July 2023
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CHEMICAL REACTORS AND REACTIONS

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1.0 SCOPE

This data sheet provides guidance for the evaluation of chemical reactivity hazards and chemical reactors, including associated hazards and equipment such as mixers, heating/cooling systems, safety interlocks, pressure-relief devices, etc. It also describes general chemical reaction hazards and concepts associated with chemical reactivity assessments, the steps and tests needed to identify process reactivity hazards and apply this knowledge to the different stages of process and equipment design, as well as to define safe process operating conditions. For general guidance on pressure vessels, piping and systems see Data Sheet 12-2, *Vessels and Piping*.

The guidance provided in this data sheet for pressure-relief devices only covers the design basis for the chemical reactivity case. For other scenarios, device selection, installation and inspection or testing and maintenance guidance, see Data Sheet 7-49, *Emergency Venting of Vessels*.

This data sheet does not include guidance for specific reactor types such as reformers and cracking furnaces, chlorine dioxide, chemical recovery boilers, ammonium nitrate neutralizers, etc., which are detailed more specifically in their respective data sheets.

1.1 Hazards

Reactive chemicals and chemical reactors present a broad range of hazards. Hazard recognition requires understanding of inherent reactivity of the chemicals involved in a reaction and whether the reaction itself requires heat to progress (endothermic and easily controlled) or gives off heat during the reaction (exothermic with controllability related to the extent of heat evolved). Many preventative steps can be taken in areas where hazardous reactions take place such as using a small reactor vessel or locating the reactor in a remote area or within a high strength barricade.

Severe reactive chemical events are largely a result of the following conditions:

- Unintentional mixing of incompatible materials
- Unintended accumulation of energy (unreacted reagents or pressure generation)
- Operation outside of established safe limits
- Failure to control chemical reaction rates and heat generation
- Handling of unstable materials

1.2 Changes

October 2024. Interim revision. Minor editorial changes were made for additional clarity.

2.0 LOSS PREVENTION RECOMMENDATIONS

2.1 Introduction

Use FM Approved equipment, materials and services whenever they are applicable. For a list of products and services that are FM Approved, see the *Approval Guide*, an online resource of FM Approvals.

2.2 Process Safety

2.2.1 Perform a reactive system assessment to determine if reactive hazards exist with the potential to generate uncontrolled chemical reactions.

2.2.1.1 Ensure raw materials, catalysts, intermediates, products, by-products, unintended products, solvents, inhibitors, quenchers, decomposition products and cleaning products are included on the analysis to determine if any of the following exist and any incompatibility between them:

a) Pyrophoric properties
b) Water reactivity
c) Oxidizing properties
d) Flammable solids, combustible dust, liquid and/or vapor flammability, or ignitability properties
e) Common contaminant reactivity (e.g., rust, heat transfer fluid, scrubber solutions)
f) Mechanical sensitivity (mechanical impact and friction)
g) Thermal sensitivity
h) Self-reactivity

2.2.2 Where reactive chemicals or reactors are used, apply all process safety elements in accordance with Data Sheet 7-43, *Process Safety*, with additional emphasis on the following:

A. Process Knowledge: Chemical reactivity tests, updated process piping and instrumentation drawings (P&IDs), details of all safety interlocks including safe operating windows, consequences of deviations and emergency procedures, vessel design specifications and codes, materials of construction, emergency relief design calculations.

B. Process Hazard Analysis (PHA): Include in the evaluation all modes of operation including startup, shutdown, idle and emergency, as well as the following upset conditions:

- Mischarge of reactants: overcharge of monomer, undercharge of limiting reagent, excess catalyst, wrong catalyst, wrong sequence of addition or inadvertent addition
- Mass load upset/composition and concentration: accumulation of unreacted materials, non-uniform distribution of gas, settling of solids, phase separation, foaming or use of re-work
- Contamination of raw materials or equipment: water, rust, chemical residue, leaking heat transfer fluid, or cleaning products
- Abnormal temperatures: reaction rate, side reactions, etc.
- Abnormal pressures: reaction rate, side reaction, etc.
- Loss of inerting media
- Loss of agitation: electric or hydraulic
- Loss of utilities: power, steam, instrument air, water (process and cooling), etc.
- Inadequate and/or loss of cooling: jacket, heat exchanger and condenser
- Equipment failures: plugged lines, stuck pressure-relief devices, failed valves, inaccurate instrumentation readings, pump failures
- Backflow of materials

C. Management of Change (MOC): Not in-kind changes to equipment, raw materials including change in concentrations or purities, catalyst, process condition modifications and batch size modifications

D. Asset Integrity: Inspection, testing and maintenance programs and frequencies, vessel history records (i.e., alterations, repairs, etc.), corrosion allowances and studies, remaining useful life (RUL), damage mechanisms, NDE tests, inspection reports (wall thickness, insulation, internal lining, heating/cooling systems, agitators, catalyst, etc.). See also Section 2.5.2.1.1 for additional information.

E. Incident investigation: Investigate and document any unplanned mixing of chemicals, out of specification batches or materials, activation of safety devices, safety interlocks failures, unintended formation of gasses or unplanned byproducts and/or operation outside the normal process operating limits. Determine the level of investigation according to the reactive chemistry hazard presented by each of these near misses/incidents.

2.3 Reactive Chemicals Management

2.3.1 Implement inventory management systems where hazardous materials are present. Include information on composition, compatibility, location of storage/processing vessel, and maximum intended inventory. The goal should be to avoid accidental mixing of incompatible materials and to minimize the inventory of high hazard materials.

2.3.2 Provide segregation of incompatible materials in warehouses and tank farms. This may include separate storage areas for different classes of materials (i.e., not putting oxidizers and reducing agents in the same room or diked area).

2.3.3 Design hazardous chemical handling systems to avoid accidental mixing of incompatible materials. This may include labeling of piping and connections, separate loading stations for incompatible materials, drains, etc.

2.3.4 Minimize the inventory of reactive chemicals in production areas. Inventories should typically be limited to the quantity needed in one operating shift.

2.4 Equipment and Processes

2.4.1 General

2.4.1.1 Design and construct reactors in accordance with applicable codes, standards, and state/local laws and regulations. Base design pressures, temperatures, and corrosion allowances on the most severe combination of conditions anticipated. For additional guidance see Section 4 and Data Sheet 12-2, *Vessels and Piping*.

2.4.2 Reactors Design

2.4.2.1 General

2.4.2.1.1 Base process development and equipment design on the results of the reactive system assessment. Consider the potential energy of the chemicals and reactions involved, reaction rates, reactive interactions (incompatibilities), secondary reactions or subproducts, upset conditions, equipment failures, etc.

2.4.2.1.2 Evaluate use of the proposed chemicals and synthesis route to optimize safety before proceeding with process and equipment design. Use the inherently safer design concepts of intensification, substitution, attenuation, and limitation throughout new products and process development to avoid hazards, thereby reducing the need for mitigation.

2.4.2.1.3 Ensure the scale-up effects are addressed systematically to prevent the presence of runaway reactions or other hazardous conditions due to improper process scalation from laboratory conditions/small-scale vessels to full production scale.

2.4.2.1.4 Where the loss of agitation is critical for process safety or to prevent runaway reactions, ensure agitators are provided with:

A. Shaft speed and/or load monitoring.

B. Adequate cooling for agitator shaft seals and bearings. Hot bearings and seals are potential ignition sources. Provide vibration or temperature sensors where this is a concern.

C. Double or tandem mechanical seals with inert seal fluid when seal failure could release flammable or other hazardous materials, particularly hydrogen. Provide low level alarms on seal fluid reservoirs.

2.4.2.2 Overpressure Protection

This section provides recommendations for design of overpressure protection of reactive systems. For design guidance of non-reactive cases see Data Sheet 7-49, *Emergency Venting of Vessels*.

Sizing calculations of pressure-relief devices for reactive systems can be performed by qualified plant personnel or contractors.

2.4.2.2.1 Provide adequate overpressure protection for all chemical reactors and pre-mix tanks.

2.4.2.2.2 Base emergency-relief vent sizing on a worst credible case evaluation considering all modes of operation. Develop the worst credible scenario based on a thorough study of the process, possible upset conditions, common causes of runaway reactions and other factors that could cause an increase in operating pressure in the vessel.

2.4.2.2.3 Ensure the sizing of the relief device is performed using adequate reactive system methodologies for the expected reaction and process conditions.

2.4.2.2.4 Where adequate overpressure protection is not practical using traditional pressure-relief devices, evaluate other methods of prevention or resistant design, isolation or barricades.

2.4.3 Reactors Construction

2.4.3.1 Arrange raw material charging systems to minimize potential mistakes and problems. Arrange feed vessels or provide protection to prevent reverse flow.

2.4.3.2 Provide an inerting/purging system or other means of explosion prevention or suppression for reactors having the potential to generate combustible/explosive mixture atmospheres. See Data Sheets 7-59, *Inerting and Purging Vessels and Equipment* and 7-76, *Combustible Dusts, for additional information.*

2.4.3.3 Arrange all process safety interlocks, including safety instrumented systems (SIS), in accordance with Data Sheet 7-45, *Safety Controls, Alarms, and Interlocks*.

2.4.3.4 For process handling of ignitable liquids and/or flammable gases refer to Data Sheets 7-14, *Fire Protection for Chemical Plants* and 7-32, *Ignitable Liquid Operations*, for additional design considerations.

2.5 Operation and Maintenance

2.5.1 Operation

2.5.1.1 Develop and implement standard operating procedures (SOPs) with clear instructions/activities addressing all modes of operation including startup, shutdown, and idle periods. Ensure the SOPs are clear, comprehensive and utilized by operators (see Data Sheet 10-8, *Operators*). Ensure the SOPs include at a minimum:

- Inspections required before initiation of operations.
- Batch recipes, including quantities and order of addition.
- Maximum batch size or fill level.
- Cleaning procedures between batches.
- Warnings for critical tasks or operations.
- Alarm management.
- Normal operating windows.

2.5.1.2 Develop and implement emergency operating procedures (EOPs). Ensure the EOPs include at a minimum:

- Upset condition management, including guidance on when to stop scheduled additions, initiate quenching, initiate dumping or add inhibitor as appropriate.
- Potential consequences of operating outside the normal boundaries, including critical safety conditions and associated safeguards.
- Shutdown authority and actions to be taken in the event of an identified upset condition even when the process is designed to fail safe.
- Management of off-specification products and instructions for rework materials. Rework may have a significant concentration of undesired materials, including unstable intermediates.

See Data Sheet 10-8, *Operators*, for additional information.

2.5.1.3 For multipurpose plants, ensure procedures are established to clean and free the equipment of incompatible materials before switching to other operations.

2.5.1.4 Avoid premixing of reactive raw materials. Where premixing is performed, provide adequate overpressure protection of premix tanks.

2.5.1.5 Where combustible atmospheres exist, add solids or liquids using closed charging systems under an inert atmosphere. Do not use open manways to add solids or liquids to a combustible headspace. See Data Sheet 7-59, *Inerting and Purging Vessels and Equipment*, for additional information.

2.5.1.6 For glass-lined reactors, ensure adequate procedures are in place to prevent lining damage caused by impact, thermal shock, operating the vessel outside the design conditions, etc. Include cleaning and inspection instructions and tools in the procedures.

2.5.2 Maintenance

2.5.2.1 General

2.5.2.1.1 Establish an asset integrity program for chemical reactors in accordance with Data Sheet 9-0, *Asset Integrity*, to ensure the integrity and reliability of the vessel, associated piping system and equipment is maintained throughout its service life. Develop the asset integrity program considering all process hazards, operating conditions, materials, and environmental conditions. Maintain records of all inspection, testing and maintenance activities. Ensure the following are included in the program:

- Welds that are prone to physical stress (e.g., at head nozzles and agitator mounts) and chemical corrosion (e.g., liquid/vapor interface)
- Vessel integrity
- Lining integrity (Glass, PTFE, cladding, etc.)
- Corrosion/thickness
- Insulation integrity
- Catalyst - functioning within design limits, poisoned or contaminated
- Piping systems
- Heating systems
- Pumps
- Agitators
- Safety controls and interlocks
- Pressure-relief devices
- Vacuum breakers
- Inerting/purging systems
- Utilities - steam, power, instrumented air, cooling water

2.5.2.1.2 When high viscosity (sticky) materials are being handled, inspect vacuum breakers and pressure-relief devices frequently to confirm the operating mechanisms are not sticking. Conduct the inspections at least monthly until sufficient information is available to establish a predictive maintenance program.

2.5.2.1.3 For new vessels and piping, ensure initial thickness readings are taken as a baseline for the asset integrity program and for additional tests to compare and establish corrosion/erosion rates for vessel half-life calculations.

2.5.2.1.4 Completely inspect the vessel at installation or when resuming operation after an extended period of inactivity, to ensure adequate conditions for vessel operation.

2.5.2.2 Contingency Planning

2.5.2.2.1 Equipment Contingency Planning

When a reactor breakdown would result in an unplanned outage to processes and systems considered key to the continuity of operations, develop and maintain a documented, viable reactor equipment contingency plan per Data Sheet 9-0, *Asset Integrity*. See Appendix C of that data sheet for guidance on the process of developing and maintaining a viable equipment contingency plan. Also refer to sparing, rental and redundant equipment mitigation strategy guidance in that data sheet.

In addition, include the following reactor-specific elements in the contingency planning process:

- Unique design/materials of construction, including any specific conditions that may affect the intended reactor service such as pressure, temperature and/or operating conditions..
- Lined or coated reactors (rubber/glass/epoxy/metal clad/explosion bonded).
- Possible contamination of sterile environment/products or solidification of process materials.
- Presence of unique or hard-to-obtain catalyst.
- Remaining useful life/fitness for service of the reactor, which can impact replacement lead time.

2.5.2.2.2 Sparing

Sparing can be a mitigation strategy to reduce the downtime caused by a reactor breakdown depending on the type, compatibility, availability, fitness for the intended service and viability of the sparing. For general sparing guidance, see Data Sheet 9-0, *Asset Integrity*.

2.5.2.2.2.1 Routine Spares

Routine reactor spares are considered consumables. These spares are expected to be put into service under normal operating conditions over the life of the furnace, but not reduce equipment downtime in the event of a breakdown. It can include sparing recommended by the original equipment manufacturer. See Section 3.6 for reactor routine spare guidance.

2.6 Utilities

2.6.1 Design processes to fail safe on loss of power. Where emergency power is needed, size the emergency power generator to handle critical equipment loads. This may include agitators, vacuum pumps and associated equipment, heat transfer fluid systems, cooling systems including cooling tower fans, transfer pumps, instrument air compressors, instrumentation and control equipment, and fire protection systems.

2.6.2 Select reactor heat transfer systems taking both material properties and process requirements into consideration. Consider the following when arranging heat transfer systems:

A. Compatibility between fluids and temperature conditions that can produce upset process conditions or runaway reactions: Use a compatible heat transfer fluid in place of water whenever water-reactive materials are present or generated by a chemical process.

B. Thermal stress assessment during heating/cooling cycles: Heating/cooling a half pipe coil with HTF too rapidly can cause cracks/leaks.

C. Provide alarms and interlocks for organic and synthetic-based heat transfer systems in accordance with Data Sheet 7-99, *Heat Transfer Fluid Systems*. For water-based heat transfer systems (e.g., steam), provide separate excess temperature interlocks and pressure-relief devices at a minimum.

2.7 Training

2.7.1 Ensure qualified and trained personnel with knowledge on chemical reactions, process hazards and controls, and emergency procedures are designated to operate chemical reactors. See Data Sheet 10-8, *Operators*, for additional guidance.

2.8 Human Factors

2.8.1 Specifically address hazardous chemical reactivity potential in all emergency response plans and keep them readily available for reference.

3.0 SUPPORT FOR RECOMMENDATIONS

Chemical reactivity hazards can be expected at any facility where hazardous materials with the potential to generate uncontrolled chemical reactions are handled, processed and/or stored—whether intended chemical reactions are present or not. Uncontrolled chemical reactions are usually accompanied by a temperature increase, pressure increase or gas evolution. Gases evolved from these uncontrolled chemical reactions can pressurize an enclosure to the point of failure or can present other hazards such as flammable, toxic, or corrosive atmospheres.

Chemical reactivity hazards are not only applicable to self-reacting materials such as organic peroxides or polymerizing monomers (which have the ability to decompose, polymerize or rearrange in an uncontrolled manner, even without being combined with other materials). These hazards will also apply to chemical interactions of incompatible materials for intended or unintended situations. The potential for an uncontrolled chemical reaction can take many forms, involving both the intrinsic material properties as well as the conditions under which the materials are used.

3.1 Reactive or Unstable Materials Identification

This process can be performed using screening methods to determine any potential chemical reactivity hazards with the materials processed, used or stored. Typically, when data is not available, safety data sheets (SDS), literature or experimental screening are used to obtained main hazards, incompatible materials, physical and chemical properties, and identification of any unstable or energetic functional group Other tools or data bases can also be used for this purpose.

Some common energetic functional groups and the typical range of decomposition energies associated to that functional groups are presented in Table 3.1-1. These compounds' families can be identified to undergo violent or explosive decompositions.

Table 3.1-1. Unstable Structure Decomposition Energies[Note 1]

Compounds (# tested)	*Molecular Structure*	*-U (kJ/mol) range*
Aromatic nitro (30)	C-NO2	220-410
Aromatic nitroso (4)	C-N = O	90-290
Oxime (5)	C = N-OH	110-170
Isocyanate (4)	C-N = C = O	50-55
Aromatic azo (5)	C-N = N-C	100-180
Hydrazo	C-NH-NH-C	65-80
Aromatic diazonium (5)	C-N2+	130-165
Peroxide (20)	C-O-O-	200-340
Epoxide (4)	CH-CH-O (ring)	65-100
Alkene (6)	C = C	40-90

Note 1. Bretherick, L. Reactive Chemical Hazards: *An Overview, International Symposium on Preventing Major Chemical Accidentsmed, 1987*

Bretherick has identified several structures susceptible to autoxidation. These structures include acetals, allyl compounds, cumene, dienes, ethers, isopropyl compounds, styrene and vinyl compounds.

Essentially all materials are unstable above certain temperatures and will thermally decompose. Thermal decompositions may be exothermic or endothermic. Exothermic decompositions are usually irreversible and frequently explosive. Organic compounds that are known to decompose before melting include azides, diazo compounds, nitramines, oxygen-containing salts and metal styphnates.

Decomposition characteristics of energetic materials can be significantly different when combined with a solvent, and different solvents may have different effects on the decomposition temperature and rate. Solids that decompose without melting usually generate gaseous products. Particle size and aging affect the decomposition rate. Age may result in crystallization of the solid surface.

Endothermic decompositions are usually reversible and are typified by hydrate, hydroxide, and carbonate decompositions. For example, a substance may have several hydrates depending on the partial pressure of water vapor. Ferric chloride, $FeCl_2$ combines with 4, 5, 7, or 12 molecules of water. The dehydration activation energy is nearly the same as the reaction enthalpy.

Oxygen balance is an analytic tool based on the difference between the oxygen content of the chemical compound and that required to fully oxidize the elements of the compound. Materials and processes approaching zero oxygen balance have the greatest heat release potential and are the most energetic. Oxygen balance calculations may be used for organic nitrates and nitro compounds. However, no correlation exists between oxygen balance and general self-reactivity. Improper application of the oxygen balance criterion can result in incorrect hazard classifications.

The ASTM program for Chemical Thermodynamic and Energy Release (CHETAH) is an analytic tool used to determine the maximum enthalpy of decomposition. It is based on molecular structure reactivity relationships. It can only predict the reactivity of organic compounds, not inorganic compounds.

A substance should be considered energetic and potentially hazardous if any of the theoretical methods indicate hazardous thermal properties or if the experimental enthalpy of decomposition in the absence of oxygen is over 50-70 cal/g (~200-300 J/g). Note that this range is highly dependent on the process conditions and does not pertain to substances that produce significant quantities of gas.

A substance has deflagration potential if the experimental enthalpy of decomposition in the absence of oxygen is greater than 250 cal/g (~1,000 J/g). (Values of 170 to 300 cal/g can be found in the literature.) A substance has detonation potential if the experimental enthalpy of decomposition in the absence of oxygen is greater than 700 cal/g (2,900-3,000 J/g) (with several exceptions including ammonium nitrate, azides, and organic peroxides that have ΔHd of less than 475 cal/g). Selected values of enthalpy of decomposition (ΔHr) are listed in Table 3.1-2

The calculated adiabatic reaction temperature (CART) also provides some indication of a compound's potential hazard. Known explosive compounds have CART values higher than 1500 K. Selected values are listed in Table 3.1-2.

