

Runaway Reactions: Ignore the Chemistry at Your Peril

Proper hazards testing is key to ensuring chemical process safety

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1. Introduction

Manufacturing chemicals is a risky business. Chemical producers must be constantly vigilant to the potential for runaway reactions, since manufacturing often requires the use of reactive chemicals, which may be potentially hazardous. Since chemical reactions involve the transfer of chemical and mechanical energy, proper management of this energy transfer is necessary to performing manufacturing operations safely without incident or accident.

Safety can be achieved by performing a complete risk assessment founded on process-specific and reaction-specific hazards test data for the desired, and undesired, chemistry and process operations. For the majority of situations these data can only be obtained from appropriately designed experiments using proper testing techniques. The basis of safety and the window of safe operations are then derived from the relevant process safety data. The main thrust of this paper is to describe the experimental methodologies for hazards testing and how that allows for quantitation of the nature and extent of runaway reactions caused by chemical process upsets. Armed with this knowledge chemical manufacturers can make valid risk assessments of their processes.

Safety is a big issue for both the Occupational Safety Health Administration (OSHA) and the U.S. Environmental Protection Agency (EPA). Both agencies have set regulatory-compliance standards. OSHA developed standard 1910.119, Process Safety Management (PSM) of Highly Hazardous Chemicals, while EPA developed the "Risk Management Program." Table 1 lists the titles of each section, or element, of OSHA's PSM standard. Of these fourteen elements, six address aspects of the process that require the employer to have reliable and pertinent hazards data addressing process safety issues.

A central aspect of both these standards is the requirement to perform an appropriately detailed process-hazard analysis (PHA) and remedying the deficiencies, if any, found by the PHA. Most PHA procedures limit the discussion of the role of chemistry to the properties of the reactant chemicals, the consequences of a release of a reactant or solvent, and the management of the reaction heat during the reaction. Often, the impact of reactivity of raw materials with each other in unintended ways, interactions with other (unintended) chemicals, and the consequences of such interactions may be only mentioned in passing. Thermodynamic and kinetic information for the desired (synthesis) reaction conditions, for process-upset conditions, and for undesired reaction scenarios, will most probably not be found in the open literature. This is not surprising, given that the majority of chemical manufacture is proprietary. The needed information may not even be available in company files.

2. Dealing with risk

Recently, process safety has been driven by a systematic risk-based approach designed to eliminate hazards that pose an intolerable risk and to reduce the hazard potential of chemical processes to a tolerable level. Generically, risk is defined as the product of the chance that a

particular hazard may actually cause injury or damage (frequency, likelihood) and the impact of an event if it occurs (consequence). Assessing risk may be qualitative or quantitative, or it can range from simple, “broad-brush” screening studies to detailed risk-assessments studying large numbers of incidents, using highly sophisticated frequency and consequence models. Figure 1 shows a decision flowchart illustrating these concepts.

The initial sequence of events - identify potential hazard, determine likelihood and determine consequence - is important. If a potentially hazardous scenario (worst-case scenario) can be shown to be unlikely, then that scenario is eliminated from further detailed consideration. However, if there is a reasonable likelihood that it can occur then a detailed examination of the nature, extent, and severity of consequences of the worst-case scenario must be carried out.

One of the more serious and common worst-case scenarios is loss of control of the heat balance of the reactor. Figure 2 illustrates the of heat balance for a liquid-filled agitated reactor. Curve AA represents the heat generation of a reaction mass, $q_{\text{generation}}$, due to chemical reaction. The energy-temperature curve, AA', illustrates that not all runaway reactions end in catastrophic thermal explosions. In this instance, the reaction terminates due to consumption of the limiting reactant. Curve BB is representative of a typical heat removal design equation for a reactor, q_{removal} . Intersection points of the two curves represent steady-state conditions at which the reactor is in thermal balance, that is, the heat removal system is capable of removing the heat generated within the reaction mass. A steady state exists as long as heat removal capability is greater than, or equal to, heat generation.

There is a long list of hazard scenarios, many of which are low probability and/or consequence. However, there are several scenarios that cannot be dismissed as “of low frequency” or “of minimal consequence.” These are commonly encountered situations in everyday chemical manufacturing activities, can develop into runaway reactions, with possible loss of containment. Some typical causes of runaway reactions are listed in Table 2.

Each one of these scenarios influence the Arrhenius equation for a general heat-production (Equation 1). For a first-order reaction, this equation encompasses relationships between thermodynamics and kinetics:

$$q_{\text{generation}} = V_M \Delta H_R A e^{-E_a/RT} C_A \dots \dots [1]; \quad q_{\text{removal}} = US(T_{\text{out}} - T_{\text{in}}) \dots \dots [2]$$

where:

V_M = volume of vessel, m^3

ΔH_R = reaction heat, J mol^{-1}

A = pre-exponential factor for Arrhenius equation

E_a = activation energy of reaction, J mol^{-1}

R = gas constant, $\text{J mol}^{-1} \text{ } ^\circ\text{K}^{-1}$

T = reaction temperature, $^\circ\text{K}$

C_A = concentration of reactant, moles liter $^{-1}$

U = heat-transfer coefficient, $\text{W}(\text{m}^2 \text{ } ^\circ\text{C})^{-1}$

S = surface area for heat transfer, m^2

T_{out} = temperature of heat-transfer fluid exiting the reactor jacket, $^\circ\text{C}$

T_{in} = temperature of heat-transfer fluid entering the reactor jacket, $^\circ\text{C}$

Table 3 provides an overview of the impact of each worst-case scenario on $q_{\text{generation}}$ and q_{removal} . Thermal control is established if $q_{\text{generation}}$ is less than q_{removal} . This condition can be violated if $q_{\text{generation}}$ increases and/or if q_{removal} decreases or if both occur; in other words, if the temperature of the reactor exceeds the upper intersection point, AB, as shown in Figure 2.

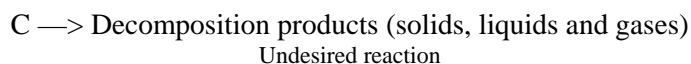
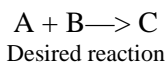
3. Design lines of defense against the credible worst case scenarios

A cost effective hazards analysis, for the six OSHA PSM elements, may be gained through a diligent examination of the safety systems measured against the potential hazards of the process. The desired process-chemistry and unit operations, and the undesired events (mal-operations) are examined in sufficient detail to provide quantitative limits on operational parameters such as maximum or minimum temperatures, pressures, feed rates, and temperature and pressure rise rates. Central to this examination is obtaining the hazard test data for the raw materials, intermediates, and final product.

