited for pulsating pressure and elevated temperature conditions. Periods of vacuum or back pressure can cause crinkling/failure of these discs. In such situations, the discs are provided with vacuum/back pressure supports.

If operating pressures some time reach pressures higher than *predoming pressure*, the disc will stretch and lift off the support when vacuum/back pressure conditions are encountered, the disc collapses against the support and produce a wrinkle deformation which shortens the life of the disc. These discs are suited for higher pressures.

Forward acting scored metal disc: This type of disc is similar to the solid metal disc, except that it is scored. This rupture disc has scored lines that will force the disc to burst along a fixed pattern. This design is a little more expensive but increases the useful *operating ratio* to about 85–90 percent. It also eliminates fragmenting, which means it can be used in combination with a relief valve. Also, there are many designs that allow this type of disc to be installed in vacuum service without requiring special supports. It still needs special supports in high back pressure service to prevent reverse buckling.

Both types of discs, that is, conventional and scored discs can be used in gas and liquid service and in fully liquid service. Figure 6.18 illustrates this design.

Forward acting composite disc: This disc can be flat or domed and is comprised of a top section preceded by a bottom seal. Flat composite discs are used for low pressure applications with burst pressures in the range of 0.07 bar (1 psi)–1 bar (15 psi). Flat designs are generally used for atmospheric storage tank applications.

The burst pressure is a function of the two sections. It is not uncommon for the bottom section to be of a totally different material of construction from that of the top section, even nonmetallic, generally plastic. Silver or gold are also not uncommon

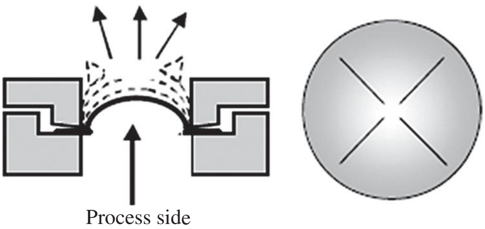


Figure 6.18 Forward-acting scored rupture disc

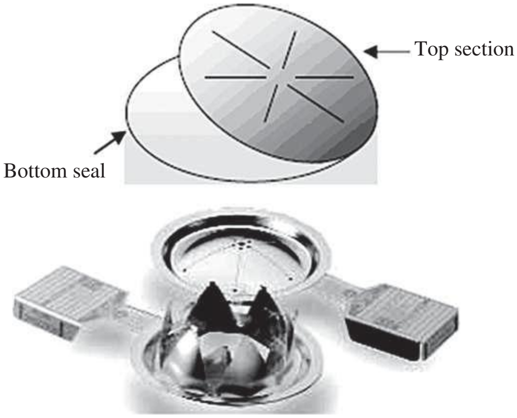


Figure 6.19 Forward-acting composite rupture disc

for the second section. Top member can be made of a less expensive material. The second section fits into the concave side of the slit disc and provides fluid seal. The domed disc design will burst due to pressure applied to the concave side whereas the flat disc may be designed to burst in either direction.

Slits in the top section control burst pressure and the bursting pattern. Purpose of the slits is to weaken the disc so that it bursts at lower pressures. The flat construction can be used for the protection of low pressure systems. Operating ratios are typically around 80 percent for the dome construction and 50 percent for the flat construction. This disc may require special supports to be used in vacuum or high back-pressure conditions. Some designs are nonfragmenting, which means they can be used in relief valve combination. Figure 6.19 illustrates this type of disc.

The composite disc is designed for systems requiring a lower burst pressure than for standard type. It is designed for non-fragmentation when used with a TEFLON seal. Allowable operating pressure for these discs can be raised to 80 percent of the burst pressure.

Reverse acting scored rupture disc: This disc is of domed shape and installed such that the pressure is on the convex side of the disc, thereby placing the rupture disc in compression. As the burst pressure rating of the disc is reached, the compression loading on the disc causes it to reverse, snapping through the neutral position and causing it to open by a predetermined scoring pattern or knife blade penetration. It is designed such that pressure pushes against the disc causing it to flex back into a forwarding acting disc and then burst.

Buckling occurs at a stress level considerably lower than that for prebulged type. It can be made out of thicker plate than prebulged type. Buckling strength is determined by Young's modulus, which is more constant and more reproducible than ultimate tensile strength and therefore these discs are easier to make for close tolerances. Unlike prebulged discs, reverse buckling discs do not creep or stretch as pressure builds up. Figure 6.20 illustrates a reverse buckling-type rupture disc.

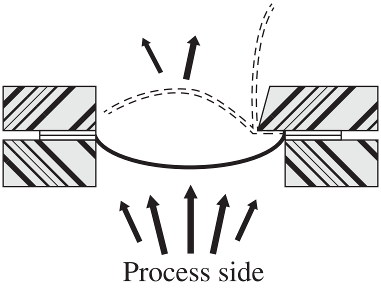


Figure 6.20 Reverse buckling-type rupture disc

Cutting of the disc on reversal depends on the energy with which it strikes the blades. For this reason, it is used on gas/vapor service or in liquid service where a substantial volume of gas/vapor is there between the liquid and the disc. In totally full liquid systems, where speed of reversal may be slow, the disc may initially come to rest on the blades and then be cut after the system pressure increases substantially, frequently exceeding burst pressure of the system.

Since, the blades are vital to the proper operation of the disc, any damage to them will adversely affect the performance of the disc. Blades can corrode and get dull as a result of being re-used over a long period of time. Edges of the blades must be kept sharp and checking and re-sharpening may be needed. This disc can be used in systems where the *operating ratio* is at about 90 percent or less. It can be, and very often is, manufactured to be nonfragmenting and thus is a good choice for use in combination with relief valves. This type of rupture disc can be used in vacuum or larger back-pressure services without special supports. Reverse acting rupture discs generally provide closer tolerances than forward-acting discs.

A reverse acting rupture disc provides some advantages, as compared to tension type rupture discs, which may warrant consideration when selecting a rupture disc. These advantages include:

Zero manufacturing range allowing the rupture disc to operate to 90 percent of its stamped burst pressure, full vacuum capabilities without the need of an additional

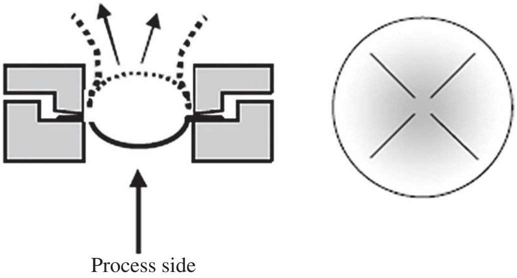


Figure 6.21 Reverse acting scored rupture disc

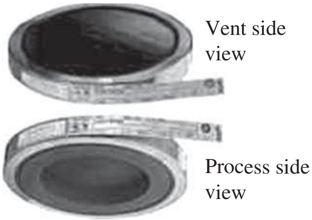


Figure 6.22 Graphite rupture disc with armored ring

support member, longer service life under cyclic or pulsating conditions. Constructed using thicker materials providing greater resistance to corrosion.

Scored reverse acting disc bursts open along the weak scored lines and bursts open in milliseconds. Figure 6.21 illustrates a reverse acting scored rupture disc.

In contrast to the situation with a conventional tension loaded disc, the reverse buckling dome does not stretch as the pressure approaches the burst pressure. Instead a dent appears which increases in size and causes the disc to snap in the direction of less pressure. As it does so, knife blades on the downstream side of the assembly penetrate more sophisticated and more expensive than prebulged type.

Ultra low pressure discs operate in both positive pressure and vacuum. Their construction involves a combination of reverse buckling and prebulged designs. This disc consists of a perforated metal section followed by a PTFE seal, a support girdle and a set of knife blades. Perforations in the metal section provide the relief area when pressure conditions force the PTFE seal against the blades. When the disc is mounted with the concave side facing the medium and exposed to positive system pressure, it acts as a prebulged composite disc. When pressure acts in the reverse direction, the PTFE seal is forced against the support girdle until the girdle reverses, with the seal snapping through and cut by knife blades. When the disc is mounted with the convex side facing the medium, the action is reversed.

Graphite discs: These are of two types, namely, resin impregnated and pure compressed graphite. Resin impregnated discs are robust and tend to perform accurately if properly installed. These withstand vacuum or back pressure equal to normal operating pressure. A typical graphite disc is illustrated in Figure 6.22.

These discs are machined from a monolithic piece of graphite and impregnated with phenolic resin. Graphite discs are corrosion resistant to many chemicals.

Some designs provide protection against two different pressures from opposite directions. A typical application involve protection of closed storage tanks against malfunctioning of primary breathers during loading/unloading operations. Operating pressure for these discs should not exceed 75 percent of burst pressure. These discs give full bore opening upon bursting irrespective of type of service, unlike ductile metal discs. Pure graphite discs are made in domed shape and normally installed as reverse buckling discs. Their normal operating pressure is 90 percent of burst pressure over a temperature range of 20–650°C. Pure graphite discs should not be

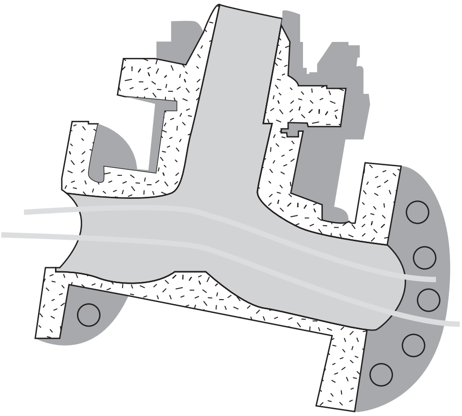


Figure 6.23 Clean sweep rupture disc assembly

exposed to erosion. Their main advantages are low burst pressure, narrow burst tolerances, and corrosion resistance. Reverse buckling metal discs can be lined with pure graphite and are particularly used for PVC reactors because of the nonstick properties of graphite to PVC.

Clean sweep disc assembly: Used in pipelines in which the flowing fluid has a tendency to build up solids under the disc if the disc is installed on a dead pipe branch. Solids build-up could prevent the disc from protecting the system from overpressure conditions. Clean sweep design eliminates the dead pocket and enables the product to sweep across the disc surface. This action tends to keep the disc from solids build up under the disc. Figure 6.23 illustrates clean sweep disc assembly.

There are a number of factors that will affect service life of rupture discs. In addition to pressure and temperature cycles, the duration of cycles are important.

Corrosion of these extremely thin metal discs is, of course, a completely independent factor that can cause discs to fail at lower pressures after short service lives. There is a legitimate concern that the gold facing on gold faced rupture discs may not stand up to more and wider cycles. If this protective barrier fails, the underlying disc will be exposed to the corrosive vapors of the system.

Burst pressure: The burst pressure of a disc is determined essentially by the thickness and the strength of the disc material. As the temperature of the disc changes, the strength of the material and hence the burst pressure, will also change. The minimum rupture pressure available will be a function of how thin the discs can be made and still be repeatable (approximately 0.03 mm), the material strength and the disc size (larger discs have lower burst pressures).

Maximum design pressure vs. Maximum operating pressure: All of the published maximum pressure and temperature ratings are calculated using the American Society of Mechanical Engineers (ASME) pressure vessel code. This code incorporates into these ratings a four times (4×) safety factor for ultimate failure and a minimum 1.5× safety factor for permanent deformation of the vessel. This code, as well as

Table 6.15 gives a summary of comparison of rupture discs and relief valves.

Table 6.15 Comparison of rupture disc and relief valve

Properties	*Rupture disc*	*Relief valve*
Type of device	Simple	Mechanical
Mounting position	Any position	Only vertical
Behavior when over-pressure ceases	It does not re-close the disc must be replaced	It closes again
Does it give over-pressure protection	Yes	Yes
Does it give proterction from vacuum?	Yes	No
Periodical check of calibration	Not required	Required
Is it possible to change calibration?	No	Yes
Calibration lower than 0.1 bar	Yes	No
Calibration higher than 500 bar	Yes	No
Availability of diameters	Large selection	Limited
Availability of materials	Large selection	Limited
Maintenance	Minimum	High
Costs	Minimum	High
Leaks during operation	No	Possible

essentially all other recognized pressure vessel codes, states that a vessel must be equipped with a rupture disc rated not higher than the maximum design pressure. A vessel that is designed to 200 bar and equipped with a standard 200 bar rupture disc should not be operated above 90 percent of its rating (185 bar).

Rupture disc selection criteria

Phase application: In selecting a particular rupture disc for installation, its phase application must be considered. This implies that *gas only* discs should be used in gas only conditions, because it may not open at all under liquid conditions. For instance, many reverse buckling discs are applied in gas conditions, with opening actuated by the energy stored in the compressed gas. Since, liquids are incompressible, stored energy due to compression is not available. Therefore, all liquid only discs should be eliminated in this stage if the application is gas.

Operating ratio: The rupture disc operating ratio indicates the pressure at which the disc can be operated and still maintain a prolonged service life. Operating ratio is achieved by dividing the maximum operating pressure by the rupture disc burst pressure. Selecting a rupture disc with a higher than required operating ratio is typically a waste of money, while selecting a rupture disc with a lower operating ratio than required will likely reduce production and require frequent change outs. Rupture discs have a recommended maximum operating ratio of about 50–95 percent, depending on the construction method and materials. They should not be selected for applications where they will be subjected to conditions above the specified maximum operating ratio. Therefore, any rupture disc that does not meet the required operating ratio requirements should not be considered for the application.

Vacuum conditions: Rupture discs are required to be vacuum resistant. In some cases, rupture discs need an additional vacuum support, while others are capable of withstanding full vacuum without additional support. It is important to know that there are both forward acting rupture discs and reverse acting rupture discs that are incapable of withstanding full vacuum service. As such, if the application is subject to vacuum conditions, it is important to understand the vacuum capabilities of the rupture disc prior to specification.

Requirement of nonfragmentation: Nonfragmenting rupture discs are usually specified for scenarios where they are located upstream of a pressure relief valve. This is because when the disc fragments lodge in the relief valve, they can obstruct the valve from closing properly. In addition, some applications require no contamination, which would make a fragmenting rupture disc totally unacceptable (e.g. sanitary applications).

The soft criteria: The plant history of the rupture disc in the same or similar scenarios is a good barometer to use when specifying a rupture disc. The end user should evaluate such soft criteria as rupture disc interchangeability, lifetime cost, operating temperature, material type, cycle life, etc. At this stage, the expertise of the rupture disc manufacturer does not really affect the final decision on the type of disc design to use in the application. Such soft criteria are previous plant history with the rupture disc design in similar or same applications, for example, interchangeability, ease of maintenance, cycle life, etc.

Rupture disc application requirements as per ASME code: In the case of rupture disc as *primary relief or sole relieving device*, it must be sized to prevent the pressure in the vessel from rising more than 10 percent or 20.7 kPa (3 psi), whichever is greater, above the maximum allowable working pressure (MAWP) of the vessel. In addition, the rupture disc marked burst pressure shall not exceed the MAWP. Figure 6.24 illustrates rupture disc as primary relief device.

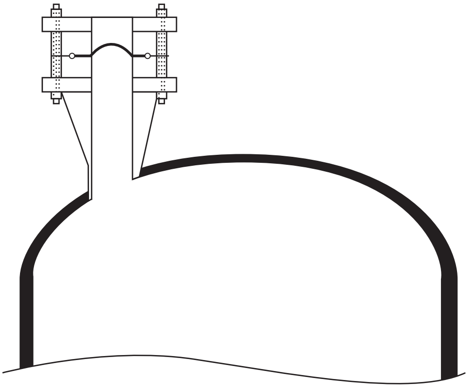


Figure 6.24 Rupture disc as a primary relief device

Figure 6.25 illustrates rupture disc as a secondary relief device to a relief valve.

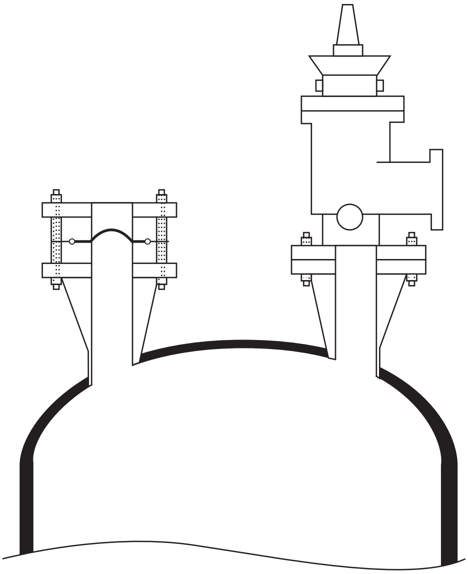


Figure 6.25 Rupture disc as a secondary relief device

The ASME code allows rupture discs to be used in *multiple* as a *secondary device* to other rupture discs or pressure relief valves. In this case, the secondary device is sized to prevent the pressure in the vessel from rising more than 16 percent or 27.6 kPa (4 psi), whichever is greater, above the MAWP. The burst pressure of the secondary device may be marked at a pressure not exceeding 105 percent of the MAWP.

When relief devices are installed for nonfire conditions and exposed to fire conditions, the operating pressure shall not exceed more than 21 percent of MAWP. Supplemental relief devices for fire conditions shall prevent pressure to rise more than 21 percent of MAWP. ΔP in inlet piping of relief valves should not be more than 3 percent of system pressure.

Another application allowed by the ASME Code is the use of a rupture disc in combination with a pressure relief valve. In this application, the rupture disc seals the pressure relief valve from the vessel contents or downstream vapors. The disc/valve combination may be used as a primary or secondary relief device. Rupture disc serves as a barrier, protecting the safety relief valve from process media. This barrier extends the life of the relief valve and prevents leakage to the atmosphere. Figure 6.26 illustrates this application.

A rupture disc may be installed between a pressure relief valve and the vessel provided:

The combination provides ample capacity to meet the overpressure requirements. The rupture disc does not interfere with proper functions of the valve (i.e. rupture disc must be a nonfragmenting design). The marked capacity of the valve is de-rated by a combination capacity factor of 0.90 or a factor certified for the specific disc/valve combination.

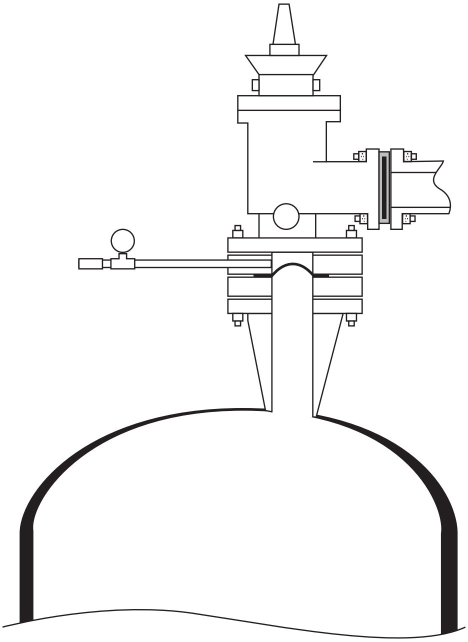


Figure 6.26 Rupture disc at inlet of relief valve in combination

General practice is that the set pressure of the disc should be as close as practical to the set pressure of the valve an in no case the set pressure to exceed MAWP of the vessel. The space between the rupture disc and valve is provided with a pressure gauge, free vent, or suitable indicator. This arrangement must be capable of detecting a leak and/or preventing a build-up of pressure in the space because any pressure build-up will affect the relieving pressure on the process side of the disc. Additionally, it should indicate if the disc ruptured. Flow opening of the disc, after burst, is to provide sufficient flow equal to the capacity of the valve.

The primary reasons for applying rupture discs upstream of pressure relief valves include:

- Prevent plugging of relief valve.
- Prevent corrosion of pressure relief valve – The rupture disc is used to prevent corrosive materials from contacting the relief valve internals during normal operating conditions. Exposure is limited to the duration of an overpressure situation.
- Avoid expensive high alloy relief valves. High alloy rupture discs are much cheaper to use.
- Prevent leakage through the relief valve.

A rupture disc may also be installed on the outlet of a pressure relief valve provided:

Discs are also used when relief valve is mounted to a common header system. In this case, the disc prevents back pressure, and contamination from reaching the relief valve. Back pressure and contamination would be caused during an upset in another part of the connecting system. The space between the valve and rupture disc is vented

Figure 6.27 illustrates installation of rupture disc at outlet of relief valve.

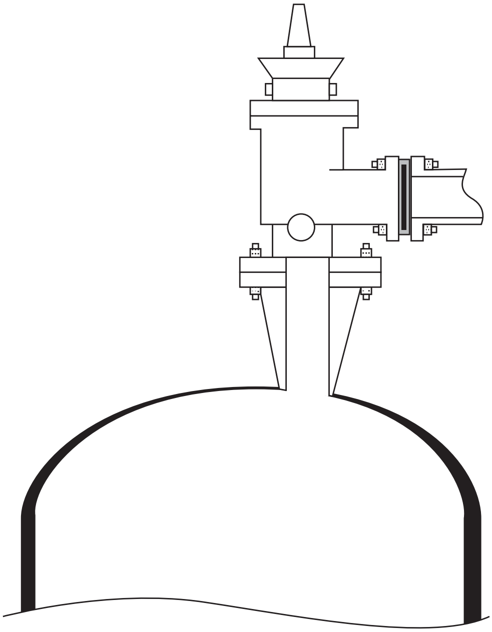


Figure 6.27 Rupture disc at outlet of relief valve in combination

or drained or the valve is designed so any accumulated pressure on the outlet of the valve will not affect the opening pressure of the valve. The marked burst pressure of the disc plus any downstream back-pressure should not exceed the set pressure of the valve.

- The rupture disc provides sufficient capacity to permit flow through the valve without exceeding the allowable overpressure.
- Fragmenting type disc can be used, provided the downstream system tolerates the ingress of fragments or the fragments are being caught. Figure 6.27 illustrates this application.
- The primary reasons for applying rupture discs downstream of pressure relief valves include:
- Prevent corrosion of relief valve – The rupture disc is used to prevent corrosive vapors in common headers from contacting relief valve internals during normal operating conditions.
- Prevent variable superimposed back pressure in a common header from affecting relief valve set pressure – Rupture discs are available that have low burst pressures but can withstand higher backpressures, hence avoiding the need for relief valves equipped with balancing bellows in some cases.
- Detect opening or leakage of relief valve – Some rupture disc types have integral burst indication that can signal the control room if the disc has been burst due to relief valve opening or leakage.

Where an a*dditional hazard is likely to be created by exposure of a pressure vessel to fire or other unexpected sources of external heat*, supplemental pressure relief devices shall be installed to protect against excessive pressure. A rupture disc in this application shall be capable of preventing the pressure from rising more than 21 percent above the MAWP and have a marked burst pressure not exceeding 110 percent of the MAWP. If the same rupture disc is also used to meet nonfire pressure relief requirements, then the marked burst pressure shall not exceed the MAWP.

A rupture disc device intended *primarily for protection against exposure of a pressure vessel to fire or other unexpected sources of heat* may be used, provided the vessel has no permanent supply connection and is used for storage of non-refrigerated liquefied compressed gases at ambient temperatures. The rupture disc shall be capable of preventing the pressure from rising more than 20 percent above the MAWP. The marked burst pressure shall not exceed the MAWP.

Table 6.16 summarizes rupture disc selection and applications.

Table 6.16 Rupture disc selection and applications

Type of rupture disc	*Applications*
Forward-acting	
(a) Forward-acting solid metal	(a) Operating pressure up to 70 percent of the marked burst pressure of the disc; not suitable for installation upstream of a pressure relief valve
(b) Forward-acting scored	(b) Operating pressure up to 85–90 percent of the marked burst pressure of the disc; withstand vacuum conditions without a vacuum support; acceptable for installation upstream of a pressure relief valve
(c) Forward-acting composite	(c) Designed to burst at a rated pressure applied to the concave side; some designs are nonfragmenting and acceptable for use upstream of a pressure relief valve
Reverse-acting (formed solid metal disc designed to reverse and burst at a rated pressure applied on the convex side)	(a) Designed to open by some methods such as shear, knife blades, knife rings, or scored lines
	(b) Suitable for installation upstream of pressure relief valves
	(c) Provided satisfactory service life with operating pressure 90 percent or less of marked burst pressure
Graphite rupture discs machined from a bar of fine graphite that has been impregnated with a binding compound.	(a) Provided satisfactory service life for operating pressure up to 80 percent of the marked burst pressure and can used for both liquid and vapor service, but not suitable for installation upstream of a pressure relief valve
	(b) Used for vacuum or back pressure conditions with furnished with a support to prevent reverse flexing.

Materials of construction of rupture discs: Most common *ductile* materials used in disc manufacture are stainless steel 316 (480), inconel (535), nickel (425), monel (425), hastelloy B and C, and aluminum (125). Titanium, tantalum, silver (125), gold, and platinum are also used. Coatings and linings used on ductile discs include PVC (80), epoxy, FEP, PFE, or TFE as coatings and polyethylene, FEP (215), TFE (260) as linings. Figures in brackets are the maximum temperatures in °C for use of the disc materials. Stainless steels are available for applications in the temperature range 480–196°C. Working temperature of discs with a lining is also dependent from lining material.

Lining materials range from polymers, stainless steels, aluminum, and copper.

Brittle material discs are mainly graphite discs, made from low ash petroleum coke, calcined at high temperatures mixed with pitch formed into blocks and heat treated. This graphite is normally impregnated with phenyl/furan resins under vacuum.

Quick change housings: To permit rapid replacement of discs after bursting, a number of quick change housings are developed. These holders require the disc device to slide sideways into the vent system. To achieve a fluid seal between the disc devices and vent system, inlet and outlet flanges of the disc device are provided with O-ring seals that are carried in dove tail grooves. When the O-rings are put under the fluid pressure, they will key into the irregularities of the mating flange face and lock the disc device firmly into position.

Double-disc assemblies are used to prevent loss of the product due to premature failure of the first disc from fatigue or corrosion. If the first disc bursts at a pressure close to the bursting pressure of the second disc, sudden pressure shock may also burst the second disc. Double-disc assembly may also be used as a quick opening valve. It may contain two reverse buckling discs designed, for example, to burst at 60 percent of system pressure. To prevent discs bursting prematurely, space between the discs can be pressurized to 50 percent of the system pressure. When this pressure is released the discs burst within milliseconds. The space between the discs should be large enough to ensure that the correct functioning of the disc is not impaired. Also, the space should be monitored for pressure or be vented by means of an excess flow valve.

Sizing considerations: Codes present equations for rupture disc sizing based on the assumptions of ideal gas laws and use of isentropic flow through the disc. Also, it is assumed that upstream velocity is small compared to flow velocity through the disc and therefore can be neglected. Where ΔP in vent system gives a flow rate different from that calculated, vent pipes severely reduce flow capacity of the discs. To prevent this, larger size disc and/or larger vent pipe is used.

Disc burst indicators: Bursting may be noted by observing pressure loss in the system, visual inspection, bursting sound, remote indication, and activation directly by the disc, or by pressure or flow change.

Applications: Discs are to perform better than relief valves (i) under conditions of runaway reactions or overpressurization where inertia of a relief valve would inhibit the required rapid release of excess pressure, (ii) where even a minute leakage of fluid to atmosphere cannot be tolerated at normal operating conditions, (iii) where fluid is highly viscous, (iv) where fluid is likely to lead to deposits of solids on the underside of relief valve that would render the valve inoperable, and (v) where low temperatures would cause seizure of the relief valve.

Discs in parallel: (i) Where one disc alone cannot satisfy relief requirements, (ii) where one disc serves as a primary relief device while the second one, set at a higher pressure, protects the pressure system against unusual overpressure conditions, and (iii) in conjunction with a switch over mechanism which puts one section of relief system on line while isolating the second relief system. When the first section has failed or needs to be serviced, the second section may be put into service by operating the switch over valve. The later must be so designed that the second part is open before the first part closes.

Discs in series: To prevent discharge of the fluid to atmosphere due to premature failure of inner disc as a result of fatigue or corrosion or to serve as a remotely operated quick opening device. The discs are, in this case, designed for a fraction of the system pressure, but re-prevented from bursting by pressurizing the space between the discs. Upon dumping the pressure between the discs, they burst within few milliseconds.

Disc parallel to a relief valve: Rupture disc downstream the valve. The valve serves as a primary device and the disc, set at a higher pressure, and protects the pressure system against *unusual overpressure conditions*. Typical application: protection of liquefied gas tanks.

