

## 24 Chemical Reaction Safety

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### 24.1 Introduction

#### 24.1.1 Need for Reactive Chemical Management

##### 24.1.1.1 Morton International, Inc.

On 8 April 1998, a vessel overpressurization, subsequent explosion, and fire injured nine employees at the Morton International, Inc. plant in Paterson, NJ (CSB, 1998). The explosion was the result of the release of flammable vapors from a vessel being used in the manufacture of a fuel additive dye. The vessel overpressurization was caused by a runaway reaction.

The dye was manufactured by reaction of *ortho*-nitrochlorobenzene (*o*-NCB) and 2-ethylhexylamine (2-EHA). The batch that resulted in the runaway reaction was the 32nd batch of this product that the company had made. The product was developed using a semi-batch mode, where the second reactant would be fed slowly or in aliquots into the vessel. This has the effect of limiting the amount of reaction energy available during a runaway reaction. On a commercial scale, however, the product manufacture was changed to batch mode, in which the full amount of both reactants is charged into the vessel. In batch operations, the full exothermic energy of the reaction is available to be released should a runaway reaction occur.

Standard procedure was to charge the full amount of the two reactants, then heat to 90 °C with the vessel vent open. The reaction normally proceeded at atmospheric pressure due to the open vent. After reaching 90 °C, the operator was to increase the temperature gradually over about 6 h to 150 °C. During batch No. 32, the operator noted that the temperature was rising much more quickly than normal. After reaching 100 °C, the operator turned off the heating and applied cooling water in an attempt to control the reaction. Despite the addition of cooling water, the temperature (and subsequently the vessel pressure) continued to rise at an increasing rate. Two 15 cm rupture disks burst when the pressure reached 0.7 barg.

An operator reported seeing the vessel temperature rise from 190 to 260 °C in less than 30 s at about the same time that the rupture disks burst. This temperature increase was the result of the onset of a decomposition reaction in the dye product. The existence of this decomposition reaction was unknown to Morton. The continuing overpressure from the decomposition caused the manway to be blown off the vessel, releasing flammable vapors into the building. The vapors contacted an ignition source, resulting in a vapor cloud explosion.

#### 24.1.1.2 MFG Chemical, Inc.

On 12 April 2004, MFG Chemical was manufacturing its first commercial-sized batch of triallyl cyanurate (TAC) (CSB, 2004). Pilot batches had been produced in a 30 gal reactor, during which the company decided to conduct the reaction in a batch mode.

In scaling up the batch size from the 30 gal (113 l) pilot reactor to the 4000 gal (15 000 l) production vessel, company personnel failed to realize that the reactor volume to surface area ratio increases considerably as the reactor size increases. This leads to less cooling capacity per unit volume of reaction mass.

After the commercial batch was heated to reaction temperature, the reaction rate, and consequently the rate of heat release, quickly exceeded the cooling capacity of the vessel. A vessel gasket blew out, releasing toxic vapor inside the reactor building. This was quickly followed by the bursting of the vessel's rupture disc, releasing toxic vapors into the surrounding community.

#### 24.1.1.3 T2 Incident

On 19 December 2007, a powerful explosion and fire occurred at T2 Laboratories in Jacksonville, FL (CSB, 2008). The explosion was equivalent to the detonation of about 1400 lb (635 kg) of TNT. The blast damaged off-site buildings up to 1500 ft (460 m) away. Debris was thrown up to 1 mile (1600 m) from the plant site. Three employees and a co-owner of the company were killed from the explosion or flying debris.

T2 produced methylcyclopentadienylmanganese tricarbonyl (MCMT). Normal procedure called for liquid chemicals and sodium metal to be added to the vessel and the mixture heated and agitated. The reaction normally produced hydrogen, which was vented to the atmosphere. When the reaction reached 150 °C, the operator would turn off the heating system. The exothermic reaction was allowed to raise the temperature to 180 °C, at which time the cooling system was used to maintain temperature. On the day of the incident, the cooling system malfunctioned, perhaps due to a pipe blockage or valve failure. The temperature and pressure in the vessel began to rise uncontrollably in a runaway chemical reaction. The vessel's rupture disk burst at 28 barg, followed 10 s later by the rupture of the vessel.

T2 had developed the reaction process in a 1 l reaction vessel, and then scaled it up directly to 2500 gal (9500 l). After producing 41 batches, the batch size was increased by one-third. During the total of 171 batches produced, T2 had periodically experienced temperature excursions that were not fully investigated.

#### 24.1.1.4 CSB Improving Reactive Hazard Management

Following the investigation of a 1998 incident involving reactive chemistry, the US Chemical Safety and Hazard Investigation Board (CSB) initiated a comprehensive review of reactive chemical incidents across the United States (CSB, 2002). The review included 167 serious incidents involving uncontrolled chemical reactions between 1980 and 2001. Forty-eight of these incidents caused 108 deaths. Hundreds of millions of dollars of property damage was incurred. Fifty of the 167 incidents impacted the public.

The CSB's conclusion was that reactive incidents are a significant chemical safety problem, which is inadequately regulated by US authorities. The Board made a total of 18 recommendations to regulatory authorities, industry groups, trade organizations, and employee unions.

#### 24.1.2

##### Summary

This chapter was included in this Handbook because reactive chemical incidents have caused and continue to cause catastrophic incidents. It is only through the thorough understating of intentional chemical reactions and the potential for unintended reactions that the frequency of these incidents can be decreased.

The scope of this chapter is limited to the hazards associated with intentional chemical reactions. Other reactivity hazards such as from mixing, blending, explosives, self-reactive or decomposing materials, and so on are not covered. This chapter describes the data, evaluation techniques, and safeguards necessary to reduce the risks associated with chemical reactions carried out intentionally.

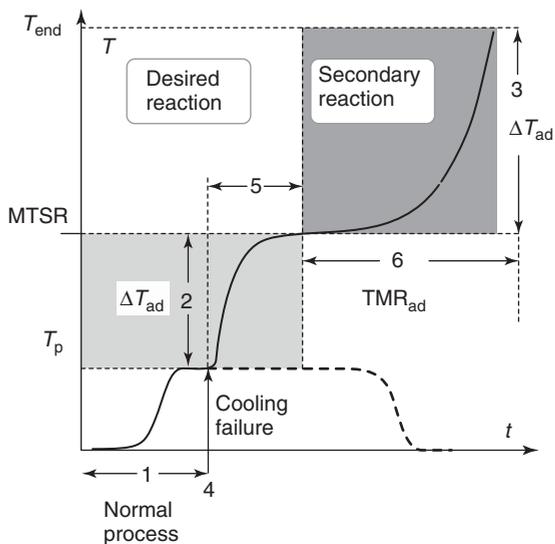
## 24.2

### Chemical Reaction Hazards

Generating a product by reacting two or more chemicals together can be done without incident hundreds or even thousands of times before a catastrophic event occurs. These catastrophic events almost always end with the overpressure and explosion of the vessel in which the reaction is carried out. The focus of safety efforts must therefore be aimed at preventing this overpressure.

Chemical reactions can be endothermic (absorbing heat) or exothermic (releasing heat). Endothermic reactions sometimes produce permanent (non-condensable) gas, which can cause overpressure of the vessel. Exothermic reactions can cause vessel overpressure in several ways:

- increased pressure due to the temperature rise occurring under normal conditions
- additional temperature increase (and subsequent pressure increase) due to loss of cooling
- initiation of a secondary or decomposition reaction at these higher temperatures



**Figure 24.1** Cooling failure scenario (Stoessel, 2008).

- permanent gas released by either the intended reaction or the secondary reaction.

Figure 24.1, taken from Stoessel (2008), demonstrates the hazards of an exothermic reaction. On the left side of Figure 24.1, labeled “Desired Reaction,” the temperature can be seen rising to the desired Process Temperature ( $T_p$ ) over the time period labeled “1.” A normal reaction would follow the dashed line, where the product is cooled and discharged from the vessel. If a loss of cooling were to occur, as shown at point 4, the temperature would increase due to reaction of any unreacted material remaining in the vessel. The temperature rise would be proportional to the amount of unreacted material in the vessel. The highest achievable temperature resulting from the reaction following the cooling failure is commonly called the maximum temperature of the synthesis reaction (MTSR). The pressure corresponding to the MTSR may in itself cause overpressure and rupture of the vessel.

Suppose, however, that the MTSR is sufficiently high to trigger the decomposition of the reactor contents. This is shown in the right half of Figure 24.1.

The heat released from this decomposition reaction could further increase the vessel temperature. While a reaction vessel may be capable of withstanding the pressure at MTSR, it may well rupture due to the increased pressure from the secondary reaction.

The maximum adiabatic temperature rise ( $\Delta T_{ad}$ ) is shown in Figure 24.1 for both the desired and secondary reactions. Also shown is the time to maximum rate ( $TMR_{ad}$ ), shown as the time from the onset of the secondary reaction until the reaction meets its maximum rate, temperature, and pressure.  $TMR_{ad}$  can be calculated for any point along the time–temperature curve.

While our concern lies in the overpressure and rupture of the vessel, the initiating events of a catastrophic incident can vary widely. Initiating events of catastrophic chemical reaction incidents can include, among other causes:

- impurities in the raw materials
- residues from prior reactions left in vessel
- incorrect amount or concentration of reaction catalyst
- overheating (vessel heating system, external fire, etc.)
- addition of reactants at a lower temperature than intended
- use of the wrong raw material
- failure of the vessel cooling system
- failure to add required solvent or diluent to the vessel.
- unplanned accumulation of reactants in the vessel
- loss of agitation
- air leaking into the vessel
- leaking of other chemicals into the vessel
- occurrence of unintended reactions, such as decomposition
- adding a raw material faster than intended.
- adding reactants in the wrong order.

#### 24.2.1

#### **Protecting Against Catastrophic Incidents**

To protect adequately against a catastrophic incident resulting from a chemical reaction, four distinct steps must be completed:

- Identify reaction hazards.
- Determine the worst-case consequences.
- Identify how the worst-case consequences could occur.
- Identify process controls – the preventive, protective, and mitigation systems necessary to prevent overpressure and rupture of the reaction vessel.

### **24.3**

#### **Identifying Reaction Hazards**

The goal of reaction hazard identification is to determine what hazards exist for the chemicals, temperatures and pressures of the process. Chemical reaction safety begins with an understanding of the hazards of the individual chemicals (toxicity, corrosivity, flammability, etc.) and the type of reaction.

#### 24.3.1

#### **Literature Survey**

The first step towards identifying the hazards of the materials and reactions is to use the work of others. Searches of relevant journal databases, using terms such as chemical names, reaction types, and so on, can produce a wealth of information.

Information such as physical properties, toxicity, flammability, stability, and limited reactivity data are often available from material safety data sheets (MSDSs). However, the data sheets are written without the knowledge of how the chemical will be used. Further information is required to understand the chemical's hazards thoroughly. Information that is important to obtain includes:

- chemical composition and source
- physical state (solid, liquid, gas)
- inventory and/or throughput quantity
- physical properties such as freezing and boiling points, vapor pressure, specific gravity, and vapor density
- physical hazards (chemical burns, irritation, corrosivity, etc.)
- acute and chronic toxicity data (occupational exposure limits, fatal exposure doses, target organs, carcinogenic and mutagenic information)
- flammability data such as flash point, upper and lower flammable concentration limits, autoignition and decomposition temperatures, and minimum oxygen concentration
- reactivity data – what other chemicals or classes of chemicals are reactive with this substance.

Manufacturers often provide this information in product bulletins, product safety literature, technical data sheets, and product stewardship manuals. While information from the specific manufacturer you are using should be used, it is good practice to review information from several manufacturers.

Some excellent sources of physical properties include:

- National Fire Protection Association (NFPA) ([www.nfpa.org](http://www.nfpa.org))
- Design Institute for Physical Properties (<http://www.aiche.org/dippr/>)
- *The Yaws Handbook of Thermodynamic Properties for Hydrocarbons and Chemicals* (Yaws, 2006)
- *The Yaws Handbook of Physical Properties for Hydrocarbons and Chemicals* (Yaws, 2005)
- National Institute of Safety and Health's *Pocket Guide to Chemical Hazards* (NIOSH, 2011)
- Knovel Critical Tables ([www.knovel.com](http://www.knovel.com))
- Knovel Solvents – A Properties Database ([www.knovel.com](http://www.knovel.com))
- National Institute of Standards and Technology Chemistry WebBook (<http://webbook.nist.gov/chemistry>).

### 24.3.2

#### **Incidents**

Information on past incidents can leverage the learnings of others with similar processes and/or process conditions. The search for incidents should not be limited to those occurring within one's own company. It is recommended that search terms used include chemical names and synonyms, Chemical Abstracts Service (CAS)

number, reaction type, and any common variations. Often chemicals and reactions are known by different names in different industries or companies.