Clearly, the absence of process upsets is the required outcome of any manufacturing process. However, there is always the possible occurrence of undesired process-conditions. Process upsets should be distinguished from normal and acceptable process deviations which impact product quality with no process safety concerns. Figure 3 shows the type of upsets in the chemistry and processing conditions that can occur.

Given that process upsets can and do occur, which of them will lead to a catastrophic outcome? The vast majority of upsets do not have serious outcomes. But how can we be sure? Basic information about the thermodynamics and kinetics of the chemically feasible reactions holds the key to a quantitative assessment of the nature, extent, and impact of these undesired reactions and process upsets. Straightforward calorimetric test data provides the distinction between undesired situations that are definitely hazardous and undesired reactions that pose a low risk, and are easily managed. The appendix provides details about choosing the right calorimeter and calorimetric technique to match the particular process safety data need.

Figure 4 shows diagrammatically a runaway scenario resulting from loss of cooling control of the desired reaction, in an adiabatic environment. In both cases the overall reactions are:



Two cases are presented that describe frequently encountered relationships between the desired and un-desired reactions. In both situations, the undesired reaction is triggered, but close inspection of Figure 4 for the two cases reveals some critical differences.

From Table 4, Case 1, we note that the desired reaction onset at 45°C, involves an adiabatic temperature rise of 80°C, and is therefore complete by 125°C ($T_{\text{onset}} + T_{\text{adiabatic,des}}$). The undesired reaction has an observed T_{onset} at 175°C (see the lower left curves of Figure 4.) The temperature-time plots, Figure 4 upper left, clearly indicate that the desired reaction is separated from the undesired reaction by a “thermal barrier.” Between 125°C and 175°C, the temperature-rise rate is less than 0.01°C/min. In practical terms, the temperature will only rise from 125°C to 175°C

under near-perfect adiabatic conditions. The presence of even modest cooling, possibly only ambient cooling, would probably be sufficient to prevent the reactor temperature from rising much above 150°C. Reactions with these kinetic and thermodynamic characteristics may be treated as being of minimal risk and straightforward to manage.

In direct contrast, Case 2 illustrates the situation where the onset of the undesired reaction overlaps the temperature range of the desired reaction. In this example, the thermal parameters for the desired reaction have been changed, with so that there is no thermal barrier between the desired and undesired reactions. While this is not inherently dangerous, it is clear that if temperature control is lost for the desired reaction, the undesired reaction is easily triggered.

This simple example assumes that there is no consumption of reactants, that the runaway begins immediately on mixing the reactants, and that the reaction is performed in the absence of a solvent that could provide a thermal barrier. Therefore, the example represents a conservative worst-case situation. The important lesson here is that by performing minimal hazards-screening tests, the nature and extent of the potential hazard of the process is immediately quantified and placed in context. For Case 1, it is reasonable to perform the reaction as a batch process, with appropriate process interlocks. However, for Case 2, serious consideration should be given to switching to a semi-batch reaction. If the product requirements or process economics do not permit this change, then significant process controls and interlocks will be necessary to reduce the inherent risk of this situation.

The Arrhenius equation, enumerated in Figure 4, is the foundation for reaction hazard-assessment and chemical process safety. It provides the kinetics of the reaction(s) by fixing the time line for thermal activity. The thermodynamics of the reaction are the key to the magnitude of the power output of the reaction(s). Equation 2 describes, in part, the ability of the equipment to manage to the heat load and power output during desired and undesired conditions.

Another complication of triggering the undesired reaction is that there is frequently a rapid and substantial pressure rise once this reaction is underway, due the formation of decomposition products that are mostly comprised of permanent gases. Pressure-rise rates are typically 10–500 bar/min and rates over 2,000 bar/min have been recorded for highly energetic runaway reactions.

Regardless of the fact that Case 1 is of minimal risk, this circumstance is not known until data of the type shown in Figure 4 have been generated and interpreted for the various aspects of the process described above.

4. Gathering Thermal Stability and Reactivity Data

The linkage of common hazards testing techniques with the six process safety elements is shown on Table 5. It makes the point that for a typical process, a thorough examination of the process, yielding process safety information in compliance with section (d) of OSHA's PSM standard, also provides the data for sections (e), (f), and (i), and most of (l). As the PHA turns up questions about worst-case scenarios, they can usually be answered from the data and analyses of the hazard testing indicated in Table 5. In particular, operating procedure limits on temperature, pressures, and other parameters, which form the basis of safety and window of safe operations, are also obtained from the test data. Plant pre-startup safety reviews and management-of-change issues have similar data requirements. However, for an accident, or incident, in addition to the

basic information from sections (d) and (e), it is probable that further hazards testing will be necessary to provide a definitive explanation of the cause of the accident.

Figure 5 presents a typical order of conducting the hazards testing. The center column of the flow chart indicates that the desired process is assessed first and missing information is obtained by hazards testing. Undesired events and mal-operations are then assessed, again using hazards testing where needed. At that point, the lines of defense, basis of safety and window of safe operations can be defined from the chemical reaction hazards data generated. The information gained from the testing becomes the basis for compliance with sections (d) and (e).

The left-hand column shows the link between the progress of the hazards testing and the contribution to the various elements of the process safety standard. It should be noted that the operating procedures, a key piece of the whole PSM standard, draws information from every step of the recommended hazards testing protocol. The right-hand column indicates the type of hazard test data and interpretation needed for each step in the process hazard analysis.

5. Operational Hazards Testing

Operational hazards relate to the risks and consequences of improperly handling process materials and chemicals. For example, exposing a chemical to high temperatures may lead to auto-ignition; subjecting a solid to an impact could lead to a detonation of the solid; mixtures of gases or vapors or solids with an oxidant, can explode in the presence of an ignition source. Commonly encountered ignition sources include:

- Metal-to-metal contact (e.g., friction)
- Overheating from worn bearings and slipping belts
- Open flames, such as direct-fired heaters and incinerators
- Static discharges, including spark, propagating brush, and conical-pile discharges
- Welding or cutting, which causes a point source discharge
- Hot surfaces

Each of these sources has a characteristic energy that it will impart to a mixture of a fuel and oxidant. However, a fire or explosion will result only if the minimum ignition energy (MIE) of the material is lower than the energy of the ignition source. MIE is defined as the lowest spark-gap energy that ignites a mixture of fuel and oxidant, and causes both the propagation of the flame, and a build up of pressure. Therefore, the determination of the minimum ignition energy for materials (gases, vapors, mists, dusts, hybrid mixtures) is an integral part of the determination of the magnitude and severity of the operational hazard, and ultimately process safety. Generally, MIE's are lowest for gases and vapors, especially mixed with air or oxygen (0.002–1.0 mJ) and somewhat higher for dusts (1.0–5000mJ). They are strongly affected by a number of factors such as increasing pressure and temperature, increasing nitrogen concentration, air-to-fuel ratios, and decreasing particle size for dusts and mists.