Disc in series upstream with a relief valve: (i) to prevent leakage past the closed valve disc to atmosphere or vent system, (ii) to prevent deposits from forming around the valve disc that would impair the valve operation, and (iii) to prevent corrosive or scaling fluids from leaking into the valve.

Rupture or Breaking Pins

Operation: The rupture pin valves relieve pressure at set point with predetermined accuracy and dependability. The valves consist of a piston on seat, restrained from movement by a slender round pin known as the buckling pin. The piston and seat have a bubble-tight seal while under pressure. The pin will buckle at set point from an axial force applied by the system pressure acting on the piston.

Each valve is self-contained and self-actuating. When the pin is buckled, the valve is full open in a matter of milliseconds. The pin is external to the system being protected and is tightly held in place at both pin ends. Figure 6.28 illustrates the working of rupture pin technology.

These pins shall not be used as single devices but only in combination between the safety or safety relief valve and the vessel.

The space between a breaking pin device and a safety or safety relief valve shall be provided with a pressure gage, a try cock, a free vent, or suitable telltale indicator. This arrangement permits detection of breaking pin device operation or leakage. Each breaking pin device shall have a rated pressure and temperature at which the pin will break.

Figure 6.28 illustrates working of rupture pin technology.

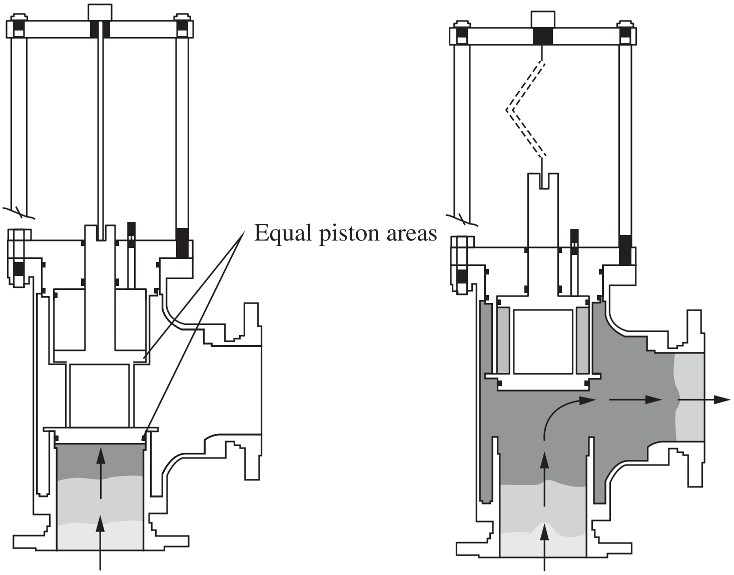


Figure 6.28 Working of rupture pin technology

The rated pressure of the breaking pin plus the tolerance shall not exceed 105 percent of the maximum allowable working pressure of the vessel to which it is applied.

Advantages of rupture pin valves: Operate at 95 percent of set pressure. The pin can be replaced in minutes and not in hours as the case is for rupture discs. Set pressure can be changed in no time. These are not subject to premature failure; their set point is insensitive to operating temperature, suitable for liquid service, and replacement pins are 1/3rd to 1/4th the cost of replacement discs. Other advantages include the following:

- No breaking the line to change the pin
- Pulsating pressures – no problem
- Extreme high or low pressures – no problem
- Telling when the pin has buckled is obvious
- No metal debris to foul the relief valve in series
- Can sense upstream, downstream or differential pressure
- Pins can be stored at the valve
- Full bore relief in milliseconds
- With toxic fluids no suiting up to change the pin (does require a valve designed for the application)
- Reliability can be checked in operation under pressure
- Bubble tight seal
- Disadvantages include greater initial installation cost and limitation of the elastomer O-ring seal to a maximum operation temperature of 230°C.

Table 6.17 gives a comparison of rupture pins and rupture discs.

Table 6.17 Rupture disc vs. rupture pin

Rupture disc	*Rupture pin*
Discs fatigue and usually fail early Working close to set point is impossible	Rupture pins cannot fatigue. Buckles at set point Maximum operating pressure to 95 percent of set point (zero leakage at set point)
Downstream fragmentation	No downstream trash possible
Senses differential pressure only	Can sense upstream pressure only or differential pressure only
Discs can be installed backwards or improperly	It is difficult to imagine a pin installed improperly
Discs are in contact with corrosive system fluids	Pins are external to the process fluid and are made of corrosion resistant metals
Costly storage and handling required	Rugged—can be stored at the valve
Costly time is required to change discs	Pin changing is done with one man in minutes, even with large valves

6.14 Breather Vents for Storage Tanks

Evaporation losses are a source of concern for storage of highly volatile organic chemicals. Rising cost on the one hand and strict implementation of environmental laws on the other hand coupled with heightened public awareness has left them with no alternative but to find ways and means of controlling emissions. Toxicity of the product stored adds an entirely new dimension and compounds the problem.

These vents are fitted to storage tanks for volatile petroleum liquids to protect them from excessive pressures or over vacuum conditions and also minimize vapor losses that would occur in free venting. Free venting is also not practiced from environmental considerations.

Normal operation of breather vents might fail through formation of waxy or crystalline deposits or ice formation during cold weather conditions on the seats of valve diaphragms or inside the nozzle connections on which the valve is fitted.

Some nonwetting materials such as PTFE used in the fabrication of diaphragms are less likely to give troubles of deposit formation and blockages.

Sometimes atmospheric and breather vents are fitted with flame arresters to prevent flame propagation into the tank.

The vents illustrated in Figure 6.9 have a cast body which is flanged for connection to the storage tank. A weather hood protects the pressure exhaust port and a mesh cover is fitted to prevent the ingress of foreign matter for valves vented to atmosphere or connected to vent systems. Both the pressure and vacuum sides of the valve incorporate a pallet and diaphragm assembly which rest on an O-ring seal to prevent leakage. This O-ring can be removed and the seat machined optically flat, producing a metal to metal seating arrangement if required. The weight of the pallet pushes the diaphragm against the seat to keep it closed. When the pressure or vacuum increases,

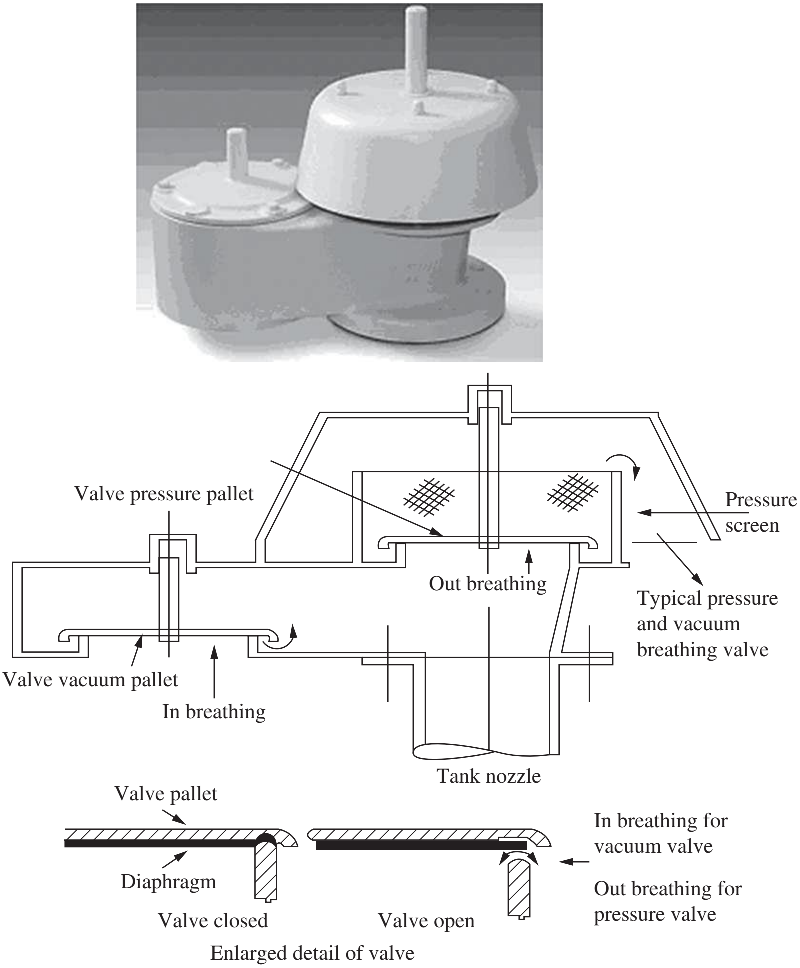


Figure 6.29 A typical breather vent

the pallet and diaphragm lifts and air/gas is allowed to flow. Pressure and vacuum breathing valves are designed to prevent evaporation from storage tanks, but to allow breathing when the pressure or vacuum exceeds that specified.

Figure 6.29 illustrates typical breather vent for storage tanks.

6.15 Explosion Vents

Explosion vent panels are low pressure relieving devices with large area. Explosion vents (rupture panels) are one of the most economical, practical and convenient solutions to preventing explosions from reaching their potential maximum pressures.

During normal venting, an explosion is freely discharged, allowing flames and dust to exit the process vessel being protected. When the process vessel is located indoors, ducts are generally used to safely convey the explosion outside the building. However, ductwork has disadvantages and may result in decreased venting efficiency.

Flameless venting in combination with explosion vents can extinguish the flame from the vented explosion without the use of expensive ducting, limitations to equipment location, or more expensive explosion protection.

Multidomed, single-membrane high-performance explosion vent has excellent service life, and is claimed to be allowing high operating pressures, with vacuum rating, and providing stable performance over a wide range of temperatures. It is designed for dynamic nonfragmenting operation during venting of explosions from industrial equipment.

Figure 6.30 illustrates a typical explosion vent.

*Source: Fike Corporation

Sizing of explosion vents: The following equations for sizing explosion vents, especially for dust explosions is proposed by Mike Ward of Fike Corporation:

$$A = B\,(1 + C \times \log10\,(L/D_E)) \tag{6.1}$$

with

$$B = (3.264 \times 10^{-5} \times P_{max} \times K_{st} \times P_{red}^{-0.569} + 0.27 \times (P_{stat} - 0.1) \times P_{red}^{-0.5}) \times V^{0.753} \tag{6.2}$$

and

$$C = (-\,4.305 \times \log_{10} P_{red} + 0.758) \tag{6.3}$$

where

A = Area of vent in m^2

V = Volume of vessel in m^3 (between 0.1 and 1,000 m^3)

K_{st} = Rate of rise of explosion pressure, bar. m/sec*

P_{max} = Maximum explosion pressure in bar* (between 5 and 10 bar for K_{st} <300 bar. m/sec and between 5 and 12 bar for K_{st} up to 800 bar.m/sec)

P_{red} = reduced explosion pressure in bar

Figure 6.30 Typical multidomed rigid panel explosion vent

P_{stat} = static opening pressure of burst panel in bar (between 0.1 and 1.0 bar)
L/D_E = length to diameter ratio (up to 20)

*Note: The equations are applicable for a reduced explosion pressure of less than 1.5 bar.

L/D_E is a measure of the *shape* of a vessel and turns out to be an important design parameter. Vessels that are near to cubic (L/D_E approximately 1) require relatively little vent area, whilst elongated vessels may need double, treble, or perhaps even more vent area in comparison.

For rectangular or cylindrical vessels, L/D_E can be calculated directly from the physical dimensions [with $D = 2 \times (\text{cross-sectional area}/\pi)^{0.5}$ in the case of rectangular vessels].

If the vessel consists of a cylindrical and conical part, or if the vent relief is at the side rather than the top, then L/D_E is estimated through the effective flame length (maximum distance the flame must travel to exit the vessel) and the effective volume (volume the flame travels through).

6.16 Flame Arresters

The primary function of a flame arrester or detonation arrester is to provide protection against an approaching flame front. In their typical applications, however, they must also allow vapors and/or air to pass through the openings in their elements so that pressure and vacuum relief may be provided so that normal processing of the vapors can be conducted. The resistance to flow through the arrestors is based on their size and configuration. The arrester must be sized to allow the required flow rate at some acceptable pressure drop. The function which a flame arrester is required to perform varies. In some cases it is required to prevent flash back of the flame, but in others where hot gases may be forced through it or where flame may stabilize on or near the arrester, it must also be capable of absorbing considerable quantities of heat. For such duties, it is necessary to not only that the arrester has apertures smaller than the quenching distance, but also it must have sufficient mass and suitable material of construction to absorb heat.

Flame arresters are used especially in flare stacks, vent pipes where their primary function is to prevent flashback. Also these are commonly used in supply lines from gas storage vessels in piping to solvent recovery units. Occasionally used in instrument systems or in connection with explosion-proof housings.

Broadly, function of a flame arrester is to quench the flame and to prevent its transmission from one location to another. Most arresters are metallic structures designed to maximize thermal heat sinking and minimize ΔP across them. Notable exceptions are liquid arresters, sometimes used in process plants.

Flame arresters are passive mechanical devices with no moving parts. They prevent the propagation of flame from the exposed side of the unit to the protected side by the use of wound crimped metal ribbon type flame cell element. This construction produces a matrix of uniform openings that are carefully constructed to quench the flame by absorbing the heat of the flame. This provides an extinguishing barrier to the ignited vapor mixture. Under normal operating conditions, the flame arrester permits a relatively free flow of gas or vapor through the piping system. If the mixture is ignited and the flame begins to travel back through the piping, the arrestor will prohibit the flame from moving back to the gas source.

Another parameter for selecting a flame arrester is directionality, which refers to the direction of flame approach for which an arrester is designed to operate in a pipeline. The pipeline connecting a flame arrester with an identified ignition source is the *unprotected side* of the arrester. The pipeline connecting the arrester with equipment at risk (equipment that must be protected from the temperature or pressure associated with flame penetration) is the *protected side*. If a flame arrester encounters a flame arriving from only one direction, a *unidirectional* arrester can be used. If a flame may arrive from either direction, a *bidirectional* flame arrester is needed. The bidirectional arrester is either symmetrically constructed or has been tested and certified for deflagrations and detonations approaching from either direction.

Flame arresters prevent flame propagation by absorbing and dissipating heat using spiral wound crimped ribbon or metal-ceramic beads or other types of flame cells. These cells allow maximum flow with maximum protection. They provide protection against flame propagation in piping systems that are main folded or have long run up distances. They disperse and cool the flame front to temperatures below self-ignition temperatures of the fuel gas in the system. To effectively quench the flame, the arrestor must rapidly transfer the heat from the flame to the arrester and sustain the heat transfer process for sufficiently long time. The arrester element must be a good heat conductor such as a metal or metal-ceramic media that readily conducts heat, withstanding high temperatures and must have large specific surface area.

If the flammable vapor should ignite, the flame burns towards the arrestor/element. As the flame attempts to pass through the element, it is slowed and cooled by contact with the metal walls of the small passages. Heat is transferred to the element until combustion cannot be maintained. The flame front is extinguished.

Arrester elements are available in a number of different configurations (perforated parallel rectangular metal plate, wound crimped metal, parallel round metal plate, expanded metal cartridge, wire gauge and wire gauge packs, sintered metal, metal shot in small housings, ceramic balls, hydraulic, or irregular such as those in random packing).

One common feature of all flame arrestors is that the flammable vapor mixture is forced to pass through a series of small openings as it flows through the arrester. The size of the openings and their length of passage can vary, depending on the arrester style.

Desirable characteristics of a flame arrester include high capacity to absorb heat from the flame, availability of high free cross-sectional area and low resistance for gas flow, freedom from blockages, and ability to withstand mechanical shock and explosion.

Crimped metal arresters have about 80 percent free cross-sectional area and are robust enough to withstand mechanical and thermal shock, and can be made to quench violent explosions.

Wire gauge arresters have a low free area (less than 50%) for fine gauges and are less effective and less robust. Not suitable for violent explosions and have limited applications.

Perforated plate arresters have low free area than wire gauges but have high heat capacity and better robustness. Not suitable for violent explosions.

Parallel plate arresters have low free area and high resistance to flow but can be designed to quench violent explosions. Used particularly on the exhaust of internal combustion engines.

Sintered arresters have low free area and high resistance for flow but can be made with very small apertures and to quench violent explosions.

Packed bed arresters have high resistance for flow but can quench violent explosions.

Hydraulic arresters contain a liquid (usually water) and serve to break-up gas stream into bubbles and so prevent passage of flame.

Size of apertures through the arrester is determined by the quenching distance of the flammable mixture. Diameter of the aperture should not be more than 50 percent of quenching diameter. Quenching distance increases with increase in temperature. It is approximately $\infty 1/\sqrt{T}$.

The required size of the channels needed to stop the flame front can vary significantly, depending on the flammability of the fuel mixture. The large openings on a chain link fence are capable of stopping the spread of a small, slow burning grass fire, but fast burning grass fires will penetrate the fence unless the holes are very small. In a coal mine containing highly explosive coal dust or methane, the wire mesh of a minor’s lamp must be very tightly spaced.

For a flame arrester used as a safety device, the mesh must be protected from damage due being dropped or struck by another object, and the mesh must be capable of rigidly retaining its shape during a forceful explosive event. Any shifting of the individual wires that make up the mesh can create an opening large enough to allow the flame to penetrate and spread beyond the barrier.

They are mounted to threaded or flanged connections on a tank or in a process piping system. In normal operation, vapors in the pipe are directed through the arrester. An arrester consists of housing and an arrester element.

On a fuel storage vent, flame arresters also serve a secondary purpose of allowing air pressure to equalize inside the tank when fuel is added or removed, while also preventing insects from flying or crawling into the vent piping and fouling the fuel in the tanks and pipes.

Figure 6.31 illustrates a typical flame arrester design.

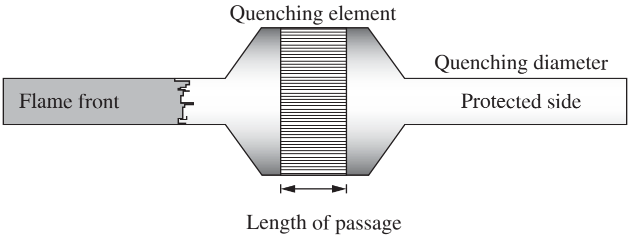


Figure 6.31 Design of a typical pipeline flame arrester

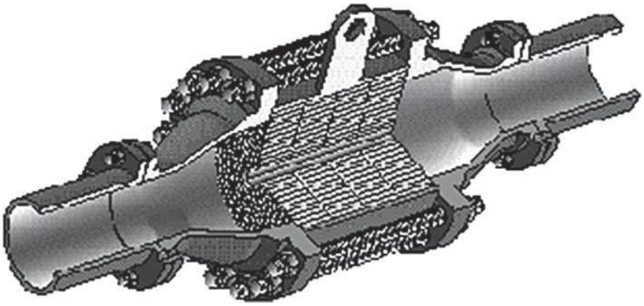


Figure 6.32 Multiple element pipeline flame arrester

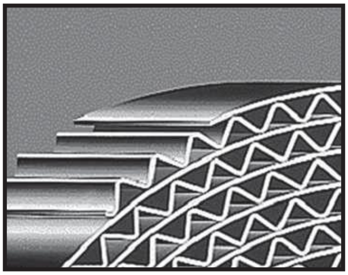


Figure 6.33 Crimped metal ribbon-type flame arrester

Figure 6.32 illustrates a typical multiple element pipeline flame arrester to extinguish high velocity flame fronts, inclusive of detonation arresting capabilities.

The optimum location for the arrester must be determined. End-of-line flame arresters are mounted on outlet flanges and they went directly to atmosphere. Vent line/in line flame arresters may be installed at some maximum distance (specified by the manufacturer) from the end of a section of open vent piping. Detonation arresters are designed so that they may be installed anywhere in a flammable vapors piping system.

Figure 6.33 illustrates spiral wound crimped ribbon flame arrester cells.

Other designs are illustrated in Figures 6.34 and 6.35.

**Sources*: Fike Corporation and Westech Industries LTD

Inline flame arresters have specifically designed heat transfer characteristics for slow moving flames and low-to-medium pressure fronts (low to medium pressure deflagration). But flames moving at higher velocity and carrying higher pressure fronts (high pressure deflagration and detonations) can pass through a standard in-line flame arrester. That is why it is critical that the proper flame arrestor be installed to meet the requirements of both the applications, operating conditions and the flame, state to which the arrester will be exposed.

Extended lengths of pipe allow the flame to advance into more severe states of flame propagation such as high-pressure deflagrations and detonations.

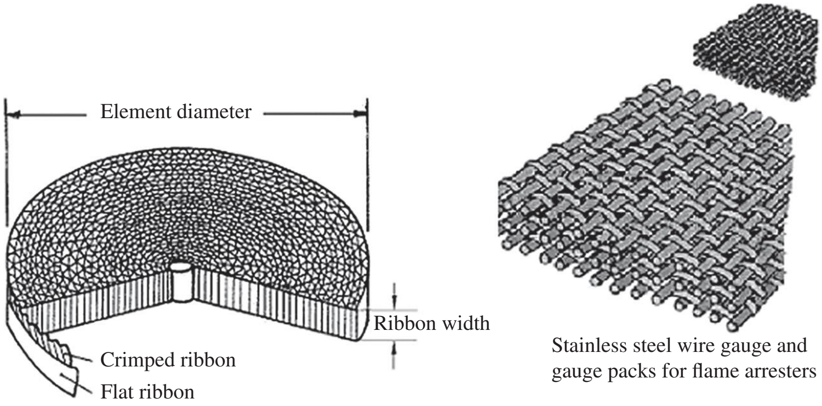


Figure 6.34 Some flame arrester designs

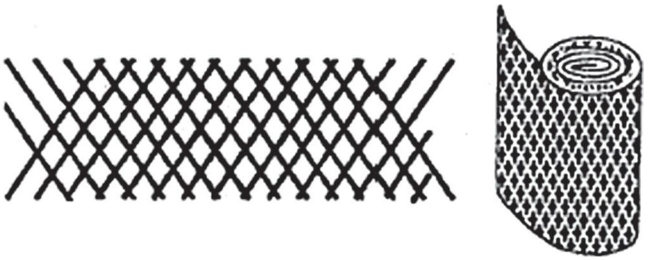


Figure 6.35 Details of expanded metal cartridge flame arrester element

Bends in piping, pipe expansions and/or contractions, valves, or flow obstruction devices of any kind, cause turbulent flow. Turbulent flow enhances the mixing of the combustible gases, greatly increasing the combustion intensity. This can result in increased flame speeds, higher flame temperatures, and higher flame front pressures than would occur in laminar flow conditions.

High-pressure deflagrations and detonations can occur more easily at higher system operating pressures than at near atmospheric levels.

Elevated pressures condense the ignitable gas giving the flame more energy to release thereby boosting flame heat intensity.

A critical concern in flame arrester installation is the possibility of a flame stabilizing on the face of the flame cell element. A flame that continuously burns against the flame arrester element for a period of time can heat the element above the gas self-ignition temperature resulting in flame propagation through the element. The time period varies with the type of element, mixture of air and gas, type of gas, and velocity at which the gas stream is moving.

Measurement of the maximum gap between two equatorial flanges on a metal sphere that will prevent a flame from being transmitted from the sphere to the surrounding flammable mixture. MESG is dependent on gas composition. Stoichiometric mixture is used to determine MESG value for a given gas.

Careful consideration must be taken to determine whether to use a flame arrester or a detonation flame arrester. Detonation flame arresters must be able to stop both deflagrations and detonations.

Deflagration flame arresters on tanks are designed to stop a flame from propagating into a tank from an unconfined atmospheric deflagration, or to prevent a flame generated from a confined volume deflagration in a vessel from escaping to the outside of the vessel. They normally cannot withstand significant internal pressure and cannot stop detonations. Typical flame speeds in a deflagration occurring in piping range from 3 to 60 m/s. Deflagrations of fuel–air mixtures typically generate pressures 8–12 times the initial pressure in closed process vessels and equipment.

Detonation flame arresters are designed to withstand and extinguish the high speed and high pressure flame front that characterizes a detonation propagating through a piping system. Therefore, a detonation arrester must be able to withstand the mechanical effects of a detonation shock wave while quenching the flame. Detonations occurring in piping have velocities of about 1,800 m/s, or greater, and in closed process vessels and equipment can generate pressures from 20 to 100 + times the initial pressure.

Detonation application: The detonation flame arrester is an advanced technology flame arrester. They are used to stop the high pressures and velocities associated with detonation. They stop confined and unconfined low-and high-pressure deflagrations, stable and overdriven detonations. Application parameters for the detonation flame arresters far exceed those of flame arresters for pipe lengths, configurations, system operating pressures, and flame stabilization.

There are two basic determinations when evaluating the intended application:

- The location of the ignition source from the flame arrester, and what needs to be protected
- First, the location of all potential ignition sources should be determined (i.e. flare, vacuum pump, blower, burner, lightning strike, and static discharge).
- Second, the system to be evaluated to determine exactly what should be protected (i.e. the gas source, process component, personnel, upstream process facility, and tank).

When one has determined the ignition source(s) and what is to be protected, the following parameters should be evaluated in order to determine the appropriate flame arrestment protective device:

- Length and configuration of pipe and pipe between ignition source and arrester
- System gas grouping
- Initial operating pressure
- Flame stabilization on element

All of these variables affect the performance of the arrester and can also affect the dynamics of flame propagation.

Inline and end of line applications: The inline flame arrester and the end of line (free vent) arrester are used to stop flame propagation of confined and unconfined low pressure deflagrations. They are typically used for limited piping applications when the system operating pressure is near atmospheric levels.

System gas grouping: The type of gas in the system and its corresponding gas group determines the design of the arrester element. The element must be designed to accommodate the specific gas group that could possibly ignite and propagate in the system. The available designs consist of International Electric Code (IEC) group gases into IIC, IIB, IIA, and I, the National Electric Code (NEC) groups gases into A, B, C, and D categories depending on the MESG value of the gas.

The materials of construction of a flame arrester or detonation arrester must be selected to ensure compatibility with the process vapors being handled. The possibility of corrosion of the arrester components or contamination of the process materials must be minimized. They are available in a wide range of materials (aluminum, stainless steel, ductile iron, hastelloy, etc.).

Flame arresters that are not routinely inspected and properly maintained can get plugged, due to condensation or corrosion by stored fluids, foreign material.

When using inline flame arresters, it is necessary to evaluate the potential for transition from deflagration to detonation in the piping system being considered.

6.17 Flare Systems

Flare systems facilitate safe burning and discharge of gases released by relief valves, rupture discs at elevated points for atmospheric dispersion of the burnt gases. A typical flare system consists of the following:

Flare header which receives the contents, both gases and liquids, of discharge, in which liquids are separated from the gases in a flare drum and recovered through recycling to suitable points in the plant.

The gases go to the flare stack, at the tip of which a pilot flame that will act as ignition source to the released gases, and facilitate their ignition and burning at the end of the tall stack. The burnt gases disperse in the atmosphere before descending to ground level at low concentrations which will not harm the populations.

Sometimes, additional liquid flows into the header, causing more entrainment in the released gases, causing raining of these liquid droplets onto the ground. For this reason, considerable ground area around the flare needs to be provided in the plant layout. This area should be kept clean, preventing dumping wastes and preventing growth of grass, as already mentioned under layout.

The flare stack should be located on the downwind side of the plant, to prevent it as ignition source to any plant leaked vapors/gases passing this area, as mentioned under layout.

The flare system should be maintained and no corrosion of the flare drum should be tolerated. Such corrosion is possible because of sulfur gases being a possibility in such gases. This reason was responsible for some accidents in the past.

Condensate handling in gas pipelines: In natural gas pipelines, condensate flows are possible, reducing line capacities through flooding. For this reason, “sphering” of these lines by introducing light weight plastic/rubber spheres on upstream points to clear and drain these condensates at designated points in these lines.

Sometimes, *open pit* burning is practiced to dispose of the condensates and also release of liquid flows from drains under emergency situations.

6.18 Safety Considerations in Instrumentation Systems:

A Safety instrumented system (SIS) is defined as an instrumented system used to implement one or more safety instrumented functions (SIF). A SIS is composed of any combination of sensors, logic solvers and final control elements for the purpose of taking a process to a safe state when predetermined conditions are violated.