Useful sources of incident data include:

- US Chemical Safety Board (CSB) ([www.csb.gov](http://www.csb.gov))
- Center for Chemical Process Safety (CCPS) Process Safety Incident Database (PSID) (<http://www.aiche.org/CCPS/ActiveProjects/PSID/index.aspx>)
- Trevor Kletz's series of *What Went Wrong* books (Kletz, 2009).

If insufficient data are available in the literature, which is fairly often the case, investigation of three main subjects must be carried out (CCPS, 1995, p. 9):

- identification of unstable molecular groups
- determination of the potential energy and reactivity of the chemicals
- determination of whether the substance is compatible with materials common in the process unit (air, water, oxidizers and combustibles, acids, alkalis, catalysts, trace metals, and process utilities).

### 24.3.3

#### Presence of Highly Unstable Atomic Groups

Many chemical groups and/or certain high-energy or strained chemical bonds can indicate a highly reactive or even detonable chemical compound. Barton and Rogers provided the following list of reactive chemical groups (Barton and Rogers, 1997, pp. 23–24):

- $-\text{NO}_2$ ,  $-\text{ONO}_2$  connected to organic or inorganic radicals – for example,  $\text{HNO}_3$ ,  $-\text{C}(\text{NO}_2)$ ,  $-\text{C}_6\text{H}_3(\text{NO}_2)_2$
- $-\text{N}=\text{N}-$  and  $-\text{N}\equiv\text{N}-$  connected to inorganic or organic radicals – for example,  $\text{PbN}_6$ ,  $\text{CH}_3\text{N}_3$
- $-\text{NX}_2$ , for example,  $\text{NCl}_3$ ,  $\text{RNCl}_2$
- $=\text{C}=\text{N}-$ , for example,  $\text{HONC}$ ,  $\text{Hg}(\text{ONC})_2$
- $-\text{OClO}_2$  and  $-\text{OClO}_4$  connected to inorganic or organic radicals
- $\text{O}-\text{O}-$  and  $-\text{O}-\text{O}-\text{O}-$  connected to inorganic or organic radicals – for example, peroxides or ozonides
- $-\text{C}\equiv\text{C}-$ , for example, acetylene, acetylenic compounds, and metallic derivatives
- A metal atom connected by an unstable bond to carbon or to certain organic radicals, for example, organic compounds of mercury, thallium, and lead.
- $\text{C}=\text{C}$  not in benzene rings, such as ethylene and styrene (CCPS, 2003)
- Metal- and halogen-containing complexes such as metal fulminates, halites, halates (CCPS, 2003).

Certain groups can be said to be:

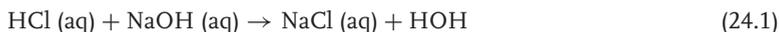
- a cause of explosibility – nitrate ester, aromatic nitro, aliphatic nitro, nitramine, azo, azide, nitroso, peroxide, ozonide, perchlorate, and acetylene
- able to make some contribution to explosibility – hydroxyl, carbonyl, ether, amino, sulfonic acid.

Refer to *Bretherick's Handbook* for a comprehensive list of groups associated with explosibility (Urben, 2007).

## 24.3.4

**Theoretical Heat of Reaction Calculations****24.3.4.1 Heats of Formation**

When the heat of reaction is not available for a specific chemical and the reaction to form the chemical is known, the heat of reaction can be calculated by subtracting the sum of the heats of formation of the reactants from the heats of formation of the products (Barton and Rogers, 1997, p. 22). For example, hydrochloric acid and sodium hydroxide react to form sodium chloride and water:



The formation energies of the reactants and products are as follows:

HCl	$-167.2 \text{ kJ mol}^{-1}$
NaOH	$-469.6 \text{ kJ mol}^{-1}$
NaCl	$-407 \text{ kJ mol}^{-1}$
HOH	$-285.8 \text{ kJ mol}^{-1}$

The heat of reaction is then:

$$(-407 + -285.8) - (-167.2 + -469.6) = -56.6 \text{ kJ mol}^{-1} \quad (24.2)$$

Note that the negative value indicates that this reaction would be exothermic.

**24.3.4.2 Bond Energy Summation**

When the heat of formation for one or more reactants or products is unknown, the reaction energy can be estimated by subtracting the total bond energies present before the reaction from the total bond energies present after the reaction. This requires only the knowledge of the structural formula of each reactant and product, and a table of average bond energies (Craven, 1987).

**24.3.4.3 Group Contribution Method of Benson**

In the group contribution method, a compound (i.e., a reactant or product for which the formation energy is unknown) is broken up into smaller groups or atoms, each of which has a known heat of formation (Benson, 1976). These heats of formation can then be summed to estimate the heat of formation of the product or reactant.

**24.3.4.4 Oxygen Balance**

The oxygen balance of an organic compound is a guide to its propensity to decompose, deflagrate, or detonate (Barton and Rogers, 1997, p. 24). A hydrocarbon with the formula  $\text{C}_x\text{H}_y\text{O}_z$  has an oxygen balance equal to:

$$-1600 \frac{2x + \frac{1}{2}y - z}{\text{mol. wt.}} \quad (24.3)$$

A negative oxygen balance indicates that oxygen must be supplied for combustion. A positive oxygen balance will have an excess of oxygen following

combustion. Almost all the recognized detonating explosives have oxygen balances between  $-100$  and  $+40$  (Barton and Rogers, 1997, p. 25). Any material with an oxygen balance of  $>-200$  should be considered a high risk and investigated further.

#### 24.3.4.5 Computer Methods

Several computer programs have been developed to assist in chemical hazard predictions. These programs, including CHETAH (CCPS, 1995, pp. 40–44), REITP2 (Yoshida, Wada, and Foster, 1995), TIGER (Cowperthwaite and Swisler, 1974), and NASA (Gordon and McBride, 1994), generally require inputs such as molecular formulas, functional groups, enthalpy of formation, and reaction products. Outputs include molecular formulas, average molecular weights, specific heat ratio ( $C_p/C_v$ ), reaction enthalpy, and entropy.

#### 24.3.4.6 Incompatibilities

Chemicals to be used in the process, including reactants, products, stabilizers, catalysts, and associated supporting chemicals such as cooling/process water and cleaning solvents, should be tested for reactivity with each other (CCPS, 2003). Possible upset conditions due to sharing of equipment (common vessels) or common piping for feeding chemicals should also be considered. For example, residue from a cleaning chemical left in a pipe could react vigorously with one of the process chemicals later traveling through it.

To evaluate the reactivity of three or more chemicals with each other, one would have to consider how the reaction product of any two chemicals might react with a third chemical in the mixture. Investigation of chemical reactivity is therefore often limited by practicality to considering the reactivity between individual pairs of chemicals. It is often also simplified by the use of resources that predict the reactivity between chemical “groups” (e.g., amides, epoxides, ethers). The reactivity between the “groups” to which the chemicals belong is assumed to be possible between the actual chemicals. Although this method is practical, it often leads to very conservative reactivity predictions. It also takes no account of the mass or mass ratios of the chemicals. For example, the explosion predicted for large amounts of fuel oil mixed with ammonium nitrate would also be predicted for a mixture of 1 tonne of fuel oil mixed with a few grams of ammonium nitrate. In some cases, verifying reactivity in a laboratory may be necessary or desired. Some resources, however, may contain information more specific than the comparison of reactive groups. Sources of chemical reactivity information include:

- *Bretherick's Handbook of Reactive Chemical Hazards* (Urben, 2007)
- *Chemical Reactivity Worksheet* (free download from NOAA at <http://response.restoration.noaa.gov/crw>)
- *Rapid Guide to Chemical Incompatibilities* (Pohanish and Greene, 1997)
- National Institute of Safety and Health's *Pocket Guide to Chemical Hazards* (NIOSH, 2011).

## 24.4

### Determine the Worst-Case Consequences

#### 24.4.1

##### Screening Tests

There are several screening tests that can be performed to obtain or verify reactivity data. These tests are relatively quick, inexpensive, and readily available from testing laboratories. Screening tests (Barton and Rogers, 1997, p. 28) are designed to give a preliminary indication of:

- the possibility of thermal decomposition
- quantity and rate of heat and gas evolution
- induction time effects (autocatalysis or the development of thermal instability after prolonged storage)
- high-rate decomposition (showing that a substance could deflagrate)
- consequences of a runaway in terms of heat and gas evolution rates should be identified.

Screening tests are useful for screening a large number of samples, testing a wide range of concentrations or mixtures, and where only small samples of materials are available. Useful tests include:

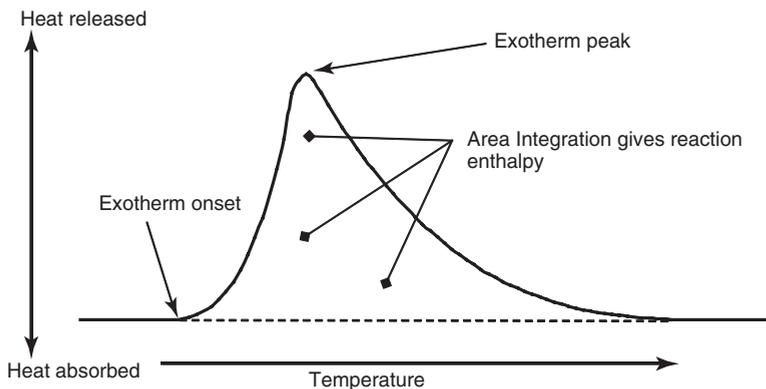
- differential scanning calorimetry (DSC)
- insulated exotherm test
- decomposition pressure test
- Carius tube
- Advanced Reactive Systems Screening Tool (ARSST)
- Rapid Screening Device (RSD)
- thermal screening unit
- micro reaction calorimeter ( $\mu$ RC).

##### 24.4.1.1 Differential Scanning Calorimetry (DSC)

DSC is an economical test that requires sample sizes of less than 10 mg. The small sample size minimizes the danger posed by highly energetic or explosive reactions. The test sample and an inert reference sample are placed in the calorimeter. The reference sample temperature is raised at a specified rate, while the heater power for the test sample is varied to maintain the test sample at the same temperature as the reference sample. The power inputs for the test sample and the reference are recorded, with the difference between the two power inputs being used to determine exothermic or endothermic activity in the test sample.

The test sample is typically placed in a sealed, high-pressure crucible to prevent volatile chemicals from escaping, and to minimize the loss of heat due to vaporization. The sample containers can be made from a variety of materials, including aluminum, stainless steel, and containers lined with glass or gold.

The reference sample is contained in an identical crucible. It should contain an identical amount of a material with a similar heat capacity.



**Figure 24.2** Example DSC results curve.

The temperature limits of the instrument can range from  $-20$  to  $500\text{ }^{\circ}\text{C}$ , with programmable heating rates from  $1$  to  $10\text{ }^{\circ}\text{C min}^{-1}$  (Barton and Rogers, 1997, p. 29). The sample should always be heated to  $300\text{--}400\text{ }^{\circ}\text{C}$  to check for decomposition of the sample. This can be important later when the maximum adiabatic temperature of the desired reaction is determined, or for considering cases where a reaction is overheated from external sources.

An example curve showing DSC results is presented in Figure 24.2. The solid line represents heat release (as measured by a decrease in power supplied to the test sample), and the baseline (dashed line) represents the power supplied to the reference sample. The integration of the area enclosed by the two lines gives the enthalpy of reaction.

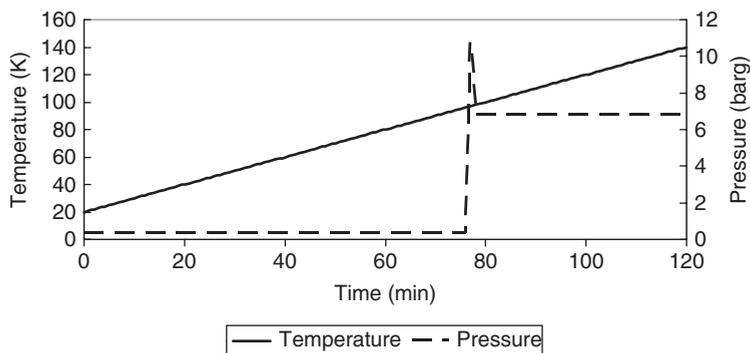
#### 24.4.1.2 Insulated Exotherm Test

The insulated exotherm test is essentially a gram-scale differential thermal analysis (DTA) technique (Cronin, Noland, and Barton, 1987). The sample and an inert reference are held in identical containers and heated together at a constant rate (e.g.,  $5\text{ }^{\circ}\text{C min}^{-1}$ ) in a Dewar vessel with additional internal insulation. The sample temperature and the temperature difference between the sample and the inert reference are recorded over time. In this device, self-heating of the sample relative to the inert reference can be determined under conditions of extremely low heat loss simply by comparing the two temperatures.

#### 24.4.1.3 Decomposition Pressure Test

In some cases, where volatile materials or permanent gas production are involved, the loss of these materials during an insulated exotherm test can produce erroneous results. In this case, the differential pressure test (DPT) can be used (Barton and Rogers, 1997).