A hazard assessment involving dusts, vapors, mists and gases needs to consider several factors. The parameters, highlighted below, are key to providing the data needed for the assessment:

Flash points. This is the lowest temperature at which gases and vapors can be ignited under the conditions defined by the test apparatus and method. Flash points are necessary for safety considerations in a hazards assessment review and are required by government agencies before

registering and transporting chemicals. Fire potential is often evaluated using the closed-cup flash point determination. Open-cup flash points are generally higher, and thus less conservative, than closed-cup determinations. The value determined in an open-cup test is subject to air movement at the open face of the cup and true vapor-liquid equilibrium probably does not occur.

Flammable limits (ranges). These are the upper and lower concentrations (in volume percent) of a vapor in air that can just be ignited by an ignition source. No ignition will occur above the upper limit and below the lower limit. Data are normally reported for air at ambient temperature and pressure. Flammable limits may be reported for atmospheres other than air (e.g., chlorine, nitric oxide, oxygen), and at temperatures and pressures other than ambient.

The basic test apparatus consists of a chamber into which a mixture of air and vapor of known concentration is introduced. After thorough mixing, ignition is attempted with a spark or a hot wire. A series of different concentrations are tested to establish the upper and lower concentration limits for flammability.

Flammable limits for most combustible gases and low-boiling liquids are known. For materials without published data, lower flammable limits can often be calculated with acceptable accuracy, but calculations for upper flammable limits are less satisfactory. Extrapolation of experimental data, by calculation, to other temperatures and pressures is possible. However, for safety-critical applications, these calculations should be confirmed by experimentally determined flammable limits at relevant process conditions.

Auto-ignition temperature. The ignition temperature of a substance, whether solid, liquid, or gaseous, is the minimum temperature required to initiate or cause self-sustained combustion, in air, with no other source of ignition. Ignition temperatures observed under one set of conditions may differ markedly in the field. Published auto-ignition temperatures should be looked upon only as approximations, since they are strongly dependent on percentage composition of the vapor or gas-air mixtures, shape and size of the space where ignition occurs, and rate and duration of heating. Test results tend to be high, and should not be used for establishing "safe" temperatures. Under process conditions, there is a potential for fuel-air mixtures to ignite at much lower temperatures, due to the many extraneous sources of ignition that are virtually impossible to eliminate.

Flammability of dusts, vapors and mists. Combustible, dusty materials, with particle sizes less than about 200 mesh, can explode if a sufficient concentration in air is present along with an ignition source. Energies of ignition sources range from 20-200 mJ (common static spark) to hundreds of joules (arcing electrical equipment). Thus, dust-explosion testing is often performed to determine the extent to which inerting process areas and equipment is necessary.

An important test to determine if a solid material of suitable particle size presents a potential dust hazard is the determination of the material's MIE, typically carried out as a function of dust concentration. This test uses a dust-dispersion system, where a dust cloud is generated inside a cylindrical-explosion chamber with a spark-gap ignition source.

A 20-liter apparatus is used to quantify the rates of pressure rise during an explosion and the maximum pressure reached. The apparatus provides reliable data for the design of vent and explosion relief systems. The maximum pressures produced in a dust explosion are typically

about 100 psig. The rates of pressure rise and the ease of ignition, however, vary considerably from material to material.

6. Less Common Stability Tests

Substances, or processes, are continually exposed to various types of external thermal stimuli. Thermal hazards testing provides insight into the nature and extent of this class of hazard. Often, the results of these tests are expressed as standard phrases, such as “no ignition”, “immediate ignition,” “partial detonation,” or merely a yes-or-no indication of sensitivity to the applied stimulus. Some tests also provide reaction violence in terms of temperature or pressure, or rate of temperature or pressure attained, or reaction heat developed.

Some of the different types of hazards covered by these tests are:

- Spontaneous decomposition to detonation transition
- Deflagration to detonation transition
- Ignitability of material
- Detonation under rapid heating or in fire scenarios
- Explosive power by cap initiation;
- Decomposition in open containers and under confinement
- Propagation by shock initiation
- Impact and friction sensitivity
- Storage stability

The results of these types of tests are often directed towards transportation issues, to a broad classification of a substance’s propensity to detonate or deflagrate, and some assessment of the nature and extent of the resultant damage. Generally, these tests are performed at the earliest stage of the new product development.

7. Offering relief

Table 6 presents a summary of the reaction hazard test methods for reactivity and thermal-hazard assessment along with the type of data obtained from each technique. Table 7 presents and defines the various parameters referenced in Table 6. As noted earlier, the risk-based approach to process hazard analysis and process-safety management is central to the assessment of the frequency and consequences of credible worst cases and the design of lines of defense. The nature and extent of the worst case can only be determined from factual data. These data may be available from a company’s loss prevention files, sometimes from the open literature, or from industry product groups. However, for most situations relevant data are not available, especially if the intention is to design an emergency relief system (ERS) using the Design Institute for Emergency Relief Systems (DIERS) approach, or determine the adequacy of a cooling system.

A typical ERS design problem illustrates these points. A common worst-case scenario is a reactor, or storage tank, surrounded by a pool of burning liquid. If the assumed outcome is that the fire will eventually cause the solvent in the vessel to evaporate, the boil-off rate of the solvent is readily estimated. Then the required (by calculation) area of the vessel’s emergency vent is compared to the in-place nozzle area to establish, or verify, the adequacy of the ERS under these fire conditions. The set pressure and other design information for the ERS also arise from these calculations. Any comprehensive physical properties database provides all the needed data. It is rare that any experimental work is needed to complete the ERS design for this situation.

However, this approach has an embedded, and frequently unchallenged, assumption that the contents of the vessel do not undergo chemical reaction(s), including decomposition, during the course of the fire and solvent loss. In many of these situations, this is not true. The undesired (or secondary) reactions that do occur are characterized by rapid evolution of large quantities of gases and vapors. The decomposition products discharged from the vent will be either gassy, liquid, or some combination of gases and liquids.