The correct operation of an SIS requires a series of equipment to function properly. It must have sensors capable of detecting abnormal operating conditions, such as high flow, low level, or incorrect valve positioning. A logic solver is required to receive the sensor input signal(s), make appropriate decisions based on the nature of the signal(s), and change its outputs according to user defined logic. The logic solver may use electrical, electronic or programmable electronic equipment, such as relays, trip amplifiers, or programmable logic controllers. Next, the change of the logic solver output(s) results in the final element(s) taking action on the process (e.g. closing a valve) to bring it to a safe state. Support systems, such as power, instrument air, and communications, are generally required for SIS operation. The support systems should be designed to provide the required integrity and reliability.

A SIF is a function to be implemented by a SIS that is intended to achieve or maintain a safe state for the process with respect to a specific hazardous event.
Examples of SIF applications include the following:

- Shut-down in a hazardous chemical process plant
- Open a valve to relieve excess pressure
- On/Off control to prevent tank overflow
- Shut-down fuel supply to a furnace
- Add coolant to arrest exothermic runaway
- Automatic shut-down when operator not present
- Close a feed valve to prevent tank overflow
- Initiate release of a fire suppressant
- Initiate an evacuation alarm

6.19 Planning for Emergencies – Considerations

Listing of hazards involved in the plant, for example, fire, explosion, toxic release, electric shock, radiation, noise, and so on.

Types and magnitudes of loss damage, injury, and hazard evaluation and analysis.

Initiating and contributing hazards that could lead to major hazards, for example, corrosion, lack of maintenance, and the like. Safeguards provided to prevent loss of control of each hazard should be listed. Examples include pressure relieving devices, inerting systems for reactive chemicals/processes, governors for speed control, and so on.

Safeguards already provided to minimize loss/damage/injury in the event of loss of control of a hazard leading to emergency, for example, monitoring/warning systems, emergency shut-down equipment, sprinkler systems for fire control, and so on.

Development of rapid reaction procedures to deal with an emergency by designated organizations/personnel. This includes review of available resources to determine deficiencies. Such an exercise must consider possible problems, locations, the unit to respond first if there are more than one, operational means of attacking the problem, consideration of availability of outside resources and when they should be sought inclusive of intercommunication procedures for timely assistance, and so on.

Actions to be taken by designated personnel/organizations at the onset of an emergency should be established. Response differs for different types of emergence, for example, response of medical services to handle injury, in case of fire, response of fire services, and so on. Prior training of personnel who receive the first communication of the emergency to obtain all pertinent information accurately and rapidly. Material Safety Data Sheets(MSDS) should be part of such training to both insiders as well as outside organizations. Means should be available to inform all personnel that an emergency exists and emergency procedures should be initiated.

- Means of communication must be established by which to alert emergency organizations regarding the required services, particularly for vehicles, stations, etc.
- Additional channels for emergency use should be clearly designated and posted.
- Consideration for a secondary emergency communication system such as radio backup network.
- Providing alarm systems, which are distinctive, different from other sounds and last long enough so that the concerned personnel are alerted, pin pointing the location of the emergency area.
- Plans for transportation services to move supplies, equipment and personnel to combat the emergency to take injured to medical facilities, to remove valuable equipment and documents, to remove hazardous materials to safe areas and to act as control points.
- Personnel handling emergency operations must know how to control utility services so that these do not cause damage but are available where necessary. An example is to cut off high-voltage power supplies to avoid shock and injury to people and initiation of fires. A circuit breaker may have to be closed to provide power to lighting or emergency equipment.
- Providing different types of emergency equipment to different personnel to meet specific types of emergencies. The equipment must be reliable and effective and must render quick response, easy to carry, and useful for emergency personnel who are under stress conditions.
- Most effective locations for emergency equipment must be established and their location at specific sites or on mobile vans must be determined to provide easy access and proximity to their use.
- Maps should be provided to each emergency service unit showing best means of getting to the concerned site and alternative routes in the event of blockage of primary route. Warning signs against parking in these routes should be provided.
- Considerations for second line of defense must be planned before any emergency arises. In case a situation goes out of control and corrections to such a situation may have to be abandoned and efforts should be redirected to safeguarding personnel saving other facilities. As personnel will not have enough time for evaluation of alternative planning, care must be exercised for prior consideration of different options.

- Safety zones and evacuation routes should be established clearly. Safe locations with structural protection to both safety zones and evacuation routes should be provided for personnel protection in the event of fast emergency developments.
- Adequacy of routes/exits to safety should be assessed for the numbers of personnel likely to be evacuated must be assessed. Routes/exits must be prominently marked. Emergency lighting system may be necessary, especially inside buildings.
- Rescue arrangements with simple and easy-to-carry emergency equipment and rescue personnel should be made available without any confusion at the site.
- A supervisor should be designated to oversee rescue process to ensure every one leaves the area when evacuation becomes necessary.
- Training and simulation of emergency exercises should be organized at intervals.
- Consideration should be given to create a voluntary emergency personnel cadre from within the work force of the plant. These personnel will be more familiar with the plant than outside organizations.

6.20 Annexure

Disaster Prevention

*Source: Material in the following paragraphs is from Safety and Health Guide, U.S. Department of Labor

There are three tasks to perform before any meaningful analysis of any disaster prevention system can begin. The first task is to identify the key processes and elements of the production process and to understand how operational processes are kept within safe bounds under normal conditions. Conceptually, it is the normal process instrumentation and control measures that provide the first and greatest degree of protection to plant employees and to the public. The four areas listed below identify some major subsystems or components that are commonly found in chemical plants. Each has a bearing on the safety of operations under normal and emergency conditions.

A management subsystem that includes management personnel, process specifications, plant design, standard operating procedures, and the written emergency plan.

A personnel sub-system that assigns and defines roles, for both normal and emergency operations, and provides appropriate training. This may also include labor/management safety committees.

A physical sub-system that may include transportation systems for materials, ventilation systems, waste removal systems, containment systems, refrigeration systems, storage areas, communications systems, and other process related equipment.

An emergency services subsystem including plant and community components.

A second task is to understand how critical failure points are identified, and what controls are used to ensure safe operations. This involves assessing the interrelation of the components and, particularly, identifying which safety features in the system should be backed up with alternative instrumentation, procedures, or equipment designed to ensure process variables are kept within safe limits.

The third task is to identify the disaster prevention system that is embedded in the operating system. Conceptually, it is a latent system that is active only when preventative measures have failed and an incident has occurred. This system is the most difficult to evaluate because it is not observable except in emergencies. The system also may involve resources and sub-systems that lie wholly or partially outside of the physical or managerial boundaries of the chemical plant

For example, local firefighters may supplement in-plant fire brigades; local hospitals may provide care to injured workers in addition to in-plant first aid; local police may be involved with traffic control, evacuating of workers and community, and expediting communications and the flow of emergency and rescue equipment.

Finally, there is the question of defining the point at which the emergency system *shuts down* and normal operations begin after an emergency.

Plant management: All the planning and preparation of safe plant operation is meaningless, unless it can be implemented. In the event of a problem, there is no time for meetings and discussions. Correct decisions have to be made at the lowest organizational level possible, and those decisions have to be communicated to other affected personnel. The following questions become very relevant for handling emergency situations.

- What are the lines of authority under normal operating conditions, in transition times like during start-up and shut-down procedures, and in emergencies?
- Can the information be transmitted quickly and easily from worker to supervisor and supervisor to worker?
- How is information exchange accomplished during transition periods (starting and stopping work)?
- Is operator jargon commonly and completely understood by those affected by the jargon? Examples: MIC – methyl isocyanate, monitor, stationary firefighting nozzles, etc.
- Are signals clear? Are audible signals distinguishable and understood?
- Are monitoring records, training records, and material safety data sheets available?

Standard operating procedures should be examined and discussed. The process of updating these procedures – including modifications, communication, and training should be understood.

Does a written emergency plan exist? It should be understood which contingencies are included in the plan, why they are included, and why management considers them to be adequate for the process, site, and situation.

The personnel subsystem: The job classifications of employees who work at the site, all the job titles present on all work shifts, and any potentially crucial omissions?

Are employees aware of their roles during emergencies? Are all critical tasks represented on all shifts?

Who is responsible for training employees? How often is training provided covering standard operating procedures? emergency procedures? How is effectiveness of training evaluated by management?

The physical subsystem: Particular attention should be given to: specific safety aspects, like separation and isolation, compatibility of the chemicals involved in the process and storage, with each other, areas of potential explosions, storage of explosives, and isolation of reaction vessels, minimization of damage and risk to employees, drainage of spilled/leaked hazardous liquids (examples such as diking provisions), provisions for control of release of hazardous gases and vapors from drains and the process, housekeeping, and confined spaces.

Compatibility of materials of construction: Are any metals, sealing compounds incompatible with the chemicals which should not be used for process equipment, piping, or storage systems?

Contamination control: Potentially reactive chemicals may have their reactions catalyzed by common materials that easily enter systems whenever seals are opened. Examples include water or rust which may easily enter a system during transfer from one vessel to another, either during hook-up or disconnect, or during pressurizing or venting of tanks.

If such potential catalysts are identified, how are they excluded from the system? Examples include the following:

- If vessels are pressurized by inert gases, are there filters in the gas lines to remove solid particles?
- If vacuum relief or pressure relief valves are on the vessels, how are they protected so potentially hazardous contaminant can enter through them when open?

When the systems are opened for maintenance purposes, what precautions are taken to prevent contamination? What is done to safeguard the system while it is open? What precautions are taken to ensure that replacement parts are free of contaminants incompatible and/or incompatible materials? When connections are made and broken (e.g. during transfer from rail cars or trucks), what measures are taken to ensure contaminants do not enter the system?

Physical facilities: Much plant equipment could be considered ancillary to the production processes. Examples of systems that may need to be present, properly inspected, and functional are emergency eye wash or shower, fixed fire suppression equipment, portable firefighting equipment, if employees or a fire brigade are to use portable firefighting equipment. How often are they tested, what are their capacity and its adequacy for the anticipated emergency?

Inspection and maintenance: When safety systems are shut- down, what backup systems or procedures are available to provide replacement protection (e.g. stop process until safety systems are available again)? If shut-off valves can isolate safety relief valves, what measures ensure that the system is protected from overpressurization? What system is in place to ensure that maintenance of critical safety features are corrected immediately? What ensures that less critical features are corrected within a reasonable period?

Pressure vessels also need periodic inspection and testing because of normal wear and potential corrosion either at welds or in the base material. The combination of pressure and volume determine the hazard: high volume, low pressure systems can have the same potential energy for release as low volume, high pressure systems.

When potentially corrosive chemicals are used (e.g. acids, caustics), or the plant atmosphere is corrosive (e.g. near the ocean, or from chemical releases within the plant), what measures are taken to ensure system integrity? Examples include periodic pressure testing, X-ray, etc.

General containment and controls: During normal operations it is difficult to keep material completely in a closed system. Vacuum must be relieved when a liquid level drops, and pressure must be relieved when the tank is refilled. For toxic, flammable, and reactive chemicals, the questions to be asked focus on minimizing such necessary releases and rendering the released chemicals harmless before discharge to the atmosphere. Examples of questions to be pursued include: Where do emergency relief vents discharge? Are they piped to scrubbers, neutralizers, incinerators, precipitators, etc., to remove hazardous materials? What precautions are taken to minimize spills when connections are broken? Is the line purged prior to disconnection? Are purge gases treated? Are quick disconnects used? Do employees wear personal protective equipment (PPE) when disconnecting? Is there a dike or some method to collect and contain small spills or releases? Is the area ventilated and is ventilated air treated?

Material handling: As long as chemicals are maintained in a closed system, they are safe and harmless. The potential problems are: introduction of raw material into the closed system and the removal of products from the closed systems. The questions involved in material handling relate to receiving, shipping, and transferring materials in a closed system, the organizations involved in such transfers, any pressurization or blanketing involved, any interchange of critical systems such as potable water by process water, incompatible reactive materials, and the like, disposal of unwanted materials, properly directed venting, flaring, scrubbing, lining of drains, treatment, provisions to segregate drains for incompatible wastes, and the like.

Instrumentation: Suitable controls and instruments should be provided for both normal conditions of operation and for emergencies. Instrumentation includes sensors, indicators, recorders, and transmitters for measurements such as temperature, pressure, flow, liquid level, and analysis. Considerations should include alternative provisions for instrument failures such as arranging control valves going into safe positions on loss of instrument air or power, for emergency air or power supplies, use of corrosion resistant materials of construction of instruments and their housings, protection of instrument leads and control locations from exposure to fires and explosions, ease of inspection and maintenance, intrinsically safe designs for hazardous locations, and the like.

Piping systems: Piping and instrument diagrams are used to follow the formulation or reaction process and also to check safety devices and system protections. Questions that may be asked include overpressure protection to equipment, venting of materials from relief valves, level, temperature rise, leak, and spill detection, design of piping, valves and fittings as per codes and standards, carrying out NDT regularly, supports and fireproofing provisions, labeling shut-off valves and other critical devices, and the like.

Protective systems: Cooling may be necessary to prevent a runaway reaction in reaction vessels. Reactive chemicals also may be cooled in storage to provide more time to respond to an initiated reaction. The relevant questions include provisions, including backup for cooling or heating systems, incompatibility of cooling or heating systems with reaction materials, automatic actuation of refrigeration in emergencies, backup for power failures, explosion suppression systems and their maintenance, inerting provisions, submerging reactive materials in safe media, for example, sodium in kerosene, and the like.

Fired systems: Provisions include adequate draft, fuel controls, combustion safeguards, relief devices, emergency shut-off facilities, back-flow protection and the like.

Electrical equipment: Selection and installation should be according codes. Equipment must be properly bonded and grounded. Lightning protection should be provided and maintained.

Pressure vessels and storage tanks: Must be designed and fabricated according codes and relief, venting should be properly provided and maintained. Inerting vapor spaces should be considered and maintained.

Pumps and compressors: Failure of moving parts or packing glands can cause escape of flammable or toxic liquids or gases. Remotely controlled switches and shut-off valves are needed to control the flow of fuel in an emergency. Vibration should be minimized by properly securing and adequate foundations.

Response to emergencies: Written emergency plans and procedures should be in place and be made known to workers, managements and concerned organizations. Training and retraining should be considered to be an essential component of any emergency plan.

Control and coordination: Prior consideration/coordination of all potential response groups or agencies such that there will not be loss of control. Safe location(s) of emergency control centers should be part of plant layout. *Detailed discussion on emergency response is given elsewhere*.

Re-entry and clean-up: When evaluating plans for reentry and cleanup of an area which has been evacuated due to an emergency situation, the questions to be considered include environmental sampling, hazard assessment of the site and residual materials, decontamination, and the like.

Safety Audit

Safety audits are frequently made by both plant managements and outside expert organizations to ensure health of the plants.

Structure includes the following:

(i) Safety policy of the company
(ii) Safety information available with the company and its visibility to the employees and management personnel
(iii) Workplace practices
(iv) Management of change
(v) Maintenance practices within the facility
(vi) Frequency of training and re-training of personnel
(vii) Incident investigations
(viii) Regular plant inspections and reviews
(ix) Hazard analyses carried out at frequent intervals
(x) Emergency planning and responses
(xi) Contract worker awareness and safety
(xii) Whether site conforms generally to safe management of hazardous substances
(xiii) Maintenance of fire alarms and protection systems
(xiv) Security arrangements and drills o security personnel
(xv) Installation and maintenance of CCTVs at strategic places

(xvi) Only accredited consultancy agencies should be employed to carry out the audits

(xvii) Structure of the safety audit report:

Executive summary
Introduction
Overview
Assessment
Findings/recommendations

Certification by the audit team, including the lead auditor and other members of the team with their signatures and date.

The above are some of the measures involved under safety audits.

Review Questions

1. What are the preventive and protective measures for a safety program in a process plant? Describe and discuss.
2. (a) What is meant by inherent safety? Give examples.
   (b) What are the ways by which inherently safer plants can be built?
3. What are the advantages in using refrigerated storage in place of normal temperature storage?
4. What are the merits of fail-safe and fail-secure systems? What is the difference between the two?
5. What are the codes of practice used in determining safe distances between equipment in a plant layout? Illustrate.
6. Give examples of specific safety provisions in plant layout.
7. What is the concept of layers of protection? Give a suitable diagram to illustrate this concept.
8. What are the considerations involved in plant security measures?
9. Name the options available for preventing explosions in a process plant.
10. What are the materials/gases used in inerting a plant under fire? Compare their merits and demerits.
11. What is a distributed control system (DCS)? Where it is practiced?
12. (a) What are the different types of alarm systems used in a process plant?
    (b) What is the color codes used for distinguishing among different alarms?
13. What is flame-less venting? What are its advantages over normal venting?
14. What are NFPA guidelines for venting?
15. What are the commonly used explosion suppression agents? What are their relatives merits?
16. What are ROSOVs? Where and under what circumstances they are used?
17. What is fire-proofing? On what types equipment this is used? What are the commonly used fire-proofing materials?
18. Where are water deluge and water spray systems are employed? What are their functions according NFPA?
19. What are the general requirements and features of cryogenic storage vessels/equipment?

20. (a) Name the electrical codes of practice used in U.S. and Europe? What are the classes of hazardous locations? How are materials grouped for the purpose of electrical classification?
    (b) What are the differences between zone and division electrical classification systems?
21. What are the different electrical protective systems? What are their applications?
22. What is meant by explosion-proof equipment? What types of equipment require explosion-proof designs? Where do they find applications?
23. What are the different types of explosion-proof equipment used in chemical industry? Name and briefly state their applications.
24. (a) Give a definition for an explosion-proof enclosure.
    (b) What are the different techniques used in various types of explosion-proof equipment?
25. (a) What are the requirements that are to be satisfied by an explosion-proof enclosure?
    (b) What is the difference between explosion-proof and flame-proof enclosures?
    (c) Is it permissible to use normal lighting systems in areas likely to have leakages of flammable vapors from equipment inside buildings? If not, what alternatives do you suggest?
26. Is an explosion-proof enclosure universal in design or it depends on the nature of flammable materials processed in the area? Explain.
27. What are the criteria that must be satisfied by electric motors and generators installed in Class I, Division I locations that involve flammable atmospheres?
28. What are the different types of electrical enclosures used in hazardous areas in chemical and petroleum plants?
29. (a) What is meant by intrinsic safety? State the principle involved in intrinsic safety?
    (b) What types of electrical enclosures use intrinsic safety?
30. Is explosion-proof housing required for instruments used in hazardous locations? What type of safety is built into instrument circuits?
31. What types of safety is used to prevent flames and fires in electrical instruments? Give reasons.
32. What is the difference between purged and pressurized enclosures? State their applications.
33. (a) What are the considerations involved in the selection of purged equipment?
    (b) Under what circumstances inert gas purging is used in process equipment in hazardous locations?
34. (a) How are hazardous areas classified for the purpose of locating different types of electrical equipment?
    (b) Describe such a classification system.
35. What are the hazards involved and procedures and precautions adopted in confined space entry?
36. What is permit-to work system? Where it is necessary? How is it operated?
36. What are lock-out and tag-out procedures? Where these are necessary and employed?
37. Name different types of personnel protective systems used in process industry.
38. What are the essential measures to be attended during plant modifications and management changes?

39. What is meant by industrial hygiene? What are the elements involved in industrial hygiene?
40. (a) What is the purpose of inerting?
    (b) What considerations are involved in determining inert gas requirements for making the vapor space of a vessel safe from ignition of flammables?
41. (a) What is the commonly used inert gas for inerting enclosed spaces? What is the other inerting gases or vapors used in some applications?
    (b) What are the precautions used in entry of personnel into inerted enclosures, such as storage tanks for petroleum products?
42. Discuss rupture discs used for pressure relief involving liquids, two phase flows and gases. Choice of discs and vent arrangements may be emphasized.
43. (a) What are the hazards associated with the handling of nitrogen gas used for inerting and purging of flammable atmospheres?
    (b) Name other gases and vapors that are used for inerting and purging purposes and compare their relative effectiveness and applications as inerting media.
44. What are the different purging methods used to initially reduce oxygen concentrations to safe levels? Name them.
45. (a) What are the advantages and disadvantages of vacuum and pressure purging systems for inerting?
    (b) State why vacuum purging is not suitable for large storage tanks?
46. Name the two methods for preventing flammable vapor concentrations in storage vessels. Compare them.
47. Describe the procedures for pressure and vacuum purging of tanks and vessels to maintain desired composition levels of oxygen in them.
48. What are siphon and sweep purging methods for inerting storage vessels?
49. (a) What is the significance of limiting oxygen concentration (LOC), and how will it be useful in determining inert gas requirements?
    (b) What are the safe levels below LOC to which inerting is normally carried out?

50 What is the use of flammability limits and flammability diagram for determining inerting requirements of a vessel? Explain.

51 What are the considerations involved in ventilation systems in process plant buildings?

52 Discuss open air installation vs. installation inside buildings for process equipment.

53 What are the differences between suction and pressure ventilation systems? Explain by means of examples.

54. What is meant by dilution ventilation? Compare dilution and local ventilation methods.
55. (a) Give the classification of flammable and combustible materials.
    (b) Why such a classification is required for determining ventilation requirements?
56. What is a sprinkler system? Give examples of applications of sprinkler systems in process industry.
57. What is the difference between sprinkler and deluge systems? Explain operation of sprinkler systems.
58. (a) What are the important functions of a sprinkler system?
    (b) What are closed head and open head sprinkler systems?

    What are their applications?

59. What are the damaging effects of using sprinkler systems in electronic and control room applications? What are the associated environmental problems?
60. What are the differences among safety valve, relief valve and safety relief valve? Explain.
61. (a) What are the various types of relief valves?
    (b) What are their features and applications?
62. Define the terms *set pressure*, *overpressure*, *accumulation, blow-down*, *back pressure*, design pressure and *maximum allowable working pressure (MAWP)*.
63. (a) What is relieving pressure?
    (b) What are the code requirements for installation of pressure relieving devices on a vessel?
64. (a) What type of valve is used on domestic pressure cookers and steam boilers?
    (b) What are the hazards involved in domestic pressure cookers when the water dries up in the cooker? Any remedy is incorporated in its design to prevent explosion of the cooker?
65. (a) Is it desirable/permissible to allow the contents of a vessel discharged to the atmosphere on pressure relief?
    (b) What types of hazards are associated with releases directly to the atmosphere and name the preventive or treatment techniques used for objectionable releases?
    (c) What types of contents can be released directly to the atmosphere? Give examples.
66. What is a pilot-operated relief valve? What are its special features? State its applications.
67. (a) What are the reasons for the requirement of pressure relief systems?
    (b) Illustrate pressure vs. time curve for a runaway reaction.
68. What are the various systems/equipment that require pressure reliefs? Give reasons.
69. What are the events that necessitate pressure relief?
70. What are the considerations involved in locating pressure reliefs? Give examples.
71. What are the considerations involved in locating pressure reliefs? Give examples.
72. How are relief devices specified for different types of applications? Name typical applications.
73. (a) Name some closed containment systems into which discharges from relief valves are directed for subsequent handling.
    (b) What are the applications of a safety valve, relief valve and safety relief valve?
74. (a) Illustrate by means of a flow diagram a relief containment system for a reactor showing relief device and a blow-down system.
    (b) What is the purpose of the blow-down/knockout drum?
75. What type of relief system is normally recommended for relieving a polymerization reactor? Give reasons.
76. What are the data requirements for sizing relief systems? Discuss.
77. (a) Is it permissible to install a stop valve on the inlet side of a relief valve? What are the consequences of such an arrangement?
    (b) What constitutes a relief system? Illustrate.
78. (a) What is a rupture disc?
    (b) What are the different types of rupture discs?
79. What types of materials can be (a) vented to the atmosphere and (b) materials that are not permitted for venting to the atmosphere? Give reasons.

80. (a) What are the primary and secondary requirements for the use of pressure relief devices on pressure systems as per codes of practice?
    (b) In what ways consideration of Maximum allowable working pressure (MAWP) is required for determining the set pressures for relief devices?
81. Can we use relief valves and rupture discs for protection against explosions and detonations? Discuss.
82. What caused Bhopal tragedy? Briefly discuss.
83. (a) What is a flare system? What is its use and where is it used?
    (b) Why is it necessary to install a knockout drum between pressure relief devices and the flare?
    (c) What is the purpose of the blow-down/knockout drum?
84. (a) What are the considerations involved in deciding whether a particular equipment or component requires over-pressure protection?
    (b) What are the ways by which releases from relief devices are disposed of.
85. How are toxic releases handled in a relief system? What are the different ways of disposal of such releases?
86. What type of pump requires a pressure relief valve on its discharge side? Explain by means of a diagram.
87. Illustrate safe installation practices for pressure relief devices by means of a logic diagram, giving the steps involved.
88. (a) What happens if a line fails, for example, a failure of a high-pressure gas line into a low pressure vessel?
    (b) What is the consequence of closing valves (block valves) on vessels or in lines that are filled with liquids and exposed to heat or refrigeration?
89. Give the guidelines for specifying relief positions, stating the equipment types, lines, pumps, and other components that require reliefs.
90. What conditions cause runaway reactions, and how are relief systems designed to handle the discharges as a result of runaway reactions?
91. What types of data are required in designing relief systems? Give details.
92. How does pressure drop in a disposal system, installed after a relief valve, affect relief valve sizing?
93. Discuss containment vs. pressure relief for a pressure system.
94. “Sometimes isolation valves become unavoidable between a vessel and relief valve”. What are the plant management steps required to avoid accidents in such situations?
95. When do relief valves have to be rated for simultaneous fire situations?
96. How are toxic releases handled in a relief system? What are the different ways of disposal of such releases?
97. Discuss containment vs. pressure relief for a pressure system.
98. (a) What happens if a line fails, for example, a failure of a high-pressure gas line into a low pressure vessel?
99. What is the consequence of closing valves (block valves) on vessels or in lines that are filled with liquids and exposed to heat or refrigeration?
100. Illustrate safe installation practices for pressure relief devices by means of a logic diagram, giving the steps involved.

101. What conditions cause runaway reactions, and how are relief systems designed to handle the discharges as a result of runaway reactions?
102. "Sometimes isolation valves become unavoidable between a vessel and relief valve". What are the plant management steps required to avoid accidents in such situations?
103. (a) Which of the two, a relief valve or rupture disc, is fast acting in relieving overpressures developed in a vessel?
    (b) What are the advantages of installing a rupture disc upstream of a relief valve? Illustrate
104. Give a sketch of a spring-operated relief valve showing the essential parts.
105. (a) What is the effect of back pressure on the operation of a relief valve?
    (b) What are the differences with respect to back pressure on the operation of spring operated and balanced pressure relief valves?
106. What are the advantages and disadvantages in using rupture discs alone as relief devices?
107. What type of relief device is normally specified for each of the following applications? Give reasons for your choice.
    (a) Corrosive service
    (b) Services involving slurries
    (c) Liquid service
    (d) Gas service
108. What are the basic variables involved in sizing relief devices for the discharge of liquids?
109. Under what type(s) of situations rupture disc–relief valve combinations are provided in series and parallel arrangements on tanks and vessels? Illustrate by means of line diagrams.
110. What is explosion venting? Where is it used?
111. What is an explosion suppression system? Under what circumstances it is used in place of pressure relieving devices?
112. (a) What type of relief device is used for vessels handling viscous liquids? Give reasons.
    (b) Show, by means of a line diagram, how a rupture disc is installed on a vessel.
113. What is clatter in relief valves? Under what circumstances clatter occurs? What are its effects on the performance of a relief valve?
114. (a) Estimate wetted surface area for a horizontal cylindrical vessel with a diameter of 2 meters and a length-to-diameter ratio of 3. The vessel is half-full. Assume that the vessel has flat ends.
    (b) Where such a calculation is useful from safety point of view?
115. How is wetted surface useful in the estimation of vaporization rates on fire exposure?
116. In the installation of a relief valve for atmospheric discharge, is it permissible to have the following?
    (a) Long outlet vent piping
    (b) Reduced size inlet piping
    (c) Discharge piping pointing downwards, ostensibly, for weather protection. What is the alternative way of doing it?
117. What are rupture panels? Where are they used? Discuss the materials used in making them.

118. What is a rupture pin? What is the principle of its operation?

    Compare rupture discs and rupture pins in their applications.

119. (a) What is a flame arrester? What is the principle involved in its operation?
    (b) What are the different types of flame arresters?