In the DPT (Cronin, Noland, and Barton, 1987), the sample is held in a glass liner within a stainless-steel pressure vessel. The vessel is provided with a bursting disc rated at  $67\text{ bar}$  ( $1000\text{ psig}$ ) and a bleed valve for venting of decomposition products.



**Figure 24.3** Typical DPT curve.

The pressure vessel is mounted inside a temperature-programmed oven, in such a way as to permit pressure relief to an external fume cupboard. A remote pressure transducer is linked to the vessel by a steel capillary tube. The oven is heated at a fixed rate over the experimental temperature range, and the sample temperature and vessel internal pressure are recorded as functions of time on a chart trace (Figure 24.3).

In the DPT, pressure from evolved gas is allowed to accumulate inside the sample holder. Following the reaction, the sample is allowed to cool to the starting temperature. Any condensable gases will condense during this cooling, with any residual pressure due to permanent gas generation

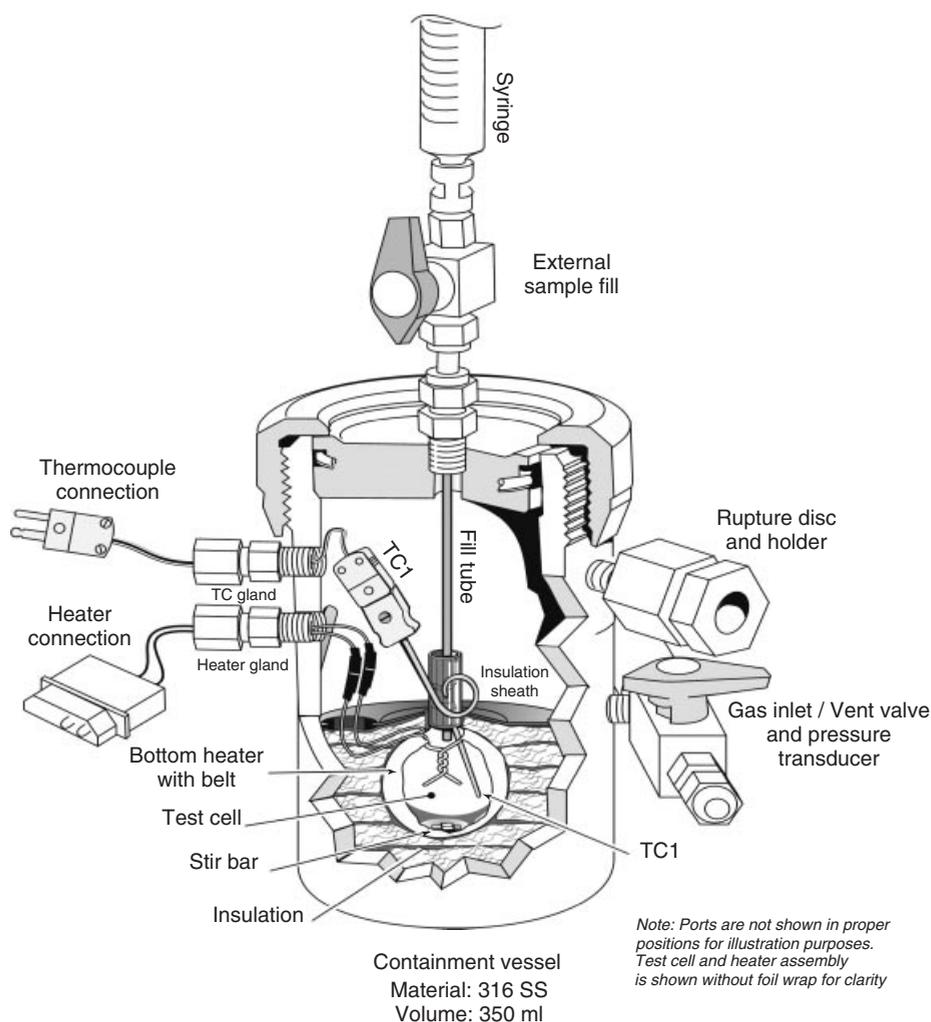
#### 24.4.1.4 Carius Tube

A Carius tube is a glass cylindrical container similar to a test tube. The neck, at the top of the tube, narrows such that a stainless-steel tube can connect it to a pressure transducer. The tube, containing about 10 g of sample material, is placed in an oven whose temperature is increased at a preselected rate (Barton and Rogers, 1997, pp. 30–32). A thermocouple at the bottom of the Carius tube measures the sample temperature. The oven temperature is compared with the sample temperature, with the difference indicating exothermic activity. The attached pressure transducer measures the pressure increase caused by gas evolution and/or vapor pressure.

As with DSC (Barton and Rogers, 1997, p. 30), this test is suitable for rapidly checking a large number of samples. The apparatus must be cooled to the starting temperature to measure permanent gas generation accurately.

#### 24.4.1.5 Advanced Reactive Systems Screening Tool (ARSST)

The basic components of the ARSST, shown in Figure 24.4, include a 10 ml open-top spherical glass test cell, sample heater, insulation, thermocouples, pressure transducer, and a 350 ml stainless-steel containment vessel that serves as both a pressure and safety vessel. The sample can be stirred using a magnetic stir bar and external stir plate. The phi factor of the instrument is fairly low, significantly less than 1.1, allowing the data to be used directly for process scale-up.



**Figure 24.4** ARSST test vessel. Graphic courtesy of Fauske and Associates, LLC.

The ARSST was developed and patented by Fauske and Associates. It is a cost-effective and easy-to-use calorimeter that is suitable for screening large numbers of samples. The low phi factor apparatus is useful for obtaining thermal hazard data that can be applied directly to process scale including emergency relief system (ERS) design (Creed and Fauske, 1990; Burelbach, 1999; Fauske, 2000; Burelbach, 2001; Theis *et al.*, 2009).

The standard test cell is a 10 ml glass sphere of low heat capacity that is typically used with a magnetic stir bar and a thermocouple is placed in direct contact with the sample. The primary mode of operation is open (vented) to a sealed high-pressure containment vessel (350 ml). This design is useful for characterizing energetic, gas-generating reactions. A heating rate is applied to the sample (power

input is determined by factory precalibration to give a prescribed net heat-up rate). Precalibration accounts for heat losses at elevated temperature and pressure. It is also possible to distinguish between foamy and non-foamy behavior, which is necessary for ERS evaluation.

#### 24.4.1.6 Rapid Screening Device (RSD)

The RSD, manufactured by Thermal Hazard Technology, is a heat flow calorimeter designed for the rapid, simultaneous screening of multiple samples (THT, 2011b). The device has a temperature range of  $-140$  to  $400$  °C and a scan rate of  $0$ – $10$  °C min<sup>-1</sup>. It uses a sample size of up to 100 g at pressures of up to 160 bar, with a detection sensitivity of less than 10 J g<sup>-1</sup>. The ability to analyze up to six samples simultaneously can shorten the screening time.

#### 24.4.1.7 Thermal Screening Unit (TSu)

The TSu, manufactured by HEL, offers the full advantages of classical DSC/DTA analysis with the added advantage of gas evolution measurement (HEL, Inc., 2011b). It operates in temperature ramp ( $0.5$ – $10$  °C min<sup>-1</sup>), isothermal, dual-scan and soak, and scan modes. The sample size is from 1 to 8 ml. The operating envelope is from 0 to 400 °C and up to 200 bar. A chilled variant is available for sub-ambient testing.

#### 24.4.1.8 Micro Reaction Calorimeter ( $\mu$ RC)

The  $\mu$ RC, manufactured by Thermal Hazard Technology, is a versatile power-compensation calorimeter (THT, 2011a). It can produce data on temperature and pressure, heat capacity ( $C_v$ ), and reaction enthalpy. With optional kinetics software ( $\mu$ RC-KIN), reaction kinetics can be obtained. Another option allows operation at pressures up to 20 bar. It can operate in three temperature modes: isothermal, step isothermal, and titration (through the use of a reactant injection system). A temperature scanning ability allows it to operate as a macro-scale DSC instrument. Working with a sample size of less than 2 ml, there may be uncertainty if the sample is not homogeneous or representative of the actual full-scale reaction mass.

#### 24.4.1.9 Interpretation of Screening Data

An important consideration during calorimetric testing is that of heat loss to the environment. In most cases, the amount of heat lost to the environment (vessel walls) in a production vessel is insignificant compared with the total heat generated by the reaction. In calorimeters, where the test cell volume to surface area ratio is much smaller, a significant proportion of the reaction heat can be lost to or through the test cell walls.

Phi ( $\phi$ ) is a unitless correction factor (Barton and Rogers, 1997, p. 40) used to account for this heat loss, where:

$$\phi = 1 + \frac{\text{heat capacity of the test cell}}{\text{heat capacity of the sample}} \quad (24.4)$$

A low phi,  $<1.1$ , is desirable to limit heat loss to the sample container, most closely mimicking plant conditions. Phi is further discussed by Townsend and Tou (1980).

After calculating phi, the observed temperature rise and reaction enthalpy are calculated as follows:

$$\Delta T_{\text{observed}} = T_{\text{max}} - T_{\text{onset}} - \Delta T_{\text{external}} \quad (24.5)$$

where

- $\Delta T_{\text{observed}}$  = temperature rise observed in the instrument.
- $T_{\text{max}}$  = maximum temperature achieved during the reaction
- $T_{\text{onset}}$  = onset temperature of the reaction
- $\Delta T_{\text{external}}$  = heating imposed by the instrument.

The adiabatic temperature rise is then

$$\Delta T_{\text{ad}} = \phi \times \Delta T_{\text{observed}} \quad (24.6)$$

Reaction enthalpy is given by

$$\Delta H_{\text{rxn}} = \frac{-\phi C_p \Delta T_{\text{observed}}}{\chi (1 - \delta_0)} \quad (24.7)$$

where

- $\Delta H_{\text{rxn}}$  = reaction enthalpy/mass of limiting reagent
- $\phi$  = phi factor
- $\Delta T_{\text{observed}}$  = temperature rise measured by the instrument
- $\chi$  = mass fraction of limiting reagent
- $\delta_0$  = fraction of reactant conversion (often assumed to be 0).

An important concept with simple reactions is the Arrhenius law, which states that the rate of reaction will decrease as the reactants are depleted (Stoessel, 2008, p. 40). If the depletion of reactants is insignificant, such as during the early stages of a reaction, the reaction rate is more heavily influenced by temperature. The reaction rate can be related to temperature by

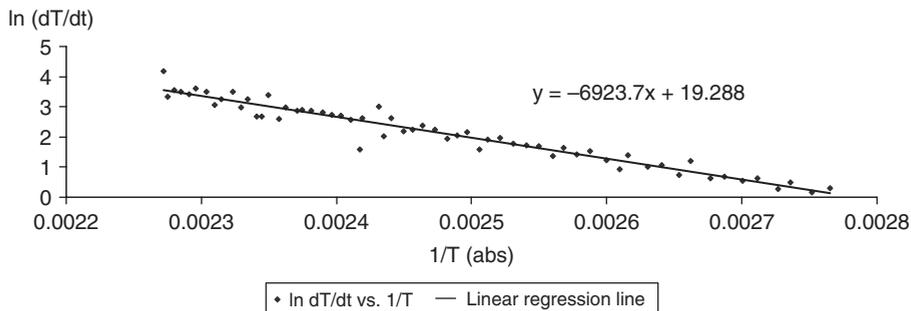
$$k = Ae^{-E/RT} \quad (24.8)$$

where

- $k$  = reaction rate constant
- $A$  = pre-exponential factor
- $E$  = activation energy
- $R$  = universal gas constant
- $T$  = absolute temperature.

If one assumes zero-order kinetics, as described above in the very early stages of the reaction (i.e., reaction <5% complete), the natural logarithm of the phi-corrected  $dT/dt$  plotted against the reciprocal of sample temperature ( $1/T$ , K) will produce a straight line. An example is shown in Figure 24.5. From this straight line,  $A = y$ -intercept = 19.288 and  $E/A = \text{slope of the line} = -6923.7$ .