Calculations using DIERS equations reveal that vent areas up to ten times the size for a “vapor only” system are required to accommodate these types of releases. The data needed to satisfy the DIERS equations center around temperature- and pressure-rise rates during the undesired reaction(s), the maximum temperature and pressure reached during these reactions, and the type of material flow through the vent. Since almost none of these data are available from the public domain, it is normally generated experimentally for the target chemical system and the worst-case scenario identified during the process hazard analysis. The consequences of not identifying the need for the DIERS approach, and therefore incorrectly sizing the emergency vent, can be a catastrophic loss of containment.

8. Conclusions

Large companies in the CPI generally do a good job of complying with the OSHA standard. Many have an internal hazards testing group that actively participates in the company’s safety, health and environmental programs. Unfortunately, as the size of a company decreases, the resources are not usually available for hazards testing to be an integral part of the process safety program. Emphasizing and requiring that test data be used to define the window of safe operations and the basis of safety generates a more fundamental knowledge of the process. This in turn leads to a decrease in the process upsets, resulting in fewer injuries to chemical workers, as well as reducing adverse community and public reaction.

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Appendix:

Choosing the right calorimeter

Choosing the Right Calorimeter

1. Introduction

Reliable hazards testing means carrying out calorimetric experiments under the conditions that most-closely mimic the full-scale manufacturing process. Such studies produce an overall heat of reaction for a particular process, including potential side reactions and phase changes. However, extracting a single heat of reaction for a particular chemical conversion can be quite challenging, often requiring an extensive chemical analysis of the reaction mixture.

Selecting the right calorimeter is key to this testing. Factors that govern the choice of calorimeter include temperature and pressure ranges of interest, reaction-initiation method, the ability to mix the contents of the sample cell, sensitivity, and amount of material available to work with. In regards to sensitivity, a direct comparison of instruments is not straightforward, since calorimeters detect heat based upon different principles (some use temperature rise, others measure heat flow) and chemical systems can be of differing heat capacities and densities. Below is a description of the various types of calorimetry available:

Mixing calorimetry. This technique is used to measure heat evolved upon instantaneous mixing of two, or more, chemicals. Generally, the calorimeter uses a differential signal from sample-cell and reference-cell thermopiles. Two or more reagents, which may be solids, liquids, or gases, are mixed with stirring in a sample cell. Resultant heat and gas evolution are then measured and the heat output is quantified by comparison with an integrated signal from an electrical calibration heater pulse. Typical quantities for mixing are: 0.1–2 ml of liquids and 0.05–1.0 g of solids. Detection sensitivity is approximately 0.02 mW, the temperature range is –50–200°C, and data collection takes roughly 20 min. This type of instrumentation is usually small, portable, and is relatively inexpensive, strengths that are important for its primary objective as a hazard-evaluation device for chemical compatibility and screening of reaction chemistry. However, one weakness of the typical mixing calorimeter is its inability to mix adequately viscous materials.

Scanning calorimetry. Differential scanning calorimetry (DSC) methods present a simple, easy and readily available method for determining heats-of-reactions. Two types of DSCs are commonly used, a heat-flux DSC and a power-compensated DSC. In heat-flux DSC, the heat flow is linearized across the entire range of temperature used so that the heat flow can be calibrated at one temperature and the calibration then used to determine heats at any other temperature. The power-compensated DSC changes the power to the sample chamber to adjust the sample temperature, so that it is the same as the reference temperature, and the difference in power between the reference and sample heaters is recorded.

Application of DSC to determine the heat of reaction has the advantage of using small quantities of sample (0.5 to 20 mg) for the determination. But this can create a sampling problem. Typical sample holders are made from aluminum, stainless steel or gold pans or glass ampoules. Aluminum can be reactive to the sample, while stainless steel or gold pans may not hold more than a few atmospheres pressure, and may allow the sample to leak from the container. On the other hand, glass ampoules, although they need to be sealed, are inert for most materials and can withstand considerable internal pressures.

While this technique has been found useful for a wide range of samples, there are some difficulties that must be considered, such as handling multiphase samples, lack of mixing within

the sample container, mimicking the role of air (oxygen) in the thermal activity of the sample, and if necessary, avoiding contamination by air. The most serious limitation is the fact that no pressure information is available from this technique, and consequently, hazard evaluation from DSC data alone is at best incomplete and possibly misleading.

Adiabatic calorimetry. Adiabatic calorimetry is used primarily as an aid in thermal hazard evaluation to measure rates of energy output, and temperature and pressure rises of desired or undesired chemical reactions. These data have application to the thermodynamics, kinetics, and engineering concerns related to process chemistries through the quantitation of potential reaction energies, rates of reaction, and scalable operating parameters. The scalable results include $\Delta T_{\text{Adiabatic}}$, ΔH , and maximum rates of temperature and pressure rise. Operating temperatures and pressures are generally from ambient up to 500°C and 2,500 psi. Adiabatic conditions are normally maintained for self-heating rates up to 20°C/min.

Two principle types of adiabatic calorimetry, distinguished by the thermal inertia of the sample container, are routinely used in the hazard-evaluation context. The energy way produced by the sample, during chemical reaction, causes a temperature rise within itself and the test cell. The apportioning of the energy between sample and test cell is characterized by the thermal inertia, ϕ . Under true adiabatic conditions, $\phi = 1$, and $\phi > 1$ for increasingly less adiabatic conditions.

High-thermal-inertia adiabatic calorimetry. This type of calorimetric testing provides an opportunity to examine the thermal stability of materials under adiabatic conditions. The overall mode of operation of the adiabatic calorimeter is known as Heat-Wait-Search (HWS). The test is conducted using a sample size of 4–8 g in a sample container made from stainless steel, or titanium of mass 10–20 g (ϕ ranges from 1.5–3.5). The data obtained from high-thermal-inertia adiabatic calorimetry is not suitable for direct use in emergency-relief design for reactive systems.

The sample is brought to the start temperature and evidence for sample self-heating is sought (Wait and Search phase). If none is seen, the sample temperature is rapidly raised 5°C or 10°C (Heat mode), and the search for self-heating repeated. Once detected, the calorimeter switches to a tracking mode, also under adiabatic conditions, and keeps pace with the temperature rise of the self-sustaining (runaway) reaction until the exotherm is complete. These data, under some circumstances, lead to estimations of heats of reaction for the reaction mixture, onset temperature of exothermic activity and pressure information, along with temperature and pressure-rise rate information. In addition, if the chemistry is not too complicated, Arrhenius-type kinetic analysis may be performed to give values of E_a and A .