Key words for Internet searches

ASME Codes for installation of relief systems
API guidelines for recommended safe distances among refinery equipment.
OSHA Websites for industrial hygiene, confined space entry
NEC and CENELEC codes for electrical systems
Websites of rupture disc manufacturers such as Fike and others referred with the figures.

*Note: *Vast number of sites is given in Appendix A of the book for the purpose of use in Internet searches for key words by enterprising teachers, students, industry professionals, and managements*.

Appendix A

Glossary of Terms, Definitions, Abbreviations, and Acronyms

ACC	*American Chemistry Council*
Accelerating rate calorimetry (ARC)	It is a technique in which a substance is heated in stages until very slow decomposition (or other reaction) is detected. The substance is then held under adiabatic conditions and the course of the decomposition (or other reaction) is monitored.
Acceptable risk	It is a risk for which, for the purposes of life or work, one is prepared to accept.
Accident	This is an unplanned event or sequence of events that results in undesirable consequences, such as ill health, damage to the environment, or damage to property.
Accumulation	This is the rise of pressure above the maximum allowable working pressure (MAWP) of the protected system, usually expressed as a percentage of the gage MAWP. A pressure increase over the set pressure of a pressure relief valve, expressed as a percentage of the set pressure.
ACGIH	American Conference of Governmental Industrial Hygienists, which develops and publishes recommended occupational exposure limits for hundreds of chemical substances and physical agents.
Acid	It is any chemical with a low pH in water solution can cause burns of skin or eyes and which undergoes dissociation in water with the formation of hydrogen ions. Acids turn litmus paper red and have pH values of 0–6.
ACIS	Automated Chemical Inventory System
ACS	American Chemical Society
Action level	This is the term used by OSHA and NIOSH to express the level of toxicant that requires medical surveillance, usually one half of the PEL.
Activation energy	It is the energy that must be overcome in order for a chemical reaction to occur. It is the minimum energy required to start a chemical reaction.
Actuator	It is a device that applies the force (torque) necessary to cause closure member of a valve to move.
Acute effect	It is the adverse health effect on a human or animal that occurs soon after a brief exposure to the offending agent.

Adiabatic calorimetry	This is a chemical testing technique that determines self-heating rate and pressure data of a chemical under near adiabatic conditions. This technique conservatively estimates the conditions for, and consequences of a runaway reaction.
Adiabatic decomposition temperature rise	An estimation of the computed temperature that a specimen would attain if all of the enthalpy (heat) of decomposition reaction were to be absorbed by the sample itself. High values represent high hazard potential.
Adiabatic flame temperature	For a combustion process that takes place adiabatically with no shaft work, the temperature of the products is referred to as the adiabatic flame temperature. This is the maximum temperature that can be achieved for given reactants.
Adsorption	To collect gas or liquid molecules on the surface of another material
Aerobic	Operating in the presence of oxygen
Aerosol	It is a collection of very small particles (dust/spray/mist/fog/fume), in the size range of 0.001–100 μm, suspended in air.
AIChE	American Institute of Chemical Engineers.
AIHA	American Industrial Hygiene Association.
ALARA	It stands for as low as reasonably achievable.
ALARP	It means as low as reasonably practicable. The philosophy of dealing with risks that fall between an upper and lower extreme. The upper extreme is where the risk is so great that it is rejected completely, whereas the lower extreme is where the risk is, or has been made to be, insignificant. This philosophy considers both the costs and benefits of risk reduction to make the risk *as low as reasonably practicable*.
Alert	It represents events that involve an actual or potential substantial reduction in the level of facility safety and protection.
Allergy	It is an abnormal response of a hypersensitive person to chemical and physical stimuli. Allergic manifestations of major importance occur in about 10 percent of the population.
Anaerobic	This means operating in the absence of oxygen.
Anhydrous	It is a substance in which no water molecules are present as hydrate or as water of crystallization.
Anoxia	It is the deficient supply of oxygen to tissues. Simple anoxia may be caused by inert gases. Toxic anoxia may be caused by certain substances like CO and HCN, which interfere with the ability of the body to transfer or utilize oxygen in the tissues. Rapid unconsciousness and death can occur in either case.
ANSI	It stands for American National Standards Institute, a voluntary membership organization (run with private funding) that develops consensus standards nationally for a wide variety of devices and procedures.

(*Continued*)

Antistatic material	It is one with an electrical resistivity that is low enough to make it incapable of accumulating hazardous concentrations of static charges when grounded.
APELL	It stands for awareness and preparedness for emergencies at local level (UNEP)
API	American Petroleum Institute
Approved	Approved by a recognized body
Aqueous	Water-based solution or suspension
ARC	Accelerating rate calorimeter
Arcing device	It is a device, such as make/break component, that under normal conditions produces an arc with energy sufficient to cause ignition of an ignitable mixture.
ARIP	Accidental release information program (EPA)
Asbestosis	It is chronic lung disease caused by inhaling airborne asbestos fibers.
ASME	American Society of Mechanical Engineers
Asphyxia	It is the result of diminished supply of oxygen to the blood and tissues and interference with the respiration function
Asphyxiant	Vapor or gas that causes unconsciousness or death by suffocation (lack of oxygen). Asphyxiation is one of the principal potential hazards of working in confined spaces.
ASSE	American Society of Safety Engineers
ASTM	American Society of Testing Materials
Asymptomatic	Neither causing nor exhibiting symptoms
ATSDR	Agency for Toxic Substances and Disease Registry
Back pressure	Pressure existing at the outlet of a relief device. The value under no-flow conditions is *superimposed* back pressure. The value under flowing conditions consists of both superimposed back pressure and built-up pressure due to piping pressure drop. Total back pressure is the sum of superimposed and built-up back pressures.
Balanced bellows safety relief valve	A balanced bellows safety relief valve is a spring-loaded relief valve that incorporates means for minimizing the effect of back pressure on the performance characteristics—opening pressure, closing pressure, lift, and relieving capacity. This is usually achieved by the installation of a bellows or other means.
Barricade/Barrier wall	An intervening approved barrier, natural or artificial, of such type, size, and construction as to limit in a prescribed manner the effect of an explosion on nearby structures or personnel. Desirable in cases involving explosives. Care must be taken such that these do not impede fire fighting by limiting access.

Battery limits	It is that portion of a chemical plant in which the actual processes are carried out, as distinguished from storage, buildings, offices and other structures.
BEI	Biological exposure index
Biodegradable	Organic material's capacity for decomposition from attack by microorganisms
Biohazard	Infective agents presenting a risk of death, injury, or illness to people
Blanketing	It is an inerting method used to provide a continuously maintained atmosphere that is either inert or fuel rich in the vapor space of a container or vessel.
Blast	Potentially damaging pressure or shock wave produced by an explosion. A transient change in gas density, pressure (both positive and negative), and velocity of the air surrounding an explosion point.
Blast wave	The air wave set in motion by an explosion. The term *blast wave* includes both sonic compression waves, shock waves, and rarefaction waves.
Blending	Mixing or homogenization of liquid or solid materials
BLEVE	Boiling liquid expanding vapor explosion: An explosion due to flashing of liquids when a vessel with a high vapor pressure substance fails. If the substance released is a fuel, the BLEVE can result in very large fire balls. Rocketing vessels are also hazards related to BLEVEs.
Blowdown	The disposal of voluntary discharges of liquids or condensable vapors from process and vessel drain valves, thermal relief or pressure relief valves. Removal of liquids or solids from a process vessel or storage vessel or a line by the use of pressure. The difference between the set pressure and the closing pressure of a pressure relief valve, expressed either as a percentage of the set pressure, or in pressure units.
BMP	Best management practice
BMS	Burner management system
Bonding	It is a safety practice where two objects are interconnected with clamps and bare wire to equalize electrical potential between the objects and help prevent static sparks that could ignite flammable materials.
Breakdown voltage	The minimum voltage at which loss of insulating properties of a medium, gas, liquid, or solid occurs in a given situation.
Brush discharge	Electrostatic discharges involve multiple brush-like discharge channels under low light conditions. In this type of discharge, the charge on an insulating surface cannot form a singular discharge channel unlike in the case of spark discharge. Maximum effective energy in brush discharges is about 4 mJ.

(*Continued*)

(Continued)

Buffer	It is a substance that reduces the change in hydrogen ion concentration (pH) that otherwise would be produced by adding acids or bases to a solution.
Built-up back pressure	This is the increase in pressure in the discharge header that develops as a result of flow after the relief device opens.
Burning rate	It is the amount of fuel consumed by the combustion process per unit time. It may also be defined as mass of fuel consumed per unit time and volume.
Burning velocity	Velocity of a laminar flame front with respect to the stationary mixture of unburnt gas immediately ahead of the flame. In hydrocarbon fuels mixed with air, burning velocities are typically less than 0.5 m/s. Burning velocity is a function of the concentration of the fuel, temperature, and pressure of the mixture.
CAAA	Clean Air Act Amendments of 1990
CAER	Community Awareness and Emergency Response
CAMEO	Computer-Aided Management of Emergency Operations
Capacitance	Any object or surface that can accumulate electrical charge can be thought of as a capacitor. Capacitance is often expressed in pico-farads
Carcinogen	It is a substance or agent that is capable of causing or producing cancer
CAS identification number	This is the number assigned to each unique chemical entity by the chemical abstracts service of ACS
Catalyst	This is a substance which, when present in a very small amount, increases the rate at which two or more chemicals react together.
Catastrophic release	This is a major uncontrollable emission, fire, or explosion, involving one or more highly hazardous chemicals that present serious danger to employees in the work place or the public.
Cause consequence	This is a procedure used to illustrate the Cause—Consequence a particular scenario, for example, an accident by means of diagrams.
Cause-and-effects diagram	This is one of the commonly used methods to show the relationship between the sensor inputs to a safety function and the required outputs. Often used as part of a safety requirements specification.
CCPS	Center for Chemical Process Safety, AIChE.
CDCIR	Community Documentation Center on Industrial Risk.
Ceiling value (CV)	It is the ceiling toxic exposure concentration limit that should never be exceeded in the breathing zone.
Cellular flame	It is a flame with a wrinkled surface due to instabilities caused by gas expansion during combustion and the combined effects of thermal and species diffusion.

CENELEC	European Committee for Electrotechnical Standardization
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act of 1980. It is commonly known as "Superfund" (U.S. EPA).
Certified equipment	This is an equipement that has been evaluated by a recognized testing agency and confirmed to be in compliance with the applicable standard(s).
CFCs	It stands for chlorofluorocarbons that are considered to be harmful to the environment.
CFR	Code of Federal Regulations
CFT	Cool flame reaction threshold
Chapman–Jouguet velocity	This is the velocity that an ideal detonation travels at as determined by the Chapman-Jouguet (CJ) condition: the burned gas at the end of the reaction zone travel at velocity of sound relative to the detonation wave front. CJ velocities can be computed numerically by solving for thermodynamic equilibrium and satisfying mass, momentum, and energy conservation for a steadily propagating wave terminating in a sonic point. CJ velocities in typical fuel–air mixtures are between 1400 and 1800 m/s.
Charge decay	It is the migration of charge across the surface or through a material leading to a reduction of surface potential at the area where the charge was deposited (relaxation).
Chatter	It is the abnormal rapid reciprocating motion of the movable parts of a pressure relief valve in which the disc contacts the seat.
Checklists	Checklists are simple means of applying experience to designs or situations to ensure that the features appearing in the list are not overlooked.
Chemical cartridge	Respirator using chemical substances to purify air being inhaled.
Chemical exposure index	This index provides a method of rating the relative potential of acute health hazard to people from possible chemical release incidents.
Chemical hygiene	It is a written plan that includes specific work practices, standard plan (CHIP) operating procedures, equipment, engineering controls, and policies to ensure that employees are protected from hazardous exposure levels to all potentially hazardous chemicals in use in their work areas. The plan, includes training, employee access to information, medical consultations, examinations, hazard identification procedures, respirator use, and record keeping practices.
Chemical incompatibility	It is a type of reactivity that occurs when a chemical is mixed or comes in contact with other chemicals, or process materials resulting in an uncontrolled and often violent reaction.

Chemical name	It is the scientific name that clearly identifies a chemical for hazard evaluation purposes.
Chemical protective clothing	Clothing, hood, boots, and gloves made from chemical-resistant materials to protect the wearer from hazardous materials.
Chemical reactivity	It is the ability of a material to chemically change. Undesirable and dangerous effects, such as heat, explosions, or the production of noxious substances, can result.
Chemical reactivity hazard	This is a situation with the potential for an uncontrolled chemical reaction that can result directly or indirectly in serious harm to people, property or the environment. The uncontrolled chemical reaction might be accompanied by a temperature increase, pressure increase, gas evolution or other form of energy release.
CHEMTREC	Chemical Transportation Emergency Center. Public service of the chemical manufacturers association that provides immediate advice for those at the scene of hazardous materials emergencies.
CHETAH	Chemical thermodynamic and energy release evaluation
CHIP	Chemicals (Hazard information and packaging) regulations
CHRIS	Chemical hazards response information system
Chronic effect	It is the adverse effect on a human or animal body with symptoms that develop slowly over a long period of time or that recur frequently.
CIMAH	Control of industrial major accident hazards
CIRC	Chemical Incidents Report Center (CSB).
Class A fire	Class A fire involves solids, normally organic, in which combustion generally occurs with the formation of embers.
Class B fire	Class B fire involves liquids or liquefiable solids.
Class C fire	Class C fire involves gases or liquefied gases.
Class D fire	Class D fire involves metals.
Classified area	It is any area that is electrically classified following the guidelines of a nationally or internationally recognized electrical code.
Clean-up operations	There are operations where hazardous substances are removed, contained, incinerated, neutralized, stabilized, cleared-up, or in any other manner processed or handled with the ultimate goal of making the site safer for people and the environment.
Closed container	It is a container so sealed that no vapors will escape from it at normal temperatures.
Code of practice	It is an international term referring to a document that describes basic safety features and methods of protection and

(Continued)

	recommends the selection, installation and maintenance procedures that should be followed to ensure the safe use of electrical apparatus.
COMAH	Control of Major Accident Hazards Involving Dangerous Substances
Combustible dust	Combustible dust when mixed with air in certain proportions can be ignited and will propagate a flame. The combustible properties of dust are dependent upon test conditions and dust particle size, chemical structure, and other particle characteristics.
Combustible dust layer	This is any surface accumulation of combustible dust that is thick enough to propagate flame or will degrade and ignite.
Combustible liquid	This is a term used by NFPA and DOT to classify certain liquids that will burn, on the basis of flash points and is defined as any liquid that has a flash point of 37.8°C (100°F) or higher.
Combustion	It is the burning of gas, liquid, or solid in which fuel is oxidized; involves heat release and often light emission. Combustion process results in increased temperature due to the transformation of chemically bound energy into heat. Products from complete combustion of a hydrocarbon fuel, for example, are mainly CO_2 and H_2O (vapor).
Common name	It is the designation for material other than chemical name, such as code, trade, brand, or generic name.
Compatibility	It is the chemical property of materials to coexist without adverse reaction for an acceptable period of time. Compatibility in storage exists when storing materials together does not increase the probability of an accident or, for a given quantity, the magnitude of the effects of such an accident.
Compressed gas	This is the material contained under pressure (dissolved gas, liquefied by compression, or refrigeration).
Condensed phase explosion	This is an explosion that occurs in the solid or liquid phase.
Conductive	It means having a conductivity greater than 10^4 pS/m or a resistivity less than 10^8 W-m.
Confined gas explosion	Explosion within tanks, process equipment, pipes, in culverts, sewage systems, closed rooms, underground installations, etc.
Confined space	This is a space that has limited openings for entry and exit and has poor natural ventilation. It is an enclosure with known potential hazards and restricted means of entrance and exit. It is not meant for normal occupancy of people and is usually not well ventilated such as vessels, boilers, storage tanks, large diameter piping, etc. The excavation more than 1.2 m deep, entry into floating roof tanks, when roof is more than 3 m down from the top, space located below ground level such as pits, drain channels etc shall also be considered as confined space.

Confinement area	This is an area having structures or systems from which releases of hazardous materials are controlled. The primary confinement systems are the process enclosures (glove boxes, conveyors, transfer boxes, and other spaces normally containing hazardous materials), which are surrounded by one or more secondary confinement areas.
Consequence	This is the direct, undesirable result of an accident, usually measured in health and safety effects, loss of property, or business costs, or a measure of the expected effects of an incident outcome case.
Contact electrification	*See Tribo-electrification*
Container	It is any bag, barrel, bottle, box, can, cylinder, drum, reaction vessel, storage tank, or the like that contains a hazardous chemical. Under hazard communication rules, pipes or piping systems, and engines, fuel tanks, or other operating systems in a vehicle are not considered to be containers.
Contamination	This is a release of hazardous material from its source to people, animals, the environment or equipment.
Contingency	It is an abnormal event which is the cause of an emergency condition.
Conventional pressure relief valve	This is a spring-loaded pressure relief valve whose performance characteristics are directly affected by changes in the back pressure on the valve.
Cool flame ignition	This is a relatively slow, self-sustaining, barely luminous gas phase reaction of the sample or its decomposition products with an oxidant. Cool flames are visible only in a darkened area.
Corona discharge	Corona discharge is a self-sustained low energy electrical discharge with non-thermal ionization that takes place in the vicinity of an electrode of sufficiently low radius of curvature, in a medium whose pressure is typically close to atmospheric. It may be accompanied by a hissing noise that increases with current and may be observed as a pinpoint of bluish light at the electrode in darkened surroundings.
Corrosion rate	This is expressed in mm or inches per year.
Corrosive	A chemical that causes visible destruction of, or irreversible alterations in, living tissue by chemical action at the site of contact or causes metals or plastics to corrode at a rapid rate.
COSHH	Control of Substances Hazardous to Health Regulations 2002
CPI	Chemical and Process Industry
CPQRA	Chemical process quantitative risk analysis
Critical mass	It is the minimum mass required to enable the occurrence of an explosion.
Cryogenic liquids	Gases that are handled in liquid form at relatively low pressures and extremely low temperatures, usually below −90°C
CSB	U.S. Chemical Safety and Hazard Investigation Board

Cutaneous	Pertaining to or affecting the skin
DCS	Distributed control system
Decision table	A table of all contingencies that are to be considered in the description of a problem, together with the actions to be taken. Decision tables can be used in place of flow charts for problem description and documentation.
Decomposition	Chemical reaction that leads to breakdown of a chemical into smaller molecules or elements, often with liberation of energy and product gases.
Decomposition energy	The maximum amount of energy which can be released upon decomposition. The product of decomposition energy and total mass is an important parameter for determining the effects of a sudden energy release, for example, in an explosion. The decomposition energy can occasionally be obtained from the literature or calculated theoretically.
Decomposition temperature	Temperature at which spontaneous decomposition occurs. In practice, it is impossible to indicate the exact value of this temperature, because the reaction rate is only zero at absolute zero temperature (0 K) conforming to the equation of Arrhenius. Therefore, in measuring the decomposition temperature both sample quantity and sensitivity of the measuring device are very important.
Decontamination	The removal of a hazardous material, chemical, biological, or radiological contaminant, or neutralizing its potential effect on, a person, object or environment by washing, chemical action, mechanical cleaning, or other techniques.
Deflagration	A rapid chemical reaction in which the output of heat is sufficient to enable the reaction to proceed and be accelerated without input of heat from another source. Deflagration is a surface phenomenon, with the reaction products flowing away from the un-reacted material along the surface at subsonic velocity. The effect of a true deflagration under confinement is an explosion. Confinement of the reaction increases pressure, rate of reaction and temperature, and may cause transition into a detonation. Flame speed relative to the unburned gas is typically 10–100 m/s and pressure rise is typically in the range 8–12 times the initial pressure.
Deflagration to detonation	In certain circumstances, a flame may transition (DDT) accelerate to high velocities (>1000 m/s) and suddenly become a detonation instead of a deflagration. The circumstances involve a sufficiently sensitive mixture (very rapid chemical reaction) in a geometrical configuration that is favorable to flame acceleration—this usually requires confinement obstructions or obstacles in the path of the flame. Such mixtures are characterized by a small detonation cell width, high flame velocity and high volume expansion ratio.

(*Continued*)

(Continued)

Deluge	The immediate release of a commodity, usually referring to a water spray release for fire suppression purposes.
Depressurization	The release of unwanted gas pressure from a vessel or piping system to an effective disposal system.
Dermatitis	Inflammation of the skin from any cause.
Dermatosis	A broader term than dermatitis and includes any cutaneous abnormality, thus encompassing folliculitis, acne, pigmentary changes, and nodules and tumors.
Design basis	The design inputs, design constraints, and design analysis and calculations. It includes areas such as seismic, fire protection, and overall safety considerations.
Design pressure	It is the maximum allowable working pressure permitted under the rules of the relevant construction code.
Detonation	A violent chemical reaction within a chemical compound or mechanical mixture evolving heat and pressure. A detonation is a reaction that proceeds through the reacted material toward the un-reacted material at a supersonic velocity. The shock compression heats the gas and triggers the combustion. Extremely high pressures are developed on the surrounding medium, forming a propagating shock wave. For hydrocarbon fuel–air mixtures at ambient pressure the detonation velocity can be up to 2000 m/s and the maximum pressures produced are close to 20 bar. The ideal detonation velocity, known as the *Chapman–Jouguet velocity*, is a function of the reactant composition, initial temperature and pressure.
Detonation cell width	This is the characteristic width of the cellular pattern that is created by the instabilities that plague all propagating gaseous detonation waves. The cell width is measured by a sooted sheet or foil of metal inserted inside a tube used for detonation experiments. Detonation cell widths are used to characterize the sensitivity or susceptibility of a mixture to detonation. Sensitive mixtures (acetylene-oxygen) have cell sizes less than 1 mm; insensitive mixtures (methane-air or any lean hydrocarbon–air mixture) can have cell sizes of up to 1 m.
Deviation	Departure from design and operating intention.
Dielectric constant	The term *dielectric* is typically used to describe materials with a high polarizability. The latter is expressed by a number called dielectric constant. A common, yet notable example of a dielectric is the electrically insulating material between the metallic plates of a capacitor.
Dielectric liquids	Dielectric liquid is a dielectric material in liquid state. Its main purpose is to prevent or rapidly quench electric discharges. Dielectric liquids are used as electrical insulators in high voltage applications, for example, transformers, capacitors, high voltage cables, and switchgear (namely high-voltage switchgear). Its function is to provide electrical insulation, suppress corona and arcing, and to serve as a coolant.

DIERS	Design Institute for Emergency Relief Systems; Institute under auspices of the American Institute of Chemical Engineers founded to investigate design requirements for vent lines in the case of two phase venting.
Differential scanning calorimetry (DSC)	Chemical testing technique that is used to establish approximate temperature ranges in which a material undergoes an exothermic decomposition and determines the energy output of those reactions; also used for endothermic processes such as melting.
Differential thermal analysis (DTA)	Chemical testing technique that produces similar data to DSC. DTA uses temperature differences to generate test results. DSC has largely replaced the DTA technique as a screening tool to obtain chemical hazard test data.
Diffusion	Diffusion describes the spread of molecullar species/particles through random motion from regions of higher concentration to regions of lower concentration.
Diffusion flame	A diffusion flame is a flame in which the oxidizer combines with the fuel by diffusion. As a result, the flame speed is limited by the rate of diffusion.
Dike	It is a barrier constructed to hold back a spill or leak spreading to other parts of plant.
DIN	Abbreviation for the Standards Institution of the Federal Republic of Germany
DOE	U.S. Department of Energy.
DOL	Department of labor; U.S. OSHA and MSHA are part of the DOL.
Domino effect	An incident that starts in one piece of equipment and affects other nearby items, such as vessels containing hazardous materials, by thermal blast or fragment impact. This can lead to escalation of consequences or frequency of occurrence. Also known as a knock-on effect.
Dose-response assessment	The process of characterizing the relationship between the exposure to an agent and the incidence of an adverse health effect in exposed populations.
DOT	Department of Transportation, U.S.
Dry chemical	Powdered fire extinguishing agent, usually composed of sodium bicarbonate or potassium bicarbonate.
DSC	Differential scanning calorimetry
DSEAR	Dangerous substances and explosive atmospheres regulations (HSE).
DTA	Differential thermal analysis

Dust-ignition proof	A term used to describe an enclosure that will exclude ignitable amounts of dusts that might affect performance or rating and that, when installed and protected in accordance with the original design intent, will not permit arcs, sparks, or heat otherwise generated or liberated inside the enclosure to cause ignition of exterior accumulations or atmospheric suspensions of a specified dust.
Dust-protected enclosure	An international term describing an enclosure in which the ingress of dust is not totally prevented, but dust does not enter in sufficient quantity to interfere with the safe operation of the equipment or accumulate in a position within the enclosure where it is possible to cause an ignition hazard.
Dust-tight	An enclosure so constructed that dust will not enter the enclosing case under specified test conditions.
Dynamic pressure	The pressure increase that a moving fluid would experience if it was brought to rest by isentropic flow against a pressure gradient.
EBV	Emergency isolation block valve
EC	European Community
Ecotoxics	Substances that present immediate risk to environment
Eddy current	Eddy currents are currents induced in conductors to oppose the change in flux that generated them. It is caused when a conductor is exposed to a changing magnetic field due to relative motion of the field source and conductor; or due to variations of the field with time.
Eddy diffusion	Any diffusion process by which substances are mixed in the atmosphere or in any fluid system due to eddy motion. In another way to define, it is mixing that is caused by eddies that can vary in size from the small Kolmogorov micro scales to sub tropical gyres.
Effective discharge area	A nominal area or computed area of flow through a pressure relief valve, differing from the actual discharge area, for use in recognized flow formulas with coefficient factors to determine the capacity of a pressure relief valve.
EHS	Extremely hazardous substance; environmental health and safety.
EINECS	European Inventory of Existing Commercial Chemical Substances.
EIS	Environmental impact statement
EIV	Emergency isolation valve
Electric arc	Results when two objects in contact, with electricity is flowing, are separated, for example, opening of switches. It can occur over a wider gap than spark for the same charge.

Electrical discharge	A current flow that occurs when the electrical field strength exceeds the breakdown value in a medium such as air.
Electrical double layer	Mechanism by which liquids are believed to become electro-statically charged is known as double-layer charging. This can occur at liquid–solid and liquid–liquid interfaces. Ions of like polarity are adsorbed at such interfaces and attract ions of opposite polarity within the liquid, thereby forming a layer. This layer is thin for conducting liquids and more diffuse for non conducting liquids, due to reduced mobility.
Electric spark	Discharge of electric current across a gap between two charged objects when these objects are brought near enough to each other.
Electrochemical potential	It is a thermodynamic measure that combines the concepts of energy stored in the form of chemical potential and electrostatics. It is expressed in the unit of J/mol.
Electron work function	It is a measure of the work required to remove an electron from a surface during contact electrification. Negatively charged materials will have a higher electron work function than the positively charged ones.
Electrostatic induction	Modification in the distribution of electric charge on one material under the influence of a nearby second object that has an electric charge. Thus, because of the electric force between charged particles that constitute materials, a negatively charged object brought near an electrically neutral object induces a positive charge on the near side and a negative charge on the far side.
Emergency	An interruption from normal operation in which personnel or equipment is endangered. A dynamic incident in which there is a continuing potential for major injury, ill-health, or damage to property, the process or environment.
Emergency planning	Act of putting an overall plan and developing it for response to emergency situations.
Emergency power	It is designed to activate on loss of the normal power supply.
Emergency power systems	The auxiliary power systems that provide power to safety and security related equipment during periods of partial or total power failure of associated primary power system.
Emergency shutdown (ESD)	A method to rapidly cease the operation of the process and isolate it from incoming and going connections or flows to reduce the likelihood of an unwanted event from continuing or occurring.
Encapsulation	An international term describing a type of protection in which the parts that could ignite an explosive atmosphere by either sparking or heating are enclosed in an encapsulant in such a way that this explosive atmosphere cannot be ignited.
Endothermic reaction	A chemical reaction that absorbs heat

Engineering controls	systems that reduce potential hazards by isolating the worker from the hazard or by removing the hazard from the work environment. Methods include ventilation, isolation, and enclosure.
Environment	This includes water, air, and land and the interrelationship that exists among and between water, air, land, and all living things.
EPA	U.S. Environmental Protection Agency.
EPCRA	Emergency Planning and Community Right-To-Know Act (U.S.).
Equivalence ratio	Ratio of fuel to oxidizer divided by the same ratio at stoichiometric conditions
Ergonomics	Study of human characteristics for the appropriate design of living and work environments
ERPG	Emergency response planning guidelines by ACGIH are intended to provide estimates of chemical concentration ranges where one might reasonably anticipate observing adverse effects.
Escape	The uncontrolled departure of personnel from an emergency area.
ESD	Electro-static discharge; emergency shutdown
ES&H	Environment, safety, and health
ESV	Emergency shudown valve
Exotherm	Heat-releasing chemical reaction
Exothermic reaction	Chemical reaction that liberates heat
Expansion ratio	Ratio of burned gas volume to initial volume for a low speed (constant pressure) flame. Expansion is responsible for flame-induced flow.
Explosion	Sudden release of energy/pressure that causes a blast or shock wave; it may lead to personal injury or property damage.
Explosion proof enclosure	An enclosure that is capable of withstanding an explosion of a gas or vapor within it and of preventing the ignition of an explosive gas or vapor that may surround it and that operates at such an external temperature that a surrounding explosive gas or vapor will not be ignited thereby. In addition, such enclosures prevent ingress of flammable or explosive materials into them. This type of enclosure is similar to a flameproof enclosure.
Explosion proof equipment (apparatus)	Equipment or apparatus enclosed in an explosion-proof enclosure
Explosive	A chemical that causes a sudden, almost instantaneous release of pressure, gas and heat when subjected to sudden shock, pressure, or high temperature.