*Table 3.1-2. Enthalpy of Decomposition, CART Values and Relative Hazard Rankings for Selected Compounds*Note 1

Compound	*Formula*	ΔH_r (kJ/g)	*CART (K)*	*Hazard Index*
Acetone	C_3H_6O	-1.72	706	N
Acetylene	C_2H_2	-10.13	2824	E
Acrylic acid	$C_3H_4O_2$	-2.18	789	N
Ammonia	NH_3	2.72	-	N
Benzoyl peroxide	$C_{14}H_{10}O_4$	-0.70	972	E
Dinitrotoluene	$C_7H_6N_2O_4$	-5.27	1511	E
Di-t-butyl peroxide	$C_8H_{18}O_2$	-0.65	847	E
Ethyl ether	$C_4H_{10}O$	-1.92	723	N
Ethyl hydroperoxide	$C_2H_5O_2$	-1.38	1058	E
Ethylene	C_2H_4	-4.18	1253	N
Ethylene oxide	C_2H_4O	-2.59	1009	N
Furan	C_4H_4O	-3.60	995	N
Maleic anhydride	$C_4H_2O_3$	-2.43	901	N
Mercury fulminate	$Hg(ONC)_2$	2.09	5300	E
Methane	CH_4	0.00	298	N
Mononitrotoluene	$C_7H_7NO_2$	-4.23	104	N
Nitrogen trichloride	NCl_3	-1.92	1930	E
Nitroguanidine	$CH_4N_4O_2$	-3.77	1840	E
Octane	C_8H_{18}	-1.13	552	N
Phthalic anhydride	$C_8H_4O_3$	-1.80	933	N
RDX	$C_3H_6N_6O_6$	-6.78	2935	E
Silver azide	AgN_3	-2.05	>4000	E
Trinitrotoluene	$C_7H_5N_3O_6$	-5.73	2066	E
Toluene	C_7H_8	-2.18	810	N

Note 1. Shanley, E.S. and Melham, G.A. On the Estimation of Hazard Potential for Chemical Substances, International Symposium on Runaway Reactions and Pressure Relief Design, 1995
N - no known unconfined explosion hazard
E - unconfined explosion hazard

No single tool should be depended upon in a chemical hazard analysis. This is obvious if the maximum enthalpy of decomposition and the CART data in Table 3.1-2 are compared. Toluene has no known self-reactivity hazard, but is in the moderate hazard category based on its enthalpy of decomposition value. Mononitrotoluene has no vigorous self-reactivity hazard, but is in the high hazard category based on its enthalpy of decomposition value. Neither the enthalpy of decomposition nor CART values adequately predicts the hazards presented by organic peroxides.

3.1.1 Chemical Interaction Matrix

The chemical interaction matrix is a tool used to understand potential reactions between materials. A typical matrix list all the chemical raw materials, catalysts, solvents, potential contaminants, materials of construction, process utilities and any other material that may be combined or contacted.

Current sources used for the development of these matrices include computer software or web databases. The basis for determining chemical incompatibilities lies in the assignment of reactive groups. The interaction between these groups is analyzed to predict the type of chemical reactions most likely to occur and the potential outcomes that those reactions produce.

3.2 Reactive Systems Assessment

Proper assessment and understanding of reactive systems are key to prevent uncontrolled chemical reactions that release enough energy to cause fires or explosions with the potential for substantial property damage and business interruption. Application of this knowledge is critical to ensure adequate design basis for reactors, heat transfer/cooling systems, emergency pressure venting, process controls and ancillary equipment, as well as for the development of operational procedures and training.

Runaway reactions related to chemical processes have commonly occurred from factors involving high temperature or pressure, gas evolution, different concentration or quantities of reactants, presence of impurities and equipment failures. In a process reactor, the thermal balance plays a very important role; and any excess energy created or applied can accelerate the reaction. Temperature increments have a linear effect on the rate of heat transfer and an exponential effect on the rate of reaction and, subsequently, on the rate of heat generation. Therefore, if the heat generated exceeds the rate of heat loss and/or equipment cooling capacity, it will lead to a runaway reaction. Figure 3.2-1 presents a typical thermal stability chart showing the heat generation curve. Any increase in the coolant temperature above the temperature of no return (TNR), will cause the loss of thermal equilibrium and, consequently, a runaway reaction.

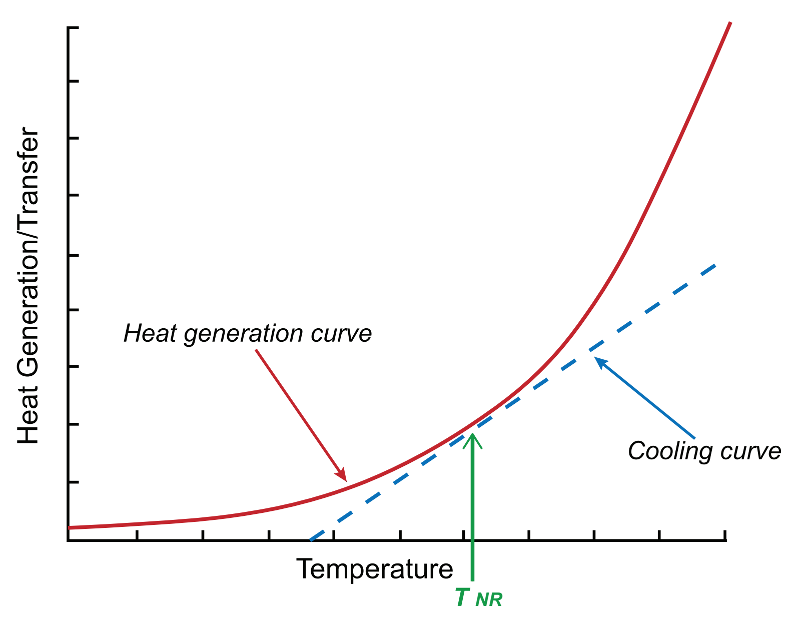


Fig. 3.2-1. Typical thermal stability chart

Heat removal rate is an important criterion for cooling system design. It can be affected if adequate agitation is not provided, resulting in inadequate cooling/heat removal capacities. Quality of raw materials is also important for safe operations. The presence of impurities can modify the actual temperature where the decomposition reaction begins. Water, for instance, (which may be considered an impurity for some processes) can create additional heat evolution. If this additional heat exceeds the reactor cooling capacity, it can lead to an increased reaction rate with a subsequent runaway reaction.

The steps involved in a reactive system assessment are presented in Figure 3.2-2. The assessment begins with the evaluation of the different properties of the materials and a preliminary characterization of chemical reactions, mainly to determine the potential of thermal instabilities and gas generating scenarios. Doing so will determine the type of analysis and the equipment to be used for main or side-reactions characterization, sizing of pressure-relief devices and process scale-up calculations.

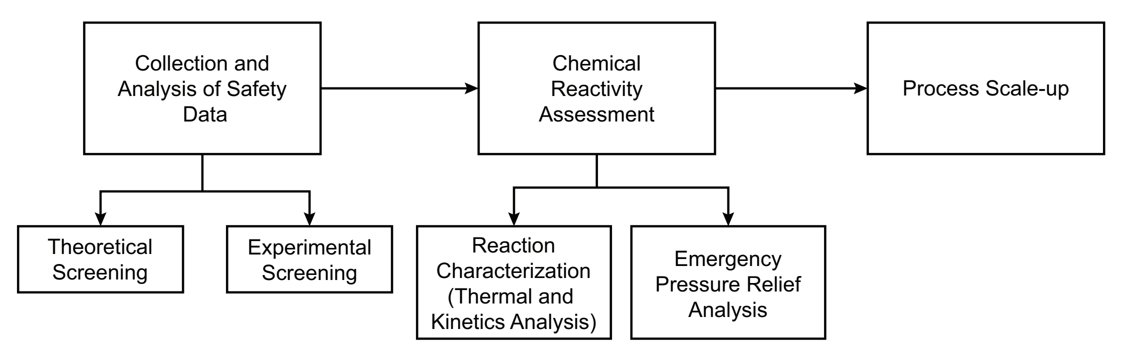


Fig. 3.2-2. Reactive systems assessment steps

3.2.1. Collection and Analysis of Safety Data

This involves collecting/reviewing physical and chemical properties for all materials in the process including raw materials, intermediate products, final products, byproducts, etc. to better understand any instability or incompatibility hazards. All pertinent properties should be evaluated in relation to the hazards of fire, explosion, toxicity, and corrosion. This phase should include the estimation of formation and reaction energies, as well as the oxygen balance (if applicable). This can be performed using literature or experimental screening when data is not available. However, since property data is frequently listed at ambient conditions, this data could be misleading. It is important to understand the physical and chemical properties of the chemicals for actual reaction conditions.

An increase in pressure raises the flash point. Conversely, a decrease in pressure lowers the flash point. An increase in pressure will also widen the flammability limits; the lower flammability limit (LFL) decreases and the upper flammability limit (UFL) increases (Figure 3.2.1-1). (Note: Lower and Upper explosive limits, LEL and UEL, are often used interchangeably with LFL and UFL). A decrease in pressure to about one-half atmosphere has minimal effect. Further decreases in pressure narrow the flammable range until it essentially disappears. An increase in pressure will decrease the minimum autoignition temperature and the minimum oxygen concentration (MOC) for combustion.

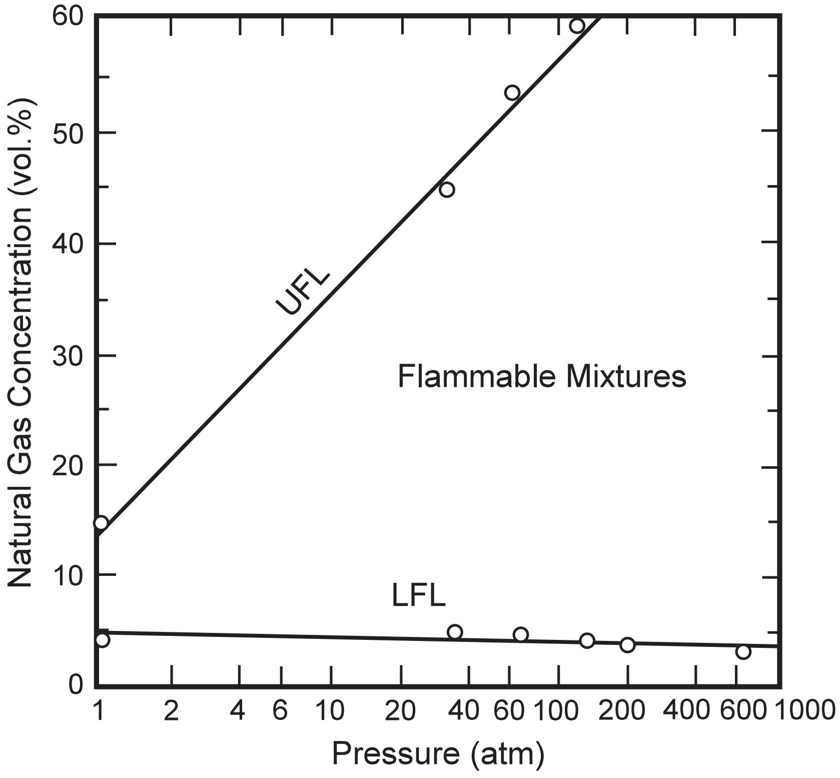


Fig. 3.2.1-1 Effects of pressure on the flammability of natural gas

Note: Zabetakis, Michael *Fire and Explosion Hazards at Temperature and Pressure Extremes,* from the AIChE Fundamentals of Fire & Explosion Hazards Course Workbook.

An increase in temperature will similarly decrease the LFL, increase the UFL, decrease the minimum autoignition temperature and decrease the MOC. Figure 3.2.1-2 shows this for two pressures P_1 and P_2, where $P_1 < P_2$. The LFLs and MOCs at one atmosphere decrease by about 8% of their values at room temperature for each 100°C increase. The UFLs at one atmosphere increase by about 8% of their values at room temperature for each 100°C increase.

Physical properties may also change significantly when a solute is put into solution. The solubility of a chemical is a function of the liquid composition and temperature. When ideal solutions are formed, there is no change

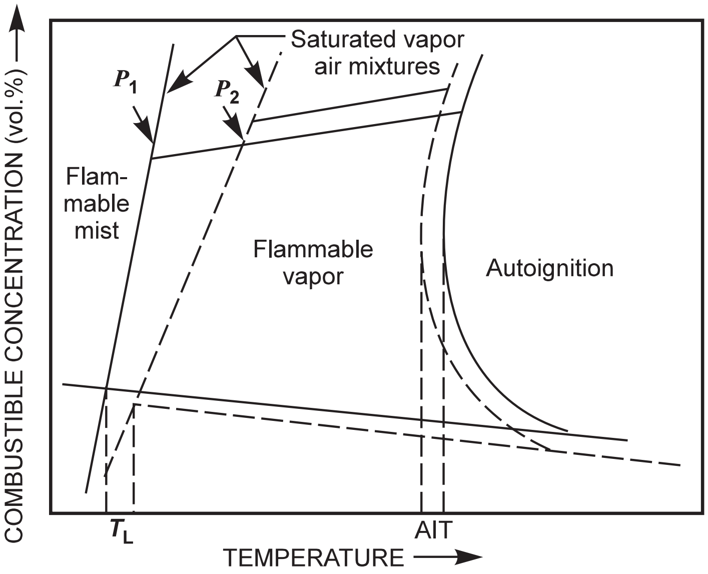


Fig. 3.2.1-2. Effects of temperature and pressure on flammability and autoignition temperature

Note: Zabetakis, Michael G. Fire and Explosion Hazards at Temperature and Pressure Extremes, from the AIChE Fundamentals of Fire & Explosion Hazards Course Workbook

in enthalpy. More commonly, however, nonideal solutions are formed, accompanied by a change in enthalpy. This heat of solution should not be confused with the heat of formation associated with a chemical reaction.

If the energy change that accompanies the dissolution of a solute is known, the effect of a change in temperature on the solubility can be determined using Le Chatelier’s principle. If the enthalpy change that accompanies the mixing ∆Hsol is positive, solubility increases as temperature increases. Likewise, if ∆Ssol is negative, solubility decreases as temperature increases. The temperature-solubility properties of three salts in water are shown in Figure 3.2.1-3. Note that temperature changes designed to increase solubility might result in solute decomposition. This is particularly true of inorganic compounds in water.

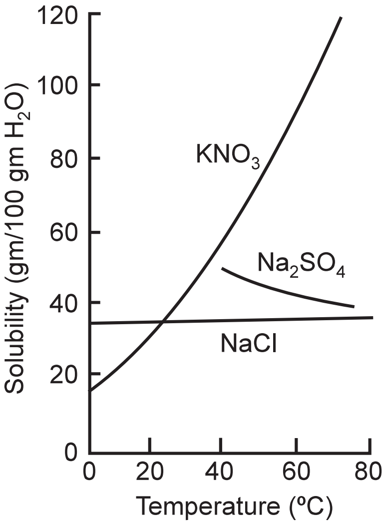


Fig. 3.2.1-3. Effects of temperature on common salt solubility

Chemical reaction analyses should also be performed initially, to predict thermodynamics of the desired reactions, as well as to identify the presence of side-reactions, the potential for gas generation or the presence of any unstable or explosive functional groups. If the risk of the process materials or reaction is high, inherent safety concepts may be introduced to reduce the process risk to tolerable levels. Inherently safer design concepts of intensification, substitution, attenuation, and limitation can be applied to eliminate hazards, thereby reducing the need for mitigation measures.

3.2.1.1 Sensitivity Assessment.

Mechanical sensitivity is divided into sensitivity to impact (shock) and sensitivity to friction. Shock sensitive materials react exothermically when subjected to pressure, and condensed-phase detonations may occur. Materials that do not exhibit an exothermic reaction during thermal stability testing are presumed not to be shock sensitive. Methods include the drop weight, confinement cap, card gap and adiabatic compression tests.

The drop weight test is conducted by dropping a weight on a sample in a metal cup. The weight and height can be varied to provide a qualitative measure of the sample’s susceptibility to decompose upon impact. This test should be applied to any material known or suspected to contain unstable chemical functional groups.

The confinement cap test is conducted using a blasting cap to determine sensitivity.

The card gap test uses a shock wave generated by an explosive charge to determine whether a propagating reaction occurs.

The adiabatic compression test is conducted by rapidly applying high pressure to a liquid in a U-shaped metal tube, then forcing hot compressed gas into the liquid. This test was designed to simulate water hammer and sloshing effects during transportation.

Sensitivity to friction tests may be conducted on solids and semi-solids by placing a sample between two rough surfaces, then rubbing the surfaces together. Methods include the ABL, BAM, and rotary friction test.

3.2.1.2 Chemical Thermodynamics

All chemical reactions involve energy changes in order to transform reactants into the products. However, is important to determine the amount of energy that can be created and released by the reaction to predict potential damage in case of an incident. The heat or enthalpy of reaction is one of the key data points and provides information on the amount of stored chemical energy. For a given chemical reaction, the total amount of energy released or required is a constant. However, the rate at which that energy is released is not a constant. The enthalpy of reaction provides some guidance as to the potential hazard, but the rate of energy release is more important than the amount of energy released. The rate of the reaction differentiates normal chemical reactions from uncontrollable chemical reactions. Enthalpy of reaction can be determined by calorimeter testing or calculated using enthalpies of formation.

The heat or enthalpy of formation provides information on the thermochemical stability of the elements involved in the subject reaction. A positive enthalpy of formation value provides a warning of a potential hazard. A negative enthalpy of formation value is of no potential use from a hazard evaluation perspective.

Reaction rate studies can vary in complexity relative to the chemical reaction. For simple reactions, the rate expression can be derived from the stoichiometric equation. For complex reactions, the rate expression is usually based on the rate expression for a similar chemical reaction and compared to the experimental data to determine its validity.

Basic factors affecting chemical reaction rates are the frequency of the molecular collisions, the reaction activation energy and the reaction activation entropy, that in practice involve temperature, pressure, concentration, and material purity. Intuitively, the greater the frequency of collisions, the faster the reaction rates. The lower the activation energy, the faster the reaction rates. The less specific the orientation required for the reaction to proceed, the faster the reaction rates. In a complex reaction, the reaction rate may also be affected by chemical and physical interactions, involving fluid dynamic properties, flow pattern, and interfacial surface area. Reaction rate studies should take all these factors into consideration.

Activation energy is generally not affected by temperature (within moderate ranges). It is dependent on pressure and is affected by the presence of a catalyst. Activation entropy is affected by the presence of a catalyst as well.

Catalysts can be thought of as forming intermediate complexes with some of the reactants. The intermediate complex then reacts with the other reactants to form the desired product and regenerate the catalyst. Catalyzed reactions have lower activation energy and/or activation entropy than uncatalyzed reactions, and the catalyzed reaction may favor one reaction mechanism over others. Catalytic reactions are classified as homogeneous or heterogeneous. In a homogeneous catalytic reaction, the reaction occurs in one phase and the reaction rate depends on the catalyst concentration. Common examples are enzymes, proteins that catalyze biochemical reactions. In a heterogeneous catalytic reaction, the catalyst is present in a different phase from the reaction mixture. Usually the catalyst is a solid, the reaction occurs at the solid surface, and the reaction rate depends on the surface area. A negative catalyst or inhibitor may be used to stop a reaction.

In an endothermic reaction, the overall energy change is positive (more heat is added than given off). Endothermic reactions generally proceed with difficulty and are slow, except at elevated temperatures. If an endothermic reaction temperature is raised too high, exothermic decompositions and side reactions may occur. The products of the endothermic reactions are typically highly unsaturated and contain high concentrations of nitrogen or nitrogen-halogen bonds. They may have an inherent tendency to spontaneously decompose. Comparison of the positive energy of activation for the decomposition reaction to the negative energy of the decomposition reaction will indicate if a self-sustained decomposition reaction is likely. In an exothermic reaction, the overall energy change is negative. Exothermic reactions generally proceed readily at ambient temperatures.

The assumption that heat addition to a reactor indicates endothermic reactions is frequently not correct. The minimum energy of activation is an important reaction rate characteristic that must be overcome. Adding heat is usually necessary to overcome the energy of activation for both exothermic and endothermic reactions (Figure 3.2.1.2-1).

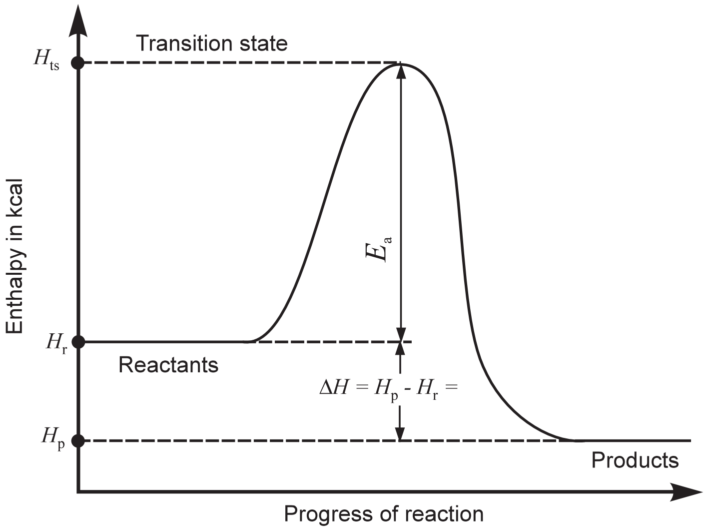


Fig. 3.2.1.2-1. Enthalpy diagram of an exothermic reaction.