Where pressure data are available from the screening apparatus, one can use  $PV = nRT$  to determine the amount (moles) of gas evolved. With  $V$ ,  $R$ , and  $T$  being



**Figure 24.5** Arrhenius plot.

constant, the number of moles of gas generated is

$$n_f = n_i \frac{P_f}{P_i} \quad (24.9)$$

where

$n_f$  = final moles of gas

$n_i$  = initial moles of gas

$P_f$  = final pressure (bara) (after cool down)

$P_i$  = initial pressure (bara)

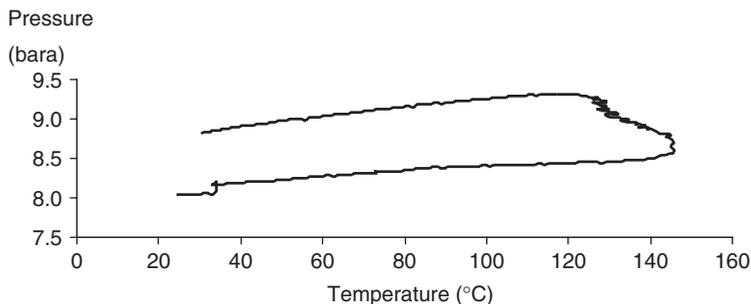
$N_i$  (adjusting for actual temperature and pressure) is given by:

$$N_i = \frac{22.4 \text{ l}}{\text{mol}} \times \frac{1}{\text{vol}} \times \frac{273 \text{ K}}{\text{act. temp}} \times \frac{\text{act. press}}{1.01 \text{ bara}} \quad (24.10)$$

where vol = volume of gas space in the sample container.

The generation of permanent gas can be observed on a  $P$  versus  $T$  graph (Figure 24.6) by comparing the pressure before and after the reaction at a fixed temperature. An increase in pressure is indicative of non-condensable gas formation. The number of moles of gas generated can be quantified using the universal gas law. This equation, assuming a 350 ml, containment vessel, reduces to

$$\text{number of moles produced} = n_2 - n_1 \quad (24.11)$$



**Figure 24.6** ARSST pressure-temperature plot.

where

$$n_1 = 4.84 \times 10^{-5} \times \frac{T_a}{P_a} \quad (24.12)$$

and

$$n_2 = n_1 \times \frac{P_{T2}}{P_{T1}} \quad (24.13)$$

where

$n_1$  = number of moles gas at the comparison temperature

$n_2$  = number of moles gas after cooling to the comparison temperature

$T_a, P_a$  = temperature (K) and pressure (bara) at beginning of the test run

$P_{T2}$  = pressure (bara) at the comparison temperature after the reaction

$P_{T1}$  = pressure (bara) at the comparison temperature before the reaction.

#### 24.4.2

#### Reaction Hazard Evaluation

##### 24.4.2.1 Introduction

The results of screening tests can be used to determine if additional testing is required, using more precise instruments. Generally, no further testing is required if *all* of the following are true, based on the screening tests:

- The maximum achievable temperature and pressure of the desired reaction are within the capabilities of the process vessel.
- Events such as secondary decomposition reactions can be accommodated or prevented at the process scale.
- There is no evidence of non-condensable (permanent) gas generation.

In the event that the above conditions cannot clearly be met, additional testing will be required to quantify more precisely (CCPS, 2003, p. 89):

- **Heat of desired reaction:** The reaction enthalpy per unit mass or mole.
- **Cooling requirements:** The amount and rate of heat that must be removed from the system to maintain safe operating conditions.
- **Maximum adiabatic temperature rise of the intended reaction:** The maximum achievable temperature increase of the reaction, based on the specific heat of the reaction mass, and total enthalpy (assuming an adiabatic system).
- **Normal accumulation of reactants (for semi-batch systems):** Quantity of the limiting reagent accumulated in the reaction mass at any point in time.
- **Critical temperature:** the temperature at which the reaction's heat generation rate is equal to the process vessel's heat removal rate (Stoessel, 2008, p. 52)
- **Unintended reactions occurring at temperatures below the maximum adiabatic achievable temperature:** Decomposition or other secondary reactions whose onset temperature is less than the maximum temperature achievable by the intended reaction. This is important to consider in loss of cooling cases, where the maximum achievable temperature of the intended reaction may be higher than the onset temperature of a decomposition reaction.

- **Heat release rate:** The rate of energy release during a runaway of the intended reaction. This information is required for sizing of emergency vents.
- **Gas generation:** The quantity and rate of non-condensable (permanent) gas generated by the reaction. This is also important for sizing emergency vents.
- **Pressure rise rate:** The maximum rate of pressure rise considering both vapor pressure increases and gas generation. This information is required for sizing of emergency vents.

Where a secondary, undesirable reaction occurs at a temperature below the maximum achievable temperature of the intended reaction, the information required for the secondary reaction will include:

- heat of reaction
- maximum adiabatic temperature rise
- critical temperature
- heat release rate
- pressure rise rate.

#### 24.4.2.2 Characterizing the Desired Reaction

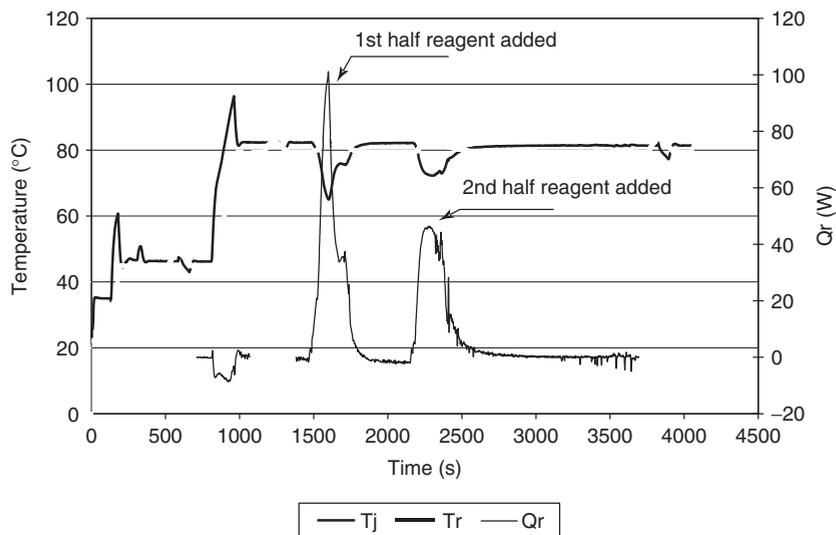
Since the early 1970s, studies of small-scale batch and semi-batch reactions have been performed by industry. These studies resulted in the development of commercially available bench-scale calorimeters which provide data crucial to ensuring the safety of chemical reactions. Reaction calorimeters are designed to mimic actual plant operations on a small (liter) scale (Stoessel, 2008, p. 95). They are most commonly operated in either isothermal or pre-programmed temperature ramp mode and have flexible features including overhead condensers, reflux condensers, and pressure/vacuum capabilities.

Most reaction calorimeters can track and record sample temperature and pressure versus time,  $dT/dt$  versus temperature, and  $dP/dt$  versus temperature. From these data, rates of pressure and temperature rise, maximum adiabatic temperature rise, reaction enthalpy, and thermokinetic information can be plotted.

##### 24.4.2.2.1 RC1 Calorimeter

The RC1 can be operated in isothermal, isoperibolic, or adiabatic mode (CCPS, 1995, p. 117). The reaction vessel is jacketed, with a heating/cooling medium circulated at high speed through the jacket. It is normally fitted with pressure measurement. In isothermal mode, the jacket fluid temperature is raised or lowered as needed to maintain the desired reaction temperature. To determine heat flow, the temperatures of the reaction mass and jacket fluid are continuously measured (Figure 24.7). The heat transfer coefficient is measured by pre- and post-reaction calibrations, and the heat transfer area is measured by physical measurement of the reaction mass volume. The modular design allows the addition of automated reactant feed systems, reflux units, agitator speed control, and agitator speed measurement.

In isoperibolic mode, the jacket temperature is held constant. The temperature difference between the jacket and the sample is plotted.



**Figure 24.7** Sample trace from RC1e.

In adiabatic mode, the jacket temperature tracks the reaction temperature, minimizing heat loss from the sample to a very low level. This allows measurement of maximum temperature and pressure during a runaway reaction. However, due to the large reactant mass used (compared with other calorimeters), a highly energetic or explosive reaction may cause substantial damage to the instrument, and also raise significant safety concerns.

The RC1 produces data important to the understanding of the normal reaction, including:

- reaction enthalpy
- conversion rate (proportional to the percentage of total heat released at time  $t$ )
- required cooling capacity and rate
- extent of reactant accumulation at any point during the reaction.

#### 24.4.2.2.2 Chemical Process Analyzer (CPA) Reaction Calorimeter

Whereas the RC1 is common in the United States, the Chemical Process Analyzer (CPA) (Figure 24.8) is frequently used in Europe (CCPS, 1995, p. 121). The CPA is a precalibrated, precision tool for analyzing chemical processes where the absolute heat production from the process is measured while accounting for stirrer torque and condenser power, yielding the truest measure of heat flow (Lamanna, Nilsson, and Reuse, 2007). The reactor is placed in a self-contained temperature bath that is a standalone unit, which lends itself to a small footprint in the laboratory.

The operating pressure ranges from vacuum to 20 bar, with an operating temperature range from  $-50$  to  $200$  °C and a volume capacity of  $10$ – $180$  cm<sup>3</sup> (CCPS, 1995, p. 123). Ports are provided in the top and base plates for auxiliary probes, such as pH or oxygen sensors, pressure measurement, or dosing. These can be inserted



**Figure 24.8** Chemical process analyzer. (Photograph courtesy of Fauske and Associates, LLC.)

directly in the reactor contents. Different types of mixers can be used, including a torque transducer for continuously measuring the mixing power input.

#### 24.4.2.2.3 Simular Calorimeter

The Simular (HEL, Inc., 2011a) calorimeter (Hazard Evaluation Laboratories) can operate as a heat flow or power compensation calorimeter. Like other reaction calorimeters, it is designed to mimic actual plant conditions. It provides standard reaction information, including reaction enthalpy, adiabatic temperature rise, pressure, temperature, and their rates of change. It accommodates gas, liquid, and solid reactant feeds, and can operate at up to 500 °C and 100 bar.

#### 24.4.2.3 Characterizing the Runaway and Secondary Reactions

Characterization of the normal reaction quantifies the heat release, gas evolution, and other properties, which can be used to determine (i) if a runaway reaction is a credible event and (ii) how to prevent a runaway reaction. If a runaway reaction is foreseeable, further testing is required to understand the consequences. The goal

**Table 24.1** Credible abnormal occurrences (CCPS, 2003).

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Not charging any of a particular ingredient
Not charging enough or charging too slowly
Charging too much or too fast, including double charging
Excessive or delayed catalyst addition
Starting temperature too high or too low
Loss of heating or cooling during reaction (including loss of agitation)
Excessive or prolonged heating or cooling during reaction
Loss of vacuum if reaction performed under vacuum
Inadequate venting of off-gases
Loss of pH or level control
Wrong sequence of addition

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is to determine the maximum achievable temperature and pressure of the reaction, and also their rates of rise, in an environment of little or no heat losses. Second, the existence of any secondary or decomposition reactions with onset temperatures below the maximum achievable temperature of the desired reaction will be identified.

It must be recognized that abnormal situations and/or occurrences can lead to thermal runaway, and that the protective systems must be capable of handling such an event. Typical abnormal situations are shown in Table 24.1.

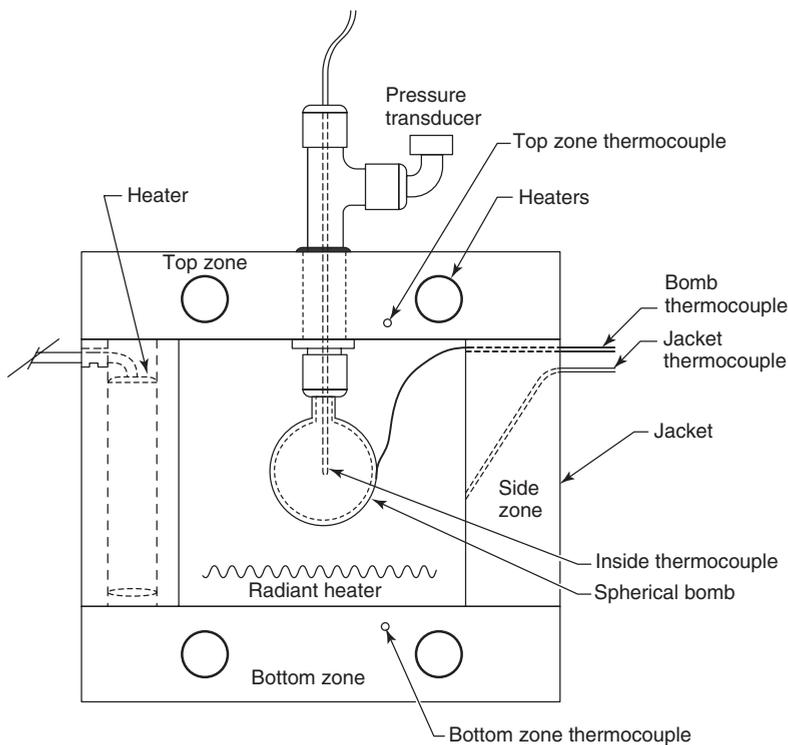
At times the worst credible occurrence is obvious, and can be determined without testing. However, multiple screening tests may be needed to determine which foreseeable abnormal situation represents the worst-case consequences.