Exposure limit	Maximum concentration of a chemical in the workplace to which most people can be exposed without experiencing harmful effects
Extinguishing media	Fire extinguisher or extinguishing method appropriate for use on specific material
Extremely hazardous	(i) Those materials that are hazardous to the extent that they generally require special handling such as licensing and training of handlers, protective clothing, and special containers and storage.
	(ii) those materials that, because of their extreme flammability, toxicity, corrosivity, or other perilous qualities, could constitute an immediate danger to people.
EU	European Union
Evacuation	The planned and controlled removal of personnel from an emergency area
Evaporation rate	Rate at which a particular material will vaporize when compared to the rate of vaporization of a known material. Useful in evaluating health and fire hazards of a material.
Event	A particular occurrence that has the potential for causing an undesirable consequence or outcome
Event tree	An inductive process which seeks to identify the ultimate consequence of an initiating event and develops the possible sequences of the event that lead to a potential accident, while fault tree analysis aims to identify the basic causes of a specific event
FA	Fire alarm
Facility	The buildings, utilities, structures, containers, or equipment that contain a chemical process.
Fail-safe	A system design or condition such that the failure of a component, subsystem or system or input to it, will automatically revert to a predetermined safe static condition or a state of least critical consequence.
Failure	Loss by a system or system element of functional integrity to perform as intended
Failure mode	It is the action of a device or system to revert to a specified state upon failure of the utility power source that normally activates or controls the device or system. Failure modes are normally specified as fail open (FO), fail closed (FC), or fail steady (FS) that will result in a fail safe or fail to danger arrangement.
Failure mode and effects analysis (FMEA)	A hazard identification technique in which all known failure modes of components or features of a system are considered in turn and undesired outcomes are noted.

F&EI	Fire and explosion index (DOW)
Fatal accident rate (FAR)	The FAR is a single number index, which is the expected number of fatalities from a specific event based on 108 exposure hours.
Fault (as applicable to systems)	A defect or electrical breakdown of any intrinsically safe component, spacing, or insulation that alone or in combination with other defects or breakdowns may adversely affect the electrical or thermal characteristics of the intrinsically safe system. If a defect or breakdown leads to defects or breakdowns in other components, the primary and subsequent defects and breakdowns are considered to be a single fault. Certain components may be considered not subject to fault when analyses or tests for intrinsic safety are made. An abnormal, undesirable state of a system or system element induced by (i) presence of an improper or absence of a proper one or (ii) by a failure. All failures cause faults but all faults are not caused by failures. A system which has been shut-down by safety features has not faulted.
Fault tree analysis (FTA)	A method for graphically representing the logical combinations of various system states (failures) which lead to a particular outcome, known as the *top event*.
FEMA	Federal Emergency Management Agency, U.S.
Fibers and flyings, easily ignitable	Fibers and flyings that are easily ignitable including rayon, cotton (including cotton linters and cotton waste), sisal or henequen, jute, hemp, tow, cocoa fiber, oakum, baled waste kapok, Spanish moss, excelsior, and other materials of similar nature.
Fibrosis	Formation of fibrous tissue, as in reparative or reactive process to particulates, in excess of amounts normally present in lung tissue walls.
Fire	A combustible vapor or gas combining with an oxidizer in a combustion process manifested by the evolution of light, heat, and flame.
Fire area	A location bounded by construction having a minimum fire resistance rating of two hours with openings protected by appropriately fire- rated doors, dampers, or penetration seals.
Fire ball	Result of a sudden and widespread release of a flammable gas or volatile liquid that is stored under pressure, coupled with immediate ignition. This is distinguished from a jet fire by the shorter duration of the event and the difference in the geometry and shape of the flame. When a pressure vessel containing a flammable gas or volatile liquid ruptures, the first result is the quick dispersion of the flammable material as the high pressure material rapidly expands to atmospheric pressure. During this expansion, the release will entrain large quantities of air as a result of the process. If the material in the vessel is a volatile liquid, this process will also cause formation of an aerosol with the dispersion of liquid droplets away from the release as a result of the vapor expansion.

Fire diamond	Symbol designed by the NFPA to give a quick number rating for the particular material's degree of health (blue), flammability (red), reactivity (yellow), and specific (white) hazard.
Fire fighting gear	Turnout gear including footwear, trousers, a coat, gloves, a helmet, and respiratory protection.
Fire loading	Quantity of combustibles within an area.
Fire point	The lowest temperature at which a material can evolve vapors fast enough to support continuous combustion.
Fire resistive	Properties of materials or designs that are capable of resisting the effects of any fire to which the material or structure may be expected to be subjected.
Fire retardant	In general a term that denotes a substantially lower degree of fire resistance than *fire resistive*. It is frequently used to refer to materials or structures that are combustible but have been subjected to treatment or surface coatings to prevent or retard ignition of the spread of fire.
Fireproof	Resistant to a specific fire exposure; essentially nothing is absolutely *fireproof* but some materials or building assemblies are resistant to damage or fire penetration at certain level of fire exposures that may develop in the petroleum industry.
Fireproofing	A common industry term used to denote materials or methods of construction used to provide fire resistance for a defined fire exposure and specified time.
Flame	This is a thin zone of combustion in which diffusion plays a dominant role. Flames in hydrocarbon fuels and air are less than 0.1 mm thick for stoichiometric mixtures.
Flame acceleration	Rapid increase in flame speed due to generation of large and small eddies—turbulence—as flow ahead of flame passes over objects or through orifices.
Flame arrester	A device used to prevent passage of a flame along a passage, for example, a pipe or duct. It is a device that stops fuel combustion by extinguishing the flame. A flame arrester functions by forcing a flame front through channels too narrow, which remove heat and free radicals from the flame fast enough to quench the flame. A mesh or perforated metal insert within a flammable material container/equipment/piping that protects its contents from external flame or ignition. Flame arresters are passive devices designed to prevent propagation of flames.
Flame proof	Describes conditions in an enclosure like an electrical equipment so that flammables will be prevented from entry to avoid ignition hazards. The enclosure should be strong enough to withstand any explosion within it due to ingress of any flammables into it.

Flame quenching	Flame propagation is suppressed if the flammable mixture is held in a narrow space. If the space is sufficiently narrow, flame propagation is suppressed completely. The largest diameter at which flame propagation is suppressed is known as the *quenching diameter*.
Flame speed	Velocity of a flame, possibly turbulent, relative to a stationary observer, that is, the ground or other fixed frame. The flame speed can be much larger than the burning velocity due to expansion of the combustion products, instability, and turbulent deformation of the flame. Flame speeds of 10–100 m/s are commonly observed for hydrocarbon-air mixtures and it is possible under exceptional circumstances to have speeds up to 1000 m/s.
Flame stretch	Measure of the rate at which the area of a propagating flame surface is changing due to curvature of flame surface and strain (gradients in velocity) in flow ahead of the flame. Units of reciprocal time.
Flame thickness	Characteristic width of flame. One simple estimate is based on the ratio of the thermal diffusivity to the flame speed.
Flameproof enclosure	An international term describing an enclosure that can withstand the pressure developed during an internal explosion of an explosive mixture and that prevents the transmission of the explosion to the explosive atmosphere surrounding the enclosure and that operates at such an external temperature that a surrounding explosive gas or vapor will not be ignited thereby. This enclosure is similar to an explosion-proof enclosure.
Flammability	Ability of a material to ignite and burn readily
Flammability limits	Flammables have a minimum concentration below which flame propagation does not occur on contact with a source of ignition. This is known as the lower flammability limit (LFL). There is a maximum concentration of vapor or gas in air above which flame propagation does not occur. This is known as the upper flammability limit (UFL). These are expressed in percent of gas or vapor in air by volume.
Flammable liquid	Any liquid having a flash point below 60°C and a vapor pressure not exceeding 280 kPa at 37.8°C
Flash back	Flame resulting from ignition of fuel travels back along the trail of fuel to its source
Flash fire	A slow deflagration of a premixed, unconfined, unobstructed gas cloud producing negligible overpressure. Thermal effects are the main hazard.
Flash point	The minimum temperature at which a liquid gives off vapor within a test apparatus, under specified conditions of test, in sufficient concentration to form an ignitable mixture with air near the surface of the liquid. It is the lowest temperature, corrected to normal atmospheric pressure, at which

(Continued)

	application of an ignition source causes the vapors of a liquid sample to ignite, but will not continue to burn without the addition of more heat. Flashpoint is lower than the ignition temperature.
FM	Factory mutual
FMEA	Failure mode and effects analysis
Frequency	The rate at which observed or predicted events occur
Galvanic isolation	A form of isolation that meets stringent standards for intrinsically safe circuits.
Gas explosion	A process where combustion of a pre mixed gas cloud leads to rapid increase of pressure
Generic name	It is the of a chemical other than its chemical name, by which it is identified.
Grounding	A procedure of connecting process equipment and materials to an electrical ground in order to bleed off any accumulated electrical charge.
Group	A classification of flammable materials of similar hazard. Consists of Groups A, B, C, D, E, F, and G to NEC and CEC standards and Groups I, IIA, IIB, and IIC to IEC standards.
HASP	Health and safety plan
HAZAN	Hazard analysis method based on statistical approach using past occurrences of similar accidents.
Hazard	A condition with the potential for causing an undesirable consequence. Inherent *potential* of a material or activity to cause danger/harm to people, damage to property, or environment.
Hazard analysis	The determination of material, system, process, and plant characteristics that can produce undesirable consequences, followed by the assessment of hazardous situations associated with a process or activity. Largely qualitative techniques are used to pinpoint weaknessses in design or operation of the facility that could lead to accidents.
Hazard categories	Conditions created by the presence of hazards that are classified as follows: *Category 1* are those with a potential for significant offsite consequences. *Category 2* are those with a potential for significant onsite consequences. *Category 3* are those with a potential for only significant localized consequences.
Hazard control audit	A safety audit done to measure the effectiveness of existing hazard controls and document them in order to prioritize them and determine if they need updating, revising, etc.
Hazard evaluation	The analysis of the significance of hazardous situations associated with a process or activity

Hazard identification	The identification of the substance of concern, its adverse effects, target populations, and conditions of exposure
Hazardous chemical	A chemical that is known to cause harmful health or physical effects to exposed personnel
Hazardous operations	Includes process operations that are subject to regulatory actions because of the presence of one or more specific hazardous materials or types of materials that meet or exceed established thresholds or guidelines
Hazard warning	Any words, pictures, symbols, or combination thereof appearing on a label that convey the hazards of the chemical(s) in the container
HAZMAT	Hazardous materials
Hazmat incident	Actual or potential unplanned release of a hazardous material.
HAZOP	Hazards and operability study. A process hazards analysis procedure. The method is highly structured and divides the process into different operationally based nodes and investigates the behavior of the different parts of each node based on an array of possible deviation conditions or guide words.
HAZWOPER	Hazardous Waste Operations and Emergency Response
Heat flux	The rate of heat transfer per unit area normal to the direction of heat flow. It is the total heat transmitted by radiation, conduction and convection.
Heat of combustion	Ideal amount of energy that can be released by burning a unit amount of fuel
Heat of decomposition	Amount of heat liberated when unit quantity of a substance decomposes to form more stable substances
Heat of formation	Heat of reaction per unit of product needed to form a species by reaction from the elements at the most stable conditions
Heat of reaction	Energy that must be supplied in the form of heat to keep a system at constant temperature and pressure during a reaction
Hermetically sealed device	A device that is sealed against the entrance of an external atmosphere and in which the seal is made by fusion. Continuous soldering, brazing, welding and the fusion of glass to metal are examples of recognized methods.
HHC	Highly hazardous chemical
High pressure	Gas pressure greater than 21 MPa gauge; liquid pressure greater than 35 MPa gauge
HIPS	High integrity protective system
HMIS	Hazardous materials identification system. The system utilizes colored bars, numbers, and symbols to convey the hazards of chemicals used in the workplace.
HMSO	Her Majesty’s Stationary Office

Hot flame ignition	A rapid, self-sustaining, sometimes audible gas phase reaction of a sample or its decomposition products with an oxidant. A readily visible yellow or blue flame usually accompanies the reaction.
Hot work	Any operation requiring the use of a flame-producing device, an electrically heated tool producing a temperature higher than 109°C, or a mechanical tool that can produce sparks or heat.
Hot zone	The area immediately around the incident site. Appropriate protective clothing and equipment *must* be worn by all personnel in the hot zone.
HPI	Hydrocarbon processing industry
HRA	Health risk assessment
HSC	Health and Safety Code (OSHA)
HSE	Health and safety executive, U.K.
HSEES	Hazardous substances emergency surveillance
Human factors	Human capacities and limitations in design, operation of processes, equipment, and work environment.
HVAC	Heat, ventilation, and air conditioning
Hybrid mixture	A mixture of a flammable gas with either a combustible dust or combustible mist.
Hydrodynamic instability	The interface between a light and a heavy fluid is stable if the fluid is accelerated in the direction of the positive density gradient. However, if the fluid is accelerating in the other direction, the interface is unstable.
Hydrophilic	Materials having large molecules that absorb and retain water, causing them to swell and frequently to gel.
Hygroscopic	Readily adsorbing available moisture in any form
Hypergolic	Property of a material which describes its ability to spontaneously ignite or explode upon contact with an oxidizing agent
IAFF	International Association of Fire Fighters.
IChemE	Institute of Chemical Engineers, U.K.
IDLH	Immediately dangerous to life and health. An atmospheric concentration of any toxic, corrosive, or asphyxiant substance that poses an immediate threat to life or would cause irreversible or delayed adverse health effects or would interfere with an individual's ability to escape from a dangerous atmosphere.
IEC	International Electro technical Commission
IEEE	Institute of Electronic and Electrical Engineers

Ignitability	Ignitability of a porous solid fuel is that characteristic which determines the ease with which the fuel may be brought to a condition of self-supporting, active oxidation. It is governed not only by the inherent chemical characteristics of the fuel that determine its rate of oxidation at various temperatures but also by its physical characteristics and surroundings that determine the rate at which it can be heated. Among these physical characteristics are (i) particle size, (ii) specific heat, (iii) thermal conductivity of particles and bulk phase, (iv) the rate at which oxygen or air is brought into contact with the fuel, and (v) the rate of heat loss to the surroundings.
Ignitable gas mixture	A gas–air mixture that is capable of being ignited by an open flame, arc or spark, or high temperature.
Ignition	The process of starting a combustion process through the input of energy. Ignition occurs when the temperature of a substance is raised to the point at which its molecules will react spontaneously with an oxidizer and combustion occurs.
Ignition delay	Time elapsed from the sudden increase in temperature until ignition is observed. Ignition delay times are very strong functions of temperature and range between minutes at low temperatures (200°C) to microseconds for shock tube testing (1500–2500°C).
Ignition source	Anything that provides heat, spark, or flame sufficient to cause combustion/explosion
IIChE	Indian Institute of Chemical Engineers
IMIS	Integrated Management Information System (OSHA)
Incendive	Ability of an energy source, such as a static discharge, to cause ignition in a given system
Incident	An undesired circumstance that produces the potential for an accident. An unplanned event causes or could cause under different circumstances injury, ill-health or damage to property or the environment.
Incompatible materials	Materials that react with process materials or products giving rise to hazardous situations, for example, fires, explosions, or toxic release.
Increased safety	This is an international term that describes a type of protection in which various measures are applied so as to reduce the probability of excessive temperatures and the occurrence of arcs or sparks in the interior and on the external parts of electrical apparatus that do not produce them in normal service.
Induction	Static electricity formation due to a charged object being brought close to an uncharged object.

Induction charging	This is the process of momentarily grounding a conductor which has been polarized by an electric field, then removing the conductor from the electric field so that it gains a net charge.
Inerting	The process of removing an oxidizer (usually air or oxygen) to prevent a combustion process from occurring normally accomplished by purging.
Ingestion	Taking a material into the body by mouth (swallowing)
Inhalation	Breathing a chemical into the lung
Inherently safe	An essential character of a process, system, or equipment that makes it without or very low in hazard or risk
Inhibited	Containing a small amount of another substance included to prevent the first material from reacting with itself or other things in its environment
Inspection	Systematic examination of a work site or equipment which, in the process is compared against an established standard
Instability	The degree of intrinsic susceptibility of a material to release energy through self-reaction (polymerizing, decomposing, or rearranging)
Interlock	(i) Instrument that will not allow one part of a process to function unless another part is functioning. (ii) A device such as a switch that prevents a piece of equipment from operating when a hazard exists. (iii) To arrange the control of machines or devices so that their operation is interdependent in order to assure their proper coordination.
Intrinsic safety	(i) A type of protection in which a portion of the electrical system contains only intrinsically safe equipment (apparatus, circuits, and wiring) that is incapable of causing ignition in the surrounding atmosphere. No single device or wiring is intrinsically safe by itself (except for battery-operated self-contained apparatus such as portable pagers, transceivers, gas detectors, etc., which are specifically designed as intrinsically safe self-contained devices) but is intrinsically safe only when employed in a properly designed intrinsically safe system.
	(ii) Design methodology for a circuit or an assembly of circuits in which any spark or thermal effect produced under normal operating and specified fault conditions is not capable under prescribed test conditions of causing ignition of a given explosive atmosphere.
	(iii) A method to provide safe operation of electric process control instrumentation where hazardous atmospheres exist. The method keeps the available electrical energy so low that ignition of the hazardous atmosphere cannot occur.

(*Continued*)

(Continued)

	(iv) A protection technique based on the restriction of electrical energy within apparatus and of interconnecting wiring, exposed to a potentially explosive atmosphere, to a level below that which can cause ignition by either sparking or heating effects. Because of the method by which intrinsic safety is achieved, it is necessary to ensure that not only the electrical apparatus exposed to the potentially explosive atmosphere but also other electrical apparatus with which it is interconnected is suitably constructed.
Intrinsic safety barrier	A component containing a network designed to limit the energy (voltage and current) available to the protected circuit in the hazardous (classified) location under specified fault conditions.
Intrinsic safety ground bus	A grounding system that has a dedicated conductor separate from the power system so that ground currents will not normally flow and that is reliably connected to a ground electrode.
Intrinsically safe circuit	A circuit in which any spark or thermal effect, produced either normally or in specified fault conditions, is incapable of releasing sufficient electrical or thermal energy to cause ignition of a specific hazardous atmospheric mixture in its most easily ignitable concentration.
Intrinsically safe equipment (Apparatus, circuits, and wiring)	Equipment and wiring that, under normal or abnormal conditions, are incapable of releasing sufficient electrical or thermal energy to cause ignition of a specific hazardous atmospheric mixture in its most easily ignitable concentration.
Intrinsically safe system	An assembly of interconnected intrinsically safe apparatus, associated apparatus, and interconnecting cables in which those parts of the system that may be used in hazardous (classified) locations are intrinsically safe circuits.
Intumesent	A fireproofing material (epoxy coating, sealing compound or paint) which foams or swells to several times its volume when exposed to heat from a fire and simultaneously forms an outer char covering, that together forms an insulating thermo layer against a high temperature fire.
I/O module	A module that provides basic input and output functions between the automation system and the field devices. Disregarding specialty modules, there are four basic types available from various vendors—analog input, analog output, discrete input, and discrete output.
Ion	An ion is an atom or molecule in which the total number of electrons is not equal to the total number of protons, giving it a net positive or negative electrical charge.
Ionizing radiation	Transfer of energy in the form of electromagnetic waves
IPL	Independent protection layer
Irritant	It is a chemical that is not corrosive but causes a reversible inflammatory effect on living tissue by chemical action at the site of contact.

ISA	Instrument Society of America
ISA	Instrumentation, Systems Automation Society
ISI	Indian Standards Institute.
ISO	International Standards Organization
Jet fire	Fire caused from flammable gas issuing from a pipe or leakage/crack in a pipe or orifice
JHA	Job hazard analysis
JSA	Job safety analysis
Label	Any written, printed, or graphic material displayed on or affixed to containers of hazardous chemicals. A diamond shape indicating a UN hazard class.
Labeled equipment	Equipment or materials, to which has been attached a label, symbol, or other identifying mark of an organization concerned with product evaluation, that may maintain periodic inspection of the production of labeled equipment or materials, and by whose labeling the manufacturer indicates compliance with appropriate standards or performance in a specified manner.
Layers of protection	Multiple, redundant, or divers safeguards to prevent an incident occurring regardless of the initiating event or the performance of any single safeguard.
LC_{50} (Lethal concentration)$_{50}$	Concentration of material in the air which causes the death of 50 percent of a group of test animals. The material is inhaled over a set period of time, usually 1–4 h.
LC_{LO} (Lethal concentration)$_{low}$	The lowest concentration of a substance in air reported to have caused death in humans or animals
LCA	Life cycle analysis
LD_{50} (Lethal dose)$_{50}$	It is the of a material, given orally or through skin, all at once, which causes death of 50 percent of a group of test animals under standard conditions.
LD_{LO} (Lethal dose)$_{low}$	The lowest dose of a substance introduced by any route, other than inhalation, reported to have caused death in humans or animals
Lean mixture	This is a mixture containing less than the stoichiometric amount of fuel, equivalence ratio less then unity. Combustion of a lean mixture will result in excess oxidizer remaining in the products.
Lewis number	Ratio of thermal diffusivity to mass diffusivity of a specified species. For light molecules diffusing in heavier mixtures, the Lewis number is less than one; for heavy molecules diffusing in lighter mixtures, the Lewis number is greater than one.
Lift	The actual travel of the disk away from the seat when a relief valve is relieving.

Lightning protection	Lightning protection involves a system designed to protect a structure from damage due to lightning strikes by intercepting such strikes and safely passing their extremely high-voltage currents to *ground*.
Liquefied natural gas (LNG)	Natural gas that has been converted to a liquid through cooling to approximately −162°C at atmospheric pressure
Liquefied petroleum gas (LPG)	Hydrocarbon fractions lighter than gasoline, such as ethane, propane and butane, kept in a liquid state through compression and/or refrigeration.
LMIE	Lowest minimum ignition energy measured at optimum concentration
LOC	Limiting oxidant concentration that is the concentration of oxidant, normally oxygen, in a mixture below which a fuel-oxidant fire or explosion cannot occur. LOC is also called MOC, minimum oxygen for combustion.
Locking out	A procedure for securing an energy-isolating device in an off, closed, or neutral position. When an energy-isolating device is locked out, a worker can safely service hazardous equipment.
LOPA	Layer of protection analysis. A method of analyzing the Likelihood (frequency) of a harmful outcome event based on an initiating event frequency and on the probability of failure of a series of independent layers of protection capable of preventing the harmful outcome.
Loss control	A system or program designed to minimize accidents and reduce financial losses
Loss prevention	A before the loss program designed to identify and correct potential causes of accidents before they result in actual injuries or financial loss
Low pressure	Gas less than 1 MPa gauge (150 psi); liquid less than 10 MPa gauge (1500 psig)
Mach number	Ratio of wave or flow speed to speed of sound. Supersonic waves or flows have M >1, this is true for detonations or shock waves. Subsonic waves or flows have M <1, this is true for most flames.
MAHB	Major Accident Hazard Bureau.
Markstein length	The larger the Markstein length, the greater the effect of curvature on burning velocity. The Markstein length divided by the flame thickness is the *Markstein number*.
MARS	Major accident reporting system
Mass charge density	The net quantity of charge carried by unit mass of a material
MAWP	Maximum allowable working pressure. The maximum allowed pressure at the top of a vessel in its normal operating position at the operating temperature specified for that pressure.

MEC	The lowest concentration of a combustible dust in air, expressed in grams per cubic meter, that will propagate a flame.
MESG	Maximum experimental safe gap. There is a maximum safe gap measured experimentally which will prevent the transmission of an explosion occurring within a container to a flammable mixture outside the container.
Microcalorimetry	Isothermal techniques of high sensitivity in which heat fluxes from the converting sample material are measured very accurately. Differential microcalorimetry is performed if the heat fluxes from the sample are compared with those of a reference material.
Minimum ignition energy (MIE)	Lowest electrical energy stored in a capacitor which, upon discharge, is just sufficient to effect ignition of the most ignitable atmosphere under specified test conditions.
Mitigating measures	Measures to reduce the consequences of a runaway to an acceptable level
Mixing calorimetry	Technique used to measure heat evolved upon instantaneous mixing of two or more chemicals
MOC	Management of change
Monitor	A self-supporting fire fighting nozzle that can function unattended and delivers a large volume of fire suppressant material
Monomers	Chemicals that are the simple starting units from which polymers are made; they are reactive and sometimes unstable
MSDS	Material safety data sheet
MSHA	Mine safety and health administration, U.S. Department of labor.
Mutagen	A chemical or physical agent that can cause a change (mutation) in the genetic material of a living cell
MWP	Maximum working pressure
NDT	Nondestructive testing
NEC	National electrical code
NEMA	National Electrical Manufacturers' Association, U.S.
Nephrotoxins	Chemicals that cause kidney damage
Neurotoxins	Chemicals that produce their primary toxic effects on the nervous system
NFPA	National Fire Protection Association, U.S.
NIOSH	National Institute of Occupational Safety and Health, U.S.
NIST	National Institute of Standards and Technology

Nitration	Chemical reaction of a substance in which the nitro group is introduced into the molecule, often accomplished under highly reactive conditions using mixtures of nitric and sulfuric acids at high temperatures. Byproducts of the reaction may have explosive properties; if reaction control is lost, vigorous and strongly exothermic runaway reactions may result due to oxidation of the reactants.
Nonincendive circuit	A circuit in which any arc or thermal effect produced in normal operating conditions of the equipment is not capable, under prescribed conditions, of igniting the specified flammable gas, vapor-in-air mixture, combustible dusts, or ignitable fibers or flyings.
Nonincendive component	A component having contacts for making or breaking a specified incentive circuit in which the contacting mechanism is constructed so that the component is not capable of ignition of the specified flammable gas or vapor-in-air mixture when tested as specified by appropriate test procedure. The housing of a nonincendive component is not intended to (i) exclude the flammable atmosphere or (ii) contain an explosion.
Nonincendive equipment	Equipment having electrical/electronic circuitry and components that are incapable under normal conditions, of causing ignition of a specified flammable gas or vapor-in-air mixture due to arcing or thermal effect, vapor hazards.
Nonincendive field wiring	Wiring that enters or leaves an equipment enclosure and, under normal operating conditions of the equipment, is not capable, due to arcing or thermal effects, of igniting a specified flammable gas or vapor-in-air mixture or combustible dust-in-air mixture. Normal operation includes opening, shorting, or grounding the field wiring.
NRC	Nuclear Regulatory Commission
NSC	National Safety Council
NTSB	National Transportation Safety Board
Odor threshold	Lowest concentration, in ppm, of a chemical in the air that is detectable by smell.
OEL	Occupational exposure limit
Operating pressure	The operating pressure is the gauge pressure to which the equipment is normally subjected in service. A process vessel is usually designed for a pressure which will provide a suitable margin above the operating pressure, in order to prevent leakage of the relief device.
Operational emergencies	Include the spectrum of significant emergency events or conditions that involve or affect facilities and activities by causing or having the potential to cause serious health and

(Continued)

	safety impacts onsite or offsite to workers or the public, serious detrimental effects on the environment, direct harm to people or the environment as a result or degradation of security or safeguards conditions or release (or loss of control) of hazardous materials.
Organic peroxide	An organic compound that contains the bivalent –O–O– structure which may be considered a structural derivative of hydrogen peroxide, in which one or both of the hydrogen atoms has been replaced by an organic radical
OSHA	Occupational Safety and Health Administration, U.S.
Overpressure	Overpressure is the pressure increase over the set pressure of the relieving device during discharge, expressed as a percentage of set pressure.
Oxidizer	A chemical that initiates or promotes combustion in other materials, thereby causing fire either of itself or through the release of oxygen or other gases
Oxidizing substances	Substances that promote combustion, or those spontaneously release oxygen at room temperature or upon slight warming, removes hydrogen from another substance, or attracts electrons. Peroxides, chlorates, perchlorates, nitrates, permanganates, etc.
Partly confined gas explosion	Occurs when a fuel is accidentally released, mixed with air, and ignited inside a building that is partly open.
PCBs	Polychlorinated biphenyls, a class of chlorinated aromatic compounds that is hazardous to human health and the environment
Peclet number	Ratio of convection speed to characteristic diffusive velocity. When the velocity is the flame speed and the length is the size of the pores in the screen of the flame arrester, a critical Peclet number determines if the flame will pass through the screen. When Pe < 40–100, a flame will extinguish or *quench*.
PEL	Legally enforced permissible exposure limit, in terms of concentration in air
Permit-to-work	A document required when the safeguards provided in normal production are unavailable and the manner in which the job done is critical to safety. It identifies conditions required for safe operation.
Peroxides	Chemicals that contain two oxygen atoms bound together. Often explosive
PFD	Process flow diagram
pH	Scale of 0–14 representing acidity or alkalinity of aqueous solution. Pure water has pH of 7.