The assumption that heat given off by a process indicates an exothermic reaction may also be false. When two or more substances are mixed to form a solution, a heat of mixing is associated with the process even though no chemical reaction takes places. Phase changes involving pure substances will exhibit latent heat effects even though no chemical reaction takes place.

The rate that energy is released depends on several factors, with temperature being the most significant. In Arrhenius' Rate Law equation, the rate of a reaction increases exponentially with temperature. Reaction rates will double or triple for every 10°C increase in temperature.

Since the rate of reaction increases exponentially with temperature, but vessel heat loss to the surroundings increases linearly with temperature, there is a temperature above which an exothermic reaction cannot be controlled simply by cooling. This is why temperature control of exothermic reactions is important. In many cases, the rate of reaction can be limited by the addition rate of the reactants or by an inhibitor to prevent excessive reaction rates.

3.2.2. Chemical Reactivity Assessment

This assessment focuses on the reaction characterization and close evaluation of any explosive or energetic material to determine its potential initiation sensitivity. The evaluation of chemical reactivity is critical to ensure safe process scale-up and operation. The assessment includes several experimental techniques that involve different tools and procedures to determine process chemistry mechanism, operating conditions and any conditions under which reactive hazards may appear.

3.2.2.1 Reaction Characterization

The reaction characterization provides basic knowledge about the chemistry of the reaction and any potentially hazardous conditions that may develop into runaway scenarios. It provides a fundamental knowledge of the stoichiometry, thermodynamics, and kinetics of the reactive system. The following items are commonly included in this analysis:

A. Thermal stability
  - Onset temperature
  - Adiabatic temperature rise
  - Kinetics and heats of reaction
  - Rate and amount of heat and gas production
  - Secondary reactions

B. Vent flow characteristics

A thermal stability analysis is needed to determine any thermal risk associated with a chemical reaction and the triggering conditions where secondary reactions or a runaway scenario may be expected. The analysis also provides data to determine safe process operating temperature and operating limits, as well as conditions where gas can be generated, creating a potential vessel over-pressure scenario. Cooling requirements can also be established based on the data obtained from this analysis.

The adiabatic temperature rise is a common criterion used to assess the severity of a runaway reaction and a good measure of the thermal hazard of a chemical system since it represents the maximum possible temperature increase. The heat of reaction is an important parameter in the safe, successful scale-up of chemical processes. Generally, heats of reaction are used to calculate or simulate temperature rises for potential hazard scenarios and to calculate heat loads for the design of heat exchange systems.

Thermal stability analysis is performed using calorimeters, a variety of which can be found in the market. They are classified based on the scale of the sample, thermal sensitivity, the way the heat balance is used (adiabatic or accumulation) and other special arrangements. Calorimeters can also be differentiated by the operating mode, specifically by the temperature control modes including isothermal, dynamic, adiabatic and isoperibolic. It is essential that the right calorimeter be used for the analysis. It must be able to reproduce normal operating conditions and be able to resist extreme conditions when runaway reactions are evaluated.

Typically, the calorimeters used for thermal stability studies are reaction or adiabatic calorimeters. Reaction calorimeters can be used to perform small-scale kinetic and thermal analysis of chemical reactions under realistic process conditions. Reaction calorimetry not only provides quantitative information on the chemical process itself (e.g., heat of reaction, reaction rate, conversion), but also on reactor parameters necessary for safe reactor operation and process design. Common applications of reaction calorimeters is to address the necessary cooling power, heat-transfer coefficients for scale-up, reactant accumulation and improve understanding of consumption rates, and whether accumulation reduction measures such as higher process temperatures, change of catalyst to increase kinetics, different mixing or addition times are needed. Reaction calorimeters must allow for controlled addition of reactants, distillation or refluxing, and reactions with gas release. In summary, they must perform the same operations as an industrial stirred tank reactor. Reaction calorimetry can be applied to reactions such as polymerization, Grignard, nitration, hydrogenation, epoxidation, etc.

Reaction calorimeters are classified (based on the measurement technique used) as Heat Flow Calorimetry (HFC), Power Compensation Calorimetry (PCC), Heat Balance Calorimetry (HBC) and True Heat Flow

Calorimetry (THF). Some of the commercially available reaction calorimeters include the differential scanning calorimetry (DSC), mixing cell calorimetry (MCC), Mettler Toledo reaction calorimetry (RC1), etc.

Adiabatic calorimeters are used to assess decompositions and undesired reactions such as thermal runaway by measuring enthalpy changes; any heat generated increases the sample temperature and serves as fuel for the reaction. These calorimeters are not fully adiabatic; therefore, an adjustment factor known as the phi-factor (ϕ) is used to account for heat loss. The phi-factor or thermal inertia is the ratio of mass and specific heat capacity of the sample and sample container to the mass and specific heat capacity of the sample only. When ϕ exceeds one (ϕ > 1), is an indication that some heat of reaction that could have heated the sample was lost to the sample container. The result is a reduced temperature increase from what would occur in process equipment. This effect is illustrated in Figure 3.2.2.1-1, where the same reaction's temperature-time function was evaluated in three different apparatus. As ϕ goes from 1.05 to 1.35 the time to reach the exotherm changes dramatically. (Note upper- and lower-time scales.) When the ϕ increases to 2.47, the exotherm is lost completely.

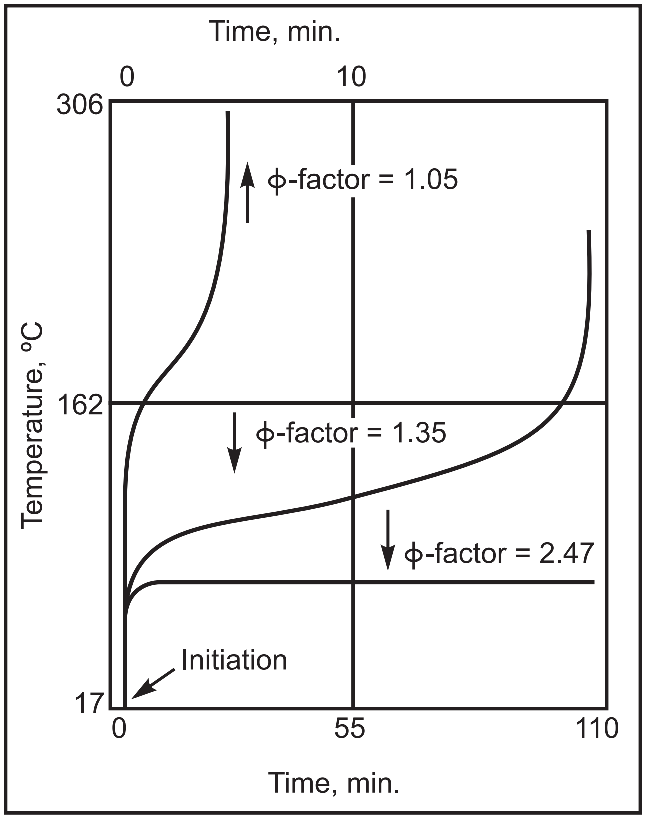


Fig. 3.2.2.1-1. Importance of ϕ-factor illustrated by amine-initiated cyanide reaction

Non-adiabaticity, or heat loss to the surroundings rather than containment in the sample, is another independent factor that could cause the simulation to not accurately represent process situations.

Adiabatic calorimetry techniques include accelerating rate calorimetry (ARC), adiabatic pressure Dewar calorimetry (ADC), the DIERS vent-sizing package (VSP2), Advanced Reactive System Screening Tool (ARSST), PHI-TEC I\T and PHI-TEC II\T.

The use and selection of the appropriate calorimetry technique for screening, thermal/reactive analysis or vent flow characterization is very important. The selection must consider the intended use of the data and that all process conditions and reactions can be adequately simulated. Additionally, trained and experienced personnel should be involved in data interpretation and calculations.

3.2.2.2 Emergency Pressure Relief

Pressure relief design for reactive systems requires a different design approach than standard non-reactive designs.

The occurrence of chemical reactions has the potential to introduce heat and volatile and/or non-condensable gas components into a system. Reaction rates can change tremendously with process conditions such as temperature and concentration. It requires an in-depth evaluation and often dynamic analysis to determine the pressure generated and the expected load to a relief device.

For these systems, no rules of thumb or nomographs allow determination of vent sizes based on simple correlating factors such as vessel volume or reaction type. Reactive systems' composition and properties are constantly changing throughout the relief event. Therefore, careful analysis must be performed to clearly identify all the mixture properties before and after the reaction, as well as pressure and temperature rates during the reaction.

For reactive systems, the proper design practices for emergency pressure relief systems are paramount, starting from the identification of hazards and potential initiating events to the selection and sizing of the pressure-relief device, discharge piping and downstream containment equipment. The design methodologies currently developed usually apply iterative steps and specialized software and techniques to determine the worst-case scenario and the adequate size of the pressure-relief device. A design approach for reactive systems commonly includes the following steps:

1. Determination of all potentially hazardous conditions
2. Sequence of events that could lead to the highest pressure and flow scenarios considering all modes of operation
3. System classification – vapor pressure/gas/hybrid
4. Determination of the nature of the discharge (single/two-phase) and the disengagement regimen
5. Selection of the relief device set pressure
6. Runaway reaction characterization at relief conditions
7. Calculation of required vent area for the worst-case scenario
8. Vent areas correction considering the effects of downstream equipment and safety factors

3.2.2.2.1 Hazardous Conditions and Worst-Case Scenario.

The key factor of success in the design of emergency pressure relief systems for reactive systems lies in a good understanding of the behavior of the reaction under relief conditions and the cause of pressure increase. The determination of all the potentially hazardous conditions and the sequence of events under all operation modes can be determined using a process hazards analysis (PHA) methodology. The PHA methodology selected for the analysis should be commensurate with the hazard and complexity of the process. Data Sheet 7-43, *Process Safety*, provides additional information about different PHA methodologies.

Evaluation of process and equipment deviations in reactive systems should include at a minimum external fire exposure, malfunctions and agitator failure, loss of cooling, contamination and mischarging of feedstocks as these are common causes of runaway reactions. External fire exposure can result in an exothermic reaction causing boiling throughout the vessel's volume from heat evolved from the reaction. This is commonly referred to as volumetric heating, which results in more liquid swell than wall heating, increasing the potential for long-duration, two-phase flow relief. Furthermore, significantly higher heat-generation rates associated with runaway reactions result in higher vapor velocities and further potential for long-duration, two-phase flow.

Insulation is commonly used to minimize heat to a vessel when it is exposed to fire. However, insulation will also minimize heat loss from the vessel during a runaway reaction. In the case of fire exposure, the insulation will prevent the vessel contents from cooling after the fire is extinguished, and this may lead to a runaway reaction. If insulation is used, consideration should be given to how the vessel contents can be drained, cooled, inhibited or utilized in the process before the runaway reaction occurs. If equipment containing reactive chemicals is insulated, obtain a clear understanding of the runaway reaction characteristics from adiabatic calorimetry data. Dynamic simulation computer models for the proposed insulation thickness can help establish the required relief capacity, time to maximum rate and required response time for corrective actions.

3.2.2.2.2 System Characterization and Disengagement Regime.

To determine the parameters for the sizing of the pressure-relief device, the reaction needs to be classified to identify the release composition, which can present as a vapor, gassy or hybrid form. In a vapor (also called tempered) system, the boiling point is reached prior to a potential gaseous decomposition. No permanent gas is generated, and the vent size will be calculated using the rate of temperature rise at the release pressure instead of the peak rate.

For gassy systems, gaseous decomposition occurs in the absence of tempering. The reactants, products and/or solvents are not volatile or have an extremely low volatility. The total pressure in the reactor is equal to the gas pressure. In these systems the maximum temperature and maximum gas generation rate can be observed during venting. The maximum rate of pressure rise is the principal parameter determining the vent size.

In hybrid systems, gases are produced prior boiling; but the rate of reaction is still tempered by vapor stripping. The total pressure in the reactor is the sum of the gas partial pressure and the vapor pressure. The principal parameters determining the vent size are the rate of temperature and pressure rise corresponding to the tempering conditions.

The size of the pressure-relief device will also be influenced by the nature of the discharge, which can present as single (vapor or liquid) or two-phase (vapor-liquid) flow. A pressure-relief device sized for all-vapor flow may be undersized if a two-phase flow occurs. A two-phase flow in a runaway reaction occurs as a result of vaporization and gas generation. Boiling takes place throughout the entire volume of the liquid, rather than solely at the surface. Each bubble occupies volume and displaces the liquid surface upwards. If a sufficient volume of bubbles becomes trapped, the liquid surface reaches the height of the relief device; and the two-phase flow occurs through it. Volumetric flow rate through a pressure-relief device is reduced when two-phase flow occurs. Therefore, a larger venting area may be required for the same venting rate. Design considerations for downstream containment equipment must include a capacity large enough to handle the two-phase flow release.

The vapor and liquid motion inside a reactor during emergency relief venting is an extremely complex hydrodynamic problem, essentially depending on the prevailing vapor/liquid disengagement regime. DIERS (Design Institute for Emergency Relief Systems) considers three main disengagement regimes: churn-turbulent, bubbly and homogeneous. In the churn-turbulent regime, a significant vapor disengagement occurs, which is reduced in the bubbly regimes and not present in the homogeneous regimes. The form and degree of bubbly and or foamy behavior are highly dependent on the system properties (i.e., viscosity) and impurities. Understanding how the system properties and the disengagement regime affect the sizing of pressure relief systems requires careful experimentation and analysis techniques.

3.2.2.2.3 Sizing Techniques.

Techniques for sizing emergency relief systems for reactive systems include:

1. Computer dynamic simulation or model-based approach: Provides design basis for difficult and complex systems, including non-ideal reactions, two-phase flow, etc., using software tools or predetermined equation models.
2. Direct empirical scaling of experimental data: Uses direct scalation from calorimetry data.
3. Semi-theoretical graphical and analytical design methods: Uses equations and nomograms to determine vent size based on predetermined properties and conditions.

Two of the most common techniques to determine the appropriate size of an emergency vent system for chemical reactions are DIERS and API 520, Part 1. Several other techniques are currently available; however, the technique selected should be fully understood and consider the complexity of the materials used, chemical reactions involved and if any specific conditions are required.

The DIERS methodology is based on the following:

a) Defining the design basis upset conditions for the reaction system
b) Characterizing the systems through bench-scale tests simulating the design basis upset conditions
c) Using a vent-sizing equation that accounts for two-phase gas/liquid vent flow

3.2.2.2.4 Reducing Emergency Relief System Capacity Requirements for Reactive Processes

For new reactive processes where the emergency relief design may be impractical or existing cases where process changes may make the installed emergency relief system inadequate, any of the examples listed below or a combination of them can be used to protect property.

A. Reduce the batch size to an amount that can readily be accommodated by existing emergency relief systems.

B. Change the process to be inherently safe. An inherently safe process is one that will not produce damaging conditions from even the most severe process upsets. These processes usually involve small volume, continuous flow operations or safe chemistry where reactions are mild, easily controlled or very stable. Inventories of unstable chemicals or reacting mixtures are small. Runaway reactions in these vessels cannot generate the energy and pressure associated with runaway reactions in large, batch-type process vessels. Hence, damage and associated production loss from an incident are usually minimal.

C. Dump the vessel contents to an open basin or tank utilizing only gravity or the pressure in the vessel. The dump basin/tank will usually contain a diluent to quench the reaction. Locate the basin/tank away from important facilities.

D. Relocate a process with the potential for a severe runaway reaction to an area where other equipment, buildings or processes will not be affected by damage from a vessel rupture. Spacing requirements can be estimated based on the size of the vessel and its pressure rating using information in Data Sheet 7-14, *Fire Protection for Chemical Plants*.

E. When the needed distances cannot be provided, barricading can be used as an alternative. Barricades should be of blast and missile resistant construction. Design data for barricades is available from several references given in Data Sheet 7-14, *Fire Protection for Chemical Plants*.

3.2.3. Process Scale-up

Chemical reactions frequently behave very differently when conducted in large-scale commercial equipment rather than in small-scale laboratory equipment. Problems observed on a commercial scale, but not necessarily on a lab scale, include non-uniform distribution of gas, settling of solids, phase separation, foaming and localized heating.

In many cases, the effect of these variables can be calculated or modeled. In other cases, only carefully designed pilot plant studies can reliably provide the needed chemical kinetic, self-heating, mass transfer and heat transfer information. Specially designed reactors may be used for this work (autoclaves, high-heat-flux reactors, microreactors, etc.).

Optimizing product yields involves changing process procedures (addition sequences, addition times, hold times, etc.), process conditions (concentrations, temperature profiles, pressure profiles, etc.), and/or process equipment. As these changes will affect the reaction and its rate, they should be carefully studied before implementing in large-scale equipment.

Some of the variables that can be affected as the scale is increased from a laboratory or small vessel to a full production reactor scale include:

- Surface-to-volume ratio effects on concentration and temperature gradients: Heat removal is a concern since the minimum temperature for a runaway reaction is not absolute. It will depend on process conditions and scale and is linked to the rate of heat loss from the system. As the volume of the reactor and reactor contents increases by a cubic function, the surface area for heat transfer to the surroundings increases at a lower relative rate by a square function. This means that as the scale increases, the ability to remove excess heat by heat loss to the vessel and its surroundings is reduced, resulting in a much higher proportion of the heat retained in the reaction mass.

- Vessel shape effects on agitation and flow patterns, which can result in excessive agitation and stagnation zones. Also, ignitability of flammable materials will change with flow rates.

- Vessel size effects on mixing capacity and flow stability, which can result in pockets of reactive and/or ignitable mixtures.

- Vapor space composition variations and potential side reactions in the vapor space.

- Use of different construction materials for the vessel, which can create different contamination levels or incompatible reactions.

- Raw material specifications and impurities: Bulk material quality may differ from lab material quality.

- Different residence time distributions and catalyst effects.

- Viscosity changes affecting adequate emergency relief venting (plugging vents).

3.3 Reaction Quenching Methods

When application of emergency cooling does not stop a runaway reaction, quenching the reaction is usually the next action taken. This can be done by adding an inhibitor, rapidly adding a cold liquid and/or dumping the reactor contents.

Inhibitors work by counteracting the catalyst or by complexing with the free radicals. For example, hydroquinone (an antioxidant) is used to inhibit some vinyl monomer polymerizations.

Cold liquids act by decreasing the temperature of the reactor contents. The cold liquid must be compatible with the reactor contents and introduced at a sufficient pressure and flow rate to be effective (to overcome runaway reaction pressure and not flash away). The reactor must be large enough to contain the combined volume or provided with overflow to a safe location. The thermal stress caused by quickly adding cold liquid to the equipment should be considered. The potential for boil-over should also be considered. Examples include gravity addition of a diluent and high-pressure water spray inside the reactor.

Dumping acts by rapidly discharging the reactor contents into another vessel. Bottom outlet discharge may be via gravity or pressurization of the reactor. It is critical that the dumping be completed before the runaway reaction compromises the reactor. The receiving vessel may be precharged with an inhibitor or a cold liquid and should be provided with a vent line.

3.4 Reactor Types

The selection of the type of reactor for a chemical process is based on many factors including mode of operation, material phases, chemical hazards, reaction kinetics, desired production rate, economics and process safety.

Reactors are designed for batch, semi-batch or continuous operation. Batch processes are primarily associated with small production rates, long reaction times and selective chemistry requirements. Continuous processes are associated with high production rates and short reaction times. In batch reactors, material composition and heat generation rates change over time. In continuous reactors, material composition and heat generation remain constant, unless process conditions are changed.

A batch reactor is an agitated vessel in which the reactants are all added at the start of the reaction and the reaction products are removed after a fixed time. Agitation is usually provided by internal impellers, gas bubbles, or pumped recirculation. Temperature control is usually provided by jackets, reflux condensers and/or pumped recirculation through an exchanger. Batch reactors present more challenges than continuous process reactors in terms of design and operation. These challenges may be increased when the batch reactor has a multipurpose use rather than being dedicated to a single process or product. Cooling, agitation systems and pressure emergency relief designs are complicated tasks for these types of multipurpose reactors as is control of potential contaminants between batches.

A semi-batch reactor is similar to a batch reactor, except that some of the reactants are fed intermittently or continuously into the vessel. This arrangement is commonly used when feed rates need to be controlled. Exothermic reactions can be slowed down and endothermic rates maintained by limiting the concentrations of some of the reactants. This arrangement is also used to increase product through-put in cases where the product volume is less than the reactant volume in the vessel.