#### 24.4.2.3.1 Accelerating Rate Calorimeter (ARC<sup>®</sup>)

The Accelerating Rate Calorimeter (ARC) is an adiabatic calorimeter developed by Dow Chemical in the mid-1970s and is a well-established tool for the evaluation of thermal hazards. It records both temperature and pressure data as a function of time for chemical reactions. These data can be used to develop kinetic models and evaluate thermal stability.

The calorimeter (Figure 24.9) consists of three zones: top, side, and bottom. Each zone contains a thermocouple and heaters which allow for adiabatic operation. The test cell, commonly referred to as a “bomb,” sits in the middle of these zones and has a thermocouple clipped to it. During adiabatic operation, the temperatures of the various zones are controlled by the heaters within them to try to match the temperature of the bomb as closely as possible. The calorimeter, made from nickel-plated copper, has a very high thermal inertia. The advantage of this is that temperatures can be held very stable, allowing the detection of self-heat rates as low as  $0.02\text{ }^{\circ}\text{C min}^{-1}$ . The disadvantage is that it only allows adiabatic tracking of an exotherm up to  $\sim 15\text{ }^{\circ}\text{C min}^{-1}$ .

Pressure measurement is done using a pressure transducer that attaches to a feed-through tube to which the sample bomb is connected. Pressure tracking is not available on the ARC. The pressure generated during a test must be self-contained. In order to do this, the ARC uses heavy-walled test cells (bombs) that are typically



**Figure 24.9** Accelerating rate calorimeter (Townsend and Tou, 1980).

constructed of titanium, Hastelloy C, or stainless steel. The combined mass of the sample and its container is kept adiabatic, so rate data from the ARC are not directly scalable and must be adjusted to correct for the thermal inertia of the sample bomb.

The ARC uses a sample container with a capacity of up to 10 g, which is held within a metal vessel containing insulation and heaters.

The instrument normally operates using the “heat–wait–search” technique, where the sample temperature is increased in small increments. After reaching each programmed temperature interval, the instrument searches for continued temperature rise which would indicate self-heating. The ARC can detect self-heating at a rate as low as  $0.02\text{ }^{\circ}\text{C min}^{-1}$  (Townsend and Tou, 1980). Once self-heating is detected, the instrument changes to temperature-tracking mode, where the environment temperature is increased at the same rate as the sample. The instrument achieves adiabaticity by maintaining the temperature outside the cell the same as that of the test mass.

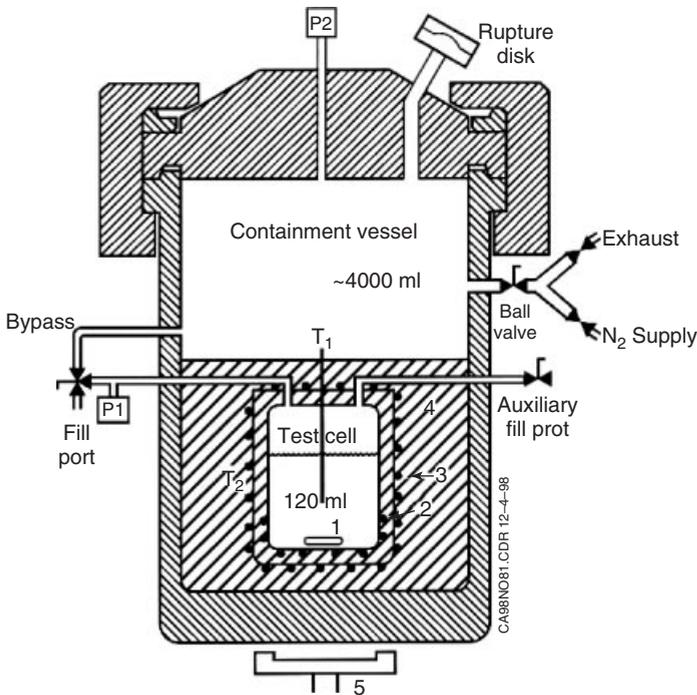
The key factor in the design of the ARC is the maintenance of a nearly perfect adiabatic environment in which the reaction under study takes place (Wilberforce, 1984). The main drawback of the ARC is its high phi factor, ranging from 1.5 to 6 (CCPS, 1995, p. 124). This is due to the robustness of the test cell, necessary to

provide adequate pressure containment. The actual phi factor will vary with sample mass and the type of test cell used.

#### 24.4.2.3.2 Vent Sizing Package 2 (VSP2)

The Vent Sizing Package 2 (VSP2, developed and manufactured by Fauske & Associates) is an adiabatic calorimeter designed to acquire thermal and vent sizing data as a result of DIERS (Design Institute for Emergency Relief Systems) research conducted in the mid-1980s. This apparatus (Figure 24.10) can be used for characterizing runaway chemical reactions and typical results have been discussed in several publications (Fauske and Leung, 1985; Leung, Fauske, and Fisher, 1986; Leung and Fauske, 1987; Fisher *et al.*, 1992; Askonas, Burelbach, and Leung, 2000).

The VSP2 can simulate multiple process operations such as batch or metered addition of reagents while maintaining adiabatic conditions. Typical sample volumes range from 40 to 80 ml. The sample is placed in a cylindrical test cell that



- |      |   |  |
|------|---|--|
| Item | 1 | Magnetic stirrer bar                               |
|      | 2 | Test cell heater                                   |
|      | 3 | Guard heater assembly with<br>aluminum can and lid |
|      | 4 | Fiberfrax insulation                               |
|      | 5 | Magnetic stirring assembly                         |
|      | T | Thermocouple                                       |
|      | P | Pressure transducer                                |

Figure 24.10 Vent sizing package 2. (Courtesy Fauske and Associates, LLC.)

can be fabricated from a variety of materials, including 304 and 316 stainless steel, Hastelloy C, titanium, glass, and glass-lined Hastelloy C. Stirring is achieved using either a magnetic stir bar (typical) or a shaft-driven stirrer. The sample temperature is measured directly and multiple thermocouples can be used to verify adequate mixing or measure vapor-phase reactions.

The VSP2 is a low phi factor apparatus that uses thin-walled test cells and a pressure balancing system. As pressure is generated in a closed test cell, pressure is added to the containment vessel via a control system. There is negligible heat transfer from the test cell surface to the surroundings over a broad range of temperature and pressure. Results obtained from VSP2 testing 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.

As its name indicates, however, the apparatus is designed to determine accurate emergency vent size requirements.

The advantage of the VSP2 over the ARC is the achievement of a low phi factor. This is accomplished by using a thin-walled sample container and automatic pressure tracking. Nitrogen is used to raise the pressure outside the sample cell to match that inside the cell. Because the sample cell will not experience a large pressure differential across the cell wall, very thin walls will contain the sample at high internal pressures. A phi factor as low as 1.05 can be achieved, depending on the sample size and cell material of construction.

#### **24.4.2.3.3 Phi-TEC II**

The Phi-TEC II instrument, from Hazard Evaluation Laboratories, is another low-phi adiabatic calorimeter used to evaluate runaway reactions and determine appropriate emergency vent sizes (HEL, Inc., 2011c). It can accommodate sample sizes from 10 to 100 ml, with magnetic stirring. Reactants can be charged at any stage of the test. The operating envelope is from 0 to 500 °C and up to 140 barg.

#### **24.4.2.3.4 Automatic Pressure Tracking Adiabatic Calorimeter (APTAC)**

The Automatic Pressure Tracking Adiabatic Calorimeter (APTAC), now produced by NETZSCH, is another low-phi adiabatic calorimeter suitable for vent sizing applications (NETZSCH-Gerätebau GmbH, 2011). Like the VSP2, it achieves a low phi factor (typically ~1.1) by utilizing automatic pressure tracking and a thin-walled test cell.

The instrument is capable of operating at up to 500 °C, with a temperature tracking limit of 400 °C min<sup>-1</sup>. Exotherm detection can be as low as 0.01 °C min<sup>-1</sup>. The containment vessel has a pressure range of full vacuum to 140 bar, with tracking capability of up to 680 bar min<sup>-1</sup>.

The 130 ml test cell can be operated in an open or closed configuration, with magnetic stirring, reagent injection, and venting abilities. The heating routines include heat-wait-search, fire exposure simulation, linear ramp, and isothermal aging.

When equipped with a VariPhi heater, the instrument heaters can compensate for the thermal inertia of the sample container. After determining the phi factor for the test, the instrument internal heater compensates for the heat lost to the sample container.

#### 24.4.2.3.5 Data Interpretation

The data obtained from the literature and testing must be properly interpreted and applied in order to determine hazard control methodology and to design adequate safety systems. This data can be used to:

- establish safe operating temperature and pressure envelope
- determine heat and gas generation rates for proper ERS design
- classify the reactive system (gassy, tempered, hybrid)
- determine the flow regime (two-phase or single-phase)
- determine kinetic data (e.g., activation energy and pre-exponential factor, which can be used to calculate TMR and temperature of no return (TNR) (The TNR is the temperature at which the rate of heat generation of a reaction or decomposition is equal to the maximum rate of cooling available (Barton and Rogers, 1997, p. 152).)).

#### 24.4.2.4 Stoessel's Criticality Classes

Stoessel *et al.* (1997) defined criticality classes for exothermic reactions (Figure 24.11). These five classes range from the least critical (classes 1 and 2) to the most critical (classes 3, 4, and 5). For semi-batch operations where a reactant is continuously fed in a manner that controls temperature, it assumes that the reaction feed will be shut off during runaway conditions. It also assumes that there is a secondary reaction which occurs at a higher temperature than that at which the desired reaction is operated. If no such reaction exists, only reaction classes 1 and 3 are possible. These classes, which evaluate criticality in a loss of cooling scenario, are based on the following parameters:

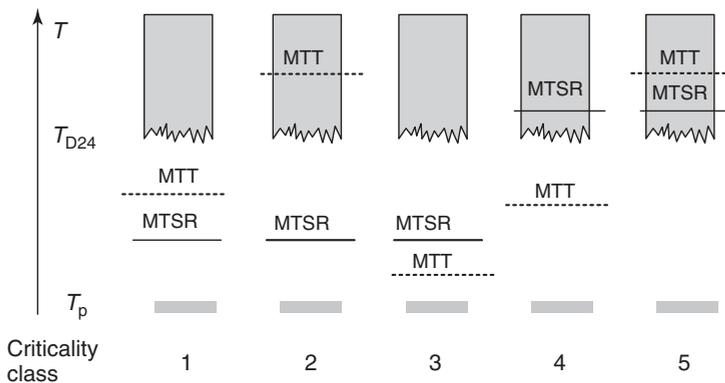
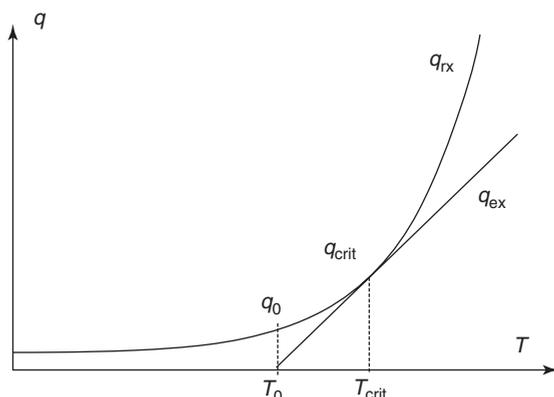


Figure 24.11 Stoessel's criticality classes (Stoessel, 2008).



**Figure 24.12** Critical temperature of a reacting system (Stoessel, 2008).

- $T_p$  – The temperature of the process at the time of cooling loss
- MTSR – This is the temperature that would be reached if the reaction proceeds from the desired process temperature with loss of cooling. Recall that this is based on the assumption that continuous reactant feed is discontinued upon detection of the runaway. For exothermic semi-batch processes, this should be taken as the point in the reaction that produces the worst-case temperature or pressure rise (e.g., the point at which the maximum accumulation of unreacted mass exists). Possible temperature rise from any foreseen abnormal conditions or occurrences must also be taken into account.
- $TMR_{ad}$  – Under adiabatic conditions. This is the time at a given temperature that it takes for a reacting mass to reach its maximum reaction rate if held in an adiabatic environment.
- $T_{crit}$  – Critical temperature. The temperature of a reaction where the rate of heat generation equals the rate heat of removed (Figure 24.12).
- $T_{D24}$  – The temperature at which the adiabatic TMR equals 24 h.
- MTT – Maximum temperature for technical reasons. In an open system, it is the boiling point of the reaction mass. In closed systems, it is defined by equipment design, equal to the maximum permissible temperature (e.g., temperature at which materials of construction begin to break down, or the temperature at which the emergency relief would activate).