Low-thermal inertia adiabatic calorimetry. A test similar in overall operation to that described above maybe used to determine times to maximum rate, t_{MR} , and given appropriate information about the process vessel, temperature of no return, T_{NR} . These data may also be used to estimate the self-accelerating decomposition temperature, T_{SADT} . For low-thermal-inertia calorimetry, the sample size is increased to 40–60 g, which allows for thermal inertia values to approach unity (1.05–1.15). The data are scalable and may be used directly in emergency-relief design for reactive systems. Key to this mode of operation is the ability to agitate mechanically the sample container, thereby guaranteeing excellent correspondence with the real process.

A significant advantage offered by adiabatic calorimetry is to obtain an experimental heat of reaction or decomposition, rather than calculate a theoretical value. The advantage of this

experimental approach is that the former does not require knowledge of the side reactions nor an overall pre-reaction and post-reaction compositional understanding or quantitation. Many times in plant operations, the rate of heat generation as a function of temperature and estimated adiabatic-temperature rise is a sufficient characterization of a decomposition process. Scenario-specific safe operating conditions can thus be rapidly evaluated and reliable recommendations made, without dedicating time and resources attempting to understand decomposition pathways.

Reaction calorimetry. Reaction calorimeters provide thermodynamic and kinetic information concerning the desired reaction under conditions closely similar to those of the larger scale plant. The strengths of reaction calorimetry include the measurement of heat flow and heat production of the desired process, the measurement of process heat generation without the knowledge of heat of reaction or the degree of conversion, and the ability to perform both isothermal and temperature-ramped experiments. Reaction calorimetry provides both process design *and* process safety information for the desired reaction.

A reaction calorimeter is essentially an automated lab-reactor configured to measure the heat flow to and from the process. These instruments are sized (typically 0.2–2 liter) such that reliable, scalable engineering design data can be obtained. Full-scale chemical processes can also be simulated; including solids handling and high pressures to at 800 psi and from -50° C to 300° C.

The heat-flow data may be used to track the progress of the reaction (or other physiochemical transformation) and to determine the process-heat load as a function of time. Integration of this heat flow gives the heat evolved from the process. Reaction calorimeters are also used for process development and optimization, process scale-up and plant design. The specific information that can be obtained from reaction calorimetry includes: heat of transformation, heat evolution rate, adiabatic temperature rise, heat transfer coefficients, specific heat of reaction mass, required cooling capacity, influence of mixing on mass and heat transfer, and crystallization behavior. Situations in which reaction calorimetry have proven to be particularly useful, even critical, include those involving continuous additions, multiphase reactions, and cases in which mass-transfer rates affect the observed rate of reaction.

However, reaction calorimetry is less sensitivity than heat-flow micro-calorimetry and incurs large experimental resources, relative to other thermoanalytical tools such as adiabatic calorimetry and DSC. It also gives little information concerning undesired conditions because of the safety concerns of simulating a process upset at the one-liter scale.

Microcalorimetry. One of the key strengths with microcalorimetry is the high sensitivity that allows heat-rate data to be collected at the temperatures of actual intended operation or storage. This is important in order to avoid the uncertainties associated with extrapolation of data collected at much higher temperatures. Operational temperature range is from -200°C to 300°C, temperature-scanning rates from 20°C/min to 0.10°C/h. With sample sizes up to 40mL of material, one can obtain detection limits on the order of tenths of mW/g of material. Typically, microcalorimetric data is collected at two or three different temperatures, giving an Arrhenius plot for activation energies of the process under investigation. The 'time-delay' of any autocatalytic events can be quantified as a function of temperature. Identical samples run in parallel under air and nitrogen can serve to immediately elucidate thermal-versus-oxidative decomposition mechanisms.

Table 1. Fourteen elements of OSHA's PSM Rule

Employee Participation: (c)	Mechanical Integrity: (j)
Process Safety Information: (d)	Hot Work Permit: (k)
Process Hazards Analysis: (e)	Management of Change (l)
Operating Procedures: (f)	Incident Investigation: (m)
Training: (g)	Emergency Plan & Response: (n)
Contractors: (h)	Compliance Audits: (o)
Pre-Startup Safety Review: (i)	Trade Secrets: (p)

Table 2. Typical Worst Case Scenarios

WCS	Description
1	loss of, or inadequate, cooling;
2	the unexpected introduction of a reactant, catalyst, or other material;
3	the unexpected depletion of an inhibitor, or other material;
4	high local temperature, caused by loss of, or inadequate, stirring;
5	lack of adequate heat conduction;
6	extended reaction and/or cycle time favoring auto-catalytic reactions;
7	accumulation of reactants because reaction is rate limited;
8	the pressurization of an enclosure by an oxidizing gaseous intermediate;
9	phase separation of a previously homogenous mixture;
10	sudden, or rapid, mixing of previously separate phases;
11	fire, or external heating, of the vessel or storage tank.

Table 3. Impact of Selected Worst Case Scenarios on Vessel Heat Balance			
WCS	Impact on Heat Balance		Principle Variable(s) Affected in Equation 1 for each WCS
	q_{removal}	$q_{\text{generation}}$	
1	$\Rightarrow 0$	↑	Increase T_m , which increases reaction rate, leading to runaway
2	↔	↑	Increase, C_A and/or decrease E_a , increase ΔH_R
3	↔	↑	Decrease E_a
4	↔	↗	Increase T_m locally, leading to global increase of T_m
5	↘	↗	Increase global T_M
6	↔	↑	Increase C_A ; New reactions increase ΔH_R ; Change E_a
7	↔	↗	Increase C_A
8	↔	↗	Increase C_A leading to loss of containment
9	↔/↘	↘/↓	Reaction may stall with unreacted material
10	↔	↑	Local increase in C_A
11	↘/⇒0	↗	Compromise cooling system; increase T_m

Table. 4 Examples of Thermal Parameters for Inherently Safe and Potentially Hazardous Reactions

	Case 1	Case 2
<i>Desired Reaction</i>		
ΔH	40 cal gm ⁻¹	120 cal gm ⁻¹
$T_{\text{ONSET,DES}}$	45 °C	35 °C
$\Delta T_{\text{ADIABATIC,DES}}$	80 °C	182 °C
Activation Energy	11 kcal mol ⁻¹	25 kcal mol ⁻¹
<i>Un-Desired Reaction</i>		
ΔH	210 cal gm ⁻¹	210 cal gm ⁻¹
$T_{\text{ONSET,UND}}$	175 °C	175 °C
$\Delta T_{\text{ADIABATIC,UND}}$	425 °C	425 °C
Activation Energy	34 kcal mol ⁻¹	34 kcal mol ⁻¹