PHA	Process hazard analysis
Physical explosion	An explosion due to the sudden release of mechanical energy that does not involve a chemical reaction
Pico	Subdivision equal to one part in 10^{12}
P&ID	Piping and instrumentation diagram
Pilot-operated pressure relief valve	A pilot-operated pressure relief valve is one that has the major flow device combined with and controlled by a self-actuated auxiliary pressure reliefs valve. This type of valve does not utilize an external source of energy.
Pipe rack	The pipe rack is the elevated supporting structure used to convey piping between equipment. This structure is also utilized for cable trays associated with electric-power distribution and for instrument tray.
Plot plan	Plot plan is the scaled plan drawing of the processing facility.
Poison	Any substance that is injurious to health and may lead to death when relatively small amounts are taken either internally or externally
Polymer	Large chemical molecule made up of repeated smaller units
Polymerization	Chemical reaction in which one or more small molecules combine to form larger molecules
Pool fire	This is a flame over a puddle or pool of liquid fuel. The heat released by the combustion of the vapor fuel supplies the energy to vaporize the liquid.
PPE	Personal protection equipment
Pressure	Stress that is exerted uniformly in all directions
Pressure generating material	A chemical substance or mixture that may spontaneously polymerize, with an increase in pressure, unless protected by the addition of an inhibitor or by refrigeration
Pressure piling	An increase in pressure within a process due to a deflagration. The pressure wave moves ahead of the reaction front, compressing the unreacted gas and increasing the reaction rate of the following reaction front.
Pressure purging	An inerting method that uses a pressurized source of inert gas to reduce the vapor concentration in a process to one that is not combustible
Preventive maintenance	All those systematically planned and scheduled actions performed for the purpose of preventing equipment, system, or facility failure
PrHA	Process hazards analysis.
Probability (P)	The likelihood of a specific outcome/event, measured by the ratio of specified outcomes to the total number of possible outcomes, the value being in the range of 0–1.

Propagating brush discharge	This is a brush type discharge with the difference that brush discharges arise when there is a single-layer charge on one side of the insulator, while propagating discharges arise when there is a double-layer charge, that is, charge on both sides of the insulating surface. These are highly energetic discharges involving effective energies as high as 2–3 J.
PSI	Process safety information
PSM	Process safety management. "A management system that is focused on prevention of, preparedness for, mitigation of, response to, and restoration from catastrophic releases of chemicals or energy from a process associated with a facility." CCPS, AIChE.
Purged enclosure	Enclosure through which clean air or inert gas is passed at a rate and pressure sufficient to keep concentration of flammables to a safe level
Purging	The process of supplying an enclosure with clean air or an inert gas, at sufficient flow and positive pressure to reduce to an acceptable safe level the concentrations of any flammable gases or vapors initially present, and to maintain this safe level by positive pressure with or without continuous flow.
Pyrophoric material	Ignite spontaneously in air at room temperature, either by oxidation or by reaction with atmospheric moisture. In hydrocarbon industries iron sulphide is the most commonly observed pyrophoric substance and is called pyrophoric iron.
Pyrophoricity	Spontaneous combustion of a material upon exposure to air (atmospheric oxygen)
QRA	Quantitative risk analysis
Quenching	This is the stoppage of combustion due to either heat transfer and mass transfer to the surface or aerodynamics effects like strain fields and rapid mixing.
Quenching distance	A characteristic length scale associated with laminar flame quenching during propagation in a narrow channel or tube. The minimum height of a channel in which a hydrocarbon-air flame can propagate at NTP is about 1.6 mm for mixtures with equivalence ratios between 1 and 2. The minimum diameter of a tube is about 2 mm. This distance varies inversely with initial pressure and is smaller for mixtures with higher laminar flame speeds. Turbulent explosions can be transmitted through openings smaller than the laminar flame quenching distance.
Reactive hazard	Reactive properties and physical conditions of a single chemical or mixture that has the potential to generate heat, energy, and byproducts that have potential to do harm to people and damage to property and environment.

Reflected pressure	Pressure measured when a blast wave hits an object like a wall head-on.
REL	Recommended exposure limit (NIOSH)
Relaxation	The process by which separated charges recombine or excess charge is lost from a system.
Relaxation time or relaxation time constant	Time required for the accumulated charge in a liquid or on a solid material to dissipate to a selected fraction of its initial value (36.8 percent of its initial value) when the material is grounded. It is also called c*harge decay time*. For comparison between materials, it is usually expressed as the time from the initial peak surface voltage to (i) 1/*e*, where *e* is the base of natural logarithm (ii) 10 percent of the peak value In general, for hydrocarbon liquids, relaxation time constant is approximated by the relationship: $\tau = 18/\sigma$ where τ = relaxation time in seconds, σ = electrical conductivity of the liquid in pS/m.
Release	Any spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment (including the abandonment or discarding of barrels, containers, and other closed receptacles) of any chemical, *extremely hazardous substance*.
Reliability	The probability that a component or system will perform its defined logic function under the stated conditions for a defined period of time.
Relief valve	A device used to open a passage on an equipment to allow fluids discharge out of it in order to prevent over pressures developing in the equipment. Relief valve opens gradually in proportion to the over pressure.
Reproductive toxins	Chemicals that affect the reproductive capabilities including chromosomal damage (mutations) or effects on fetuses (teratogenesis)
Required relief rate	The required relief rate is the venting rate required to remove the volume being generated within the protected equipment when the equipment is at its highest allowed pressure.
Rescue	The recovery of personnel from an area of danger to safe location
Residence time	The length of time that a product remains in a grounded conductive delivery system from the point at which a charge is generated before it reaches the point of delivery, for example, from the outlet of an inline filter or a micro filter to the inlet of a tank truck or a tank. Residence time is determined by system configuration and operation.
Resistivity (rv)	The volume resistance of a sample of material having unit length and unit cross-sectional area. If the length is expressed

(*Continued*)

(Continued)

	in meters and the area in square meters; the resistivity is given in ohm-meters.
Restricted area	A location within 50 m of a facility that might release hazardous materials
RHI	Reactivity hazard index
Risk	A measure of the chances that damage to life, property, or the environment will occur if a hazard occurs. It requires exposure and includes consideration of the severity of the damage. It is the product of the probability of a particular failure (or event) occurring and the consequence.
	Risk = Probability × Consequences.
	Consequences may relate to *individuals* (individual risk), to particular *groups*, to *profits* (economic risk), or to *society* as a whole (social risk).
Risk analysis	Use of available information to estimate the risk to individuals or populations, property, or the environment, from hazards.
Risk assessment	The process of risk analysis and risk evaluation. It is the s of systematic evaluation of the risk associated with a potential accident.
Risk management	A program or activity involving the application of management principles and risk assessment techniques to help ensure the safety of any facility. Brings together risk evaluation, exposure control and risk monitoring.
RMP	Risk management program (EPA)
Root cause	Primary reason why an incident occurred or developed through systematic analyses
Root cause analysis (RCA)	Root cause analysis is a systematic technique that focuses on finding a real cause of problem and dealing with that, rather than just dealing with its symptoms.
ROSOV	Remotely operated shut off valve
Routes of entry	Means by which material may gain access to the body (inhalation, ingestion, skin contact).
RTECS	Registry of toxic effects of chemical substances
Runaway reaction	A reaction that occurs when the heat released by the reaction exceeds the heat removal, resulting in a temperature and pressure increase.
Rupture disc	A device designed to function by the bursting of a pressure-retaining disc assembly which consists of a thin, circular membrane usually made of metal, plastic, or graphite that is firmly clamped in a disc holder. When the process reaches the bursting pressure of the disc, it ruptures and releases the pressure.

SADT	Self-accelerating decomposition temperature: The lowest ambient temperature at which auto accelerative decomposition of an unstable substance is observed (minimum self-heating rate of 5°C/week), when the substance as packaged in its commercial container and is subjected to that temperature during one week in the testing facility.
Safe work permit	Written permit issued to a worker/crew by an authorized person in-charge of the work site to do a specific job, after ensuring safety for the work and specifying work details.
Safety	Converse of risk. Safety = 1/Risk.
Safety can	This is an approved container of not more than five gallon capacity having a spring closing lid and a spout cover and so designed that it will safely relieve internal pressure when subjected to fire exposure.
Safety relief valve	It is a pressure relief valve with mechanical design or adjustments to allow either relief or safety service.
Safety valve	Fully opens or pops up on over pressure development in an equipment to allow fluids to escape in order to relieve the over pressure. It is used on air or steam equipment.
SARA title III	Superfund amendments and reauthorization act. Title III of SARA, the emergency planning and community right-to-know act, EPCRA, includes detailed provisions for community planning (U.S.).
SCBA	Self-contained breathing apparatus which includes a seal tested mask, positive pressure regulator and a pressurized air supply.
Seal, cable, explosion proof	A cable terminator filled with compound and designed to contain an explosion in the enclosure to which it is attached or to minimize passage of flammable gases or vapors from one location to another. A conduit seal may also be used as a cable seal. This method differs from the international practice, which requires cable glands.
Seal, conduit, explosion proof	A sealed fitting, poured with a cement-like potting compound, designed to contain an explosion in the enclosure to which it is attached and to minimize passage of flammable gases or vapors from one location to another.
Self-ignition temperature (SIT)	Lowest temperature required to initiate or cause self-sustained combustion in materials, whether solid, liquid, or gaseous, in the absence of an external source such as a spark or flame. Also called auto-ignition temperature (AIT).
Semiconductive	Possessing a conductivity between 10^2 and 10^4 pS/m or a resistivity between 10^8 and 10^{10} W-m.
Sensitizer	A chemical that causes a substantial proportion of exposed people or animals to develop an allergic reaction in normal tissue after repeated exposure to the chemical.

SHEL	Safety, health, environmental, and loss prevention reviews; performed during design.
Shelter in place	Protect people without evacuating by keeping them inside a building with indows and doors closed and external ventilation systems shut off until a hazardous situation has resolved.
SHI	Substance Hazard Index
Shock-sensitive	A relatively unstable material, the energetic Decomposition of which can be initiated by merely the input of mechanical energy at normal ambient conditions. Materials are considered shock-sensitive if they are more easily initiated than dinitrobenzene in a standard drop-weight test.
Shock wave	A fully developed compression wave of large amplitude, across which density, pressure, and particle velocity change drastically. A shock wave propagates at supersonic velocity relative to the gas immediately ahead of the shock, that is, the gas ahead is undisturbed by the shock. The propagation velocity of the shock wave depends on the pressure ratio across the wave. Increasing pressure gives higher propagation velocity.
Short-circuit proof	The ability of an intrinsic safety barrier or isolator to withstand the shorting of its intrinsically safe connections to ground. Determined by dividing the rated voltage by its' internal resistance. If the resulting value is less than the fuse rating, the barrier is said to be short-circuit proof.
SI	Systeme international and unites (International system of units).
Side-on pressure	Pressure measured perpendicular to the propagation direction of a blast wave.
Signal words	Distinctive words on MSDS s which alert the reader to the existence and relative degree of hazards. Signal words: (i) Danger materials that are highly toxic, corrosive to living tissue, extremely flammable, or are suspected human carcinogens. (ii) Warning Materials that are moderately toxic, have severe skin-irritation potential, cause allergic skin reactions, or are flammable. (iii) Caution Materials that have a low order of toxicity, produce only slight to moderate skin irritation, or are combustible.
Simple apparatus (as applied to intrinsic safety)	A device that will not generate nor store more than 1.2 V, 100 mA, 25 mW, or 20 µJ. Examples are switches, thermocouples, light-emitting diodes, and resistance temperature devices.
Skin absorption	Toxic exposure limit involving skin and eye absorption

Soot	A general term that refers to impure carbon particles resulting from the incomplete combustion of a hydrocarbon. It is more properly restricted to the product of the gas phase combustion process but is commonly extended to include the residual pyrolyzed fuel particles such as cenospheres, charred wood, petroleum coke, etc. That may become airborne during pyrolysis and which are more properly identified as cokes or chars.
SOP	Standard operating procedure
Spark discharge	A short duration electric discharge accompanied by a momentary flash of light, called spark. Spark discharge involves distinct and singular discharge channel which is described as spark discharge. The effective energy in spark discharges can be approximated as energy stored on an isolated conductor, which can be modeled as a simple capacitor by the equation,
	$E = 0.5\ CV^2$
	where E is energy in J, C is capacitance in Farads and V is voltage.
Split loading	Using separate compartments of the same vehicle to hold different products.
Spontaneous ignition	Ignition of a combustible material caused by the accumulation of heat from oxidation reactions.
Spontaneous/self-heating	Slow oxidation of an element or compound which causes the bulk temperature of the element/compound to rise without the addition of an external heat source.
Sprinkler system	A network of piping an discharge nozzles throughout a structure or process through which water is discharged during a fire.
Stagnation pressure	The pressure that a moving fluid would have if it was brought to rest by isentropic flow against a pressure gradient.
Static electricity	The class of phenomena recognized by the presence of electrical charges, either stationary or moving, and the interaction of these charges, this interaction being solely by reason of the charges themselves and their position and not by reason of their motion. Static electricity is produced by any means of relative motion between surfaces. The movement separates positive and negative charges which can accumulate, creating high potential differences that can discharge as sparks capable of igniting flammable vapors.
Static eliminators	Static eliminators neutralize static electricity charges. In a wide variety of industrial processes.
Static pressure	(i) The pressure that would exist at a point in a medium if no sound waves were present
	(ii) The normal component of stress exerted across a surface moving with the fluid, especially across a surface that lies in the direction of the flow

STCC identification numbers	Standard transportation commodity Code. A seven digit identification number commonly used for materials shipped by rail. Numbers beginning with 49 are hazardous materials.
Steam curtains	Usually consist of a steam pipe with jets, mounted on a 1.5 m high wall. Used in highly hazardous plant.
STEL	Short-term toxic exposure limit.
Stoichiometric ratio	The proportions of fuel and oxidizer that will result in optimal combustion are known as a stoichiometric ratio. The optimal ratio is determined by finding the amount of air that will result in the products of the combustion reaction containing only water and carbon dioxide with no left over oxygen.
Stray currents	Electric currents that wholly or in part do not follow the original circuits designed for them.
Stress corrosion cracking	Deep cracking in a metal part due to the combination of tensile stress and a corrosive environment, causing failure in less time than could be predicted by simply adding the separate effects of stress and the corrosive environment.
Sublime	To change from a solid state to a gaseous state without becoming a liquid.
Superimposed back pressure	The static pressure that exists at the outlet of a pressure relief device at the time the device is required to operate. It is the result of pressure in the discharge system, for example, flare system, and therefore may be constant or variable.
Surface charge density	The net quantity of charge per unit area of surface of a solid or liquid expressed in Coulomb/square meter
Switch loading	The practice of loading a low conductivity, low vapor pressure (<77.5 mm Hg under actual loading condition) organic liquid product into a fixed or portable tank, truck, trailer or railroad tank car that was loaded with an organic liquid with a vapor pressure of 77.5 mm Hg (1.5 psia) or greater immediately preceding the transfer. Such a practice can result in a flammable atmosphere while loading the low vapor pressure product.
Synergistic	Exposure to more than one chemical can result in health effects greater than when expected when the effects of exposure to each chemical are added together.
Synonyms	Other names for the same chemical
Systemic toxicity	This term is applied when a substance affects a system in the organism other than and often distant from the site of application or exposure.
Tagging out	A procedure for placing a warning tag or sign—a tag out device—on an energy-isolating device.
Tank spacing	Unobstructed distance between tank shells, or between tank shells and the nearest edge of adjacent equipment, property lines, or buildings.

Temperature identification number (Temperature class)	A system of classification by which one of 14 temperature identification numbers (internationally, six temperature classes) is allocated to an electrical apparatus. The temperature identification number represents the maximum surface temperature of any component that may come in contact with the flammable gas or vapor mixture.
Teratogen	This is a substance that can cause birth defects.
Termination panel	A mechanical assembly which resides in front of the I/O system and performs signal conditioning, electrical isolation, and other functions
TGA	Thermo gravimetric analysis. Chemical testing technique that precisely measures weight loss, due to gas forming reactions, as a function of temperature and time.
Threshold limit value (TLV)	A time-weighted average concentration under which most people can work consistently for eight hours a day, day after day, with no harmful effects.
TNO	Netherlands Organization for Applied Scientific Research
TNT	Trinitrotoluene
Toxicity	Ability of a substance to cause harmful health effects
TQ	Threshold quantity, the minimum amount of a toxic, reactive, or flammable chemical as capable of causing a catastrophic event.
Trade name	Trademark name or commercial trade name for a material given a by the manufacturer.
Transitional brush discharge	A partial discharge from a nonconductive layer on a conductive substrate. The effective energy is highly dependent on the breakdown voltage of the layer and is intermediate between brush discharges and propagating brush discharges. The more energetic of these discharges might ignite dust in air.
Triboelectrification	In static electric generation, one surface will have a propensity to donate electrons (and in doing so become positively charged), while the other surface will receive them (and become negatively charged). This mechanism is known as tribo-electrification or contact electrification.
TSCA	Toxic Substances Control Act
Turbulence intensity	Characteristic magnitude of the velocity fluctuations in a turbulent flow
Turbulent flow	Turbulent flow is characterized by an irregular random fluctuation imposed on mean flow velocity.
TWA	Time weighted average toxic exposure limit
UCVCE	Unconfined vapor cloud explosion.
UL	Underwriters laboratories

Ullage	This is the volume in a liquid fuel tank that is not occupied by liquid fuel. This is sometimes referred to as the vapor space since it is filled with a mixture of fuel vapor and a cover gas, air in the case of commercial airplanes.
UN identification number	An international four-digit number assigned to all hazardous materials regulated by the United Nations.
Unconfined gas explosion	A deflagration in an unconfined, unobstructed gas cloud. Occurs in an open area
UNEP	United Nations Environmental Program.
Unstable (reactive)	A chemical that in the pure state, or as produced or transported, will vigorously polymerize, decompose, condense, or will become self-reactive under conditions ions of shocks, pressure, or temperature.
Upper flammability or explosive limit	UFL or UEL. Highest concentration of vapor or dust in air at or above which a burning or explosive reaction cannot be sustained.
USCG	U.S. Coast Guard
Vapor cloud explosion (VCE)	An explosion which occurs when a large quantity of flammable vapor or gas is released, mixes with air, and is ignited.
VCM	Vinyl chloride monomer
Venting	Emergency flow of vessel contents out of the vessel. The pressure is reduced by venting, thus, avoiding a vessel rupture due to over-pressurization. The vent flow can be single or multi-phase with consequent differences in mass flux and depressurization characteristics.
VOCs	Volatile organic compounds
Waiting period	The elapsed time after the completion of product dispensing into storage or transportation containers (i.e., storage tanks, tank trucks, and tank cars) before sampling or gauging activities.
Water hammer	Water hammer (or, more generally, fluid hammer) is a pressure surge or wave resulting when a fluid (usually a liquid but sometimes also a gas) in motion is forced to stop or change direction suddenly (momentum change). Water hammer commonly occurs when a valve is closed suddenly at an end of a pipe line system, and a pressure wave propagates in the pipe.
Water reactive material	A chemical substance or mixture that reacts vigorously with water to release heat or gas which is flammable or toxic. Examples include alkali metals, metal hydrides, alkyl lithiums and alkyl aluminums.
Weaver flame speed number	Used to characterize flame speed. It is simply calculated as ratio of burning velocities of the fuel to that of H_2. It is less than 100 percent.

What-if	At each process step, what-if and answered to evaluate the effects of component failures or procedural errors.
WHMIS	Workplace hazardous materials information system
Work area	A room or defined space in a workplace where hazardous chemicals are produced or used and where personnel are present.
Work function	The minimum energy required to extract the weakest bound electron from a particle surface and remove it to infinity.
Workplace	An establishment, job site, or project at one geographical location containing one or more work areas.
Zero energy state	The lowest possible energy that a quantum mechanical physical system may have and is the energy of the ground state.
Zone	Classification system for electrical and electronic equipment and wiring for all voltages in locations where fire or explosion hazards may exist.

Note: This glossary, selective and by no means exhaustive, is drawn from different sources, including statutory bodies that are responsible for industrial and public safety.

Appendix B

Selected Literature Sources

General

- Crowl, Daniel A. and Joseph F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, 2nd ed., Prentice Hall, 2001.
- Fawcett, H. N. and W. S. Wood, *Safety and Accident Prevention in Chemical Operations*, Inter Science.
- Hammer, Willie and Dennis Price, *Occupational Safety Management and Engineering*, McGraw-Hill, New York, 2000.
- Marshall, V. C. and Steve Ruhemann, *Fundamentals of Process Safety*, IChemE, 2001.
- King, Ralph, *Safety in the Process Industries*, Butterworth-Heinemann, 1990.
- Lewis, Bernard and Guenther Von Elbe, *Combustion, Flames and Explosions of Gases*, Academic Press, New York, 1987.
- Glassman, I., *Combustion*, 3rd ed., Academic Press, New York, 1996.
- Kuo, K. K., *Principles of Combustion*, John Wiley and Sons, New York, 1986.
- Bradley, J. N., *Flame and Combustion Phenomena*, Methuen, London, UK, 1969.
- Griffiths, J. F. and J. A. Barnard, *Flame and Combustion*, 3rd ed., Blackie Academic & Professional/Chapman & Hall, New York, 1995.
- Strahle, W. C., *An Introduction to Combustion*, Gordon and Breach, New York, 1993.
- Cox, G. (Ed.), *Combustion Fundamentals of Fire (Combustion Treatise)*, Academic Press.
- Blackshear, P. L. (Ed.), *Heat Transfer in Fires: Thermophysics, Social Aspects, Economic Impact*, Scripta Book Co., Washington, DC, 1974.
- Mannan, Sam, *Lees' Loss Prevention in the Process Industries*, 3 Vols, Butterworths, London, 2004.
- Slote, Lawrence and William F. Dalton, *Handbook of Occupational Safety and Health*, John Wiley and Sons, 1987.
- Mumford, C., *Chemical Process Safety, Occupational Health and Safety*, Department of Design, Portsmouth, UK.
- Richardson, Mervyn (Ed.), *Chemical Safety: International Reference Manual*, John Wiley, 1994.
- Buschmann, C. H., *Loss Prevention and Safety Promotion in the Process Industries*, Elsevier.
- ACGIH, *Encyclopaedia of Occupational Health and Safety*, 4th ed., Pub No: 0590, ACGIH, ILO, 1998.
- Blake, Roland P. (Ed.), *Industrial Safety*, 10th ed.
- Alaimo, Robert J., *Handbook of Chemical Health and Safety*, ACS Handbooks, 2001.
- CCPS, *Guidelines for Process Safety Fundamentals in General Plant Operations*, AIChE, 1995.

- CCPS, *Safety, Health and Loss Prevention in Chemical Processes – Problems for Undergraduate Engineering Curricula – Instructor's Guide*, AIChE, 1990.
- Sanders, Roy E., *Chemical Process Safety: Learning from Case Histories*.
- NSC, *The Dictionary of Terms Used in the Safety Profession*, 4th ed., National Safety Council, US, 2001.
- NSC, *Pocket Guide to Safety Essentials*, National Safety Council, US, 2001.
- Factory Mutual, *Handbook of Industrial Loss Prevention*, McGraw-Hill.
- ACGIH, *Occupational Safety and Health for Technologists, Engineers, and Managers*, 3rd ed.
- Diberardinis, Louis J. (Ed.), *Handbook of Occupational Safety and Health*, 2nd ed., Pub No: 9839, ACGIH, ©1999.
- Cheremisinoff, Nicholas P., *Practical Guide for Industrial Safety: Methods for Process Safety Professionals*.
- Reynolds, Joseph P. and Kevin Morris, *Health, Safety and Accident Prevention: Industrial Applications: A Self-Instructional Problem Workbook*, E T S Incorporated, 1996.
- *Health, Safety and Accident Management in the Chemical Process Industries*, Technology, 2001.
- Heinrich, H. W., *Industrial Accident Prevention*, McGraw-Hill, 1980.
- *Staff of Chemical Engineering, Plant and Personnel Safety*, www.che.com
- Benuzzi, A. and J. M. Zaldivar, *Safety of Chemical Batch Reactors and Storage Tanks*, Technology, 1991.
- AIChE, *Guidelines for Process Safety in Batch Reaction Systems*, Pub No: G-62, AIChE, 1999.
- Keith Furr, A., *CRC Handbook of Laboratory Safety*, 2000.
- Speegle, Michael, *Safety, Health and Environmental Concepts for the Process Industry*, 2005.
- Krishnan, N. V., *Safety Management in Industry*, Jaico Publishing House, Bombay.
- Reese, Charles D. and Reese D. Reese, *Occupational Health and Safety Management: A Practical Approach*, Business and Economics, 2003.
- Angle, James S., *Occupational Safety and Health in the Emergency Services*, Technology, 2004.
- Kletz, T. A., *Learning from Accidents*, 3rd ed., Technology, 2001.
- Kletz, T. A., *Critical Aspects of Safety and Loss Prevention*, Butterworth-Heinemann, 1990.
- IChemE, *Engineering for Safe Operations*, BP Process Safety Series, IChemE.
- AIChE, *Plant Safety*, Pub No: Q-1, AIChE, 1996.
- Fthenakis, V. M., *Prevention and Control of Accidental Releases of Hazardous Gases*, Van Nostrand-Reinhold, New York, 1994.
- Hughes, Phil, *Introduction to Health and Safety at Work*, Elsevier, 2005.
- Ridley, John, *Safety at Work*, Elsevier, 2003.
- Taylor, Geoffrey A., Kellie Easter, and Roy Hegney, *Enhancing Occupational Safety and Health*, Butterworth-Heinemann, 2004.
- Cote, Arthur E., Editor-in-Chief, *National Fire Protection Association Handbook*, 17th ed., 1991.