A continuous reactor is a vessel in which the reactants are being continuously added at one point and the products are being continuously removed at another point. The two most common reactor types are continuous-flow, stirred-tank reactors (CSTR) and tubular flow reactors (TFR).

Continuous stirred tank reactors (CSTR) are continuously stirred to maintain uniform concentrations within the reactor. They are adaptable to either batch or continuous operation and may be used in series. They are best suited for small or medium production rates. They can be used for a wide range of pressures and temperatures. Agitation is furnished by stirrer blades, or by forced circulation using external pumps. Jacketed walls, internal coils, external heat exchangers, direct fire or electric resistance heaters can be used to provide heat transfer. If the reaction occurs with evolution of vapors, reflux condensers can be used for cooling. CSTRs are generally cylindrical vessels, installed vertically (Figure 3.4-1). Horizontal reactors are used for processing of slurries where greater liquid surface is desired, where the boiling point rise due to hydrostatic heat is a concern, where headroom is limited, or if the material is very viscous.

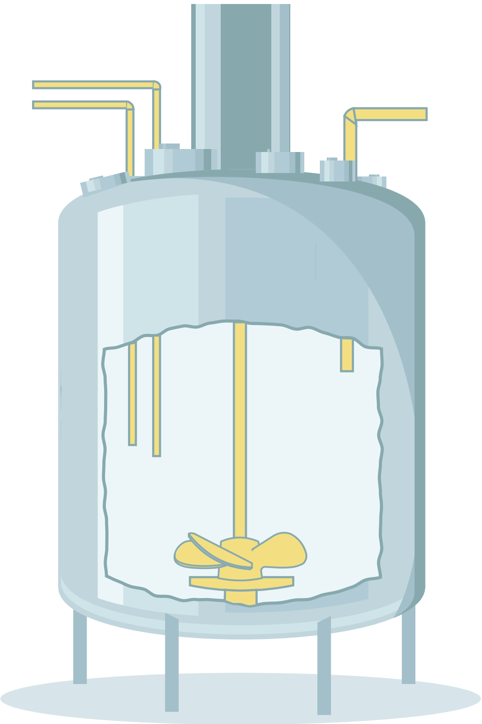


Fig. 3.4-1. Pfaudler CSTR.

Bioreactors are CSTRs used in biochemical and biotechnology applications (Figure 3.4-2). High heat flux process reactors are CSTRs that employ a cryogenic heat transfer system.

Fig. 3.4-2. Braun bioreactor.

Tubular flow reactors (TFRs) have continuous concentration gradients in the direction of flow, as the reactants are continuously fed in one end and the products are continuously removed from the other end. They are used in continuous operations with medium to high production rates. TFRs may have several pipes or tubes in parallel. Individual tubes are jacketed, or shell-and-tube construction is used when auxiliary heat transfer is needed. With shell-and-tube construction, the reactants may be on either the shell or the tube side. The reactant side may be filled with solid particles, either catalytic or inert, to improve heat transfer through increased turbulence or to improve interphase contact. Both horizontal and vertical orientations are common. Tubular reactors are also known as plug flow, slug flow and piston flow reactors.

Plug flow reactors (PFRs) are large-diameter tubular flow reactors with packing or trays that mimic plug flow behavior (Figure 3.4-3).

Membrane reactors are plug-flow reactors that contain an internal cylinder of porous material—the membrane (Figure 3.4-4). The membrane is a barrier that allows only certain components to pass through; selectivity is based on pore diameter. Catalytic membrane reactors combine reaction with separation to increase conversion and are used for catalyzed reactions such as dehydrogenations. Two types of catalytic membrane reactors are commercially available: 1) the inert membrane reactor with catalyst on the feed side (IMRCF) and 2) the catalytic membrane reactor (CMR). The IMRCF has an inert membrane that contains the catalyst. The CMR membrane is either coated with or comprised of a material containing the catalyst.

Tube furnaces are a type of tubular flow reactor. They consist of a combustion chamber lined with refractory and tubes mounted on the walls, ceiling and sometimes on the floor. In the radiant section, the tubes are in direct view of the flames. In the convection section, tubes serve to preheat the charge, to maintain the reaction temperature attained in the radiant section and/or recover heat by preheating combustion air or generating steam.

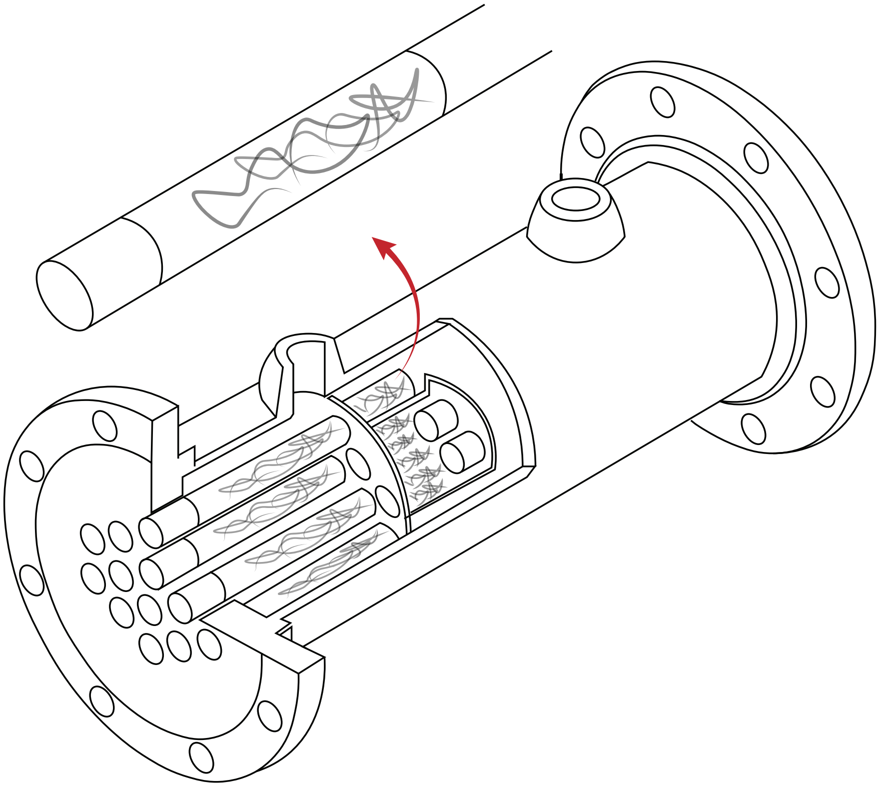


Fig. 3.4-3. Plug Flow Reactor.

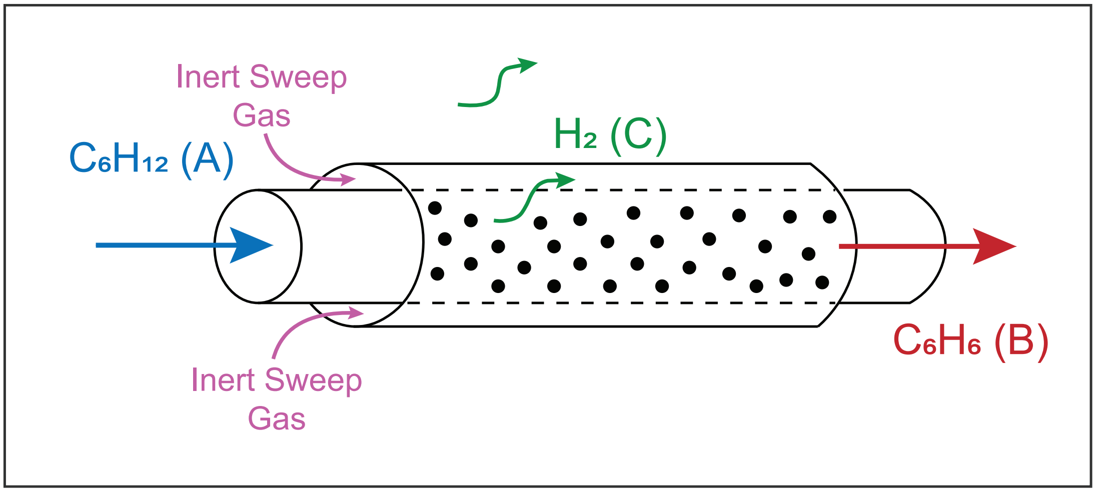


Fig. 3.4-4. Membrane Reactor.

Microreactors are also a type of tubular flow reactor. Micrometer-scale channels and chambers are used to conduct reactions. Because of the very high surface to volume ratio, good control of extremely exothermic reactions is possible. Custom microreactors are being developed for continuous processes and may be used in parallel to feed downstream equipment. Microreactors, at this time, are best suited for conducting gas-phase reactions with very small production rates (lb./day). They can be used over a wide range of pressures and temperatures. The hazard is minimal due to the small quantities of material present.

Table 3.4-1. Advantages and Disadvantages of Various Reactor Types

Reactor Type	*Advantages*	*Disadvantages*
Batch	Agitation	Large inventory Low throughput rate Heat transfer problems Cycling effects
Semi-batch	Agitation Addition rates controllable	Potential accumulation of reactants Precipitation problems
CSTR	Agitation Addition rates controllable Stationary conditions	Large inventory Low throughput rate Heat transfer problems Precipitation problems
TFR	Low inventory High throughput rate Stationary Conditions	Potential for hot spots Agitation only if in-line mixers are available Inflexible

Reactor selection also depends on the phase of the materials being processed. There are vapor phase reactors, liquid phase reactors, solid phase reactors, gas/liquid reactors, and gas/liquid/solid reactors. Catalysts may be retained in the vessel or separated out downstream. Beds may be fixed, moving, or fluidized. Gas/liquid reactors include tray tower, packed tower, falling liquid film, spray tower, bubble tower, venturi mixer, static in-line mixer, tubular flow, looped and stirred tank. Liquid/liquid reactors include tray tower, packed tower, spray tower, rotating disk contactor and stirred tank. Gas/liquid/solid reactors include trickle bed, flooded fixed bed, fluidized bed, bubble columns, slurry and stirred tank. Solid reactors include horizontal rotary kilns, vertical kilns, multiple hearth, fluidized bed and vertical moving bed (blast furnace). The bottoms of these reactors may be cone, slope or dish shaped.

3.5 Reactor Aging and Corrosion Resistance

Accelerated aging and corrosion can result in unexpected equipment failure. Inspections alone may not be an adequate predictor of reliability. Understanding the factors that influence corrosion, the effect corrosion may have on the chemical process, and the effect corrosion may have on the reliability of the process equipment is important. Changes in process chemistry, even relatively minor ones, may significantly change corrosion resistance. Frequent start-ups and shutdowns accelerate aging and may cause corrosion fatigue.

Corrosion may be localized. Pitting is a form of very localized corrosion. Crevice corrosion occurs within or adjacent to a crevice. Oxygen-concentration corrosion frequently occurs under gaskets. Galvanic corrosion occurs when dissimilar metals are used in contact with each other and are exposed to an electrically conducting solution. Intergranular corrosion occurs from selective corrosion in the grain boundaries of a metal or alloy without a significant attack on the grains themselves. This type of corrosion is unusual in that the loss of strength and ductility is not proportional to the amount of metal lost due to the corrosion. Stress corrosion occurs from either internal stress or externally applied stress and can result in cracking. Liquid-metal corrosion occurs when liquid metal attacks metal grain boundaries, potentially resulting in catastrophic failure. Erosion is a form of corrosion associated with material flow. Cavitation corrosion occurs when bubbles collapse on a surface. Fretting corrosion occurs when metal pieces slide over one another. Hydrogen embrittlement occurs when a significant amount of hydrogen is present at elevated temperatures. The National Association of Corrosion Engineers has published charts detailing recommended operating limits for various hydrogen partial pressures, temperatures and steel alloys.

Corrosion may also be structural. Graphite corrosion usually involves gray cast iron or carbon steel heated above 455°F (235°C) for prolonged periods and occurs when the metal is converted into corrosion products. Dealloying corrosion occurs when only one alloy is attacked by corrosion; the most common type is dezincification of brass. Biological corrosion occurs due to metabolic activity of microorganisms. Microbiologically induced corrosion (MIC) is one type of biological corrosion that occurs when the microorganism attaches to a metal.

As a general rule, one volume of steel yields twenty volumes of corrosion. This accounts for what is known as rust-jacking - a process whereby rust forces surfaces apart. The following conditions may increase corrosion:

- Chlorides. The presence of chlorides increases localized corrosion problems. Pitting of aluminum and stainless steel in aqueous solutions containing chlorides is an example. Inhibitors can be used to prevent pitting. Chlorides may be present in either process materials or utilities.
- Water (presence or absence): The presence of water may increase the corrosiveness of non-aqueous compounds. The absence of water may increase the corrosiveness of some organic halides.
- pH affects the stability of the oxide films on metal alloys. Significant changes in pH may change the corrosivity of some chemicals, particularly the halides.
- High Temperature: High temperature and hot spots increase corrosion rates. Temperature also indirectly affects corrosion rates by impacting the solubility of air (oxidizer) and material phases.
- High Flow Rates: High flow rates, or velocity, can increase abrasion and friction, resulting in erosion. Using harder materials, reducing flow rates, and minimizing directional changes can minimize erosion.
- Low Oxygen Concentration.
- Oxidizing Agents: Oxidizing agents may accelerate or retard corrosion depending on the characteristics of the metal. Reduced oxygen concentrations accelerate corrosion.
- Environmental Conditions (internal and external): Environmental conditions, both internal and external, affect corrosion rates. Essentially every metal alloy has environmental conditions that produce stress corrosion cracking. Steel cracking from caustic is an example. External chloride corrosion may result from external insulation materials, chemical spills, sea mist and road salt. Reference Data Sheet 12-2, *Vessels and Piping*.
- Equipment Stress: Equipment stress may be caused during fabrication, by unbalanced cooling from high temperature or by external modifications (rivets, bolts, etc.).

- Equipment Arrangement: Equipment arrangement may also affect corrosion. Glass-lined reactors are commonly supplied with a conventional jacket or with a half-pipe jacket constructed by welding a half-pipe coil around the outside of the tank. The conventional jacket is less susceptible to crevice corrosion and provides better thermal shock protection. Improper agitation and pumping can generate excessive amounts of bubbling that result in mechanical damage. If not properly lubricated, friction from metal pieces sliding over one another can cause surface wear.

The resistance of materials to similar environments and process conditions is a good screening tool. However, materials selected should be evaluated under proposed conditions whenever possible. Supercritical process conditions are particularly challenging due to accelerated corrosion from high temperature/pressure and shifting of reaction mechanisms.

The general applicability of materials in oxidizing and reducing acids is shown in Figure 3.5-1. Chromic, nitric, and greater than 70% sulfuric acid are common oxidizing acids. Formic, hydrochloric, phosphoric, and less than 70% sulfuric acid are common reducing acids.

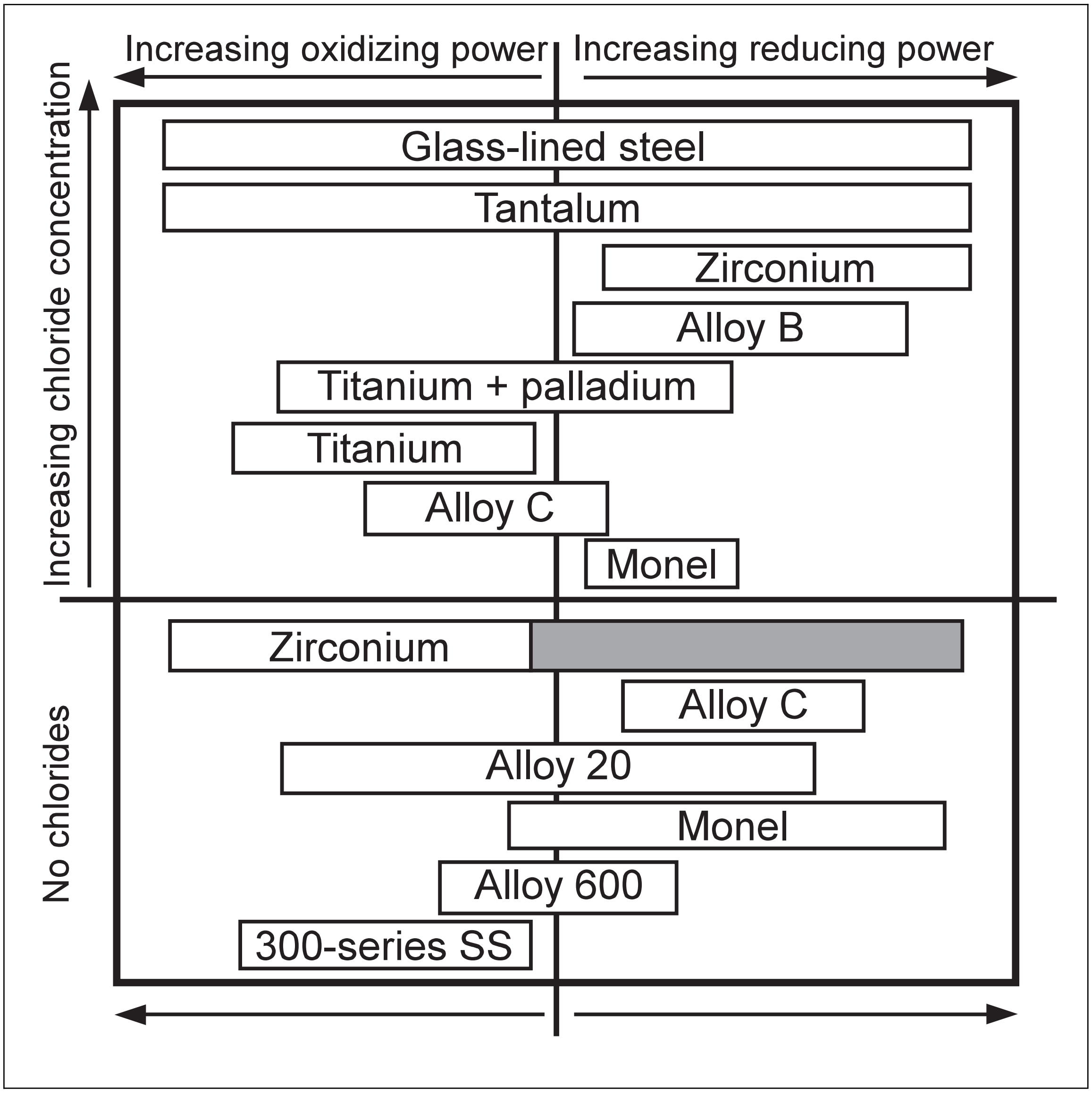


Fig. 3.5-1. Applicability of Materials in Oxidizing and Reducing Acids
Illustration courtesy of Te-Lin Yu Consultancy

Nonmetals, such as plastics, may exhibit deterioration similar to corrosion. However, this is physiochemical deterioration rather than corrosion.

3.6 Routine Spares

The following are common routine spares for reactors. Store and maintain the routine spares per the original equipment manufacturer's recommendations to maintain viability. Refer to Data Sheet 9-0, *Asset Integrity*, for additional guidance.

- Tube bundles
- High-wear components

If non-repairable materials of construction are used (e.g., graphite) or if the materials of construction are unique, rare, or special (i.e., requiring long lead times), consider maintaining complete sets of routine spare components such as tube bundles and common high-wear components such as agitators.

4.0 REFERENCES

4.1 FM

Data Sheet 7-14, *Fire Protection for Chemical Plants*
Data Sheet 7-43, *Process Safety*
Data Sheet 7-45, *Safety Controls, Alarms and Interlocks*
Data Sheet 7-49, *Emergency Venting of Vessels*
Data Sheet 9-0, *Asset Integrity*
Data Sheet 10-8, *Operators*
Data Sheet 12-2, *Vessels and Piping*

4.2 Other

American Society of Mechanical Engineers (ASME), *Boiler and Pressure Vessel Code Section VIII. Rules for Construction of Pressure Vessels*.

Standard EN 13445, *Unfired Pressure Vessels*.

AS 1210-2010, *Pressure Vessels*.

APPENDIX A GLOSSARY OF TERMS

Activation Energy (Ea): The critical energy needed for a reaction to occur.

Activation Entropy (S_j): The relative position or orientation of the molecules needed for a reaction to occur.

Adiabatic: A condition where no heat is exchanged between a system and its surroundings.

Catalyst: A substance that increases the rate of a reaction but is recovered, unchanged, at the end of the reaction.

Chemical Reactor: A vessel designed to contain a chemical reaction. Chemical reactors can operate above atmospheric pressure, at atmospheric pressure or under vacuum. Vessels can be open tanks, enclosed cylindrical vessels and tubular or pipe-like vessels.

Enthalpy (ΔH): The heat content of a substance or the heat of reaction. Compounds that release energy when formed usually have a negative enthalpy.