Table 5. Types of Hazards Test Data Needed to Satisfy Six OSHA PSM Elements						
Hazards Testing Procedure	PS Info (sect. d)	PHA (sect. e)	Operating Procs (sect. f)	Pre-Start Up Rev (sect. i)	Management of Change (sect. l)	Incident Investigation (sect. m)
Calculations/Books/ Open literature	●	○	○	○	○	●
Flammable Limits and Flash Points	●	○	○	○	○	●
Mixing Calorimetry	●	●	○	○	●	●
DSC / DTA	●	●	○	○	●	●
Adiabatic High ϕ Calorimetry	●	●	○	○	●	●
Reaction Calorimetry	●	○	○	○	○	○
Adiabatic Low ϕ Calorimetry	●	●	○	○	○	●
Venting requirements	●	●	○	○	○	●
Flammability / Explosion	●	○	○	○	○	●
Impact Sensitivity	●	○	○	○	○	●
Dust Explosion potential	●	○	○	○	○	○

Note: ● means (additional) data may need to be obtained; ○ means data from other PSM sections will apply

Table 6. Summary of Reaction Hazard Testing Methods			
HAZARDS TEST STAGE	METHOD	TYPICAL INFORMATION (See Table 7 for definitions)	COMMENTS
Hazard Screening	Desk Calculation (Note 1)	<ul style="list-style-type: none"> Reaction enthalpy, ΔH_{RXN} 	<ul style="list-style-type: none"> Need formation energy data or derive it Must know precise stoichiometry Known reactions only, no rate information
	Mixing Calorimetry (Note 2)	<ul style="list-style-type: none"> Instantaneous heat of mixing, ΔH_{MIXING} Gas generation rates 	<ul style="list-style-type: none"> Isothermal, from ambient to 150C No mixing Cannot test multi-phase liquids
	DSC / DTA (Note 3)	<ul style="list-style-type: none"> Reaction enthalpy, ΔH Reaction 'onset' temp, T_{ONSET} 	<ul style="list-style-type: none"> Very quick (~2 hours), needs little sample No mixing, no pressure data, no multi-phase Difficult to get representative mixture.
	Adiabatic Screening (Note 4)	<ul style="list-style-type: none"> $\Delta H_{UNDESIRE}$, T_{ONSET} ΔT_{ADIAB} P, T, t, dP/dt, dT/dt Simple kinetics, E_A, A 	<ul style="list-style-type: none"> Sample ~ a few grams Reasonably quick to test (~1/2 day) Poor/moderate sample agitation Not reliable for scale-up (high-factor).
Develop desired reaction	Reaction Calorimetry (Note 5)	<ul style="list-style-type: none"> $\Delta H_{DESIRED}$ Power output, Q_{RXN} Heat transfer rate Accumulation, X_{AC} 	<ul style="list-style-type: none"> Normally 0.1 to 2 liter scale Mimics normal operation Essential information for safe scale-up Very useful for process development.
Detailed Hazard Assessment	Low Thermal Inertia (ϕ -factor) Adiabatic Calorimeter (Note 6)	<ul style="list-style-type: none"> $\Delta H_{UNDESIRE}$, ΔT_{ONSET} ΔT_{ADIAB} dT/dt; dP/dt; T_{SADT}, T_{NR}, t_{MR}, Vent sizing data 	<ul style="list-style-type: none"> Sample size ~ 100 ml Safe for general laboratory work Good mimic of large-scale runaway Ideal for 'what-if' scenario study.
Special Studies	High Sensitivity Calorimetry (Note 7)	<ul style="list-style-type: none"> $\Delta H_{DESIRED}$, $\Delta H_{UNDESIRE}$ dT/dt; ΔT_{ADIAB} Kinetics, E_A, A 	<ul style="list-style-type: none"> Sample size 1 – 50ml, $\mu W/g$ sensitivity Shelf life studies by accelerated aging Combine with low adiabatic to confirm solids low self-heating rate studies

Note 1: Based entirely on heats of formation type data on reactants and products; Note 2: For example, CRC-90.

Note 3: Differential scanning calorimetry or other simplified methods; Note 4: ARC or PHI-TEC I are examples

Note 5: SIMULAR, autoMATE or RC-1 are examples; Note 6: PHI-TECH II or VSP are examples; Note 7: Seteram C-80 and Calorimetry Sciences Corporation are examples.

Table 7. Data Available from Thermal and Reactivity Hazards Testing

Parameter	Definition
ΔH_{RXN}	Enthalpy for specified chemical reaction
$\Delta H_{\text{MIXING,T}}$	Enthalpy of isothermal mixing two chemicals, at temperature T
ΔH	Enthalpy obtained from a temperature induced, non-specific reaction or reactions
T_{ONSET}	Observed, by calorimeter, onset of thermal activity
ΔT_{ADIAB}	Temperature rise resulting from adiabatic release of energy from sample
$\Delta H_{\text{UNDESIRE D}}$	Enthalpy for undesired chemical reaction, usually measured by adiabatic calorimetry.
$\Delta H_{\text{DESIRED}}$	Enthalpy for specified chemical reaction, usually measured by isotherm reaction calorimetry.
Q_{RXN}	Power output from chemical reaction, usually measured by isotherm reaction calorimetry.
X_{AC}	The unreleased reaction heat due to accumulation of un-reacted feed material, as a fraction
T_{SADT}	Self accelerating decomposition temperature for a fixed mass of material held isothermally for an extended period in a container of a particular geometry.
T_{NR}	The temperature of the reaction mass above which a self sustaining runaway reaction will occur despite totally available cooling being applied to the reactor.
t_{MR}	The time to maximum dT/dt from a particular temperature.
E_{A}, A	Arrhenius Parameters, activation energy and pre-exponential factor.
Vent Size	Emergency relief area, for 2 phase flow, determined from adiabatic calorimetry and DIERS theory and methodology.