The criticality classes are defined by what order MTSR, MTT, and  $T_{D24}$  follow each other as the temperature increases:

- **Criticality class 1** – The reaction cannot reach MTT or the onset of the decomposition reaction unless held for a long time under heat accumulation conditions. In the event of a runaway reaction, the MTSR is below the MTT and  $T_{D24}$ . No special precautions are required for this type of reaction.
- **Criticality class 2** – The reaction again cannot reach MTT or the onset of decomposition unless held for a long time under adiabatic conditions. However,

if the decomposition is reached, say from external fire exposure, the decomposition reaction will raise the temperature above MTT. For this type of reaction, emergency relief is a common Basis of Safety.

- **Criticality class 3** – This reaction type is characterized by MTSR exceeding MTT, yet  $T_{D24}$  again cannot be reached. The safety of this reaction depends on the rate of heat release and pressure rise at MTT. Evaporative cooling, controlled depressurization, a backup cooling system, dumping the reaction mass, reaction quenching, or emergency venting are all options to be considered for the Basis of Safety.
- **Criticality class 4** – In this class, MTSR exceeds both MTT and  $T_{D24}$ , with MTT less than both  $T_{D24}$  and MTSR. During a runaway reaction, the reaction temperature will first exceed MTT, and then exceed  $T_{D24}$ . The Basis of Safety would be similar to that of a Class 3 reaction. However, it must be noted that if these safeguards fail, the decomposition reaction will likely be triggered. Safety systems must be designed to accommodate the heat release rate of the decomposition reaction.
- **Criticality class 5** – Upon runaway of the synthesis reaction, the decomposition reaction will be triggered. This second reaction will then heat the reaction mass above the MTT. This is a critical situation because the heat release rate of the synthesis reaction and decomposition reaction must be simultaneously accommodated. It is unlikely that evaporative cooling or emergency relief can achieve this. Because there is no barrier between the synthesis and decomposition reactions, only quenching or dumping can be used as a Basis of Safety. Alternative system designs such as reduced concentration, semi-batch operation, or aliquot addition of reactant should be considered.

## 24.5

### Assessing Chemical Reaction Risks

At this point in the evaluation, the risks of the chemical reaction are known. Potential increases in pressure and temperature and their rates, and also their ability to overpressure and rupture the process vessel, are understood. We now must evaluate the risk, accounting not only for what is possible, but also how probable each event is. Risk is often understood to be a function of both the consequences and likelihood of an event:

$$\text{risk} = \text{frequency} \times \text{severity} \quad (24.14)$$

#### How Safe Is Safe Enough?

When a reaction is judged to be “safe” to conduct, it does not mean that it can be done without risk. In fact, in most cases, the risk of a reactive chemistry incident cannot be reduced to zero unless the reaction is not carried out.

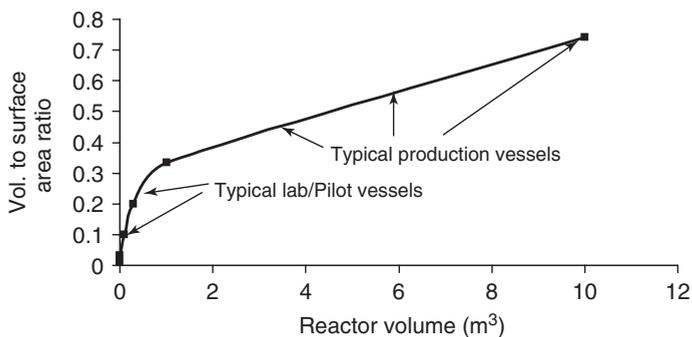
The concept of “risk” is often used to determine whether or not to proceed. Risk is the combination or consideration of both the severity of the incident

which might occur and the likelihood of its occurrence. Generally, the more severe the potential incident, the lower the likelihood of its occurrence should be. There are many facets involved in determining the acceptability of risks to which employees and the public should be exposed from a process operation. These include legal requirements, public opinion, financial risks, and others. In the end, this is a decision for those at the highest level of a company. More information on this topic is available from the Center for Chemical Process Safety (CCPS, 2009).

To understand how likely it is that an incident will occur, one must identify the events that can initiate the incident sequence, and the pathways followed to arrive at the undesired consequences. There are many ways that a runaway reaction can be initiated, as shown earlier in Table 24.1.

Many process hazard analysis (PHA) techniques exist to identify what might go wrong, initiating an accident sequence, and also to estimate how likely the event might be. Most are undertaken with a team of people representing various experience levels, backgrounds, and disciplines. Most often the team is formed from process operating employees, engineers (chemical, mechanical, controls), process safety specialists, chemists, maintenance, and safety, health, and environment representatives. These teams apply the various PHA methodologies to identify process errors or conditions that might lead to a runaway reaction incident. Table 24.2 shows some of the more common techniques.

In addition to identifying errors or maloperations that might occur, one must consider issues related to scaling the batch size from bench or pilot scale to a commercial-sized vessel. As experienced in the MFG Chemical example described in the Introduction, scaling a reaction from bench- or pilot-sized vessels to production-sized vessels can cause significant changes in cooling ability. Smaller vessels have a much smaller volume to vessel/cooling coil surface area ratio than larger vessels. This difference can result in decreased cooling ability by a factor of up to 15 (see Figure 24.13).



**Figure 24.13** Reactor volume:cooling area ratio.

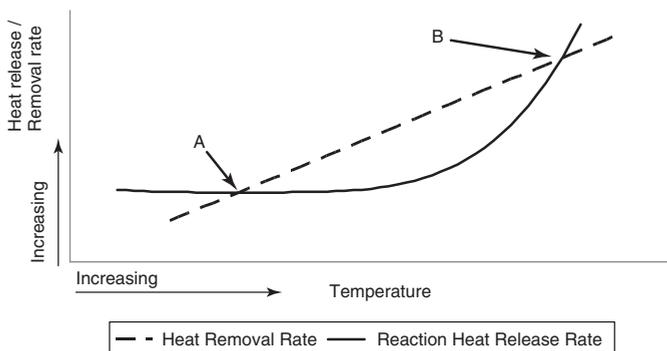
**Table 24.2** Hazard identification methodologies.

Analysis technique	Methodology	Best for analyzing what type of processes?	Dis advantages	Time investment
Checklist analysis	A team experienced with the process under study completes a checklist questionnaire listing potential initiating events	Simple process with which the analysts are familiar	Limited to consideration of the items included on the checklist	Low
What-if analysis; what-if/checklist review	A brainstorming technique conducted by a team experienced with the process under study. Often combined with a checklist analysis to provide more comprehensive hazard identification	Used for both continuous and batch processes. Can also be used for conducting a procedure-based study	Limited to consideration of the items identified by brainstorming or included on the checklist	Medium
Hazard and operability (HAZOP) study	A detailed study conducted by a multi-disciplinary team. The technique uses guide-words to prompt consideration of various deviations from process intent	Suitable for continuous, batch, and procedure-based studies. Accounts for multiple safeguards. Often used with a risk matrix to prioritize risk abatements	Generally limited to evaluation of a single cause at a time	High

Agitation, which is typically much better in bench- and pilot-sized vessels, can also play a part in decreased cooling ability. Less agitation can result in decreased heat transfer throughout the reaction mass, resulting in less heat transfer to the cooling medium.

Another issue to examine is the change in heat removal versus heat production rates as the reaction temperature increases. As shown in Figure 24.14, the heat removal rate increases in a linear fashion as the reaction temperature increases. This happens because the heat transferred to the coolant is directly proportional to the temperature difference between the reaction and the coolant.

Heat production, however, increases exponentially as the reaction temperature increases. Figure 24.14 shows the reaction rate heat release curve crossing the heat removal rate line at two points. To the right of point A, the heat removal capacity is higher than the heat release rate, until point B is reached. To the right of point B, the heat release rate will always be higher than the heat removal capability, and the reaction will run away. Reactions with a constant coolant temperature and flow, and constant reactant feed, will always move along the lines to point A, where the heat production and heat removal rates are balanced. Events such as loss of cooling or



**Figure 24.14** Comparison of heat removal and release rates with reaction mass temperature

decreased coolant flow, loss of agitation or mixing efficiency, or decrease in cooling ability for any other reason can cause the system to exceed point B, resulting in a runaway reaction.

Increasing coolant temperature, as might occur on a hot day or if several reactors share the same cooling tower, has the effect of moving the heat removal rate line to the right. If this line moves to the right of the reaction heat release rate line, such that the two do not cross, a runaway reaction will likely occur in the absence of any safeguards.

Throughout this risk assessment, the assessment team should work to eliminate or minimize hazards as much as possible by increasing the inherent safety of the system. Safety systems must then be developed for whatever risks that cannot be eliminated.

## 24.6 Identifying Process Controls

Relevant calorimetric data for the reaction are used to determine if adequate hazard control measures are available or can be put in place to perform a reaction safely. Information must be used appropriately to determine the safeguards required to conduct the reaction safely. It is most effective to take an inherently safer approach to reducing the risk or minimizing the hazards associated with a chemical reaction. Preferably, one would eliminate the hazard wherever possible. In cases where the hazard cannot be eliminated, the concepts of minimization, substitution, moderation, and simplification (summarized below, with examples) are used to reduce the hazards (CCPS, 2009).

- 1) **Minimize** – Minimize the quantity of materials and/or energy contained in the process:
  - a. Operate the process at atmospheric pressure instead of as a pressurized system.

- b. Use a smaller reaction vessel, or continuous reactor.
- 2) **Substitute** – Replacement of a hazardous process or material with an alternative that reduces or eliminates the hazard:
  - a. Use an alternative process route that allows for the use of less hazardous materials.
  - b. Replace volatile organic solvents with aqueous systems or less hazardous solvents.
- 3) **Moderate** – Use of materials under less hazardous conditions:
  - a. Use more dilute concentrations of hazardous materials.
  - b. Operate the process at lower temperature and pressure.
- 4) **Simplify** – Design the process to eliminate unnecessary complexity, reducing the opportunities for error and maloperation:
  - a. Perform the reaction in a reactor capable of withstanding the highest pressure generated from a runaway reaction, making the use of complex safeguards to shut the process down less critical.

#### 24.6.1

##### **Selection of Reactor Type**

Selection of a reactor type can play an important role in making one process inherently safer than another. Reactors can represent a large portion of the risk in a chemical process (CCPS, 2009, pp. 32–36).

Use of batch, semi-batch, or continuous reactions can provide various advantages and disadvantages from a safety perspective. Selection of the most appropriate reactor type requires a complete understanding of the reaction mechanism and kinetics, including mass transfer, heat transfer, and mixing.

##### **24.6.1.1 Batch Reactors**

A batch reactor consists of a tank, often pressure rated, with a mechanical agitator. The identifying characteristic of a batch reactor is that no addition or removal of materials takes place during the reaction. In a batch reaction, the entire charges of reactants, catalyst, solvent, and so on, are added to the vessel before heating it to reaction temperature. The relatively large amount of unreacted material in the vessel possesses the full reaction energy, with no simple way to stop or slow the release rate on loss of cooling. This type of reactor is often used for low-energy exothermic reactions, but can also be designed with robust cooling systems, including backup cooling, for higher energy reactions.

##### **24.6.1.2 Semi-Batch Reactors**

Semi-batch reactors are often of similar design to the batch reactor, with one major difference – the capability to meter in slowly one or more reactants. This has the effect of limiting the amount of unreacted material in the vessel, thus limiting the amount of available energy at any given point in the reaction. In the event of a runaway reaction, the addition of reactant can be shut off, limiting the temperature

and pressure of a runaway reaction. For many reactions, in the event of cooling loss, a runaway reaction can be avoided simply by discontinuing the reactant addition.

Semi-batch reactors are often used for high-energy reactions, where cooling of a batch reaction would not be feasible. The amount of reactant accumulation occurring during a semi-batch reaction must be well understood, as even semi-batch reactions can accumulate reactants during normal operations. Also, reactants fed at a lower than desired temperature can accumulate quickly if the reactor temperature is below the reaction's onset temperature.

#### 24.6.1.3 Continuous Reactors

Continuous reactors are designed such that the mass of unreacted chemicals is always at a minimum. Finished product is continuously removed, as fresh reactants are continually added. The product removal rate is controlled by the reactant addition rate, keeping the two in balance at all times if designed properly (Stoessel, 2008, p. 181). This requires very careful consideration of the mass and energy balances, and the simultaneous balancing of the two. In some situations, they can be designed with no cooling, as reaction heat is carried away with the product.

If designed with cooling, the concentration of unreacted reactants is typically low. This limits the total temperature rise should cooling loss occur. The temperature rise on loss of cooling can also easily be calculated.

#### 24.6.1.4 Continuous Stirred Tank Reactor (CSTR)

The continuous stirred tank reactor (CSTR) often looks similar to the batch reactor, except that reactants are continuously fed into the vessel as product is removed. Product is removed from either the top or bottom of the vessel, depending on the relative densities of the reactants and products. If products are removed from the bottom, robust controls are required to ensure that the reaction mass remains constant, ensuring a constant heat capacity.