Entropy (ΔS): The degree of disorder in a chemical system. Reaction systems that result in greater disorder have positive entropy.

Hazard Analysis: The systematic identification of chemical or physical characteristics, processing conditions and/or operating conditions that could lead to undesired events.

Ignitable Liquid: Any liquid or liquid mixture that is capable of fueling a fire, including flammable liquids, combustible liquids, inflammable liquids or any other reference to a liquid that will burn. An ignitable liquid must have a fire point.

Inhibitor: A substance that retards a chemical reaction, usually by affecting the required activation energy. Inhibitors are also commonly called negative catalysts or reaction poisons.

Isoperibolic Calorimetry: A system where the controlling external temperature is constant; external temperature is compared to internal temperature to determine onset temperature.

Isothermal: A system where the (internal and external) temperature is constant; internal temperature changes are quickly manifested as pressure and volume changes.

Onset Temperature: The temperature at which a self-sustaining chemical reaction can occur.

Phi-Factor (ϕ): The phi-factor or thermal inertia is the ratio of mass and specific heat capacity of the sample and sample container to the mass and specific heat capacity of the sample only.

$$\phi = \frac{(mCp)_{sample} + (mCp)_{(sample\ container)}}{(mCp)_{sample}}$$

or

$$\phi = 1 + \frac{(mCp)_{(sample\ container)}}{(mCp)_{sample}}$$

Runaway Reaction: An uncontrollable, accelerating reaction rate that results in rapid increases in temperature and pressure. The heat generated exceeds the heat removed by the cooling system and/or vaporization.

Temperature of No Return (TNR): The temperature at which the rate of heat generation of a reaction or decomposition is equal to the maximum rate of cooling available.

Tempered: A term that describes an exothermic reaction involving a volatile reaction mass where the heat loss from latent heat of vaporization balances the heat of reaction. In this situation, the temperature and reaction rates do not increase; hence, the reaction does not runaway.

Vapor Pressure: The pressure exerted when a solid or liquid is in equilibrium with its own vapor. The higher the vapor pressure at standard temperature and pressure, the easier a liquid will evaporate.

Worst Credible Case: An event or combination of events that could result in a runaway reaction, creating the largest or fastest pressure excursion.

APPENDIX B DOCUMENT REVISION HISTORY

The purpose of this appendix is to capture the changes that were made to this document each time it was published. Please note that section numbers refer specifically to those in the version published on the date shown (i.e., the section numbers are not always the same from version to version).

October 2024. Interim revision. Minor editorial changes were made for additional clarity.

July 2023. This document has been completely revised. The following significant changes were made:

A. Reorganized the document to provide a format that is consistent with other data sheets.

B. Created new recommendations for reactive systems and reactor evaluations.

C. Added information to support new recommendations (Section 3.0).

D. Added new guidance on the design of pressure-relief devices for reactive systems.

E. Relocated and updated information for calorimetry analysis from Data Sheet 7-49.

January 2022. Interim revision. Minor editorial changes were made.

July 2020. Interim revision. Updated contingency planning and sparing guidance.

October 2015. Interim revision. A definition was added for chemical reactor.

July 2013. Minor editorial and formatting changes were made.

April 2013. Information in Section 3.1 on estimating the effects of vessel rupture has been eliminated. Guidance can be found in Data Sheet 7-0, *Causes and Effects of Fires and Explosions.*

January 2012. Terminology related to ignitable liquids has been revised to provide increased clarity and consistency with regard to FM Global's loss prevention recommendations for ignitable liquid hazards.

January 2003. Editorial changes were done for this revision. Section 3.16 was revised.

January 2002. Data Sheet 7-46 has been completely rewritten.

Major revisions are as follows:

1. The recommendation section has been expanded and segmented to highlight recommendations dealing with an inherently safer design philosophy, chemical hazard analysis, process hazard analysis, and reactor selection. Reference is made to other data sheets rather than repeating information contained elsewhere.

2. The chemical reaction section has been streamlined and includes the information previously located in Data Sheet 7-43/17-2, *Process Safety*, (February 1974 edition).

3. A section on photochemical reactions has been added.

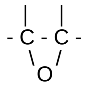
4. A section on chemical properties and thermodynamics has been added under Support for Recommendations.

APPENDIX C. HAZARDOUS COMPOUNDS AND CHEMICAL REACTIONS

C.1. Compounds with the Potential to Generate Uncontrolled or Explosive Decompositions

The chemical families presented in Table C.1-1 deserve special attention due to their structural elements and hazards, which can present or generate uncontrolled polymerization reactions, formation of unstable materials or explosive decompositions.

Table C.1-1. Hazardous Compounds with the Potential to Generate Uncontrolled or Explosive Decompositions

Chemical Family	*Chemical Structure*	*Hazards*	*Examples*
Alkenes	$R - CH = CH - R$	Uncontrolled polymerization and formation of unstable peroxides.	Vinyl acetate, vinyl benzene (styrene), vinyl chloride
Carbonyl compounds	$- C = O$	Rapid oxidation or reduction, uncontrolled polymerization and formation of unstable peroxides. Note: aldehydes (RCHO) and ketones (R_1R_2CO) are both included in the carbonyl compound group. The hydrogen atom versus organic group attached to the carbonyl group makes a significant difference in their reactivity. Aldehydes are easily oxidized, whereas ketones are oxidized only with difficulty. Aldehydes more readily undergo nucleophilic addition—the characteristic reaction of carbonyl compounds—than do ketones.	Acetaldehyde, butyraldehyde
Conjugated unsaturated compounds (two or more double bonds)	 $- \overset{\vert}{C} = \overset{\vert}{C} - \overset{\vert}{C} = \overset{\vert}{C} -$	Uncontrolled polymerization and formation of unstable peroxides.	Acrylonitrile, 1,3 butadiene
Epoxides (oxirane ring)	 $\underset{\setminus\,O\,/}{- \overset{\vert}{C} - \overset{\vert}{C} -}$	Explosive decomposition and contaminant catalyzed uncontrolled polymerization.	Ethylene oxide, propylene oxide
Alkynes (triple-bonded hydrocarbons)	$R_1 - C \equiv C - R_2$	Explosive decomposition.	Acetylene, propargyl alcohol
Haloacetylene derivatives	$- C \equiv C - X$	Explosive decomposition.	Acetylene, propargyl alcohol
Peroxides	$R - O - O - R$	Self-accelerating decomposition initiated at low temperatures.	Alkylperoxides and metal peroxides included benzoyl peroxide
Nitro-Alkanes	$R - NO_2$	Highly exothermic reaction with inorganic acids and instability.	Nitromethane, dinitrotoluene, trinitrotoluene (TNT)
Azo compounds	$R - N = N - R$	Explosive decomposition.	p-hydroxyazobenzene
Diazo compounds	$R = N = N$	Explosive decomposition/ detonation.	o-toluenediazonium chloride (salt)
Azides	$- N_3$	Explosive decomposition.	Sodium azide

C.2. Common Types of Reactions, Relative Energies, and Critical Processing Parameters

Chemical reactions and processes may be simple or complex. Chemical reactions and processes may present very little hazard or be extremely hazardous. Because of the large number of possible chemical reactions and processes, it is impossible to provide specific guidance for every possible scenario. However, most chemical reactions can be classified into a limited number of categories. Table C.2-1 summarizes common types of reactions, relative energies, and critical processing parameters.

Table C-2.1. Common Types of Reactions

Type	*Energy*	*Potentially Critical Processing Parameters*	*Notes*
Alkylation	Moderately to Highly Exothermic	1, 2, 6	Excess reagent may be needed
Amination	Endothermic to Highly Exothermic	1-5 12 (diazo)	
Aromatization	Endothermic to Moderately Exothermic	1-4	Dumping/Suppressant may be needed
Calcination	Endothermic	1, 6 (offgas)	
Condensation	Moderately Exothermic	1-5	
Double Decomposition	Endothermic to Mildly Exothermic	6, 7, 8	NH3 decomposition potential
Electrolysis	Endothermic	5, 6, 7, 9	pH, electrical variables
Esterification (organic acids)	Mildly Exothermic	1, 2, 5	Moisture, contaminants
Fermentation	Mildly Exothermic	1	
Halogenation	Endothermic to Highly Exothermic	5, 8, 11 (some), 12 (some)	
Hydration	Mildly Exothermic	1, 2	Excluding acetylene production
Hydrogenation	Moderately Exothermic	1, 2, 3, 5, 6, 7	
Hydrolysis	Mildly Exothermic	1, 2	Includes enzymes
Isomerization	Mildly Exothermic	1, 2, 3	
Neutralization	Mildly Exothermic	1, 2	
Nitration	Highly Exothermic	1-6, 8, 12	Contamination, Dumping may be needed, Detonation potential
Organometallic	Highly Exothermic	1-5, 8, 10, 12	
Oxidation	Endothermic to Moderately Exothermic	1, 3, 4, 5, 11 (some)	
Polymerization	Mildly to Moderately Exothermic	1-7, 12 (some)	Viscosity issues
Pyrolysis and Cracking	Endothermic	1, 2, 8	
Reduction	Endothermic to Mildly Exothermic	1, 2, 10 (some)	
Reforming	Endothermic to Moderately Exothermic	1, 3, 4, 5	
Substitution	Endothermic to Mildly Exothermic	1, 2	
Sulfonation	Mildly Exothermic	1, 2, 5	

Processing Parameters:

1. Temperature
2. Pressure
3. Agitation
4. Cooling/Heating
5. Addition Rate
6. Concentration
7. Flammable gases (LEL detection)
8. Inerting
9. Liquid Level
10. Water reactive
11. Reactive metals
12. **Critical that adequate and reliable process control be provided**

C.3 Chemical Reactions

Exothermic reactions known to be highly reactive or difficult to control include nitrations, bulk polymerizations, Friedel-Craft alkylations and Grignard reactions. Additional information on these and other chemical reactions, including a general description, process chemistry, equipment and hazards is presented below.

Addition

Addition reactions are reactions in which two molecules combine to form a single molecule of product. These reactions are best described by the functional group of the reagent; see alkylation, amination, halogenation, hydration, hydrogenation, organometallic compounds, oxidation, polymerization, sulfonation, etc.

Alkylation

Alkylation is the addition or insertion of an alkyl group (C_nH_{2n+1}) into a molecule. Alkylation reactions are diverse in nature and include carbon-carbon, carbon-nitrogen, and carbon-oxygen reactions. Friedel-Crafts reactions, aluminum chloride or similar -RX catalysts in the presence of a Lewis acid, are primarily carbon-carbon alkylations. Quaternization is an example of carbon-nitrogen alkylation. Williamson reactions are carbon-oxygen alkylations. Grignard reactions and many other organometallic reactions are also alkylation reactions but are better considered separately; see organometallic compounds.

No inclusive, universal method for conducting alkylations exists. Carbon-oxygen alkylations can use acids or bases as catalysts. Temperatures in this class of alkylation reaction vary widely, ranging from ambient to 750°F (400°C) for processes conducted in the vapor phase. Pressures also vary considerably. In some processes, pressure is applied to keep the volatile reactants liquid. In other cases, high pressure is applied to promote completion of the reaction. Pressures can be in excess of 1000 psi (7 MPa).

Alkylation of saturated hydrocarbons is performed catalytically. In addition to RX catalysts, hydrofluoric, sulfuric, and phosphoric acids are also used. With catalysts, temperatures of alkylation reactions vary considerably depending upon the reactants and the catalyst used; but most range from 0° to 150°F (- 18° to 65°C). Pressures are normally only high enough to maintain the reactants in the liquid state.

Alkylation products include ethyl benzene, cumene, detergents, dyes, ethers, glycols, and synthetic lubricants.

Process Chemistry

a) Substitution of hydrogen attached to a carbon atom with an acid catalyst:

$CH(CH_2)(CH_3)_2$	+	$CH(CH_3)_3$	$\rightarrow$	$(CH_3)_2CHCH_2C(CH_3)_3$
isobutylene		isobutane	acid	2,2,4-trimethylpentane (iso-octane)

b) Addition of an alkyl group onto a benzene ring to produce a larger aromatic hydrocarbon:

C_6H_6	+	CH_3CHCH_2	$\rightarrow$	$C_6H_5CH_2(CH_3)_2$
benzene		propylene		cumene

c) Substitution of the hydrogen attached to a nitrogen atom:

$C_2H_5NH_2$	+	$2CH_3OH$	$\rightarrow$	$C_6H_5N(CH_3)_2$	+	H_2O
aniline		methanol		dimethylaniline		water

d) Substitution of the hydrogen attached to an oxygen atom:

C_2H_5OH	+	$(CH_2)O$	$\rightarrow$	$C_2H_5OC_2H_4OH$
ethanol		ethylene oxide		Cellosolve

Equipment

Alkylation reactors are normally constructed of steel. Where a highly corrosive catalyst or reagent is used, a corrosion-resistant lining must be used. Special attention should be given to moving parts and instruments to protect them from corrosion. Pumps, valves, and instruments are often made from special alloys such as Monel.

Large-scale alkylations are generally continuous processes. Small-scale alkylations may be performed in batch reactors. Because of pressure requirements, an autoclave is typically used. The autoclave may have agitation and may need heating, cooling, pressure relief and instrumentation.

Amination

Amination is the replacement of another functional group with NH_2 or NH3 in an unsaturated compound or by the reduction of NO_2 to NH_2 with hydrogen.

Amination by ammonolysis is the replacement of constituents in a compound such as -Cl, -OH, $-SO_3H$, $-NO_2$, and -O- with $-NH_2$ to form an amine. It can also involve the addition of ammonia to an unsaturated compound.

Amination by reduction is the preparation of amines by the reduction of an $-NO_2$ or similar oxidized nitrogen component of a compound to an $-NH_2$ group. The process usually involves reaction of a material with ammonia in water solution but can also involve reaction with liquid or gaseous anhydrous ammonia.

For reduction processes using hydrogen, see hydrogenation.

Aqueous ammonolysis are usually performed without catalysts. Temperatures and pressures vary, but pressures are usually high. For example, the chlorobenzene process below operates at 355-430°F (180-220°C) and 950 psi (6.5 MPa). Ammonolysis using liquid anhydrous ammonia is less common than aqueous solutions since higher pressures must be used to maintain the liquid state. Process pressures of 3000 psi (21 MPa) are not unusual. Ammonolysis using gaseous anhydrous ammonia is usually performed in the presence of a catalyst.

Process Chemistry

a) Ammonolysis of ethylene oxide produces a mixture of monoethanolamine, diethanolamine, and triethanolamine:
$(CH_2)_2O + NH_3\ (aq) \rightarrow NH_2(CH_2)OH + NH((CH_2)_2\ OH)_2 + N((CH_2)_2\ OH)_3$
ethylene ammonia monoethanolamine diethanolamine triethanolamine

b) Ammonolysis of chlorobenzene produces aniline:
$C_6HCl + 2NH_3\ (aq) \rightarrow C_6H_5NH_2 + NH_4Cl$
chlorobenzene ammonia aniline ammonium chloride

c) Ammonolysis of carbon dioxide produces ammonium carbonate as an intermediate, which must be dehydrated to produce urea. The overall reaction is:
$CO_2 + 2NH_3\ (l) \rightarrow (NH_2)_2CO + H_2O$
carbon dioxide ammonia urea water

d) Ammonolysis of methanol with an aluminum oxide catalyst to produce methylamines:
$CH_3OH + NH_3\ (g) \rightarrow NH_2CH_3 + NH(CH_3)_2 + N(CH_3)_3 + H_2O$
methanol ammonia methylamine dimethylamine trimethylamine water

Equipment

Aminations by ammonolysis are usually conducted most economically at elevated temperatures and pressures. For pressures up to 800 psi (5.6 MPa), autoclaves are normally used as both batch and continuous reactors. Reactions at pressures above 800 psi (5.6 MPa) are usually conducted in tubular reactors. Vessels may be solid-walled or built up of successive layers. Small diameter tubes are commonly employed where the reaction is rapid, or the heat of reaction must be removed rapidly. Some gas-phase reactions are conducted continuously in reactors that are essentially shell-and-tube heat exchangers.

Aromatization

Aromatization is the conversion of aliphatic compounds to aromatic compounds (benzene ring derivatives). These reactions involve the rearrangement of the atoms in an organic molecule without changing the number of carbon atoms. Operations are typically conducted at elevated temperatures and pressures in the presence of a catalyst.

Conversion is primarily by catalytic reforming; see reforming.

Process Chemistry

$CH_3CH_2CH_2CH_2CH_2CH_3 \xrightarrow{\text{catalyst}} C_6H_5CH_3 + 4H_2$
n-heptane toluene hydrogen

Equipment

In large-scale processes, continuous reactors are used. In small-scale processes, batch reactors are used.

Biochemistry: Biocatalysis, Bioconversion, Biotechnology and Biotransformation

Biocatalysis, bioconversion, biotechnology, and biotransformation are all names for the use of biological substances in a biochemical reaction.

Biochemical reactions are classified as fermentation reactions because of their use of biological substances. This is true despite the fact that the actual reaction mechanism may be an addition, amination, dehalogenation, epoxidation, esterification, hydrolysis, hydroxylation, polymerization, or reduction. See fermentation for process equipment and hazard descriptions.

Biotechnology increasingly refers to processes using recombinant DNA technology, commonly used in the agricultural, chemical and pharmaceutical industries.

Calcination

Calcination is the heating of a material to a high temperature to remove moisture or another volatile component. It is most common in the cement, lime, gypsum, and soda ash manufacturing.

Process Chemistry

a) Calcination of lime at 2200 to 2370°F (1200 to 1300°C):
$CaCO_3 \rightarrow CaO + CO_2$
calcium carbonate calcium oxide carbon dioxide

b) Calcination of gypsum at 250 to 375°F (120 to 190°C):

$CaSO_4 \cdot 2H_2O$	$\rightarrow$	$CaSO_4$	+	$2H_2O$
gypsum anhydrite		gypsum		water

c) Sodium bicarbonate is converted to sodium carbonate (soda ash) at 350 to 440°F (175 to 225°C):

$2NaHCO_3$	$\rightarrow$	Na_2CO_3	+	CO_2	+	H_2O
sodium bicarbonate		sodium carbonate		carbon dioxide		water

d) Calciners are also used in heating petroleum coke to 2550°F (1400°C) to drive off flammable volatile materials before converting the coke to graphite.

Equipment

Large steel kilns are used for calcining. Horizontally rotating kilns are most common. Vertical kilns are often used for lumpy material. Kilns may be heated by gas, oil, pulverized coal, waste fuels/gases or electricity.

Additional information on kilns is provided in Data Sheet 6-17/13-20, *Rotary Kilns and Dryers*. Additional information on off-gas treatment is provided in Data Sheet 6-11, *Thermal and Regenerative Catalytic Oxidizers* and Data Sheet 7-2, *Waste Solvent Recovery*.

Combustion

Combustion is the reaction of a solid, liquid, or gaseous hydrocarbon with air to produce carbon dioxide, water, and heat. The principal objective normally is to produce heat; see Data Sheet 6-0/12-1, *Elements of Industrial Heating Equipment* and the appropriate heating equipment data sheet. Combustion reactions are also used to generate gas for use as an inerting agent; see Data Sheet 6-9, *Industrial Ovens and Dryers* and Data Sheet 6-10, *Process Furnaces*.

If the combustion is intentionally incomplete (producing carbon monoxide or other unburned combustion products) or if other elements such as sulfur are burned, then the reactions are better considered separately; see Oxidation.

Condensation

Condensation is the joining together of two or more molecules by two carbon atoms, while simultaneously splitting off a small molecule such as water or hydrochloric acid (HCl).

Condensation reactions are diverse in nature. They may be catalyzed by bases or acids or conducted at elevated temperatures.

Aldol condensations are an example of an aldehyde or ketone condensation. Claisen, Dieckmann, Doebner, Knoevenagel, and Perkin condensations are closely related to the Aldol condensation. Condensation reaction conditions vary, but they are usually conducted at moderately elevated temperatures and near atmospheric pressures with or without catalysts.

Some condensation reactions are also alkylation or polymerization reactions; see the appropriate reactions for additional information.

Condensation reactions are frequently used to produce the active ingredients in flavorings, perfumes, dyes, and pharmaceuticals. They are also used to produce heterocyclic compounds such as imidazoles, pyrazoles, quinalines, and thiazoles.