- Craig Schroll, R., *Industrial Fire Protection Handbook*, 2nd ed., Technomic Pub Co., 2002.
- Wells, G., L. Segrave, and R.M.C. Whiting, *Flow Sheeting for Safety*, IChemE, Rugby, UK.
- Flynn, Ann Marie and Louis Theodore, *Health, Safety, and Accident Management in the Chemical Process Industries*, Marcel Dekker Inc., 2002.
- Theodore, L., J. P. Reynolds, and F. B. Taylor, *Accident and Emergency Management*, John Wiley and Sons Inc., 1989.
- Finucane, Edward W., *Definitions, Conversions, and Calculations for Occupational Safety and Health Professionals*, 2nd ed., Pub No: 9543, ACGH, ©1998.
- Freeman, R. A. and D. C. Hendershot, *Loss Prevention: Process Safety Information Archives*, (Two CD-ROM Set) SACHE Package, CCPS, AIChE, 1999.
- NFPA, *Fire Prevention Code Handbook*, NFPA, Quincy, MA.
- Bolmen, Richard A. Jr. (Ed.), *Semiconductor Safety Handbook: Safety and Health in the Semiconductor Industry*, Noyes Publications, Westwood, NJ, 1998.
- Foley, Stefen N. (Ed.), *Fire Department Occupational Health and Safety Standards Handbook*, 1st ed., NFPA, 1998.
- Benedette, Robert P. (Ed.), *Flammable and Combustible Liquids Code Handbook*, 6th ed., NFPA, 1996.
- Laughlin, J. and David G. Trebisacci (Eds.), *Hazardous Materials Response Handbook: With the Complete Text of the 2002 Editions of NFPA 471, Recommended Practice for Responding to Hazardous Materials Incidents, NFPA 472*, 4th ed., 2002.
- Lemoff, Theodore C. (Ed.), *Liquefied Petroleum Gases Handbook*, 4th ed., NFPA, 1995.
- Klein, Burton R. and Thomas W. Gardner, *Health Care Facilities Handbook*, 1999.
- Wallace, Ian G., *Developing Effective Safety Systems*, IChemE, 1995.
- CCPS, *Guidelines for Preventing Human Error in Process Industry*.
- CCPS, *Guidelines for Safe Automation of Chemical Processes*.
- CCPS, *Safe Design and Operation of Process Vents and Emission Control Systems*, Wiley, 2006.
- CCPS, *Guidelines for Safe Process Operations and Maintenance*, AIChE.
- CCPS, *Plant Guidelines for Technical Management of Chemical Process Safety*, Revised Edition, 1992.
- CCPS, *Inherently Safer Chemical Processes*.
- CCPS, *Safety, Health and Loss Prevention in Chemical Processes – Problems for Undergraduate Engineering Curricula – Instructor's Guide*, CCPS, AIChE, New York, 1990.
- Townsend, Arthur (Ed.), *Maintenance of Process Plants*, 2nd ed., 1992.
- HSE, *A Guide to the Control of Major Accident Hazards Regulations 1999 (As Amended)*, HSE Books, 2006.
- Wallace, Ian G., *Developing Effective Safety Systems*, Gulf Pub. Co. 1995.
- Lipton, S. and J. Lynch, *Health Hazard Control in the Chemical Process Industry*, John Wiley, New York, 1987.

- ACGIH, *Encyclopaedia of Occupational Health and Safety*, 4th ed., Pub No: 0590, ACGIH, International Labour Office, 1998.
- Richardson, Mervyn (Ed.), *Chemical Safety: International Reference Manual*, John Wiley and Sons, 1994.
- Burns, Thomas, *Serious Incident Prevention: How to Sustain Accident-Free Operations in Your Plant or Company*, Technology, 2002.
- AIChE, *Guide to Containment*, Pub No: U-58, AIChE, 1999.
- IChemE, *Safety Integrity – The Implications of IEC 61508 and other Standards for the Process Industries*, EPSC, IChemE, 2000.
- CMA, *Process Safety Manual*, CMA, Washington, DC, 1985.
- de Lasa, Hugo I., G. Dogu, and A. Ravella, *Chemical Reactor Technology for Environmentally Safe Reactors and Products*, NATO Advanced Science Institutes Series: E Volume 225, Kluwer Academic Publishers, Dordrecht, 1993.
- Kletz, T. A., *What Went Wrong? Case Studies of Process Plant Disasters*, 4th ed., 1998.
- Kletz, T. A., *Learning from Accidents*, Butterworth Heinemann, 1994.
- NSC, *Accident Prevention Manual: Administration and Programs*, 12th ed., National Safety Council, US, 2001.
- NSC, *Accident Prevention Manual: Engineering and Technology*, 12th ed., 2001.
- NSC, *Accident Prevention Manual: Security Management*, National Safety Council, US, 1997.
- NSC, *Accident Prevention Manual: Environmental Management*, National Safety Council, US, 2000.
- NSC, *Occupational Health & Safety*, 3rd ed., National Safety Council, US, 2000.
- NSC, *Basics of Safety and Health*, National Safety Council, US, 2004.
- NSC, *Nine Elements of a Successful Safety and Health System*, National Safety Council, US, 2005.
- NSC, *Fundamentals of Industrial Hygiene*, 5th ed., National Safety Council, US, 2002.
- NSC, *On-Site Emergency Response Planning Guide*, National Safety Council, US, 2002.
- NFPA, *Flammable and Combustible Liquids Code Handbook*, NFPA, Quincy, MA, 1996.

Design and Safety

- Wells, G. L., *Safety in Process Plant Design*, George Godwin, London.
- Kletz, T. A., *Plant Design for Safety*, Hemisphere Pub. Corp., Washington, DC, 1990.
- Kletz, T. A., *Process Plants: A Handbook for Inherently Safer Design*, 2nd ed., Taylor and Francis, 1998.
- Bollinger, R. E., D. G. Clark, A. M. Dowell, R. M. Ewbank, D. C. Hendershot, W. K. Lutz, S. I. Meszaros, and E. D. Wixom, *Inherently Safer Chemical Processes: A Life Cycle Approach*, AIChE, 1996.
- CCPS, *Guidelines for Engineering Design for Process Safety*, AIChE.
- CCPS, *Design Solutions for Process Equipment Failures*.

- CCPS, *Safe Design and Operation of Process Vents and Emission Control Systems*, Wiley, 2006.
- CCPS, *Inherently Safer Chemical Processes – A Life Cycle Approach*, 2nd ed., AIChE, New York, 2009.
- Lieberman, Norman P., *Process Design for Reliable Operations*, Gulf Publishing, Houston, 1988.
- NSC, *Safety through Design*, National Safety Council, US, 1999.
- API Std 2510, *Design and Construction of Liquefied Petroleum Gas Installations (LPG)*, 7th ed., 1995 (ANSI/API Std 2510-1996).
- Hirst, Nigel, Mike Brocklebank, and Martyn Ryder, *Containment Systems: A Design Guide*, IChemE, 2002.
- BP Process Safety Series, *Engineering for Safe Operations*, IChemE, 2006.
- IP, *Refining Safety Code*, Institute of Petroleum, London.
- Cheremisinoff, Nicholas P., *Pressure Safety Design Practices for Refinery and Chemical Operations*, Noyes Data Corporation, 1998.
- Pilkington, Stan (Ed.), *Process Vessels Subject to Explosion Risk: Design Guidelines for the Pressure Rating of Weak Process Vessels Subject to Explosion Risk*, British Materials Handling Board (BMHB), IChemE, 2000.
- Gruhn, Paul and Harry L. Cheddie, *Safety Shut-Down Systems: Design, Analysis, and Justification*, ISA, 1998.

Hazards and Properties

- Sax, N. I., "Dangerous Properties of Industrial Materials," in *Sax's Dangerous Properties of Industrial Materials*, Richard L. Lewis, Sr. (Ed.), 3 Vols, Van Nostrand-Reinhold, New York, 1996.
- *TLVs and BEIs*, Pub No: 0100, ACGIH, 2000.
- Williams, Phillip L. and James L. Burson (Eds.), *Industrial Toxicology: Safety and Health Applications in the Work Place*, John Wiley and Sons, 1997.
- Sittig, Marshall, *Handbook of Toxic and Hazardous Chemicals and Carcinogens*, 2 Vols, 3rd ed., Noyes Publications, 1991.
- Urben, Peter (Ed.), *Bretherick's Handbook of Reactive Chemical Hazards*, 7th ed., Academic Press, 2006.
- Lewis, Richard J., *Hazardous Chemicals Desk Reference*, John Wiley, 1996.
- NFPA, *Hazardous Chemicals Data*, NFPA 49, Quincy, MA, 2001.
- ACGIH, *Occupational Safety and Health for Technologists, Engineers, and Managers*, 3rd ed.
- ACGIH, *TLVs CD-ROM Demo, TLVs® and other Occupational Exposure Values*, 1999.
- ACGIH, TLVs and Beis: Based on the Documentation of the Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices … and Biological Exposure Indices for 2006, Spiral Bound.
- ACGIH, *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 6th ed., Pub No: 0206, ACGIH.

- Coward, H. F. and G. W. Jones, *Limits of Flammability of Gases and Vapors*, U. S. Bureau of Mines Bulletin 503, US Department of the Interior, Washington, DC, 1952.
- Zabetakis, M. G., *Flammability Characteristics of Combustible Gases and Vapors*, U. S. Bureau of Mines Bulletin 627, US Department of the Interior, Washington, DC, 1965.
- NSC, *NIOSH Pocket Guide to Chemical Hazards and Other Databases*, National Safety Council, US, 2003.
- Dahn, C. James, *Explosivity and Pyrophoricity of Metal Powders, Metals Handbook*, 9th ed., Vol. 7, Powder Metallurgy.
- Jacobson, M., A. R. Cooper, and J. Nagy, *Explosibility of Metal Powders*, Bureau of Mines, US Department of the Interior, 1965.
- Walters, David and Karola Grodzki, *Dealing with Chemical Risks at Work in Europe*, Elsevier Science, 2006.
- *Proctor and Hughes' Chemical Hazards of the Workplace*, 4th ed., John Wiley, 1996.
- *Cooper's Toxic Exposures Desk Reference with CD-ROM*, Lewis Publishers, 1996.
- ANSI Z400.1, *Hazardous Industrial Chemicals – Material Safety Data Sheets – Preparation*.
- Grewer, Theodor, *Thermal Hazards of Chemical Reactions*, Elsevier, 1994.
- Lewis, Richard J. Sr., *Rapid Guide to Hazardous Chemicals in the Workplace*, 4th ed., Wiley, 2000.
- Patnaik, P., *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, Van Nostrand Reinhold, 1992.
- API Recommended Practice 750, *Management of Process Hazards*, 1st ed., API, Washington, DC, 1990.
- Marshall, V. C., *Major Chemical Hazards*, John Wiley, New York, 1987.
- Pohanish, Richard P. and Stanley A. Greene, *Rapid Guide to Chemical Incompatibilities*, John Wiley and Sons, 1997.
- Yaws, Carl L., *Handbook of Chemical Compound Data for Process Safety: Comprehensive Safety and Health Related Data for Hydrocarbons and Organic Chemicals*, Gulf Pub. Co.
- *Hazardous Substances in Refineries*, BP Process Safety Series, IChemE, 2005.
- Bennet, G. F., S. F. Franks, and I. Wilder, *Hazardous Materials Spills Handbook*, McGraw-Hill, New York, 1982.
- NFPA, *Guide to Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids*, NFPA 325, Quincy, MA, 1994.
- *Fire Protection Guide to Hazardous Materials*, 13th ed., 2002.
- Babrauskak, V., *Ignition Handbook*, Fire Science Publishers, Issaquah, WA, 2003.
- Bond, John, *Sources of Ignition: Flammability Characteristics of Chemicals and Products*, Butterworth-Heinemann, 1991.
- API, *Ignition Risk of Hydrocarbon Vapors by Hot Surfaces in the Open Air*, 2nd ed., Pub No: 2216, 1991.
- Barton, John and Richard Rogers (Eds.), *Chemical Reaction Hazards*, 2nd ed., Gulf Pub. Co., 1997.
- Burgess, William A., *Recognition of Health Hazards in Industry: A Review of Materials Processes*, 2nd ed., John Wiley and Sons, 1995.

- *Hazards of Nitrogen and Catalyst Handling*, BP Process Safety Series, IChemE, 2004.
- *Hazards of Air and Oxygen*, BP Process Safety Series, IChemE, 2004.
- *Hazards of Steam*, BP Process Safety Series, IChemE, 2004.
- *Hazards of Water*, BP Process Safety Series, IChemE, 2004.
- Compressed Gas Association, *Handbook of Compressed Gases*, 3rd ed., Van Nostrand Reinhold, New York, 1990.
- Finkel, A. J. (Ed.), *Hamilton and Handy's Industrial Toxicology*, John Wright, Boston, 1983.
- Banerjee, S., *Industrial Hazards and Plant Safety*, 1st ed., Taylor and Francis, 2002.
- Grewer, T., *Thermal Hazards of Chemical Reactions (Industrial Safety Series)*, Elsevier Science, 1994.
- NSC, *Natural Gas Safety Handbook for Utility Workers and Contractors*, The American Public Gas Association, U.S. DOT, and NSC prepared this Handbook, 2003.
- NSC, *Lock out/Tag out: The Process of Controlling Hazardous Energy*, National Safety Council, US, 1995.

Hazards and Control

- Johnson, R. W., S. W. Rudy, and S. D. Unwin, *Essential Practices for Managing Chemical Reactivity Hazards*, Wiley, 2003.
- Wells, Geoff, *Major Hazards and Their Management*, Pub No: U-41, AIChE, 1997.
- Lipton, Sydney and Jeremiah Lynch, *Handbook of Health Hazard Control in the Chemical Process Industry*, 1994.
- Mumford, Clive J. and Philop Carson, *Control of Industrial Chemical Hazards*, Vols. 1 and 2, Halsted Press, 1989.
- Carson, P. A. and C. J. Mumford, *The Safe Handling of Chemicals in Industry*, Vols. 1 and 2, Mercel Dekker, New York, 1988.
- Lees, Frank P. and M. L. Ang (Eds.), *Safety Cases within the Control of Industrial Major Accident Hazards*, Butterworth-Heinemann 1990.

Static and Electrical Hazards

- Greenwald, E.K.K. (Ed.), *Electrical Hazards and Accidents: Their Cause and Prevention*, John Wiley and Sons, Incorporated, 1997.
- Fordham-Cooper, W. and D. A. Dolbey Jones (Eds.), *Electrical Safety Engineering*, Newnes, 1998.
- Cadick, John, *Electrical Safety Handbook*, McGraw-Hill Companies, 1993.
- *National Electrical Code Handbook and Code Set*, 1999.
- API RP 2003, *Protection Against Ignitions Arising Out of Static, Lightning, and Stray Currents*, 6th ed., 1998 (7th ed., being published during 2006).
- Klinkenberg, A. and J. L. Van Der Minne, *Electrostatics in the Petroleum Industry: The Prevention of Explosion Hazards*, D. Van Nostrand, New York, 1958.
- Haase, H., *Electrostatic Hazards, Their Evaluation and Control*, Verlag Chemie, Weinheim, Germany, 1977.

- Bustin, W. M. and W. G. Dukek, *Electrostatic Hazards in the Petroleum Industry*, Research Studies Press, Letchworth, UK, 1983.
- Glor, Martin, *Electrostatic Hazards in Powder Handling*, John Wiley and Sons, 1988.
- Cross, J., *Electrostatics Principles, Problems & Applications*, Adam Hilger, IOP, Bristol, UK, 1987.
- Glor, M. and G. Luttgens, *Understanding and Controlling Static Electricity*, Expert-Verlog, Eliningen bei Boblingen, Fedaral Republic of Germany, 1989.
- NFPA 77, *Recommended Practice on Static Electricity*, NFPA, 2000.
- BS 5958, *Code of Practice for Control of Undesirable Static Electricity*, British Standards Institute, London, 1991.
- API RP2003, *Protection against Ignitions Arising Out of Static, Lightning, and Stray Currents*, 6th ed., American Petroleum Institute, Washington, DC.
- API Publ 2214, *Spark Ignition Properties of Hand Tools.*
- Britton, L. G., *Avoiding Static Ignition Hazards in Chemical Operations*, 3rd ed., CCPS.
- Pratt, Thomas H., *Electrostatic Ignitions of Fires and Explosions*, CCPS, 2000.
- *Hazards of Electricity and Static Electricity*, BP Process Safety Series, IChemE, 2005.
- Jones, T. B. and J. L. King, *Powder Handling and Electrostatics*, Lewis Publishers/CRC Press, Boca Raton, FL, 1987.
- Luttgens, Gunter and Norman Wilson, *Electrostatic Hazards*, Butterworth-Heinemann, 1997.
- BS 5958, "Code of Practice for Control of Undesirable Static Electricity," Part 1 "General Considerations" and Part 2 "Recommendation for Particular Industrial Situations," British Standards Institution, London.
- Sheehan, Josef V., John M. Caloggero, and Jeffrey Sargent (Eds.), *National Electrical Code 2005 Handbook*, 10th ed., Delmar Pub., 2005.
- NFPA, *National Electrical Code 2002 Handbook.*
- Adams, J. Maxwell, *Electrical Safety: A Guide to the Causes and Prevention of Electrical Hazards*, Technology, 1994.
- NFPA 499, *Classification of Combustible Dusts and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas*, 2004.
- API RP 500, *Recommended Practice for Classification of Locations for Electrical Installations at Petroleum Facilities Classified as Class I, Division 1 and Division 2*, 2nd ed., 1997 (ANSI/API RP 500-1998).
- API RP 505, *Recommended Practice for Classification of Locations for Electrical Installations at Petroleum Facilities Classified as Class I, Zone 0, Zone 1, and Zone 2*, 1st ed., 1997 (ANSI/API RP 505-1998).
- API RP 540, *Electrical Installations in Petroleum Processing Plants*, 4th ed., API.
- NSC, *Electrical Inspection Illustrated*, 3rd ed., National Safety Council, US, 1993.
- ISA S12.11, *Electrical Instruments in Hazardous Dust Locations*, Instrument Society of America, Research Triangle Park, NC, 1973.
- IP IP-MCSP-P1, *Model Code of Safe Practice for the Petroleum Industry – Part 1: Electrical Safety Code*, 7th ed., Energy Institute (Formerly Institute of Petroleum), 2003.

- Alonzo, Robert J., *Electrical Safety for Petroleum Facilities*, American Society Of Safety Engineers, 1997.
- Magison, Ernest C., *Electrical Instruments in Hazardous Locations*, 3rd ed., Instrument Society of America, Pittsburgh, 1978.
- Greenwald, E.K.K. (Ed.), *Electrical Hazards and Accidents: Their Cause and Prevention*, Wiley, 1997.
- NFPA 496, *Standard for Purged and Pressurized Enclosures for Electrical Equipment*, 2003.
- Hattangadi, A. A., *Brooke Stauffer, Electrical Fires and Failures: Prevention and Troubleshooting*, McGraw-Hill Professional Publishing, 1999.
- Cadick, John, *Electrical Safety Handbook*, 1st ed., McGraw-Hill Companies, 1993.
- Euring, Alan Mcmillan, *Electrical Installation in Hazardous Areas*, Butterworth-Heinemann, 1998.
- Adams, J. M., *Electrical Safety*, Institution of Electrical Engineers, 1994.
- Winburn, D. C., *Practical Electrical Safety*, Marcel Dekker, Inc., 1988.
- Levy, Samuel C. and P. Bro, *Battery Hazards and Accident Prevention*, Plenum Publishing Corporation, 1994.
- NFPA 497, *Classification of Flammable Liquids, Gases, or Vapors and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas*, NFPA, Quincy, MA, 1997.
- ISA RP 12, *Installation of Intrinsically Safe Systems for Hazardous (Classified) Locations (ANSI Approved)*, Instrument Society of America, Research Triangle Park, NC, 1987.
- ISA S12.16.01 (IEC 79-7 MOD), *Electrical Apparatus for Use in Class I, Zones 1 and 2, Hazardous (Classified) Locations: Type of Protection—Increased Safety "e"*, Instrument Society of America, Research Triangle Park, NC.
- ISA S12.22.01 (IEC 79-1 MOD), *Electrical Apparatus for Use in Class I, Zone 1 Hazardous (Classified) Locations: Type of Protection—Flameproof "d"*, Instrument Society of America, Research Triangle Park, NC.
- ISA S12.23.01 (IEC 79-18 MOD), *Electrical Apparatus for Use in Class I, Zone 1 Hazardous (Classified) Locations: Type of Protection—Encapsulation "m"*, Instrument Society of America, Research Triangle Park, NC.
- ISA S12.25.01 (IEC 79-5 MOD), *Electrical Apparatus for Use in Class I, Zone 1 Hazardous (Classified) Locations: Type of Protection—Powder Filling "q"*, Instrument Society of America, Research Triangle Park, NC.
- ISA S12.26.01 (IEC 79-6 MOD), *Electrical Apparatus for Use in Class I, Zone 1 Hazardous (Classified) Locations: Type of Protection—Oil Immersion "o"*, Instrument Society of America, Research Triangle Park, NC.
- ISA-S84.01-1996, *Application of Safety Instrumented Systems for the Process Industries*, Instrument Society of America, Research Triangle Park, NC.
- NFPA 499, *Classification of Combustible Dusts and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas*, 2004 Edition, NFPA, Quincy, MA.
- NFPA 496, *Standard for Purged and Pressurized Enclosures for Electrical Equipment*, 2003 Edition, NFPA, Quincy, MA.

Other Ignition Hazards

- API RP 2027, *Ignition Hazards and Safe Work Practices for Abrasive Blasting of Atmospheric Storage Tanks in Hydrocarbon Service*.
- API Publ 2009, *Safe Welding and Cutting Practices in Refineries, Gasoline Plants, and Petrochemical Plants*, 6th ed., 1995.
- API RP 2214, *Spark Ignition Properties of Hand Tools*.
- API RP 2216, *Ignition Risk of Hydrocarbon Liquids and Vapors by Hot Surfaces in the Open Air*.
- API Publ 2201, *Procedures for Welding or Hot Tapping on Equipment in Service*, 4th ed., 1995.

Fires and Explosions

- Davletshina, Tatyana A. and Nicholas P. Cheremisinoff, *Fire and Explosion Hazards Handbook of Industrial Chemicals*, Noyes Data Corporation 1998.
- Gugan, K., *Unconfined Vapour Cloud Explosions*, George Godwin, London.
- Eckhoff, Rolf K., *Dust Explosions in the Process Industries*, 2nd ed., Butterworth-Heinemann, 1997.
- Stull, D. R., *Fundamentals of Fire and Explosion*, AIChE, New York, 1977.
- *Liquid Hydrocarbon Tank Fires: Prevention and Response*, BP Process Safety Series, IChemE, 2005.
- *SFPE Handbook of Fire Protection Engineering*, 3rd ed., NFPA, 2002.
- Cote, Arthur E., *Fire Protection Handbook*, 19th ed., NFPA, 2003.
- *Fire Protection Guide to Hazardous Materials*, NFPA, 1997.
- API Publ 2510A, *Fire Protection Considerations for the Design and Operation of Liquefied Petroleum Gas (LPG) Storage Facilities*, 2nd ed., 1996.
- CCPS, *Guidelines for Fire Protection in Chemical, Petrochemical and Hydrocarbon Processing Facilities*.
- API RP 2021, *Management of Atmospheric Storage Tank Fires*, 4th ed., API.
- Nolan, Dennis P., *Handbook of Fire and Explosion Protection Engineering Principles for Oil, Gas, Chemical, and Related Facilities*, Noyes Publications, 1996.
- Bond, J., *Sources of Ignition–Flammability Characteristics of Chemicals and Products*, Butterworth-Heinemann, Boston, MA, 1991.
- CCPS, *Understanding Explosions*, AIChE.
- Bodurtha, F. T., *Industrial Explosion Prevention and Protection*, McGraw-Hill, New York.
- *Fires and Explosions CD Rom*, IChemE.
- Medard, Louis A., Peter Fawcett, and V. C. Marshall (Trans.), *Accidental Explosions: Physical and Chemical Properties*, Ellis Horwood Series in Applied Science and Industrial Technology.
- Medard, Louis A., *Accidental Explosions*, Vols. I & II, Prentice Hall, 1989.
- Fickett, W. and W. C. Davis, *Detonation*, University of California Press, Berkeley, 1979.
- Crowl, Daniel A., *Understanding Explosions*, Wiley, 2003.
- NFPA 69, *Standard on Explosion Prevention Systems*, NFPA, 1997.

- *Process Vessels Subject to Explosions Risk*, Pub No: U-65, AIChE, 1999.
- *Confined Vented Explosions Health and Safety Executive*, 1992.
- CCPS, *UVCES & BLEVES*, AIChE.
- Baker, W. E., P. A. Cox, P. S. Westine, J. J. Kulesz, and R. A. Strehlow, *Explosion Hazards and Evaluation*, Elsevier, 1983.
- NFPA 654, *Standard for the Prevention of Fire and Dust Explosions from the Manufacturing, Processing and Handling of Combustible Particulate Solids*, NFPA, 2000.
- EPSC, *Explosion Protection: Practical Understanding of Recent Standards & New Legislation in Process Safety*, IChemE, 2003.
- Gugan, K., *Unconfined Vapor Cloud Explosions*, George Godwin.
- *Guidelines for Evaluating the Consequences of Vapor Cloud Explosions, Flash Fires, and BLEVES*, IChemE, 1994.
- Nettleton, M. A., *Gaseous Detonations: Their Nature, Effects and Control*, Chapman and Hall, New York, 1987.
- Hussaini, Y. A., A. Kumat, and R.G. Voight (Eds.), *Major Research Topics in Combustion*, Springer-Verlag, Berlin, 1992.
- Woodward, John Lowell, *Estimating the Flammable Mass of a Vapor Cloud*, Pub No: G-60, AIChE, 1999.
- Fawcett, H. H. and W. S. Wood, *Fire and Explosion: Investigations on Chemical Plant and Oil Refineries*, 2nd ed., John Wiley, 1984.
- Davletshina, Tatyana A. and Nicholas P. Cheremisinoff, *Fire and Explosion Hazards Handbook of Industrial Chemicals*, Noyes Data Corporation, 1998.
- *Guidelines for Evaluating Process Plant Buildings for External Explosions and Fires*, AIChE, 1995.
- Bartknecht, W., *Explosions Course Prevention Protection*, Springer Verlag, Berlin, 1981.
- Bartknecht, W., *Dust Explosions: Course Prevention Protection*, Springer Verlag, New York, 1989.
- Eckhoff, Rolf K., *Dust Explosions in the Process Industries*, 2nd ed., Butterworth-Heinemann, 1997.
- Field, Peter, *Dust Explosions, Handbook of Powder Technology*, J.C. Williams and T. Allen (Eds.), Vol. 4, Elsevier, Amsterdam, 1989.
- Field, Peter, *Explosibility Assessment of Industrial Powders and Dusts*.
- *Guide to Dust Explosion Prevention and Protection, Parts 1 – 3*, IChemE, 1992.
- Barton, John (Ed.), *Dust Explosion Prevention and Protection: A Practical Guide*, IChemE, 2002.
- Schofield, C. and J. A. Abbott, *Guide to Dust Explosion Prevention and Protection, Vol. 2: Ignition Prevention, Containment, Inerting, Suppression and Isolation*, IChemE, Rugby, Warwickshire, UK, 1988.
- Kauffman, C. W., *Agricultural Dust Explosions in Grain Handling Facilities, Fuel-Air Explosions*, University of Waterloo Press, Waterloo, Ontario, Canada, 1982.
- Palmer, K. N., *Dust Explosions and Fires*, Chapman and Hall, London.
- ASTM E 1226, *Standard Test Method for Pressure and Rate of Pressure Rise for Combustible Dusts*.
- NFPA 68, *Guide for Venting of Deflagrations*, NFPA, 2002.

- NFPA, *Fire Protection Handbook, Guide for Explosion Venting, Hazardous Chemicals Data, etc.*, NFPA.
- NFPA, *Fire Protection Guide for Hazardous Materials*, 13th ed., 2002.
- API 2218, *Fireproofing Practices in Petroleum and Petrochemical Processing Plants*, 2nd ed., API.
- NFPA 69, *Standard on Explosion Protection Systems*, NFPA, Quincy, MA, 1997.
- Van Dolah, R. W. and D. S. Burgess, *Explosion Problems in the Chemical Industry*, American Chemical Society, Washington, DC, 1974.
- Korver, W. O. E., *Classifying Explosion Prone Areas for the Petroleum, Chemical and Related Industries*, William Andrew/Applied Science Publishers, 1995.