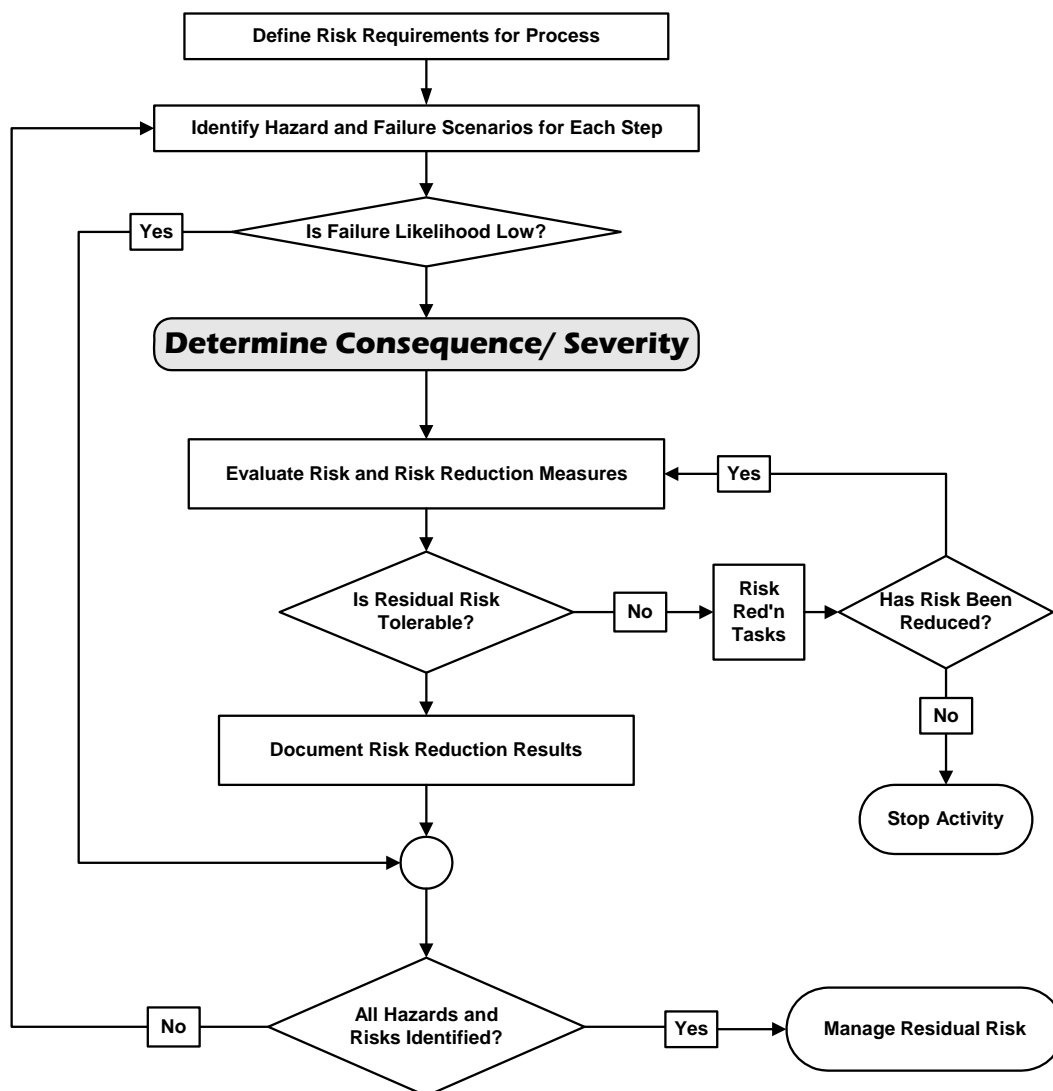


Figure 1. Risk Assessment and Reduction Flowchart

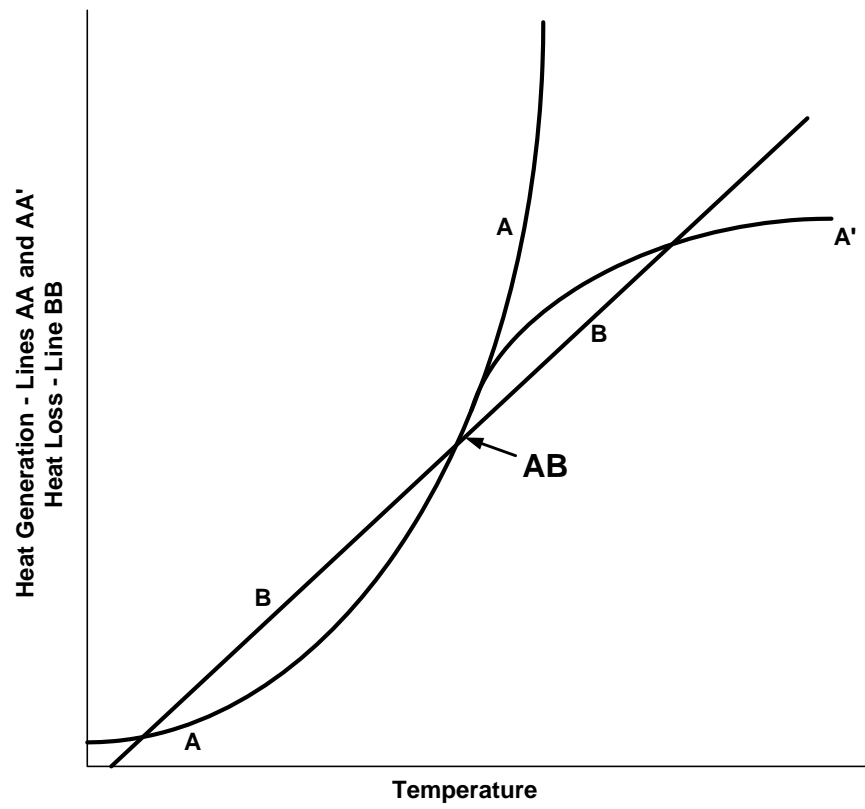


Figure 2. Semenov Plots for Heat Gain and Heat Loss of Reaction Vessel

CHEMISTRY	UNDESIED	<ul style="list-style-type: none"> • Runaway Reactions • Mal Operations • Materials of Construction • Unexpected Side Reactions • Not Fully Characterized • Unknown Decomposition Onset 	<ul style="list-style-type: none"> • Lines of Defense Not Developed • Basis of Safety Incomplete • Unknown Envelope of Safe Operations • Undesired Chemistry & Undesired Process
	DESIRED	<ul style="list-style-type: none"> • Thermodynamics and Kinetics • Rates of Change $\delta X / \delta t ; \delta X / \delta T$ for X = P, T, Q, C • Vent design, Cooling Duty • Process Control • Physical & Organic Chemistry • Required Unit Operations 	<ul style="list-style-type: none"> • Failure or Loss of Critical Unit Operations: <ul style="list-style-type: none"> • Agitation • Cooling • Sensors • Leaks Into Processing Vessel • Fire, External and Internal • Loss of Containment • Extended Reaction Times
		DESIRED	UNDESIED
		<u>PROCESS</u>	

Figure 3. Relationship between Desired and Undesired Processes and Chemistry. P = pressure, T = temperature, Q = reaction power, C = material quantity, t = time.