Process Chemistry

a) Aldol condensation using sodium hydroxide or sodium ethoxide as the catalyst:

C_6H_5CHO	+	CH_3CHO	$\rightarrow$	$C_6H_5CH = CHCHO$	+	H_2O
benzaldehyde		acetaldehyde		cinnamaldehyde		water

b) Condensation using sulfuric acid as the catalyst at 250°F (120°C):

$C_6H_4(CO)_2O$	+	$2C_6H_5OH$	$\rightarrow$	$C_6H_4C(C_6H_4OH)_2COO$	+	H_2O
phthalic anhydride		phenol		phenolphthalein		water

c) Condensation at a higher temperature, 560°F (293°C):

$CH_3CH_2CH_2CH_3$	+	S	$\rightarrow$	C_4H_4S	+	H_2S
n-butane		sulfur		thiophene		hydrogen sulfide

Equipment

Most condensation reactions take place in stirred batch reactors, with corrosion resistant linings when necessary. Equipment may be constructed of stainless steel or special alloys (Hastelloy, Inconel, Monel, Alloy B, Alloy C, etc.) to improve corrosion resistance.

Double Decomposition

Double decomposition reactions involve an exchange of one or more constituents between two reacting molecules, usually in water. An inorganic salt generally exchanges a constituent with an acid, base, or another salt.

Some double decomposition reactions are also halogenation, esterification, or condensation reactions; see the appropriate reactions for additional information.

These reactions are common in water softening and the manufacture of sodium, potassium, calcium, and magnesium salts, inorganic acids, and pigments.

Process Chemistry

a) Double decomposition of two inorganic salts:

$NaNO_3$	+	KCl	→	$NaCl$	+	KNO_3
sodium nitrate		potassium chloride		sodium chloride		potassium nitrate

b) Double decomposition of an inorganic salt and an acid:

$2NaCl$	+	H_2SO_4	→	Na_2O_4	+	$2HCl$
sodium chloride		sulfuric acid		sodium sulfate		hydrochloric acid

c) Double decomposition of an inorganic salt and a base:

$(NH_4)_2S_2O_8$	+	$2NaOH$	→	$2NH_4OH$	+	$Na_2S_2O_8$	+	NH_3	+	H_2O
ammonium persulfate		sodium hydroxide		ammonium hydroxide		sodium persulfate		ammonia		water

Equipment

These reactions are conducted in steel reactors or ordinary tanks. The reactor may also be used for separation, as a still or as a crystallizer. Special linings or materials may be used for corrosion resistance.

Electrolysis

Electrolysis is the separation of ions by means of electric current. The ionic compound may be in a water solution in the form of a molten salt or present as the anode. Highly reactive products or by-products can be generated.

The most common electrolytic process in a water solution is the electrolysis of sodium chloride in diaphragm cells. Chlorine is evolved at the anode, and sodium reacts with the water to generate hydrogen at the cathode. Fluorine is also produced commercially using an electrolytic process.

Electrolysis is frequently used to extract or purify metals. As a general rule, metals and/or hydrogen are discharged at the cathode (-). Non-metals and/or oxygen are discharged at the anode (+).

Process Chemistry

a) Electrolysis of water, using a dilute sodium hydroxide solution to improve conductivity, in diaphragm cells to produce hydrogen and oxygen:

H_2O	→	H_2	+	O_2
water		hydrogen		oxygen

b) Electrolysis of anhydrous hydrofluoric acid in potassium bifluoride, at medium temperature and operating currents >6000A to produce fluorine.

HF	+	$KF \cdot HF$	→	$KF \cdot 2HF$	→	F_2
Hydrofluoric acid		potassium biflouride		electrolyte		fluorine

c) Electrolysis of ammonium sulfate or sulfuric acid produces ammonium persulfate or persulfuric acid, respectively:

$2H_2SO_4$	→	$H_2S_2O_8$	+	H_2
sulfuric acid		persulfuric acid		hydrogen

d) Aluminum is produced by electrolysis of alumina dissolved in molten cryolite (Na_3AlF_6). The oxygen reacts with the carbon anode to form carbon dioxide:
$2Al_2O_3 \quad + \quad 3C \quad \rightarrow \quad 4Al \quad + \quad 3CO_2$
Alumina carbon aluminum carbon dioxide

Equipment

Electrolytic cells are normally made of steel. They may be lined with carbon, fire brick, or rubber. They may also be constructed partly of concrete or plastic. Electrodes may be copper, platinum, carbon or other metals.

Esterification

Esters are organic compounds corresponding in structure to salts in inorganic chemistry. Esters are most often prepared by reacting an acid and an alcohol. Acids can also be converted into their esters using acid chlorides. This section covers only esters of organic acids.

Where the acid is a strong inorganic acid such as nitric, sulfuric, or hydrochloric acid, the reaction may also be classified as a nitration, sulfonation, or halogenation. Esterifications involving strong inorganic acids are better considered separately; see nitration, sulfonation or halogenation reactions, as appropriate.

Esterification of an organic acid and an alcohol is an equilibrium reaction. This reversibility is a disadvantage; in order to make the reaction go to completion, the equilibrium must be shifted by either removing one of the products or by using an excess of one of the reactants. It has the advantage, however, of being a single step. Esterification via the acid chloride route is essentially irreversible but has multiple steps. Operations are conducted at moderate temperatures and pressures.

Transesterification is the replacement of one alcohol with another alcohol in an ester.

Many esters are used in fragrances, flavors, or food additives because of their pleasant odor. They are also used widely as solvents, particularly in lacquers.

Process Chemistry

a) Esterification of an alcohol with an organic acid to form an acetate:
$C_6H_5CH_2OH \quad + \quad CH_3COOH \quad \rightarrow \quad C_6H_5CH_2OCOCH_3 \quad + \quad H_2O$
benzyl alcohol acetic acid benzyl acetate water

b) Esterification via the acid chloride route. Thionyl chloride ($SOCl_2$) is the catalyst for the first step. Ethanol is used as the solvent for the second step:
$(CH_3)_3CCOOH \quad + \quad (CH_3)_3CCOCl \quad \rightarrow \quad (CH_3)_3CCOOC_2H_5$
trimethylacetic acid acid chloride ethyl trimethylacetate

c) A mixture of methyl esters and glycerol is prepared by reacting a glyceride (fat) with methanol, catalyzed using either an acid or base (transesterification).

Equipment

Esterification reactions between an alcohol and an organic acid are usually conducted in stirred batch reactors with a distillation column attached to the reactor.

Fermentation

Fermentation was originally defined as the anaerobic (without oxygen) metabolism of organic compounds by microorganisms (yeast, bacteria, algae, molds and protozoa) or their enzymes. This definition has been expanded over time to also include aerobic (with oxygen) microbial processes.

Fermentation processes are classified based on whether they are catalyzed by microorganisms (microbial) or by enzymes (enzymatic). In microbial fermentation, the catalytic agent reproduces itself as part of the microbe's metabolism; the desired product could be a cell waste product or a cell component. In enzymatic fermentation, the catalytic agent does not reproduce. This difference is significant because it influences the addition of reactants and equipment selection.

Fermentations are typically aqueous; and in some aerobic fermentation reactions, supplemental oxygen may be added. Ammonia may be used to regulate pH and as a nitrogen source for the microbe. Operational temperatures are typically a little above ambient. Operational pressures vary depending on whether the fermentation is an anaerobic or aerobic.

Fermentation is used to produce active pharmaceutical ingredients (antibiotics, monoclonal antibodies, proteins and vitamins) and to replace chemical synthesis steps or as an alternative to petrochemical routes in the fine chemical and chemical intermediate industries.

Fermentation is most commonly used to produce alcoholic beverages through the enzymatic breakdown of carbohydrates to simple sugars with subsequent yeast metabolism to produce ethanol. Fermentation processes are also used to produce foodstuffs (tea, yogurt, sauerkraut, and pickles), citric acid, lactic acid and to purify organic wastes (sewage).

Process Chemistry

a) Anaerobic fermentation of sugar cane or starch, by yeast, to produce ethanol and fusel oil (mixture of primary alcohols):

$$C_6H_{12}O_6 \rightarrow CH_3COCOOH + CO_2\ N \rightarrow NCH_3CHO \rightarrow 2C_2H_5OH + \text{fusel oil} + CO_2$$

glucose pyruvic acetaldehyde ethanol carbon dioxide

b) Aerobic fermentation of molasses, by the mold *Aspergillus niger*, to citric acid:

$$\underset{\text{glucose solution}}{C_6H_{12}O_6/\text{water}} + \underset{\substack{\text{calcium}\\ \text{hydroxide}}}{Ca\,(OH)_2} + \underset{\substack{\text{sulfuric}\\ \text{acid}}}{H_2SO_4} + \underset{\text{oxygen}}{O_2} \rightarrow \underset{\substack{\text{citric}\\ \text{acid}}}{C_6H_8O_7} + \underset{\text{gypsum}}{Ca\,SO_4} + \underset{\substack{\text{carbon}\\ \text{dioxide}}}{CO_2}$$

Equipment

Most fermenters are stirred tank reactors constructed of stainless steel. Toroidal fermenters (ring-shaped) may be used where air mixing is part of the process. Tower fermenters may be used to retain heavily coagulated cells.

Most fermenters are equipped with sparger systems having large openings to prevent clogging by microbial growth. Mechanical anti-foaming devices may be provided and are usually accompanied by surface-active, antifoam agent delivery systems.

Fermenters operate in batch or semi-batch mode and are as large as 50,000 gal. (187,000 L). A batch may take several days or up to three weeks to complete. Downstream processing equipment is usually sized to operate continuously, supplied from multiple fermenters.

Utility reliability is critical throughout the fermentation process. Large quantities of electric power, chilled water and compressed air are needed to achieve optimum yield from a batch. See the appropriate data sheets for additional utility equipment information and safeguards.

Fuel Gas Processes

See Oxidation.

Grignard Reactions

See Organometallic Compounds.

Halogenation

Halogenation is the process of introducing halogen atoms (fluorine, chlorine, bromine, or iodine) into an organic molecule. This may be accomplished by adding to an unsaturated bond or by replacement of an -H, -OH, or -SO_3 H group.

Halogenation reactions are conducted at moderate temperatures and pressures. Reactions are often initiated by a light source within the reactor as an alternative to operating at higher temperatures.

The reactivity of the halogen atoms varies a great deal. Fluorinations usually proceed so vigorously that even in the dark and at room temperature, reactions must be carefully controlled. Chlorinations and brominations proceed at relatively reasonable rates. Iodinations can be difficult to initiate and proceed at relatively slow rates.

Process Chemistry

a) Halogen addition to a double bond: phosgene (highly poisonous gas):

$$\underset{\text{carbon monixide}}{CO} + \underset{\text{chlorine}}{Cl_2} \rightarrow \underset{\text{phosgene}}{COCl_2}$$

b) Halogen replacement of hydrogen: chlorination of methane to produce any of the four degrees of chlorinated methanes. The reaction is usually carried out in the vapor phase with an excess of hydrocarbon at a temperature of 650 to 700°F (345 to 370°C). The products are recycled to get the degree of chlorination desired:

CH_4	+	Cl_2	$\rightarrow$	CH_3Cl	+	CH_2Cl_2	+	$CHCl_3$	+	CCl_4	+	HCl
methane		chlorine		methyl chloride		methylene chloride		chloroform		carbon tetrachloride		hydrochloric acid

c) Halogen replacement: Because fluorine is violently reactive with many compounds, fluorination is often conducted by first chlorinating the compound and then substituting the fluorine for chlorine:

CCl_4	+	$2HF$	$\rightarrow$	CCl_2F_2	+	$2HCl$
carbon tetrachloride		hydrofluoric acid		dichloro-difluoromethane		hydrochloric acid

Equipment

Halogenations are normally conducted in reactors designed for the corrosive characteristics of the chemicals present. They may be glass or ceramic lined. If the gases involved are dry, steel may be used.

Continuous tubular reactors, with thin tubes for good heat transfer, are preferred for the exothermic reactions.

Hydrogenation

Hydrogenation is the addition of hydrogen atoms to both sides of a double or triple bond, such as C = C, C = O, or C = N, usually through the use of hydrogen gas and a catalyst. The reaction takes place on the surface of the catalyst, and localized high temperatures will exist on the catalyst surface. In the absence of a catalyst, hydrogenations usually proceed at a very slow rate, even at high temperatures. Hydrogenation reactions can be conducted at low to very high pressure.

The most common use of hydrogenation is the conversion of unsaturated animal and vegetable fats and oils into more highly or completely saturated oils. Hydrogenation not only changes the physical properties of fats, but also the chemical properties. Because of the presence of the catalysts, unsaturated compounds may undergo isomerization as well as hydrogenation. Hydrogenations are also used in many petrochemical processes, in the production of synthetic natural gas and in the preparation of amines.

Process Chemistry

a) Oil hydrogenation at 250 to 300°F (120 to 150°C) and 50 to 250 psi (350 to 1750 kPa) with a nickel catalyst.

$(C_{17}H_{31}COOO)_3C_3H_5$	+	$3H_2$	$\rightarrow$	$(C_{17}H_{33}COO)_3C_3H_5$
linolein		hydrogen		olein

b) Hydrogenation of carbon monoxide to form methanol. This process is conducted at 570°F (300°C) and 4500 psi (31 MPa). The catalyst is silver or copper, with oxides of zinc, chromium, manganese, or aluminum.

CO	+	$2H_2$	$\rightarrow$	CH_3OH
carbon monoxide		hydrogen		methanol

c) Amination and hydrogenation. The reaction of an unsaturated carbonyl compound with ammonia and hydrogen.

$CH_2 = CHCHO$	+	NH_3	+	$2H_2$	$\rightarrow$	$CH_3CH_2CH_2NH_2$	+	H_2O
acrolein		ammonia		hydrogen		n-propylamine		water

d) Amination by reduction.

$C_6H_5NO_2$	+	$3H_2$	$\rightarrow$	$C_6H_5NH_2$	+	$2H_2O$
nitrobenzene		hydrogen		aniline		water

Equipment

Hydrogenations are usually conducted under pressure in steel reactors. Since hydrogen gas attacks carbon steels, the vessel is normally of an alloy resistant to hydrogen or has a corrosion resistant lining. Since the hydrogen molecule is small, it tends to leak through packings, valves and fittings more than other gases. Care should be taken to see that these are tight, particularly when operating at high pressures and when conducted indoors. Possible points of hydrogen leakage from equipment should be regularly checked. Leaks should be promptly corrected. Approved hydrogen gas analyzers should be provided in indoor hydrogenation process areas, arranged to sound an alarm at a minimum detectable concentration (not more than 2%).

Hydration, Hydrolysis and Saponification

Hydration is the addition of water to a compound.

Hydrolysis is the reaction of a compound with water. The water effects a double decomposition, with the hydrogen ion (H+) going to one component and the hydroxyl ion (OH-) going to the other. The general formula is $XY + H_2O \rightarrow HY + XOH$. Inorganic hydrolysis generally involves water alone. Organic hydrolysis involves acidic solutions, alkaline solutions or enzymes.

Saponification is the hydrolysis of fat to form a fatty acid and glycerin. Since water is not soluble in fats, the reaction takes place on the interface between the liquids. A sulfoaromatic-emulsifying compound is usually added to increase the interface area and promote the reaction.

In many hydration and hydrolysis reactions, catalysts or high temperatures and pressures must be used for the reaction to proceed at a reasonable speed.

Hydration is used in the manufacturing of alcohols from alkenes, glycols from oxides, and acetaldehyde. Hydrolysis is used to manufacture soaps, high purity carboxylic acids and sucrose derivatives.

Process Chemistry

a) Hydration of ethylene to ethanol, using a phosphoric acid catalyst at 570°F (300°C) and 1000 psi (7 MPa).

$$\underset{\text{ethylene}}{C_2H_4} + \underset{\text{water}}{H_2O} \rightarrow \underset{\text{ethanol}}{C_2H_5OH}$$

b) Hydration of ethylene oxide to ethylene glycol.

$$\underset{\text{ethylene oxide}}{(CH_2)_2O} + \underset{\text{water}}{H_2O} \rightarrow \underset{\text{ethylene glycol}}{(CH_2OH)_2}$$

c) Hydration of calcium carbide to acetylene (See Data Sheet 7-51, *Acetylene* for additional information).

$$\underset{\text{carbide}}{CaC_2} + \underset{\text{water}}{H_2O} \rightarrow \underset{\text{acetylene}}{C_2H_2} + \underset{\text{lime}}{Ca(OH)_2}$$

d) Saponification of glyceryl tristearate to stearic acid and glycerine.

$$\underset{\text{glyceryl tristearate}}{C_3H_5(C_{18}H_{35}O_2)_3} + \underset{\text{water}}{3H_2O} \rightarrow \underset{\text{stearic acid}}{3C_{17}H_{35}COOH} + \underset{\text{glycerine}}{C_3H_5(OH)_3}$$

Equipment

Materials of construction vary depending on whether the process is conducted in acid or alkaline solution. Alkaline materials can usually be handled in steel vessels. With acids, special corrosion resistant materials or linings must be used.

Isomerization and Stereoisomers

Isomerization reactions involve the rearrangement of the atoms in an organic molecule without changing the molecular formula. For example, ethyl alcohol and methyl ether are isomers (C2 H6 O). Isomerization can be a simple rearrangement, such as a change from a straight chain to a branched molecule, or a relocation of a double bond within the molecule that produces a significant change in physical and chemical properties. Isomerization can also result in a very small change that produces only subtle differences in spatial orientation.

Stereoisomers are isomers that are different from each other only in their three-dimensional orientation. They are classified by appearance. Enantiomers are mirror-image stereoisomers. They have identical physical properties, except for the direction of rotation of the polarized light plane, and identical chemical properties, except toward optically active reagents. Diastereomers are stereoisomers that are not mirror-image. Diastereomers have different physical properties and similar, but not identical, chemical properties. Stereoisomers can also be further classified by how they are formed.

Isomerization reactions are initiated either by heat or light.

Isomerization reactions are used in petroleum refining and in the preparation of many biopharmaceutical active ingredients. Some optically active compounds are obtained from natural sources. Other optically active compounds can be made from the naturally occurring compounds.

Process Chemistry

a) Isomerization and chlorination of n-butane

$CH_3CH_2CH_2CH_3 + Cl_2 \rightarrow CH_3CH_2CHClCH_3 + CH_3CH_2CH_2CH_2Cl$

n-butane chlorine sec-butyl chloride n-butyl chloride

b) Aldohexose stereoisomers ($C_6H_{12}O_6$):
There are sixteen stereoisomers including (+)-glucose, (-)-glucose, (+)-mannose, and (+)-galactose.

Equipment

Process equipment should be specified depending on the properties of the materials involved. Special linings or materials may be needed for corrosion resistance.

Neutralization

Neutralization is a reaction between an acid and a base to produce a salt.

Reactions normally take place in aqueous solutions at or near ambient conditions.

Neutralization is used widely in fertilizer manufacturing, inorganic salt processes, water treating and in soap manufacturing.

Process Chemistry

a) Acid reacts with a base to form a salt; see Data Sheet 7-89, *Ammonium Nitrate*, for additional information.

$HNO_3 + NH_3 \rightarrow NH_4NO_3$

nitric acid ammonia ammonium nitrate

b) Acid reacts with a metal to form a salt and hydrogen

$2HCl + Mg \rightarrow MgCl_2 + H_2$

hydrochloric acid magnesium magnesium chloride hydrogen

c) Metal carbonate reacts with acid to form a salt and water

$Na_2CO_3 + 2HNO_3 \rightarrow 2NaNO_3 + CO_2 + H_2O$

sodium carbonate nitric acid sodium nitrate carbon dioxide water

Equipment

Neutralization is often done in ordinary tanks or in closed reactors or absorbers. Equipment materials should be able to resist any corrosive acids or bases present.

Nitration

Nitration is the introduction of one or more nitro groups ($-NO_2$) into a compound, normally through replacement of a hydrogen atom. Nitrations of aromatic and alcohol compounds are typically performed using nitric acid, often in the presence of sulfuric acid. If the hydrogen in the -OH group of an alcohol is replaced, the reaction is also an esterification.

Nitration reactions are very sensitive to temperature. If the temperature is too low, the nitrating agent may not react when introduced and may accumulate. When the temperature later rises, the nitrating agent may react all at once. If the temperature is too high, side reactions such as oxidation or decomposition may result and become violent. Reaction temperatures range from 30°F (0°C) to 750°F (400°C). Pressures range from atmospheric to about 100 psi (700 kPa).

Nitration is common in the manufacture of high-energy materials, dyes, perfumes, pharmaceutical intermediates, herbicides and fungicides.

Process Chemistry

a) Nitration of benzene to produce nitrobenzene (aromatic nitration).

$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$

benzene nitric acid nitrobenzene water

b) Nitration of glycerine to produce nitroglycerine (alcohol nitration).

$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(ONO_2)_3 + 3H_2O$

glycerine   nitric acid   nitroglycerine   water

c) Nitration of propane produces a variety of nitrated products (alkane nitration).

$CH_3CH_2CH_3 + HNO_3 \rightarrow CH_3CH_2CH_2NO_2$ (25%) $+ CH_3CHNO_2CH_3$ (40%) +

propane   nitric acid   1-nitropropane   2-nitropropane

$CH_3CH_2NO_2$ (10%) $+ CH_3NO_2 + CO_2 + H_2O$

nitroethane   nitromethane   carbon dioxide   water

Equipment

Nitration of alkanes is normally performed as a vapor phase reaction in a high-pressure continuous reactor (NO_2+ ions do not react readily with alkanes).