#### 24.6.1.5 Plug Flow Reactors

Plug flow reactors are generally tubular vessels, with the reaction occurring in a relatively short section of the tube. The high surface-to-volume ratio of the tube provides the capability for excellent cooling (Stoessel, 2008, p. 193). This high ratio also serves to limit the temperature rise after loss of cooling, as much of the heat goes to heat the high surface area vessel wall. Feedstock is often mixed using a static mixer before entering the reaction zone. As with the overflow CSTR, the product removal rate is controlled by reactant addition rate.

### 24.6.2

#### Process Safeguards

Once the principles of inherent safety have been applied, and the reactor type has been selected, one is left with the residual hazards or risks that could not be eliminated or sufficiently reduced. A sufficient number of safeguards must be

designed for each remaining hazard, such that the overall risk from the reaction is sufficiently low.

Process safeguards might include alarms, interlocks and administrative controls, emergency shutdown systems, and so on. Process safeguards might be categorized by both type (CCPS, 2009) and purpose (CCPS, 2007). The types of safeguards, in order of desirability, include:

- **Passive** – Does not require any device to sense and/or actively respond to a process variable and has very reliable mechanical design.
- **Active** – Requires devices to monitor a process variable and function to mitigate a hazard.
- **Procedural** – requires a person to perform an action to avoid a hazard.

Safeguard purposes, in order of effectiveness, include:

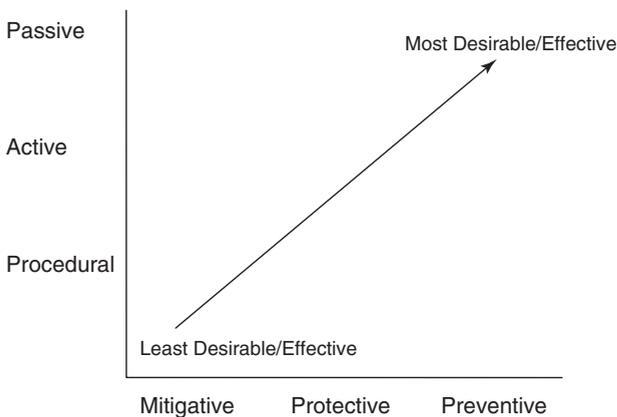
- **Prevention** – Designed to prevent the occurrence of a runaway reaction.
- **Protection** – Generally these are designed to prevent the worst possible consequence by allowing a less hazardous consequence to happen.
- **Mitigation** – This type of safeguard acts only after the incident has occurred, and serves to minimize the severity of the consequences.

Taken together, the types and purposes of safeguards form a continuum, from the least to most effective/desirable safeguards, as shown in Figure 24.15.

Examples of various safeguards, and the type and purpose of each, are given in Table 24.3.

Process safeguards should be selected on a case-by-case basis, covering each of the hazardous scenarios individually. At times, safeguards can provide prevention, protection, or mitigation for more than one scenario.

The continuum shown in Figure 24.15 should be followed by first selecting available passive, preventive safeguards, then moving towards the procedural,



**Figure 24.15** Effectiveness of various types of safeguards

**Table 24.3** Examples of Safeguards, Their Type and Purpose.

Safeguard	Safeguard type			Safeguard purpose		
	Passive	Active	Procedure	Prevention	Protection	Mitigation
Safety instrumented system <sup>a</sup> (SIS) interlock closes reagent block on loss of agitator rotation confirmation		×		×		
Basic process control system <sup>b</sup> (BPCS) interlock closes vessel nitrogen valve at 2.5 barg		×		×		
Safety relief valve opens 0.7 bar (10 psi) below the vessel's pressure rating		×			×	
Vessel pressure rating is higher than the maximum pressure achievable by the reaction	×				×	
Automatic sprinklers activate on detection of fire/explosion		×				×
Operator initiates emergency cooling			×		×	
Process vessel is located in a remote section of the plant	×					×
Operator initiates injection of reaction inhibitor			×		×	

<sup>a</sup>A safety instrumented system is an independent system whose sole function is to perform the stated action. It is typically a system designed to be highly reliable, often with integral system diagnostics (CCPS, 2007, pp. 239–265).

<sup>b</sup>The basic process control system (BPCS) is the electronic system used by operators to control the basic functions of the process, such as chemical addition, venting, heating, and cooling. It often includes programmed alarms and interlocks, but is not considered to be a highly reliable system compared with a safety instrumented system (CCPS, 2007, pp. 239–265).

mitigative sources. These should be used only as a last resort. Examples of potential safeguards are presented in the next section.

### 24.6.3

#### Potential Safeguards

Chemical reaction safeguards are, of course, tailored to the subject reaction and its potential hazards. Designs are unique and varied, depending on things such as reaction type, vessel pressure, and the availability of various ancillary system components. There are, however, safeguards that are applicable for a wide range of situations. Some of these are described below.

### 24.6.3.1 Addition Rate Control

Semi-batch reactions are conducted by charging all of reactant A, then slowly feeding in reactant B. This leaves only small amounts of reactant B available to react, limiting the amount of unreleased energy in the vessel at any point in time. The addition rate of reactant B is typically balanced between reaction rate and the cooling ability of the reactor to maintain the desired reaction temperature. In the event of cooling loss, the reactant B feed is shut off, limiting the temperature rise.

It must be understood that semi-batch reactions may naturally accumulate a certain amount of reactant as the reaction proceeds. This accumulation amount can vary over the duration of the reaction. The resultant temperature rise on cooling loss is not only affected by accumulation amount but also by the total mass in the vessel, which will absorb reaction energy as sensible heat. There may exist a point in the reactant feed that produces the maximum temperature rise on cooling loss.

In addition to natural accumulation, there are several other ways in which an excess of reactant B can be accumulated:

- Addition below the reaction onset temperature.
- Failure to add catalyst, or too little catalyst charged, prior to initiation of the reactant B feed.
- Loss of agitation, allowing the reactant to accumulate as a separate layer with reaction at the interface level. This localized reaction can generate high temperatures at the reaction site, leading to runaway.
- Contaminants in the reaction mass.

Regardless of the accumulation mechanism, accumulation of unreacted chemical can easily lead to a runaway reaction if the temperature is raised to reaction temperature, or the catalyst is added after the reactants have accumulated.

### 24.6.3.2 Addition Temperature

The temperature at which the reactants are charged, and/or the temperature at which the reaction is conducted, can have an impact on maximum achievable temperature on runaway (Stoessel, 2008, Figure 3.2). Suppose, for example, a temperature rise of 100 °C is expected on loss of cooling. Further, assume there is a decomposition reaction possible with an onset temperature of 200 °C. If the desired reaction temperature is 100 °C, the decomposition reaction onset temperature can easily be reached. If the reaction temperature is lowered to 60 °C, the possibility of reaching the decomposition temperature is significantly reduced (with a safety margin of 40 °C).

### 24.6.3.3 Crash Cooling

If a runaway reaction can be detected early enough, it may be possible to initiate emergency cooling (Barton and Rogers, 1997, p. 106). This may take the form of turning on full cooling, or switching to a chilled cooling fluid. This is preferably initiated automatically by a safety instrumented system (SIS), but should also have manual activation capability.

#### 24.6.3.4 Inhibitor Injection

With some reactions, it is possible to inject a “poison” substance that prohibits the reaction from progressing further (Barton and Rogers, 1997, p. 123). This inhibitor is often stored in a pressurized container connected to the vessel, and activated in a similar manner to crash cooling. Again, an SIS should be used to detect the runaway as early as possible, and to activate the system.

#### 24.6.3.5 Safety Instrumented Systems

CCPS defines the following terms (CCPS, 2007, pp. 239–265):

*Safety instrumented function (SIF)*: A safety function allocated to a safety instrumented system (SIS) with a safety integrity level (SIL) necessary to achieve the required risk reduction for an identified hazardous event involving a catastrophic release.

*Safety instrumented system (SIS)*: Composed of a separate and independent combination of sensors, logic solvers, final elements, and support systems that are designed and managed to achieve a specified safety integrity level. An SIS may implement one or more SIFs.

*Safety integrity level (SIL)*: Represents one of four discrete ranges used to benchmark the integrity of each SIF and the SIS, where SIL 4 has the highest and SIL 1 the lowest reliability.

In short, a potential safeguard may be a safety instrumented function (SIF) that is separate from the system used to control the process. The system is designed for high reliability when a demand is placed on it. When several SIFs are implemented, they may be part of a single system or an SIS. As potential incident severity increases, and/or as non-SIF safeguards decrease, the reliability (integrity) of the SIF must increase. Safety integrity level (SIL 1) systems are basic instrumented systems that satisfy the lowest SIL level (SIL 1). SIL 4 systems, although possessing the highest reliability, are rarely used in industry owing to the enormous costs of testing and maintenance. SIL 3 systems are avoided wherever possible for the same reasons.

While SIL 1 and SIL 2 systems are those most commonly used in industry, the goal remains to implement the principles of inherently safety design to eliminate the need for such systems.

#### 24.6.3.6 Emergency Relief System Design

Overpressure and subsequent bursting of a reaction vessel must be avoided during a runaway reaction. Vessel bursts can cause enormous pressure waves over short distances, causing severe injury to those nearby. Fragments from the vessel walls can fly like missiles over considerable distances, further endangering those within range. If a flammable material in the vessel is released when the vessel bursts, the likelihood of a second explosion or fire can be high.

Design of emergency vents for reacting systems is a highly specialized and complex field (Stoessel, 2008, pp. 253–257). It is important to verify that the

ERS provides adequate vent area to relieve the vessel contents for the identified worst-case upset scenario. Two-phase flow through the vent should be considered since this required vent area is much larger compared with all vapor flow. Depending on the chemical system, various strategies can be employed to reduce the required vent size. It is recommended to consult with a professional who can make proper recommendations based on adiabatic calorimetric data. Appropriate ERS design should also include effluent handling equipment to mitigate toxic releases or quench contents that are discharged through the relief device.

## 24.7

### Basis of Safety Selection

The concept of a Basis of Safety (Barton and Rogers, 1997) for the process is useful to help document process hazards and systematically develop safeguards. The Basis of Safety for a process contains the following information:

- a brief description of the process
- a list of process chemicals and their hazards
- a list of process hazards, their causes, and worst-case consequences
- the Safety Objectives that must be achieved in order to operate the process in a safe manner
- the safeguards or control measures implemented to achieve the Safety Objectives
- the Safe Operating Envelope for the process.

The Basis of Safety document can be used to train operators on the process safety-critical information for the process. It gives the operator an understanding of the process (Process Description), what might happen if the process is not operated as intended (Process Hazards and Worst-Case Consequences), the hazards of the chemicals being used, what objectives the process safeguards are intended to achieve (Safety Objectives), how those objectives are achieved (Safeguards and Control Measures), and the boundaries within which he must maintain the process (Safe Operating Envelope).

#### 24.7.1

##### Process Description

The Process Description should be a concise but complete description of the reaction, written in a manner such that a trained operator can understand what is taking place. A process description for a semi-batch reaction might look like the following:

Epichlorohydrin is reacted with sodium bisulfite (plus water as a diluent) to form a chlorohydroxy compound. The sodium bisulfite is charged to the vessel first, through a bottom valve using vacuum. The epichlorohydrin is then charged through a flow meter from the bulk storage tank. The reaction is addition controlled, adjusting the feed rate and cooling water flow to maintain

**Table 24.4** NFPA ratings.

Chemical	NFPA rating		
	Health	Fire	Reactivity
Epichlorohydrin	3	3	2
Sodium bisulfite	2	0	0

the temperature at 50–60 °C throughout addition. The reaction is exothermic, producing up to a 50 °C temperature increase (70 °C if water is omitted).

### 24.7.2

#### Process Chemicals

For the above reaction, the chemicals and their hazards could be listed as shown in Table 24.4. In this example, the NFPA Hazard Rating (National Fire Protection Association, 2012) is used to communicate the chemical hazards. Text from an MSDS might also be used.

### 24.7.3

#### Process Hazards, Causes, and Consequences

Each process hazard should be identified, along with potential causes and the worst-case consequences (as if all safeguards have failed). This information can be listed in a table, as shown in Table 24.5.

In this example, two hazards unrelated to the reaction have been included as items 2 and 3. The Basis of Safety could be expanded further to include all process hazards.

### 24.7.4

#### Safety Objectives

The Safety Objectives are the conditions required for the reaction to be performed safely. They can usually be written based on a list of the identified hazards of the reaction under consideration. A list of hazards and potential corresponding Safety Objectives is shown in Table 24.6. Again, process hazards unrelated to the reaction itself can be included.

Specification of the Safety Objectives is important to understanding the purpose of the required safeguards. Each safeguard should assist in meeting one or more of the Safety Objectives, and documentation should link the safeguard to both the Safety Objective and the hazard. The reason for the safeguard should be clearly documented.