Analysis

- *Dow Chemical Company, Fire and Explosion Index: Hazard Classification Guide*, 7th ed., AIChE, 1994.
- *Dow's Chemical Exposure Index*, AIChE, 1994.
- DOE Handbook, *Process Safety Management for Highly Hazardous Chemicals, DOE-HDBK-1101-2004*, August 2004.
- DOE, *Chemical Process Hazards Analysis, DOE-HDBK-1100-2004*.
- Arendt, J. S., *Evaluating Process Safety in the Chemical Industry, a User Guide to Quantitative Risk Analysis*, 2000.
- CCPS, *Guidelines for Chemical Reactivity Evaluation and Application for Process Design*, AIChE, 1995.
- *Guidelines for Hazard Evaluation Procedures*, Prepared by Battelle Columbus Division, AIChE, New York, 1992.
- CCPS, *Guidelines for Safe Process Operations and Maintenance*.
- Crawley, Frank and Brian Tyler, *Hazard Identification Methods*, EPSC, IChemE, 2003.
- Sutton, Ian, *Process Hazards Analysis*.
- Sutton, Ion, *Fault Tree Analysis*.
- Hignett, K. C., *Practical Safety and Reliability Assessment*, Technology, 1996.
- Henley, E. J. and H. Kumamoto, *Reliability Engineering and Risk Assessment*, Prentice Hall, New York, 1981.
- Hyatt, Nigel, *Guidelines for Process Hazards Analysis, Hazards Identification & Risk Analysis*, CRC Press.
- Bateman, Mike, *Tolley's Practical Risk Assessment Handbook*, 4th ed., Butterworth-Heinemann, 2003.
- Ferry, T. S., *Modern Accident Investigation and Analysis*, John Wiley, New York, 1981.
- *Hazard Communication Made Easy: A Checklist Approach to OSHA Compliance*, Government Institutes, 2000.
- Stone and Webster Engineering Corporation, *Risk Assessment and Risk Management for the Chemical Process Industry*, John Wiley and Sons, 1991.
- Tyler, Brian, Frank Crawley, and Malcolm Preston, *HAZOP: Guide to Best Practice: Guidelines to Best Practice for the Process and Chemical Industries*, EPSC/IChemE, 2000.

- Nolan, Dennis P., *Application of Hazop and What-If Reviews to the Petroleum and Petrochemical Industry*, Technology, 1994.
- Kletz, Trevor A., *Hazop and Hazan: Identifying and Assessing Process Industry Hazards*, 4th ed., Taylor and Francis, Inc., 1999.
- *Practical Risk Assessment*, IChemE.
- CCPS, *Guidelines for Quantitave Risk Analysis*, AIChE, 1999.
- CCPS, *Guidelines for Chemical Process Quantitative Risk Analysis*, 2nd ed., G-42 AIChE, 2000.
- *Guidelines for Hazard Evaluation Procedures*, with Worked Examples, 2nd ed., G-18, AIChE, 1992.
- Tyler, Brian J., Frank Crawley, and Malcolm Preston, *HAZOP: Guide to Best Practice*, IChemE, 1999.
- Mattheck, Claus, *The Body Language of Trees: A Handbook for Failure Analysis: Research for Amenity Trees*, The Stationery Office, 1995.
- *Guidelines for Consequence Analysis of Chemical Releases*, G-63, AIChE, 1999.
- API 760, *Model Risk Management Plan Guidance for Petroleum Refineries*.
- CCPS, *Safe Use of Vapor Cloud Dispersion Models*, 2nd ed.
- CCPS, *Guidelines for Process Equipment Reliability Data*, AIChE, 1989.
- Todinov, Michael, *Reliability and Risk Models*, Wiley, 2005.
- Frank, W. L. and David K. Whittle, *Revalidating Process Hazard Analyses*, Wiley, 2001.
- Steinbach, Jorg, *Safety Assessment for Chemical Processes*, John Wiley, 1999.
- *Tools for Making Acute Risk Decisions: With Chemical Process Applications*, AIChE, 1995.
- CCPS, *Guidelines for Hazard Evaluation Procedures with Worked Examples*, 2nd ed., AIChE, 1992.
- CCPS, *Layer of Protection Analysis, Simplified Process Risk Assessment*.
- CCPS, *Revalidating Process Hazard Analyses*.
- Crawley, Frank and Brian Tyler, *Hazard Identification Methods, European Process Safety Center*, IChemE, 2003.
- Skelton, Bob, *Process Safety Analysis: An Introduction*, IChemE, 1997.
- EPA, *Workbook of Screening Techniques for Assessing Impacts of Toxic Air Pollutants*, Revised Edition, EPA-454/R-92-024, 1992.
- EPA, *Guidance on the Application of Refined Dispersion Models to Hazardous Air Pollutant Releases*, EPA-454/R-93-002, 1993.
- Chemical Industries Health and Safety Council, *Hazard and Operability Studies*, Chemical Industries Association, London, 1977.
- CEFIC, *Views on the Quantitative Assessment of Risks from Installations in the Chemical Industry*, European Chemical Industry Council, Brussels, 1986.
- Ellis, Knowlton R., *An Introduction to Hazard and Operability Studies*, Chemetics International Ltd., Vancouver, BC, 1981.
- Dayan, A. D., "Interpretation of Data," in *Toxic Hazard Assessment of Chemicals*, M.L. Richardson (Ed.), Royal Society of Chemistry, London, 1986.
- *Guidelines on Risk Analysis*, 1st ed., Chlorine Institute, Arlington, VA, Pub No: 83, 1989.

- *Evaluating Process Safety in the Chemical Industry, a Manager's Guide to Quantitative Risk Assessment*, CMA, Washington, DC, 1989.
- *Guidelines for Use of Vapor Cloud Dispersion Models*, AIChE, 1987.
- *Workbook of Test Cases for Vapor Cloud Source Dispersion Models*, AIChE, 1989.
- API 760, *Model Risk Management Plan Guidance for Petroleum Refineries*, 3rd ed., API.
- Walters, David and Karola Grodzki, *Dealing with Chemical Risks at Work in Europe*, Elsevier, 2006.
- Greenberg, H. R. and J. J. Cramer, *Risk Assessment and Risk Management for the Chemical Process Industry*, Van Nostrand Reinhold, New York, 1991.
- Apostalakis, G. and G. Volta (Eds.), *Synthesis and Analysis Methods for Safety and Reliability Studies*, Plenum, New York.

Confined Spaces

- NSC, *Complete Confined Spaces Handbook*, National Safety Council, US, 1994.
- *Confined Space Entry*, BP Process Safety Series, IChemE, 2005.
- Mcmanus, Neil, *Safety and Health in Confined Spaces*, Technology, 1998.
- Finkel, Martin H., *Guidelines for Hot Work in Confined Spaces: Recommended Practices for Industrial Hygienists and Safety Professionals*, American Society of Safety Engineers, 1999.
- Rekus, John, *Complete Confined Spaces Handbook*, CRC Press/Lewis Publishers, 1994.
- API RP2016, *Guidelines and Procedures for Entering and Cleaning Petroleum Storage Tanks*, 1st ed.
- API Std 2015, *Safe Entry and Cleaning of Petroleum Storage Tanks, Planning and Managing Tank Entry from Decommissioning Through Recommissioning*, 5th ed., 1994.
- API Publ 2217a, *Guidelines for Work in Inert Confined Spaces in the Petroleum Industry*, 2nd ed., 1997.
- *Control of Work*, BP Process Safety Series, IChemE, 2006.
- ANSI Z117.1, *Safety Requirements for Confined Spaces*.
- *Hazards Xxviii Process Safety – Sharing Best Practices*, IChemE, 2004.
- *Safe Ups and Downs for Process Units*, BP Process Safety Series, IChemE, 2005.
- *Safe Handling of Light Ends*, BP Process Safety Series, IChemE.
- *Safe Tank Farms and (Un) Loading Operations*, Bp Process Safety Series, IChemE.
- *Safe Furnace and Boiler Firing*, BP Process Safety Series, IChemE, 2005.

Prevention and Protection

- *Loss Prevention and Protection for Chemical and Petrochemical Plants*, Industrial Risk Insurers, Hartford, CT.
- *Accident Prevention Manual: Engineering & Technology*, 11th ed., National Safety Council, US.
- Burns, Thomas, *Serious Incident Prevention: How to Achieve and Sustain Accident-Free Operations in Your Plant or Company*, Gulf Pub. Co., 1999.

- NFPA, *Fire Protection Guide to Hazardous Materials*, 13th ed., 2002.
- API RP 920, *Prevention of Brittle Fracture of Pressure Vessels*, 1st ed., 1990 (ANSI/API Publ 920-1992).
- API RP 2350, *Overfill Protection for Storage Tanks in Petroleum Facilities*, 2nd ed., 1996.
- API RP 2001, *Fire Protection in Refineries*.
- Schroll, R. Craig, *Industrial Fire Protection Handbook*, 2nd ed., Technomic Pub Co., 2002.
- API RP 520, *Sizing, Selection, and Installation of Pressure-Relieving Devices in Refineries: Part I – Sizing and Selection*, Part I – *Sizing and Selection* – 7th ed., Part II – *Installation* – 5th ed., API.
- Grossel, Stanley S., *Deflagration and Detonation Flame Arresters*, Wiley, 2002.
- API Publ 2028, *Flame Arresters in Piping Systems*, 2nd ed., 1991.
- HSE, *Flame Arresters*, HSE Book HS(G)158, Health and Safety Executive, UK, 1996.
- API STD 670, *Machinery Protection Systems*, 4th ed., API.
- NSC, *PPE Made Easy: A Comprehensive Checklist Approach to Selecting and Using Personal Protective Equipment*, National Safety Council, US, 1998.
- NSC, *Chemical Protective Clothing Performance Index*, 2nd ed., National Safety Council, US, 1999.
- FMEC, *Inerting and Purging of Tanks, Process Vessels and Equipment*, Loss Prevention Data Sheet No. 7–59, Factory Mutual Engineering Corporation, Norwood, MA.
- Forsberg, Krister and S. Z. Mansdorf, *Quick Selection Guide to Chemical Protective Clothing*, 3rd ed., John Wiley, 1997.
- API 2218, *Fireproofing Practices in Petroleum and Petrochemical Processing Plants*.
- API RP 571, *Damage Mechanisms Affecting Fixed Equipment in the Refining Industry*, 1st ed., API.

Inspection

- API RP 576, *Inspection of Pressure-Relieving Devices*, 2nd ed., API.
- API Std 510, *Pressure Vessel Inspection Code: Maintenance Inspection, Rating, Repair, and Alteration*, 8th ed., 1997 (ANSI/API Std 510-1997).
- API Std 653, *Tank Inspection, Repair, Alteration, and Reconstruction*, 2nd ed., 1995.
- API RP 580, *Risk-Based Inspection*, 1st ed., API.
- API RP 572, *Inspection of Pressure Vessels (Towers, Drums, Reactors, Heat Exchangers, and Condensers)*, 2nd ed., API.
- API RP 573, *Inspection of Fired Boilers and Heaters*, 2nd ed., API.
- API RP 574, *Inspection Practices for Piping System Components*, 2nd ed., API.
- API RP 575, *Guidelines and Methods for Inspection of Existing Atmospheric and Low Pressure Storage Tanks*, 2nd ed., API.
- API STD 598, *Valve Inspection and Testing*, 8th ed., API.
- NSC, *OSHA Inspections: Preparation and Response*, National Safety Council, US, 2004.

- API 581, *Risk-Based Inspection Base Resource Document*, 1st ed., API.
- API STD 610, *Centrifugal Pumps for Petroleum, Petrochemical and Natural Gas Industries*, 10th ed., ISO 13709 Adoption, API.
- API STD 660, *Shell-and-Tube Heat Exchangers for General Refinery Services*, 7th ed., ISO 16812 Adoption, API.
- API STD 661, *Air-Cooled Heat Exchangers for General Refinery Service*, 5th ed., ISO 13706: 2000 Adoption, API.
- API STD 662, *Plate Heat Exchangers for General Refinery Services*, 2nd ed., ISO 15547: Adoption, API.

Case Studies

- Garrison, P. E., *100 Largest Losses*, 7th ed., M&M Protection Consultants, Chicago, 1988.
- Kletz, T. A., *What Went Wrong? Case Studies of Process Plant Disasters*, 4th ed., 1998.
- Kletz, T. A., *Still Going Wrong! Case Histories of Process Plant Disasters and How They Could Have Been Avoided*, IChemE, 2003.
- *Lessons from Disaster: How Organizations Have No Memory and Accidents Recur*, IChemE, 1993.
- Eckerman, Ingrid, *The Bhopal Saga:Causes and Consequences of the World' Largest Industrial Disaster*, Universities Press.
- *The Flixborough Cyclohexane Disaster*, HMSO, London, 1975.
- NSC, *Case Studies in Safety & Productivity*, Vol. 1, 2000, Vol. 2, 2003, National Safety Council, US.
- Drogaris, G., *Major Accident Reporting System: Lessons Learned from Accidents Notified*, Elsevier Science Publishers B.V., Amsterdam, 1993.

Human Factors

- Kletz, T. A., *An Engineer's View of Human Error*, IChemE, 2001.
- Kletz, T. A., Paul Chung, Eamon Broomfield, and Chaim Shen-Oor, *Computer Control and Human Error*, IChemE, 1995.
- CCPS, *Guidelines for Preventing Human Error in Process Safety*, AIChE, 1994.
- API 770, *A Manager's Guide to Reducing Human Errors Improving Human Performance in the Process Industries*.
- *A Manager's Guide to Reducing Human Errors, Improving Human Performance in the Chemical Industry*, CMA, Washington, DC, 1990.
- *Human Error Reduction and Safety Management*, ACGIH, 3rd ed.
- *Guidelines for Preventing Human Error in Process Safety*, Pub No: G-15, AIChE, ISBN No: 0-8169-0461-8 1994.
- Mill, Robert C. (Ed.), *Human Factors in Process Operations*, 1992.
- NSC, *Ergonomics: A Practical Guide*, 2nd ed., National Safety Council, US, 1993.
- MacLeod, Dan, *The Rules of Work: A Practical Engineering Guide to Ergonomics*, National Safety Council, US, 2000.
- Salvendy, Gavriel (Ed.), *Handbook of Human Factors and Ergonomics*.
- NSC, *Fitting the Task to the Human*, 5th ed., National Safety Council, US, 1997.

- Sanders, M. S. and E. J. McCormick, *Human Factors in Engineering and Design*, 7th ed., McGraw-Hill, New York, 1993.
- API RP 752, *Management of Hazards Associated with Location of Process Plant Buildings*, 2nd ed., API.

Investigations

- *Guidelines for Investigating Process Safety Incidents*, 2nd ed., Pub No: G-65 AIChE, 2000.
- Vincoli, Jeffrey W., *Basic Guide to Accident Investigation and Loss Control*, Van Nostrand Reinhold, 1997.
- Ferry, Ted S., *Modern Accident Investigation and Analysis*, John Wiley.
- *Investigating Accidents and Incidents*, HSE Books, 2004.

Releases

- NFPA, *Recommended Practice for Handling Releases of Flammable and Combustible Liquids and Gases*, NFPA 329, Quincy, MA, 1999.
- CCPS, *Guidelines for Post-Release Mitigation in the Chemical Process Industry*, AIChE, 1996.
- CCPS, *Guidelines for Vapor Release Mitigation*, AIChE, 1988.
- Hackman, Christian L., Matthew E. Hackman, and Elsworth Hackman, *Hazardous Waste Operations & Emergency Response Manual and Desk Reference*, Technology, 2001.
- NFPA 471, *Recommended Practice for Responding to Hazardous Materials Incidents Guidelines for Use of Vapor Cloud Dispersion Models*, AIChE, 1987.
- *Workbook of Test Cases for Vapor Cloud Source Dispersion Models*, AIChE, 1989.
- *Guidelines Technical Planning for On-Site Emergencies*, AIChE, 1995.
- API STD 537, *Flare Details for General Refinery and Petrochemical Service*, 1st ed., API.
- NSC, *On-Site Emergency Response Planning Guide*, National Safety Council, US, 2003.

Relief

- API RP 521, *Guide for Pressure-Relieving and Depressuring Systems*, 4th ed., 1997.
- API RP 520, *Recommended Practice for the Design and Operation of Pressure Relieving Systems in Refineries*, Parts I and II.
- API RP 520/1&2, *Sizing, Selection, and Installation of Pressure Relieving Devices in Refineries*, Parts I and II.
- API RP 2210, *Flame Arresters for Vents of Tanks Storing Petroleum Products*.
- CCPS, *Deflagration and Detonation Flame Arrestors*, AIChE.
- *Guide for Explosion Venting*, NFPA, Quincy, MA, Latest Edition.
- CCPS, *Guidelines for Pressure Relief and Effluent Handling Systems*.
- Parry, Cyril F., *Relief Systems Handbook*, IChemE, 1992.

Storage and Handling

- Hughes, J. R., *Storage and Handling of Petroleum Liquids*, 2nd ed., Charles Griffin & Co. Ltd., London, 1978.
- CCPS, *Guidelines for Storage and Handling of Chemicals Guidelines for Safe Storage & Handling of High Toxic Hazard Materials*, Pub No: G-3, AIChE, 1988.
- *Guidelines for Safe Storage and Handling of Reactive Materials*, Pub No: G-30, AIChE, 1995.
- *Safe Warehousing of Chemicals*, Resource Manual, CMA, Washington, DC, 1989.
- API Publ 340, *Liquid Release Prevention and Detection Measures for Aboveground Storage Facilities*, 1997.
- API Publ 2510A, *Fire Protection Considerations for the Design and Operation of Liquefied Petroleum Gas (LPG) Storage Facilities*, 2nd ed., 1996.
- API Std 2000, *Venting Atmospheric and Low-Pressure Storage Tanks: Non-refrigerated and Refrigerated*, 4th ed., 1992 (ANSI/API Std 2000-1992).

Miscellaneous

- CCPS, *Guidelines for Technical Management of Chemical Process Safety*, AIChE, New York, 1989.
- *Guidelines for Implementing Process Safety Management Systems*, AIChE, New York, 1994.
- *Safety Guidelines for the Manufacture of Chlorine*, 1st ed., 2nd rev., 1981.
- *Guidelines for Process Safety Management Documentation*, AIChE, 1995.
- ACGIH, *Industrial Ventilation—A Manual of Recommended Practice*, 19th ed., American Conference of Governmental Hygienists, Cincinnati, OH, 1986.
- CMA, *A Resource Guide for Implementing the Process Safety Code of Management Practices*, Chemical Manufacturers Association, Washington, DC, 1990.
- ANSI Z535 Series, *Safety Color Code - Environmental Facility Safety Signs - Criteria for Safety Symbols - Product Safety Sign & Labels and Accident Prevention Tags*, Contains ANSI Z535.1, Z535.2, Z535.3, Z535.4, and Z.
- *Safety Guidelines for the Manufacture of Chlorine*, 1st ed., 2nd rev., Pub No: 67, Chlorine Institute, Arlington, VA, 1981.
- *Management of Process Hazards*, API Recommended Practice 750, 1st ed., API, Washington, DC, 1990.
- *Evaluating Process Safety in the Chemical Industry, a Manager's Guide to Quantitative Risk Assessment*, CMA, Washington, DC, 1989.
- Thumann, Albert and K. L. Petrocelly, *Facilities Evaluation Handbook: Safety, Fire Protection and Environmental Compliance*, 2nd ed., Fairmont Press, 1999.
- Gruhn, P. and H. Cheddie, *Safety Shutdown Systems: Design, Analysis and Justification*, ISA, 1998.
- *Process Safety Management (Control of Acute Hazards)*, CMA, Washington, DC, 1985.

- *Managing Process Changes: Implementing and Improving Management of Change Programs*, CMA, Washington, DC, 1993.
- CCPS, *Plant Guidelines for Technical Management of Chemical Process Safety*, AIChE, 1992.
- CCPS, *Guidelines for Implementing Process Safety Management Systems*, AIChE, 1994.
- Petersen, Dan, *Authentic Involvement*, National Safety Council, US, 2001.
- NSC, *On the Practice of Safety*, 3rd ed., National Safety Council, US, 1997.
- NSC, *Supervisors' Safety Manual*, 9th ed., National Safety Council, US, 1997.
- NSC, *Techniques of Safety Management: A Systems Approach*, 4th ed., National Safety Council, US, 2003.
- NSC, *Lockout/Tagout: The Process of Controlling Hazardous Energy*, National Safety Council, US, 1995.
- Manuele, Fred A., *Innovations in Safety Management: Addressing Career Knowledge Needs*, National Safety Council, US, 2001.
- NSC, *Safety Metrics: Tools and Techniques for Measuring Safety Performance*, National Safety Council, US, 2003.
- NFPA 170, *Standard for Fire Safety Symbols*, NFPA, Quincy, MA, 1996.
- Nimmo, I., *Abnormal Situation Management*, Instrument Society of America, New Orleans, 1996.
- Sutton, I., *Writing Operating Procedures for Process Plants*, Southwestern Books, Houston, TX, 1995.

Regulations, Codes of Practice, and Industry Standards

- API RP 2210, *Flame Arresters for Vents of Tanks Storing Petroleum Products*, 3rd ed., American Petroleum Institute, Washington, DC, 2000.
- API RP 521, *Guide for Pressure-Relieving and Depressuring Systems*, 4th ed., American Petroleum Institute, Washington, DC, 1997.
- ASTM F-1273-91, *Standard Specification for Tank Vent Flame Arresters*, American Society for Testing and Materials, West Conshohocken, PA, 1991.
- CEN (Comité Européean de Normalisation) Std, *Flame Arresters- Specifications, Operational Requirements and Test Procedures*, EN12874, European Committee for Standardization, Brussels, Belgium, 2001.
- CGA (Compressed Gas Association, Inc.), (Reaffirmed 1984), *Acetylene Transmission for Chemical Synthesis (Recommended Minimum Safe Practices for Piping Systems)*, Publication G-1.3, Compressed Gas Association, Inc., Arlington, VA, 1970.
- HSE (Health and Safety Executive), *Guide for Flame Arresters and Explosion Reliefs*, Booklet HS(G)11, Health and Safety Executive, Her Majesty's Stationery Office, London, UK, 1980.
- IEC (International Electrotechnical Commission) IEC 79-1A, First supplement to Publication 79-1 (1971), *Electrical Equipment for Explosive Gas Atmospheres*, Part 1, Appendix D, 2nd impression, *International Electrotechnical Commission*, 1 rue de Varembe, Geneva, Switzerland, 1982.
- NFPA 30, *Flammable and Combustible Liquids Code*, NFPA, Quincy, MA, 2000.

- NFPA 325, *Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids*, NFPA, Quincy, MA, 1994.
- NFPA 497, *Recommended Practice for the Classification of Flammable Liquids, Gases, or Vapors and of Hazardous (Classified) Locations for Electrical Installations in Chemical Process Areas*, NFPA, Quincy, MA, 1997.
- 29 CFR 1910.106, *Flammable and Combustible Liquids, Code of Federal Regulations*, Washington, DC, 1969.
- 33 CFR Part 154, Subpart E—*Vapor Control Systems*, U.S. Department of Transportation, Coast Guard, June 21, 1990.
- UL 525, *Standard for Flame Arresters*, 6th ed., Underwriters Laboratories, Inc., Northbrook, IL, 1994.
- Flessner, M.F. and R.A. Bjorklund, "Control of Gas Detonations in Pipes," *CEP Loss Prevention Manual*, 14, 113–126, 1981.
- Grumer, J., M.E. Harris, and V.R. Rowe, *Fundamental Flashback, Blowoff, and Yellow-Tip Limits of Fuel Gas-Air Mixtures*, U.S. Bureau of Mines Report of Investigations 5225, July 1956.
- Howard, W.B., C.W. Rodehorst, and G.E. Small, "Flame Arresters for High-Hydrogen Fuel–Air Mixtures," *CEP Loss Prevention Manual*, 9, 46–53, 1975.
- HSE, *Flame Arresters and Explosion Vents*, Health and Safety Series Booklet HS(G)11, Health and Safety Executive, London, UK, 1980.
- NMAB, *Classification of Gases, Liquids and Volatile Solids Relative to Explosion-Proof Electrical Equipment*, Report NMAB 353-5. National Academy Press, Washington, DC, August 1982.

Professional Societies/Institutions/Organizations

- American Institute of Chemical Engineers (AIChE), New York.
- Center for Chemical Process Safety (CCPS), AIChE, New York.
- American Chemical Society (ACS), Washington, DC.
- Institution of Chemical Engineers (IChemE), Rugby, UK.
- National Fire Protection Association (NFPA), Boston.
- Occupational Safety and Health Administration (OSHA).
- Health and Safety Executive (HSE), UK.
- Her Majesty Stationary Office (HMSO), London.
- National Academy of Sciences, Committee on Hazardous Materials, Washington, DC.
- Manufacturing Chemists Association (MCA), US.
- American Conference of Governmental Industrial Hygiene (ACGIH), Cincinnati, OH.
- American Industrial Hygiene Association (AIHA), Akron, OH.
- Environmental Protection Agency (EPA), US.
- Chemical Industries Association, London.
- Underwriter's Laboratories (UL), US.
- National Safety Council (NSC), US.
- National Institute of Occupational Safety and Health (NIOSH), US.
- Chlorine Institute, New York.
- Department of Transportation, U.S. Coast Guard, Washington, DC.

- American Petroleum Institute (API), Washington, DC.
- Energy Institute, London.
- National Electrical Code (NEC), US.
- Instrument Society of America (ISA), Pittsburgh.
- American National Standards Institute (ANSI).
- British Standards Institute (BS).
- International Organization for Standardisation (ISO), Geneva.
- American Society of Mechanical Engineers (ASME), New York.
- American Society for Testing Materials (ASTM), Philadelphia.
- Swiss Society of Chemical Industry, Basle, Switzerland.

Periodicals

- Chemical Engineering Progress, AIChE, New York.
- Chemical Health and Safety, ACS, Washington, DC.
- The Chemical Engineer, IChemE, Rugby, UK.
- Chemical Engineering, McGraw-Hill, New York.
- Hydrocarbon Processing, Gulf Publishing Co., Houston, TX.
- Oil and Gas Journal, Gulf Publishing Co., Houston, TX.
- Journal of Hazardous Materials, Pergamon Press.
- Reliability Engineering and System Safety.
- Fire Safety Journal.
- Journal of Fire and Flammability.
- Combustion and Flame.
- Process Safety Progress, AIChE.
- Process Safety and Environmental Protection.
- Journal of Loss Prevention in the Process Industries.
- Journal of Chemical and Engineering Data, American Chemical Society, Washington, DC.
- Plant/Operations Progress.
- Journal of Occupational Accidents.
- NSC, Safety+Health® Magazine, National Safety Council, US.

Journals

- IChemE.
- Chemical Engineering Research and Design.
- Food and Bio products Processing.
- Education for Chemical Engineers.
- Journal of Safety Research, National Safety Council & Pergamon Press.
- Publications on Safety & Codes of Practice By API, ASME, ANSI, ISA, HSE, HMSO, ACS, OSHA, ACGIH, Manufacturing Chemists Association, Chemical Industries Association, BS, etc.
- AIChE, CCPS Guidelines, Manuals and Symposium Series on Loss Prevention, Ammonia Plant Safety, National Safety Council, etc.
- IChemE, Symposium Series and Other Publications on Safety.

OSHA Standards

- 1910.38 Employee Emergency Plans and Fire Prevention Plans.
- 1910.38 (a) Emergency Action Plan.
- 1910.106 Flammable and Combustible Liquids.
- 1910.109 Explosives and Blasting Agents.
- 1910.119 Process Safety Management of Highly Hazardous Chemicals.
- 1910.120 Hazardous Waste Operations and Emergency Response.
- 1910.252 General Requirements (Welding, Cutting, and Brazing).
- 1910.252 (a) Fire Prevention and Protection.
- 1910.1200 Hazard Communication.
- 1910.1200 (g) Material Safety Data Sheets.

Professional Societies and Associations

- Chlorine Institute, 1300 Wilson Boulevard, Arlington, VA. 22209, (703) 741-5760.
- American Chemistry Council, 1300 Wilson Boulevard, Arlington, VA. 22209, (703) 741-5000.
- Center for Chemical Process Safety, American Institute of Chemical Engineers (AIChE), Park Avenue, New York, 10016-5991, (212) 591-7319.

Note: Categorization of books may involve overlapping of the subject topics.

Index