The acid and the material to be nitrated are usually not soluble in one another and form two non-miscible layers. Vigorous agitation or tubular flow is needed to bring the reactants in contact and promote the reaction.

Organometallic Compounds

Organometallic compounds are simply a combination of an organic molecule and a metal. Grignard reagents (RMgX) are probably the best known of these compounds. Others include organocadmium reagents, lithium dialkyl copper reagents (Corey-House synthesis), and organozinc compounds (Simmons-Smith reaction and Reformatsky reaction).

Organolithium compounds (RLi) resemble Grignard reagents in their preparation and reactions, except they are even more reactive. Organosodium compounds are so reactive that their use is limited to the synthesis of symmetrical alkanes (Wurtz reaction).

Reactions involving these compounds can also be classified as alkylation, condensation or reduction reactions; but they are covered separately because of the unique hazards they present.

Process Chemistry

a) Grignard reagent preparation: Grignard reagents can be purchased for laboratory or small-scale commercial use, but usually are prepared as part of the process. Typically, magnesium chips or turnings (Mg) are charged into a vessel after it has been purged with nitrogen. Ethyl ether or tetrahydrofuran (THF) is pumped in and an organic halide (RX) is added. This forms an alkymagnesium halide of the general formula RMgX. The reaction is highly exothermic and the temperature must be controlled by limiting the rate of addition of the organic halide, making sure that it reacts as it is added, and by providing cooling to the reactor jacket.

$C_6H_5Br + Mg \rightarrow C_6H_5MgBr$

bromobenzene   magnesium   phenyl-magnesium bromide

b) Grignard reactions: Grignard reagents react with a wide variety of compounds. Phenylmagnesium bromide reacts with ethylene oxide, followed by treatment with an acid to produce phenylethanol (a compound with a rose-like odor widely used in perfumes).

$C_6H_5MgBr + (CH_2)_2O \rightarrow C_6H_4CH_2CH_2OMgBr$

ethylene oxide   intermediate

$C_6H_5CH_2CH_2OMgBr + HCl \rightarrow C_6H_5CH_2CH_2OH + MgClBr$

hydrochloric acid   phenylethanol   magnesium chlorobromide

c) Grignard reactions: Grignard reagent reaction with an organic or inorganic halide.

$CH_3CH_2MgCl + C_6H_5Cl \rightarrow C_6H_5CH_2CH_3 + MgCl_2$

ethyl magnesium chloride   chlorobenzene   ethyl benzene   magnesium chloride

d) Grignard reactions: Grignard reagents react violently with water to produce an ignitable liquid or flammable gas.

$CH_3CH_2CH_2CH_2MgCl + H_2O \rightarrow CH_3CH_2CH_2CH_3 + MgOHCl$

n-butylmagnesium chloride   water   n-butane   (mixture of magnesium hydroxide and chloride)

Equipment

Agitated, semi-batch type reactors constructed of carbon steel are frequently used. Nitrogen blanketing is provided both for safety reasons and to prevent depletion of the reagent by reaction with oxygen and moisture.

Oxidation

Oxidation is any process that increases the proportion of oxygen or acid forming elements in a compound. Oxygen is usually added to an organic molecule; but electrons may be lost, or hydrogen removed. Oxidation also includes the combination of oxygen with inorganic chemicals, such as sulfur, phosphorus and metals. In this data sheet, oxidation differs from combustion only in that the reaction is stopped at a point where only carbon dioxide and water is generated.

Organic oxidation processes can take place either in the liquid or vapor phase. In vapor phase oxidation, an excess of the material to be oxidized is vaporized and mixed with air or oxygen. A low oxygen concentration and temperature control are used to prevent completion of the reaction. A catalyst is used to promote the reaction at the low temperature. In liquid phase oxidation, air or oxygen in bubbled through the liquid solution with a catalyst. Liquid phase oxidations are performed when a higher temperature may cause the molecule to disintegrate.

Common oxidizing agents are oxygen, hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), potassium dichromate ($K_2Cr_2O_7$), chromic (VI) acid (CrO_3), dilute nitric acid (HNO_3) and numerous chlorine derivatives. The chlorine derivatives include potassium perchlorate ($KClO_4$), sodium chlorate ($NaClO_3$), perchloric acid ($HClO_4$), chlorous acid ($HClO_2$), sodium chlorite ($NaClO_2$) and chlorine dioxide (ClO_2). Tollens' reagent contains a silver ammonia ion, $Ag(NH_3)_2+$, used to oxidize aldehydes and aldoses in an alkaline solution. Fehling's solution and Benedict's solution, containing a complexed cupric ion, are also used to oxidize aldoses and ketoses.

Ozonolysis is another form of oxidation. It is the addition of ozone (O_3) to a double bond to form an ozonide. Hydrolysis of the ozonide usually follows to yield the cleavage products consisting of aldehydes and ketones. Formaldehyde can be produced from isoprene via ozonolysis. Cycloalkenes and cycloalkynes do not cleave but simply open up into a six carbon molecule containing two aldehyde groups.

Oxidation is common in fuel gas processes, such as purification of natural gas and the production of fuel gases from coal. Oxidation of primary alcohols is used to produce aldehydes and carboxylic acids. Oxidation of secondary alcohols is used to produce ketones. Oxidation of alkylbenzenes is used to produce carboxylic acids. Upon treatment with periodic acid (HIO_4), compounds containing two or more OH or = O groups attached to adjacent carbons undergo oxidation with cleavage of the carbon-carbon bond. A common application of this is the oxidative cleavage of carbohydrates into sugar derivatives. Many biological processes involve oxidation reactions.

Inorganic oxidation is most common in the metallurgical refining (mining) industry. It is used to produce pure metals from metal minerals—typically gold, copper, nickel and zinc. Oxygen selectively reacts with undesired metallic sulfides (pyrite), iron and other metals to free up the desired valuable metals. This process may be completed pyrometallurgically in smelters or roasters using a high concentration of oxygen to produce gaseous sulfur dioxide, or hydrometallurgically in autoclaves to produce liquid sulfates. While smelters and roasters operate at high temperature and low (atmospheric) pressure, autoclaves operate at high temperatures and pressures.

Process Chemistry

a) Oxidation of coal: fuel gases are produced by the reaction between carbon and steam or oxygen. Oxygen is obtained from air in the production of producer gas or low BTU gas. Pure oxygen produces medium BTU gas.

$C + H_2O \rightarrow H_2 + CO \text{ or } CO_2$
carbon water hydrogen carbon monoxide carbon dioxide

$C + O_2 \rightarrow CO \text{ or } CO_2$
carbon oxygen carbon monoxide carbon dioxide

b) Oxidation of methane at flame temperature (1500°F [815°C]), and at 850°F (454°C) with a nickel catalyst.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O +$ heat (complete combustion)
methane oxygen carbon dioxide water

$6CH_4 + O_2 \rightarrow 2C_2H_2 + 2CO + 2H_2$
methane oxygen acetylene carbon monoxide hydrogen

$CH_4 + H_2O \rightarrow CO + 3H_2$
methane water carbon monoxide hydrogen

c) Oxidation of an alkene using permanganate

$CH_3CHC(CH_3)_2 + KMnO_4 \rightarrow (CH_3)_2CO + CH_3COOH$
2-methyl-2-butene potassium permanganate acetone acetic acid

d) Oxidation of sulfur to form sulfuric acid. In the first and second steps, sulfur is oxidized. Step one is performed in an ordinary furnace. Step two is performed in a converter at a temperature of 1065°F (575°C), using a platinum or vanadium catalyst. In the third step, the oxide is hydrated with water to produce the acid.

$S + O_2 \rightarrow SO_2$
sulfur oxygen sulfur dioxide

$2SO_2 + O_2 \rightarrow SO_3$
sulfur dioxide oxygen sulfur trioxide

$SO_3 + H_2O \rightarrow H_2SO_4$
sulfur trioxide water sulfuric acid

Equipment

The greatest problem in the design of organic oxidation reactors is the removal of heat in vapor-phase reactors. Removal of heat is essential to prevent destruction of apparatus, catalyst, or raw material. Maintaining temperature at the proper level is necessary to ensure the correct rate of oxidation. Another problem in the design of oxidation reactors is the possible introduction of liquid into vapor-phase reactors; the liquid may flash resulting in overpressurization. In liquid-phase reactors, the temperature is usually low; and the rate of heat generation can be readily controlled by the rate at which air or another oxidizing agent is introduced. Good mixing of reactants is important.

Autoclaves used in metallurgical refining are often constructed of special corrosion resistant alloys such as titanium.

Construction materials should be able to resist any corrosive substances present.

Photochemical

This type of reaction falls outside the common classification systems. Photochemical reactions proceed in the presence of light; the rate is dependent on the intensity of incident radiation. Classification is based on the reactions themselves.

a) Halogenation using UV light

$CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl$
ethane chlorine chloroethane

b) Isomerization of 1,3-butadiene to cyclobutene
$CH_2 = CHCH = CH_2 \rightarrow CH_2CH = CHCH_2$ (cyclic compound)
1,3-butadiene cyclobutene

Polymerization

Polymerization is the joining together of small molecules, known as monomers, to form a much larger molecule, known as a macromolecule or polymer. Polymers are formed in many ways as shown in Figure C.3-1.

The catalyst used in addition polymerization may be an organic peroxide, an inorganic peroxide, an acid, a base or an organometallic compound.

Addition polymerization can be conducted via a homogeneous system (need only one phase for the reaction to proceed) or a heterogeneous system (need at least two phases for the reaction to proceed).

In bulk polymerization, the monomer, polymer and catalyst are the only materials in the reactor. Because of the high concentration of reactants, polymerization is the most difficult process to control. The heat given off is difficult to remove, specifically as the polymerization progresses and the mix increases in viscosity. Bulk polymerization is often completed in two stages. In the first stage, the monomer is only partly polymerized into a resin. In the second stage, the reaction is completed by molding or extruding the resin into sheets, rods or tubes (acrylic polymers), spraying onto forms and curing (fiberglass reinforced polyester polymers) or extruding into sheets or films. Bulk polymerization has the advantage of being free of solvents and impurities.

In solution polymerization, the monomer is dissolved in a solvent. Because of the dilution of the monomer, the reaction is easier to control; and the viscosity is reduced. This facilitates heat removal and temperature control. However, the product is usually of a lower molecular weight; and the solvent must be separated from the polymer after the reaction is completed.

In emulsion polymerization, monomer particles are suspended in a water emulsion using soap or another emulsifying agent. The monomers are converted to a colloidal suspension of polymer particles, forming latex. The water absorbs the heat of reaction and keeps the reaction mass flowing to simplify agitation. This process is common in the polymerization of vinyl chloride. The disadvantage of this process is that the addition of emulsifying or stabilizing agents makes preparing a pure or clear polymer difficult.

In suspension or pearl polymerization, the monomer droplets are usually suspended in water without an emulsifying agent. However, solvents can be used (e.g., hexane is used in an older polypropylene process). The droplets are larger (0.1 to 1 mm) than in the emulsion process. The catalyst is dissolved in the water. Polymers usually form as small beads that are easily filtered out, washed, and dried to form molding powders.

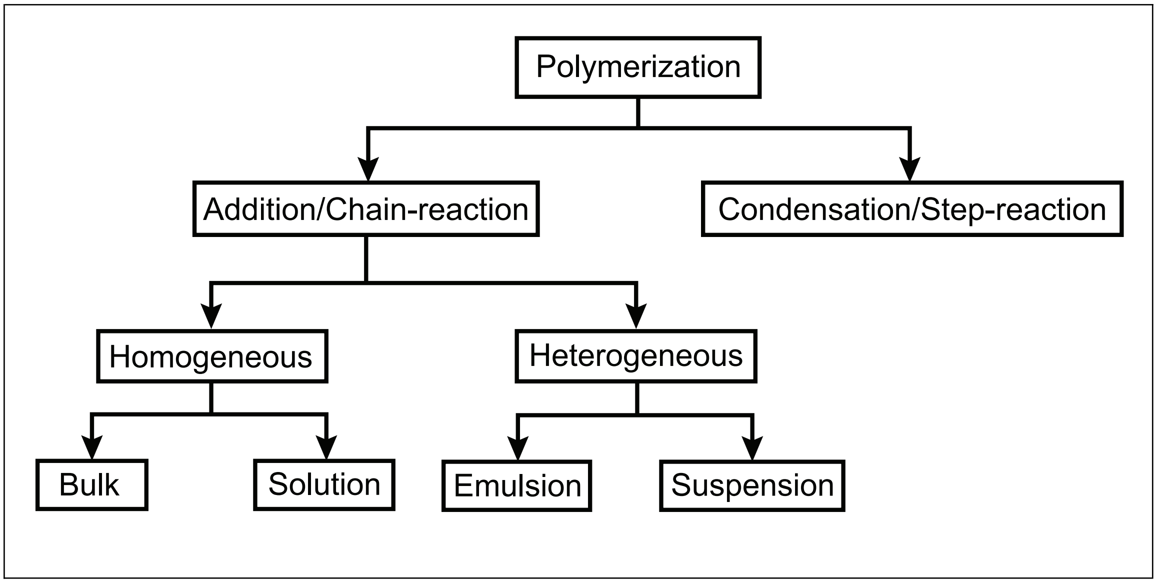


Fig. C.3-1. Types of polymerization reactions.

In both emulsion and suspension polymerization, if agitation can be maintained, absorption of heat by the water or solvent readily controls the reaction. However, if agitation is lost or the emulsifying agent is inadequate, the monomer will concentrate; and uncontrolled bulk polymerization will ensue. Therefore, reliable agitation is vital as is relief venting equal to that provided for bulk polymerization processes.

Condensation polymerization can be conducted in an aqueous or a solvent medium, or the reactants may be liquids. The reaction is usually interrupted while the polymers are still soluble or fusible. A curing process completes the polymerization of the final product. The catalyst used in condensation polymerization is usually an acid or base. Since water or a similar condensation product is produced and must be removed, the process is normally easier to control than addition polymerization.

Copolymers are polymers that contain two or more different monomers. Copolymerization processes are similar to polymerization processes, except that the relative concentrations and reactivities of the monomers become important process parameters.

Synthetic polymers include elastomers, fibers and plastics. Elastomers have the elasticity characteristics of rubber. Elastomeric Materials, published by the International Plastics Selector, identifies over 20 different generic types of synthetic rubber, including acrylic, butadiene, butadiene/styrene/vinyl pyridine, butyl, ethylene-propylene, halogenated, nitrile, styrene-butadiene and urethane rubbers. Fibers are thread-like. Synthetic fibers include polyamides (Nylon 66), polyesters (Dacron, Terylene, Vycron), polyacrylonitriles (Orlon, Acrilon), polyurethanes (Spandex, Lycra) and isotactic polypropylene.

Plastic characteristics depend on the molecular structure. Plastics are classified as thermoplastics or thermosetting.

Thermoplastic or thermosoftening polymers are linear and branched polymers that are basically crystalline. On heating, these polymers soften. Addition polymerization is commonly used to produce thermoplastics including acid-catalyzed phenyl-formaldehyde, polyethylene, polystyrene and polyvinyl chloride.

Thermosetting polymers are highly cross-linked, and form rigid, irregular, three-dimensional structures. On heating, these polymers may actually become harder due to the formation of additional cross-links. Condensation polymerization is commonly used to produce thermosetting resins, including alkaline-catalyzed phenyl-formaldehyde and melamine.

Process Chemistry

1. Addition polymerization of ethylene to polyethylene:

    a) Bulk polymerization of ethylene to produce low density polyethylene (LDPE, 0.910-0.940 g/cm^3) at high-pressure using small quantities of oxygen, an organic peroxide or another strong oxidizer as the catalyst. The ethylene gas is compressed up to 60,000 psi (420 MPa) at up to 660°F (350°C). Note that at very high pressures ethylene can be decomposed by shock and by an excess of catalyst.

    b) Solution polymerization of ethylene to produce high density polyethylene (HDPE, 0.941-0.970 g/cm^3) at low-pressure using an organic or an inorganic peroxide as a catalyst. The ethylene is dissolved in an inert hydrocarbon. The solvent helps absorb the heat of reaction. If the temperature rises, the ethylene is driven out of solution, reducing its concentration and automatically slowing the reaction.

    $$\underset{\text{ethylene}}{CH_2 = CH_2} \rightarrow \underset{\text{polyethylene}}{(\text{-}CH_2\ CH_2\text{-})_n}$$

2. Condensation copolymerization of adipic acid and hexamethylenediamine to Nylon 66:

    $$\underset{\text{hexamethylenediamine}}{H_2N(CH_2)_6NH_2} + \underset{\text{adipic acid}}{HOOC(CH_2)_4\ COOH} \rightarrow \underset{\text{nylon}}{\text{-}NH(CH_2)_6NHCO(CH_2)_4CO\text{-}} + \underset{\text{water}}{H_2O}$$

3. Condensation copolymerization of phenol or substituted phenol and an aldehyde to prepare phenolic resins, such as phenol-formaldehyde: The type of catalyst used (caustic or acid), the ratio of the reactants and the reaction conditions (time and temperature) determine the properties of the resin and the reaction hazards.

Formaldehyde to-phenol ratios of 0.5 to 0.8 are used with an acid catalyst to produce novolaks. Novolaks are thermoplastic and react with cross-linking substances to give the resin desired properties; they are generally solids. Novolaks are produced in both continuous and batch processes. Molten phenol is usually charged into the reactor, followed by a precise amount of acid catalyst. The formaldehyde solution is then introduced in a slow, continuous or stepwise addition.

Formaldehyde to-phenol ratios of 1.0 to 3.0 are used with a caustic catalyst to produce resoles. Resoles are generally of lower molecular weight and may be liquid or solid. Most resoles are produced in a multi-step batch process.

Acid catalyzed phenol-formaldehyde reactions are historically easier to control than caustic catalyzed reactions.
$C_6H_5OH + HCHO \rightarrow C_6H_4OH(CH_2OH) + C_6H_5OH \rightarrow C_6H_5OH\text{-}CH_2\text{-}C_6H_5OH \rightarrow \text{polymer}$
phenol formaldehyde o-hydroxymethyl phenol intermediate

Equipment

Batch, semi-batch or continuous reactors are used, depending on the type of polymerization. Polystyrene is prepared in batch and semi-batch reactors. Polyethylene is typically prepared in tubular flow reactors. These reactors may be 1.25 miles (2 km) long by 2.5 in. (6.4 cm) in diameter, or 20 ft (6.1 m) high by 9 in. (22.9 cm) in diameter with 4.5 in. (11.4 cm) thick walls. Polyvinylchloride is prepared in large batch reactors.

Pyrolysis and Cracking

Pyrolysis is the decomposition of large molecules into smaller ones by heat. Coal may be pyrolyzed to form coke, ammonia, and light and heavy oils.

Cracking is the pyrolysis of alkanes, particularly petroleum.

In thermal cracking, alkanes are simply heated to a high temperature. Large alkanes are converted to smaller alkanes, alkenes, and hydrogen. Cracking of natural gas is conducted at temperatures up to 3000°F (1650°C).

In steam cracking, alkanes are diluted with steam, briefly heated to 700-900°F (370-480°C), then rapidly cooled. This method is used to produce many hydrocarbon chemicals, including ethylene, propylene, butadiene, isoprene, and cyclopentadiene.

Hydrocracking is conducted in the presence of hydrogen at high pressure and lower temperatures, i.e., 250-450°F (120-230°C).

In catalytic cracking, higher boiling petroleum fractions are contacted with a catalyst at moderate temperatures and pressures, i.e., 900°F (480°C) and 8-20 psi (50-140 kPa). This method produces alkanes with the highly branched structures desired in fuels.

Process Chemistry

1. Pyrolysis of natural gas (methane) in a continuous furnace to produce industrial carbon and hydrogen.
   $CH_4 \rightarrow C + 2H_2$
   methane carbon hydrogen

If the gas is heated in an electric arc, acetylene may be formed. Its decomposition can be prevented by rapid quenching:
$2CH_4 \rightarrow C_2H_2 + 3H_2$
methane acetylene hydrogen

2. Catalytic cracking of butane to form 1,3-butadiene (used in synthetic rubber).
   $CH_3CH_2CH_2CH_3 \rightarrow CH_3CH = CHCH_3 + CH_3CH_2CH = CH_2 \rightarrow CH_2 = CHCH = CH_2$
   n-butane 2-butene 1-butene 1,3-butadiene

Equipment

Pyrolysis and cracking equipment is very large and is designed for the specific application.