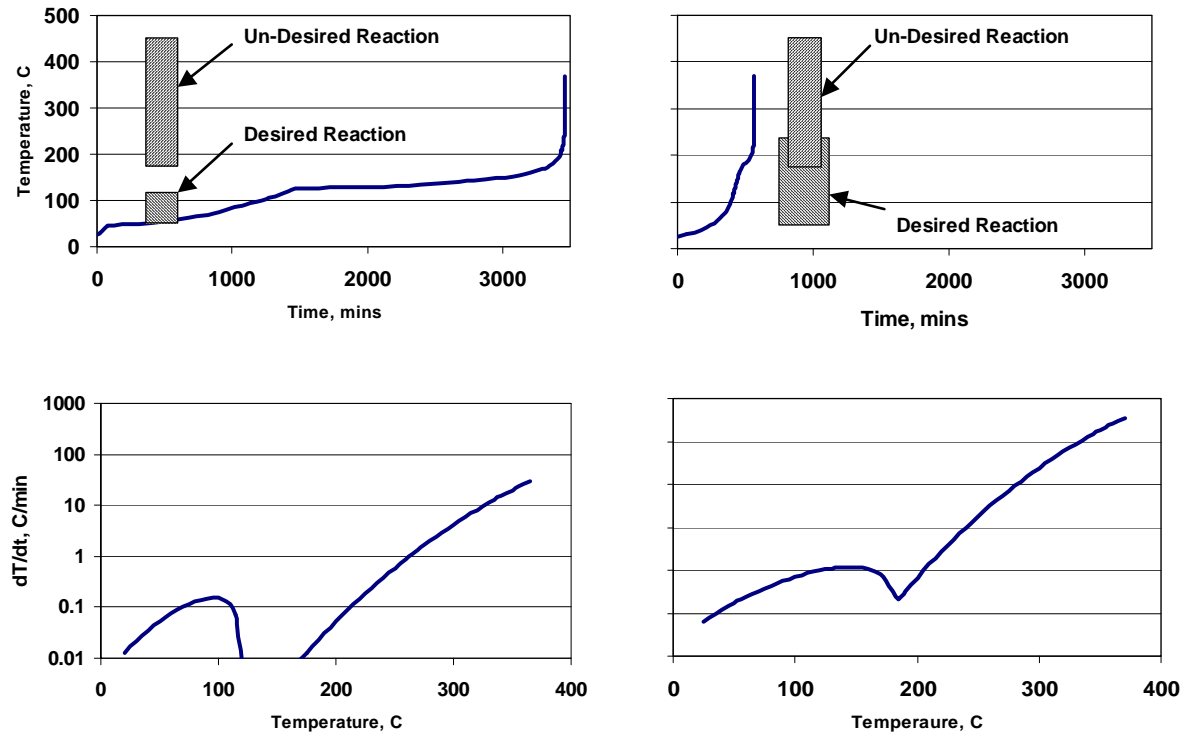
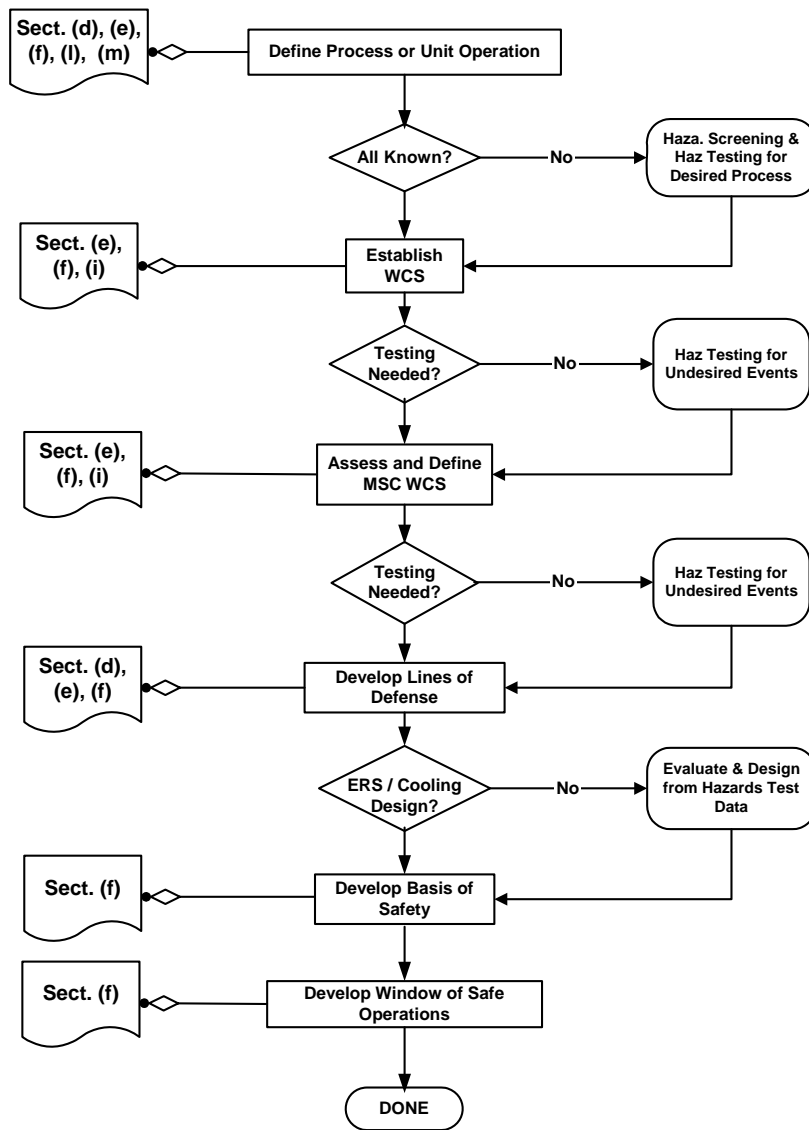
Case 1Case 2

Figure 4. Time vs. temperature and Temperature rise rate vs. temperature plots for Desired and Un-Desired sequential reactions, under adiabatic conditions.



WCS Worst Case Scenario; MSC WCS Most Severe Credible Worst Case Scenario

Figure 5. Flowchart Showing Links Between PSM Elements Data Requirements, Hazard Testing, and Stages in Hazard Assessment