**Table 24.5** Hazards, causes, and consequences.

Hazard	Cause	Consequences
1. Overpressure of vessel due to runaway reaction	A. Loss of epichlorohydrin addition control	Toxic release, flash fire, on-site fatalities
	Loss of cooling	Toxic release, flash fire, on-site fatalities
	B. Epichlorohydrin added at a too low temperature, followed by heating	Toxic release, flash fire, on-site fatalities
	C. Omission of water	Vessel overpressure, relief of epichlorohydrin from PSV (platform supply vessel), toxic release, on-site overexposure to epichlorohydrin
	D. Loss of agitation	Toxic release, flash fire, on-site fatalities
2. Release of epichlorohydrin through PSV due to vessel overpressure	E. Overheating (from external source) of epichlorohydrin-containing vessel	Toxic release, flash fire, on-site fatalities
	F. Nitrogen overpressure of epichlorohydrin-containing vessel	Toxic release, flash fire, on-site fatalities
3. Overpressure of vessel due to internal ignition	G. Loss of nitrogen inerting and ignition source	Explosion, on-site fatalities

#### 24.7.5

##### Process Safeguards

The Basis of Safety should list all process safeguards related to the hazards in Table 24.5. Safeguards should be listed in such a way that the operators can determine which hazard–cause–consequence scenario the safeguard protects against. Table 24.7 shows one method of accomplishing this, using the hazards listed in Table 24.5.

#### 24.7.6

##### Safe Operating Envelope

The Safe Operating Envelope specifies limits on various process parameters which must be maintained to avoid a reaction incident. These are typically high and low limits on parameters such as pressure and temperature, but could also include items such as maximum oxygen concentration in a vessel, maximum level of reactant accumulation, batch size, and cooling water temperature. The Safe Operating

**Table 24.6** Reaction hazards and safety objectives.

Hazard	Safety objective
Exothermic reaction	Avoid accumulation of reagents Prevent loss of cooling Prevent loss of agitation
Flammable process materials	Maintain an inert atmosphere Avoid ignition sources Avoid loss of containment
Toxic process materials	Use closed handling systems Avoid loss of containment Use closed handling systems
Process materials have high vapor pressure	Avoid overheating

**Table 24.7** Process Safeguards.

Safeguard	Hazard scenario(s)
High-temperature trip shuts off reactant feed on high temperature	1A, 1B, 2G
Interlock prevents addition of epichlorohydrin if vessel temperature is below 35 °C	1C
Operating procedure requires addition of water before charging epichlorohydrin	1D
Interlock shuts off reactant feed on loss of agitator run confirm signal	1E
Interlock shuts of nitrogen feed to vessel on high pressure	2G
Procedure requires vessel to be inerted prior to charging flammable epichlorohydrin	3H

Envelope should be comprehensive enough that the risk of a reactive incident is sufficiently low whenever the process is operating within it.

## 24.8 Conclusion

Catastrophic incidents involving reactive chemistry continue to occur in manufacturing and storage facilities around the world. Inherent hazards in the materials and process conditions continue to cause fires, explosions, and toxic releases. Only through a thorough understanding of the reactions under both normal and abnormal conditions can these incidents be prevented.

Every chemical reaction must be screened for reactive hazards. Where required information cannot be found in references and literature searches, screening tests must be conducted.

While thermodynamics can be estimated by calculation, these values should only be used as rough estimates to select the proper screening test methods. Multiple screening apparatus is available for obtaining necessary data. Screening

must be conducted for the normal reaction in addition to any foreseeable abnormal conditions such as loss of cooling, over-/undercharging, catalyst failure, and so on.

Once the scenarios producing the worst-case consequences have been identified, further testing can be limited to these circumstances. Characterization of the normal reaction can be achieved using reaction calorimeters. Runaway reactions are best evaluated utilizing adiabatic calorimeters. Information obtained from these types of devices can also be used to design emergency vent systems.

Once the hazards of the process are understood, design of necessary safeguards can begin. The first effort should always be to implement the principles of inherent safety wherever possible. Selection of the appropriate Basis of Safety can then begin.

The Basis of Safety includes the specification of the Safe Operating Envelope and the Safety Objectives for the process. Safeguards are selected such that the risk of operating the process will be acceptably low.

Process safeguards might include inerting, limiting addition temperature and rate, emergency cooling or other methods of “killing” the reaction, and SIS. Emergency venting is typically the final layer of protection to prevent the worst-case consequences, although it may create undesirable consequences, such as release of toxic or flammable materials.

Due diligence and understanding the hazards associated with chemicals and operating conditions can reduce the frequency of chemical reaction incidents. Companies should continue to improve their knowledge of the chemicals and reactions for processes at their facilities.

## References

- Askonas, C.F., Burelbach, J.P., and Leung, J.C. (2000) The versatile VSP2: a tool for adiabatic thermal analysis and vent sizing applications. Presented at the North American Thermal Analysis Society 28th Annual Conference, Orlando, FL, October 4–6, 2000.
- Barton, J. and Rogers, R. (1997) *Chemical Reaction Hazards*, 2nd edn, Institute of Chemical Engineers, Rugby.
- Benson, S.W. (1976) *Thermochemical Kinetics*, 2nd edn, Wiley-Interscience, New York.
- Burelbach, J.P. (1999) Advanced reactive system screening tool (ARSST). Presented at the Process Safety Center Symposium, College Station, TX, October 26–27, 1999.
- Burelbach, J.P. (2001) Vent sizing applications for reactive systems. Presented at the AIChE 2001 Spring National Meeting, 5th Bi-Annual Process Plant Safety Symposium, Pressure Relief Session, April 25, 2001.
- CCPS (Center for Chemical Process Safety) (1995) *Guidelines for Chemical Reactivity Evaluation and Application to Process Design*, Wiley–AIChE, New York.
- CCPS (Center for Chemical Process Safety) (2003) *Essential Practices for Managing Chemical Reactivity Hazards*, CCPS–John Wiley & Sons, Inc., Hoboken, NJ.
- CCPS (Center for Chemical Process Safety) (2007) *Guidelines for Safe and Reliable Instrumented Protective Systems*, John Wiley & Sons, Inc., Hoboken, NJ.
- CCPS (Center for Chemical Process Safety) (2009) *Inherently Safer Processes – A Life Cycle Approach*, 2nd edn, John Wiley & Sons, Inc., Hoboken, NJ.
- Cowperthwaite, M. and Swisler, W.H.T. (1974) TIGER Computer Program Documentation, Stanford Research Institute, distributed by National Technical Information Service, US Department of Commerce, Washington, DC.

- Craven, A.D. (1987) A simple method of estimating exothermicity by average bond energy summation. Presented at the Institute of Chemical Engineers Symposium 102, UMIST, Manchester, June 16–18, 1987.
- Creed, M.J. and Fauske, H.K. (1990) *Chem. Eng. Prog.*, **86**, 45–49.
- Cronin, J.L., Noland, B.F., and Barton, J.A. (1987) A strategy for thermal hazard assessment in batch chemical manufacturing. Presented at the Institute of Chemical Engineers Symposium 102, UMIST, Manchester, June 16–18, 1987.
- CSB (Chemical Safety and Hazard Investigation Board) (1998) Chemical Manufacturing Incident. Investigation Report No. 1998-06-I-NJ, National Technical Information Service, US Department of Commerce, Washington, DC.
- CSB (Chemical Safety and Hazard Investigation Board) (2002) Improving Reactive Hazard Management. Report No. 2001-01-H, National Technical Information Service, US Department of Commerce, Washington, DC.
- CSB (Chemical Safety and Hazard Investigation Board) (2004) Toxic Chemical Vapor Cloud Release. Investigation Report No. 2004-09-I-GA, National Technical Information Service, US Department of Commerce, Washington, DC.
- CSB (Chemical Safety and Hazard Investigation Board) (2008) T2 Laboratories Inc Runaway Reaction. Report No. 2008-3-I-FL, National Technical Information Service, US Department of Commerce, Washington, DC.
- Fauske, H.K. (2000) Properly Size Vents for Non-Reactive and Reactive Chemicals, *Chemical Engineering Progress* **96** (12), PP 17–29.
- Fauske, H.K. and Leung, J.C. (1985) *Chem. Eng. Prog.*, **81** (8), 39–46.
- Fisher, H.G., Forrest, H.S., Grossel, S.S., Huff, J.E., Muller, A.R., Noronha, J.A., Shaw, D.A., and Tilley, B.J. (1992) *Emergency Relief System Design Using DIERS Technology: the DIERS Project Manual*, AIChE, New York.
- Gordon, S. and McBride, B. (1994) Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications. I. Analysis. <http://www.grc.nasa.gov/WWW/CEAWeb/RP-1311.htm> (last accessed 15 July 2011).
- HEL, Inc. (2011a) Similar, <http://www.helgroup.com/reactor-systems/safety-calorimetry/similar-heatflow-reaction-calorimeter/> (last accessed 10 September 2011).
- HEL, Inc. (2011b) Thermal Screening Unit (TSU), <http://www.helgroup.com/product/pdf/fed74cfab4fae7e2/994d33ad8c49669a.pdf> (last accessed 5 September 2011).
- HEL, Inc. (2011c) Phi-TEC II, <http://www.helgroup.com/reactor-systems/safety-calorimetry/phitec-ii-precise-stability-reaction-safety-calorimetry/> (last accessed 5 September 2011).
- Kletz, T.A. (2009) *What Went Wrong? Case Histories of Process Plant Disasters and How They Could Have Been Avoided*, 5th edn, Gulf Professional Printing, Burlington, MA.
- Lamanna, P., Nilsson, H., and Reuse, P. (2007) On-line reaction calorimetry optimization of safety parameters. Presented at the 35th Annual Conference of the North American Thermal Analysis Society (NATAS), East Lansing, MI.
- Leung, J.C. and Fauske, H.K. (1987) *Plant Oper. Prog.*, **6** (2), 77–83.
- Leung, J.C., Fauske, H.K., and Fisher, H.G. (1986) *Thermochim. Acta*, **104**, 13–29.
- National Fire Protection Association (2012) *704 Standard System for the Identification of the Hazards of Materials for Emergency Response*, 2012 edition, National Fire Protection Association, Quincy, MA.
- NETZSCH-Gerätebau GmbH (2011) Adiabatic Reaction Calorimetry, Method, Technique, Applications, [http://www.netzsch-thermal-analysis.com/download/ARC-APTAC\\_E\\_0411\\_en\\_456.pdf](http://www.netzsch-thermal-analysis.com/download/ARC-APTAC_E_0411_en_456.pdf) (last accessed 10 September 2011).
- NIOSH (2011) *Pocket Guide to Chemical Hazards*, National Institute of Safety and Health, Atlanta, GA.
- Pohanish, R.P. and Greene, S.A. (1997) *Rapid Guide to Chemical Incompatibilities*, John Wiley & Sons, Inc., New York.
- Stoessel, F. (2008) *Thermal Safety of Chemical Processes, Risk Assessment and Process Design.*, Wiley-VCH Verlag GmbH, Weinheim.
- Stoessel, F., Fierz, H., Lerena, P., and Kille, G. (1997) Recent developments in the

- assessment of thermal risks of chemical processes. *Org. Process Res. Dev.*, **1** (6), 428–434.
- Theis, A.E. *et al.* (2009) *Process Saf. Prog.*, **28** (2), 135–140.
- THT (Thermal Hazard Technology) (2011a)  $\mu$ RC Micro Reaction Calorimeter, [http://www.thermalhazardtechnology.com/uploaded\\_images/files/uRC/uRC%20Flyer\\_2010.PDF](http://www.thermalhazardtechnology.com/uploaded_images/files/uRC/uRC%20Flyer_2010.PDF) (last accessed 10 September 2011).
- THT (Thermal Hazard Technology) (2011b) RSD Rapid Screening Device, [http://www.chemshow.cn/UploadFile/datum/1000/tht\\_2008229142410806079.pdf](http://www.chemshow.cn/UploadFile/datum/1000/tht_2008229142410806079.pdf) (last accessed 20 August 2011).
- Townsend, D.I. and Tou, J.C. (1980) *Thermochim. Acta*, **37**, 1–30.
- Urban, P.G. (ed.) (2007) *Bretherick's Handbook of Reactive Chemical Hazards*, 7th edn, Elsevier, Oxford.
- Wilberforce, J.K. (1984) Applications of the accelerating rate calorimeter in thermal hazards evaluation. Presented at the Institute of Chemical Engineers Symposium 85, UMIST, Manchester.
- Yaws, C.L. (2005) *The Yaws Handbook of Physical Properties for Hydrocarbons and Chemicals*, Gulf Publishing, Houston, TX.
- Yaws, C.L. (2006) *The Yaws Handbook of Thermodynamic Properties for Hydrocarbons and Chemicals*, Gulf Publishing, Houston, TX.
- Yoshida, R., Wada, H., and Foster, N. (1995) *Safety of Reactive Chemicals and Pyrotechnics*, Elsevier, Amsterdam.