Reduction

Historically, a reduction reaction occurred when oxygen was removed from a molecule. However, reduction is really any process where the number of electrons in the chemical substance increases. In addition to removal of oxygen, reduction reactions also include removal of halogens, sulfur or ammonia, as well as the addition of hydrogen to a metal or the generation of hydrogen. Note the oxidation state of hydrogen is +1 in all its compounds, except for those with metals where it is commonly 1.

Reduction reactions are frequently thought of as the reverse of oxidation reactions. Redox reactions occur when reduction and oxidation reactions occur simultaneously. Standard redox or electrode potentials can be used to determine simple reduction potentials.

Process conditions vary widely, depending on whether organic or inorganic materials are involved.

Among the most common organic reduction processes are the manufacture of amines from nitro compounds. These generally involve the generation of hydrogen and subsequent addition of hydrogen to the compound. Hydrazine, diborane, sodium hydride or hydrogen may be used in organic reduction reactions.

The most common inorganic reduction processes are the removal of oxygen from inorganic chemicals, such as the reduction of metal oxides to pure metals (i.e., metallic sodium, aluminum or magnesium).

Process Chemistry

1. Reduction of nitrobenzene to aniline by iron, using an acid ferrous chloride catalyst.
   $4C_6H_5NO_2 + 9Fe + 4H_2O \rightarrow 4C_6H_5NH_2 + 3FE_3O_4$
   nitrobenzene iron water aniline iron oxide

2. Reduction of calcium phosphate to prepare phosphorus with carbon monoxide as a by-product.
   $Ca(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + 2P + 5CO$
   calcium phosphate sand coke calcium silicate phosphorus carbon monoxide

3. Iron extraction from haematite in a blast furnace.
   a) Coke is oxidized to form carbon dioxide
      $C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)$
      carbon oxygen carbon dioxide
   b) Carbon dioxide is reduced to carbon monoxide
      $CO_2\ (g) + C\ (s) \rightarrow 2CO\ (g)$
      carbon dioxide carbon carbon monoxide
   c) Iron oxide is reduced to iron (with impurities) by carbon monoxide.
      $Fe_2O_3\ (s) + 3CO\ (g) \rightarrow 2Fe\ (s) + 3CO_2$
      iron oxide carbon monoxide iron carbon dioxide

Equipment

Inorganic reduction is often done in furnaces.

Organic reductions are normally conducted in ordinary steel reactors, suitably designed for the corrosive conditions that may be present.

Reforming

Catalytic reforming may result in dehydrogenation, cyclization and isomerization of alkanes into cycloalkanes and aromatic hydrocarbons.

The most common commercial application of these reactions is in ammonia synthesis and petroleum refining.

Process Chemistry

1. Reforming of methylcyclohexane to produce toluene, using a catalyst at 560°F (293°C), 300 psi (2.1 MPa) (dehydrogenation).
   $C_6H_{11}CH_3 \rightarrow C_6H_5CH_3 + 3H_2$
   methylcyclohexane toluene hydrogen

2. Reforming of 1,3-dichloropropane to produce cyclopropane, using a catalyst and a salt (cyclization).
   $CH_2Cl\ CH_2CH_2Cl \rightarrow \text{intermediate} \rightarrow (CH_2)_3$
   1,3-dichloropropane cyclopropane

Equipment

Ammonia synthesis and catalytic steam hydrocarbon reformers are detailed in Data Sheet 7-111G, *Ammonia and Ammonia Derivatives* and Data Sheet 7-72, *Reformer and Cracking Furnaces*.

Saponification - See Hydration, Hydrolysis and Saponification

Silicon, Silane, Silicone, and Siloxane

Silicon (Si) is an element that is a component of many different minerals. It should not be confused with inert silica (SiO_2) or silicates ($M_2O \bullet mSiO_2 \bullet nH_2O$ where M is an alkali metal and m and n are the number of moles of SiO_2 and H_2O, respectively, per mole of M_2O) from which it is derived. Silicon is used extensively in the semiconductor and nonferrous metal industries.

A silane is a compound containing a hydrogen-silicon bond and is also known as a silicon hydride. Silane (SiH_4) is the simplest hydride. Thousands of inorganic silane and organosilane compounds exist. Inorganic silanes undergo many different types of reactions, including oxidations and halogenations. Organosilanes also undergo a variety of chemical reactions including additions, aminations, hydrolysis, oxidations and photolysis. The addition of organosilanes to olefins is called hydrosilylation.

Silicone, $R_nSiO_{(4-n)/2m}$,is a synthetic polymer where $n = 1\text{-}3$ and $m \leq 2$. A silicone has a repeating silicon-oxygen backbone and has organic groups attached by silicon-carbon bonds to a significant number of the silicon atoms. Preparation of silicone involves a number of steps. Simply, a silane monomer is hydrolyzed to siloxane; the siloxane is hydrolyzed to an intermediate; and then the intermediate is rearranged, reduced, polymerized or copolymerized. The final product could be a fluid, a resin or an elastomer. Silicone elastomers are further categorized by their cure-system chemistry, e.g., room-temperature-vulcanizing (RTV) or heat-cured.

Silicones have several unusual properties that make them commercially important. Silicones are relatively stable and inert. They are resistant to weathering, have good dielectric strength and have a low surface tension. Silicone fluids are used as hydraulic fluids, lubricants, surfactants and for waterproofing. Silicone resins are used in adhesives, electrical insulations, laminates, paint and varnishes. RTV elastomers are used in adhesives, electrical insulations, gaskets, glazings and sealants. Heat-cured elastomers are used in belts, calendering rollers, fabric coatings, hoses and penetration seals.

Process Chemistry

1. Chlorination of silicon using methyl chloride in the presence of a copper catalyst and at elevated temperatures to produce methylchlorosilanes.

CH_3Cl	+	Si	→	CH_3SiCl_3	+	$(CH_3)_2SiCl_2$	+	$(CH_3)_3SiCl$
methyl chloride		silicon complex		methyltrichlorosilane		dimethyldichlorosilane		trimethylchlorosilane

2. Chlorination of silicon, ferrosilicon, or calcium silicide in the presence of a copper catalyst to produce trichlorosilane.

HCl	+	Si	→	$HSiCl_3$
hydrogen chloride		silicon complex		trichlorosilane

3. Reduction of hydrochloric acid and silane to produce chlorosilane, using an aluminum chloride catalyst. Hydrogen is generated.

HCl (g)	+	SiH_4 (g)	→	SiH_3Cl (g)	+	H_2
hydrochloric acid		silane		chlorosilane		hydrogen

Equipment

Because of the wide range of silicon, silane, silicone, and siloxane processes, equipment must be designed for the specific application, taking into consideration material characteristics and process conditions.

Sulfonation

Sulfonation is the process by which the sulfonic acid group, HSO_3, is added to a carbon in an organic compound. Normally, this is accomplished by reacting a compound with SO_3, H_2SO_4, or oleum (SO_3 dissolved in H_2SO_4). SO_3 is the most vigorous sulfonating agent, but it tends to initiate side reactions with materials that are easily sulfonated. Therefore, the sulfonating agent used is generally no stronger than necessary. Most sulfonation reactions are readily reversible.

Sulfonation is one of the reactions used to dissolve lignin when processing sulfite pulp in paper mills. It is also used in the manufacture of detergents.

Process Chemistry

1. Sulfonation of phenol to o-phenolsulfonic acid at 15 to 20°F (-9 to -7°C) and p-phenolsulfonic acid at 100°F (38°C).

C_6H_5OH	+	H_2SO_4	→	$C_6H_4(OH)(SO_3H)$
phenol		sulfuric acid		phenolsulfonic acid

2. Sulfonation of an alcohol to a sulfate.

$$\underset{\text{lauryl alcohol}}{n\text{-}C_{11}H_{23}CH_2OH} + \underset{\text{sulfuric acid}}{H_2SO_4} \rightarrow \underset{\substack{\text{lauryl hydrogen}\\ \text{sulfate}}}{n\text{-}C_{11}H_{23}CH_2OSO_3H} + \underset{\substack{\text{sodium}\\ \text{hydroxide}}}{NaOH} \rightarrow \underset{\substack{\text{sodium lauryl}\\ \text{sulfate}}}{C_{11}H_{23}CH_2OSO_3\text{-}Na+}$$

Equipment

Sulfonations may be conducted in ordinary batch reactors equipped with agitators, heat transfer systems and condensers. They may also be conducted in continuous tube reactors with tube-bundle reactors (about 100, 1 in. [2.5 cm] diameter tubes inside a water-cooled vessel) and falling film reactors (single, 30 in. [72.2 cm] ID tube).

Equipment should be constructed of materials able to withstand concentrated sulfuric acid, such as glass-lined steel.

APPENDIX D. TEST CALORIMETERS

Many tools are available for measuring reaction rates and revealing reaction behavior. However, selection of the right tool that can safely replicate a runaway reaction in a laboratory, under a variety of conditions, with a degree of confidence, is of paramount importance to better understand process conditions that can result in a runaway reaction and for the establishment of adequate process controls. Numerous devices and instruments are commercially available, designed specifically to measure reaction behavior for the evaluation of thermal hazards and for determination of reaction parameters. Some of these calorimeters are summarized in Table D-1.

Table D-1. Common Calorimeters

Equipment	*Main Use*	*Data Obtained*	*Test Description*	*Advantages*	*Disadvantages*
Differential Scanning Calorimetry (DSC)	Screening tool for thermal and oxidative stability	• Heat of Reaction (ΔHr). • Onset temperature. • Explosive properties.	Small quantity of sample (greater than 20 mg). Test cells constructed of stainless steel, aluminum, or gold, which may or may not be sealed high pressure cells. Sample temperature increased to detect temperature range where reaction (exothermic or endothermic) occurs. The parameters measured are heat flow, time, and temperature.	• Test can be performed under air or nitrogen atmospheres. • Sensitive to small changes on heat flow and mass. • Economic and simple to operate. • Short testing time.	• No pressure generation is detected. • Results are not directly scalable. • Expect appreciable heat loss to the surroundings. • No agitation in the sample container. • All materials must be added before testing.
Reaction Calorimetry (RC1)	Screening. Intended Chemistry.	• Heat of Reaction (ΔHr). • Adiabatic temperature rise. • Heat flow.	The test is conducted to simulate actual process conditions. Materials are charged into a jacketed reactor in batches of about 1.5 liter, with efficient agitation. Predefined dosing (liquids and gases) over time can be used.	• The heat of reaction can be determined under isothermal or isoperibolic conditions. • Instantaneous identification of the effect of process changes such as concentration, temperature and feed rates. • Loss of cooling effects can be determined using the heat of reaction.	• The system accuracy decreases with viscosity. • Solid reactions cannot be analyzed.
Micro-Reaction Calorimeter (μRC)	Screening. Upset Conditions.	• Heat capacity (Cp). • Thermodynamics. • Reaction kinetics.	Power compensation calorimeter controls the sample temperature to maintain equal temperatures between the sample and reference cell.It allows for operation at a pressure up to 290 psi (20 bar) and a sample size of less than (2 ml).	• Shorter calorimetry study times.	• Uncertainty if the sample is not homogeneous or representative of the actual full-scale reaction mass.

Table D-1. Common Calorimeters (continued)

Equipment	*Main Use*	*Data Obtained*	*Test Description*	*Advantages*	*Disadvantages*
Accelerating Rate Calorimetry (ARC)	Upset Conditions. Thermal stability. Secondary reactions.	• Heat generation rates. • Onset temperature (Tonset). • Adiabatic temperature rise (ΔTad). • Rate of temperature rise (dT/dt). • Rate of pressure rise (dP/dt). • Time to maximum rate (TMRad). • Self-accelerating decomposition. temperature (SADT). • Volume of gas generated.	A small sample (1-6 grams) is placed in a small spherical metal container (bomb) (7-10 ml). The test will measure the system's adiabatic pressure and temperature response/ time under adiabatic conditions. The sample is heated to a pre-set temperature and allowed to equilibrate. If a temperature increase greater than 0.02°C/min is detected, the unit's controller maintains the heater at the current setting and starts recording temperature and pressure data in the container as the sample is allowed to runaway. This data can be adjusted for the thermal inertia of the sample container using a correction factor. The adjusted data may be used to estimate kinetic properties of the reaction for calculation purposes, or it can be used for comparing the results of different upset scenarios to determine which one causes the worst case.	• Testing conditions representative of large-scale processing units. • The automatic dosing unit allows additions at any time during the test. • Sensitive at low reaction rates. • Built to withstand internal pressure.	• High phi factor (1.5-3). Corrections and data adjustments are needed. • No agitation provided. • Cannot track very fast reactions.
Advanced Reactive System Screening Tool (ARSST)	Upset Conditions. Screening test. Data for vent sizing.	• Heat of reaction or mixing. • Onset temperature. • Adiabatic temperature rise (ΔTad). • Rate of temperature rise (dT/dt). • Rate of pressure rise (dP/dt). • Time to maximum rate (TMR). • SADT assuming simple kinetics.	The test uses a small (5-20ml) spherical glass cell heated to temperatures up to 752 ˚F (400°C) in a quasi-adiabatic mode, which prevents heat loss to the surroundings. Self-heat rate is obtained as a function of temperature and pressure.Test can be performed on open or closed cells, can be used to determine the potential for runaway reactions and to measure the rate of temperature and pressure rise for gassy reactions.Data obtained can be applied directly to simulate process upset conditions and for process scale. The ARSST has increased temperature ramp rates to simulate fire exposure, a heat-wait-search operation mode with increased onset detection sensitivity and an isothermal operation at elevated temperature mode.	• Stirring. • Low phi-factor (1.04). • Easy setup for fast testing. • Flow regime detector distinguishes between foamy and non-foamy behavior. • High pressurization rates. • Operates well for reactions that are moderately or strongly exothermic.	• Difficulty detecting weak exothermic reactions

Table D-1. Common Calorimeters (continued)

Equipment	*Main Use*	*Data Obtained*	*Test Description*	*Advantages*	*Disadvantages*
Vent Sizing Package (VSP2)	Upset conditions.Data for vent sizing.	• Required size of emergency relief system (ERS). • Adiabatic temperature and pressure rise rates (dT/dt, dP/dt). • Total adiabatic temperature rise (ΔTad). • Heat of reaction or mixing. • Vapor pressure data. • Time- to-maximum rate (TMR). • Temperature of no return (TNR). • Self-accelerating decomposition temperature (SADT).	VSP2 is an adiabatic calorimeter designed to acquire thermal and vent sizing data (DIERS). Typical sample volumes range from 40 to 80 ml. Results obtained from the test can be directly applied to process scale and used for Emergency Relief System (ERS) design. Results can also be used to perform flow regime characterization, which is necessary for ERS evaluation. Test can be performed on open or closed cells. A blowdown test can also be conducted to assess the foamy nature of a material or the vented materials atmospheric pressure boiling point. Data obtained can be applied directly to simulate process upset conditions and for process scale.	• Can simulate multiple process operations such as batch or metered addition. • Low phi factor (1.05), using thin-walled test cells and a pressure balancing system. • Stirring. • Test performed under adiabatic (zero heat loss) and high pressure1500-2000 psig (100-140 barg) conditions. • External cooling or heating can be added. • Flow regime detector distinguishes between foamy and non-foamy behavior. • Can track very fast reactions	• Solid additions can be problematical. • Very highly energetic reactions may be prohibited from study. • Not sensitive al low reaction rates.

APPENDIX E. REACTIVE MATERIALS (MONOMERS, WATER-REACTIVE AND PYROPHORIC)

Reactivity in a substance or material refers to the tendency to undergo a chemical change or reaction under the right conditions. The reaction can occur on its own or with other incompatible materials, generally accompanied by the release of energy and gas generation. Reactive materials may initiate a reaction by themselves when exposed to conditions such as heat, pressure, shock, friction, catalyst or by contact with air or water.

Reactive materials, when used under controlled process conditions, allow a wide variety of materials to be synthesized. However, a thorough process evaluation should be performed to ensure that these materials will not pose a process hazard where uncontrolled reactions develop into fires and explosions. Listed below are some of the common practices used in processes where reactive materials are present:

- Process and equipment designed to operate with small quantities of reactive materials.
- Presence of reactive materials in process areas limited to the smallest possible quantities, while maintaining the storage conditions required to prevent undesired reactions (i.e., temperature controls, inhibitors, stabilizers, heat/light exposure, etc.).
- Process designed to prevent a double catalyst dose.
- Reactors operated under conditions where the reactive chemical is used in the process as quickly as it is introduced.
- Reliability of cooling systems and process controls.

E.1 Monomers

A monomer is a molecule that can react with other monomers or compounds to produce polymers. These materials are highly reactive and can polymerize during storage, resulting in heat release, runaway reactions, fires and explosions. Monomer polymerization effects are different from those of liquid and gases. Liquid monomers may polymerize in a runaway reaction, whereas monomer gases may polymerize to form solid materials that can block pressure release vents and devices.

Different types of inhibitors and stabilizers are used to prevent polymerization reactions during transportation and storage. Some of the most common inhibitors include tertiary-butyl catechol (TBC), diethylhydroxylamine (DEHA), hydroquinone (HQ) and methyl ether of hydroquinone (MEHQ). Typically, inhibitors are effective only in the presence of oxygen. Therefore, a specific oxygen concentration is required, even when an inert gas blanketing system is present, to ensure the inhibitor's effectiveness.

In general, the following practices are recommended for monomer storage to prevent polymerization reactions:

- Follow manufacturers recommendations for handling and storage operations.
- Inhibitor presence: Inhibitor and concentrations may vary according to monomer type and storage conditions.
- Oxygen presence in the vapor space to keep the inhibitor active: Keep it below the Limiting Oxygen Concentration (LOC). Some monomers do not need oxygen.
- Testing and monitoring: Usually includes temperature, oxygen, inhibitor concentration and storage life (typically 6-12 months for quality purposes).
- Inhibitor addition and stabilization system.
- Pressure-relief devices or weak roof tank construction for scenarios with impractical vent size areas.
- Emergency procedures with clear instructions for monomer stabilization or short stop addition (reaction killer).

E.2 Water-Reactive Materials

Water reactive materials are chemicals that can react violently with water or moisture to produce flammable and/or toxic gases and heat. Water-reactive materials are labeled as such because they may undergo hazardous hydrolysis or reduction-oxidation (redox) reactions with water. Most water-reactive materials undergo exothermic hydrolysis reactions. The rate of the reaction and the characteristics of the reaction products cause concern, not the type of reaction. The rapid reaction rate produces significant heat generation and gaseous products that are flammable and/or toxic. Examples include aluminum carbide and water reacting to form methane, and calcium carbide and water reacting to form acetylene. Sodium metal in water produces hydrogen gas that is ignited by the heat of the reaction.

Common practices for safe handling, storage and processing of water-reactive materials are listed below:

- Evaluate storage, handling and processing operations during Process Hazard Analysis.
- Store materials in a small, detached building of noncombustible construction.
- Transport materials in watertight containers.
- Limit quantities in manufacturing areas to one shift usage.
- Do not use water or steam for heating/cooling, equipment cleaning or as barrier fluid in mechanical seals.
- Use only dry compressed air and inerting gas streams.
- Check raw materials before processing to ensure they are dry.
- Arrange scrubbers, if provided, to prevent backflow to equipment processing water-reactive materials.

E.3 Pyrophoric Materials

Pyrophoric materials are liquids, solids, or gases that will ignite spontaneously upon contact with air. A gas is classified as pyrophoric if it ignites at or below 130°F (54°C) after air contact. Solids and liquids are classified as pyrophoric if they ignite within five minutes. Examples of pyrophoric materials include:

- Organo-metallic reagents (i.e., Grignard reagents).
- Alkali earth elements (sodium, potassium, cesium).
- Finely divided metals (Raney nickel, aluminum powder, zinc dust).
- Metal hydrides (sodium hydride, germane, lithium aluminum hydride).
- Alkyl metal hydrides (butyllithium, trimethylaluminum, triethylboron).
- Metal carbonyls (nickel carbonyl, iron pentacarbonyl).
- Gases (arsine, diborane, phosphine, silane).
- Silicon halides (dichloromethylsilane).

Exposure to air or moisture can cause these materials to generate heat, fire or flammable/corrosive gases. They are usually packaged and stored in airtight containers under an inert atmosphere of nitrogen or argon, oil or solvents, depending on the pyrophoric's physical form. Appropriate methods must be utilized to preserve the material and prevent direct air contact during storage, dispensing or processing.

Common practices for safe operations of pyrophoric materials, are listed below:

- Design process equipment to prevent the accumulation of pyrophoric materials inside the equipment. Where accumulation is unavoidable, design equipment so that the pyrophors can be safely and easily removed on a periodic basis.
- Design process equipment to withstand deflagration pressures. Where this is not practical, provide explosion suppression systems.
- Use closed feed systems.
- Use low-volume equipment to limit the quantity of pyrophoric material present.
- Provide interlocks to prevent opening of the equipment during processing.
- Provide equipment isolation valves.
- Provide oxygen detection interlocked to an emergency purge and isolation system.