

Microcalorimetry and its role in thermal hazard quantification

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Industrial level exothermic chemical reactions and thermally unstable chemical compounds continue to be areas of intense research. Lack of adequate knowledge of the exothermicity of reactions and runaway reaction chemistry at plant level operations have caused casualties and material loss. Nevertheless, through recent advances in the field of microcalorimetric techniques even hazardous runaway reaction potential could not only be identified, but also quantified. This article broadly describes the causes, several contributing factors for thermal runaway and instability, analyses the methodologies of the new instrumental techniques. The article also suggests a tested protocol for the effective application of microcalorimetry in thermal hazard quantification.

EXOTHERMIC chemical reactions are often accompanied by significant heat release, and therefore, need a thorough investigation before they are taken to a plant scale. The heat losses in laboratory scale apparatus are relatively large and it is difficult to quantify the rate of heat release associated with the chemistry. Sudden thermal energy releases from exothermic decompositions and runaway reactions have contributed to serious fire and explosions in several chemical process plants. Similarly, thermal runaway had also occurred in storage and transportation of reactive chemicals. The secondary events of thermal runaway reactions can be rupture of process vessel, toxic spills and release of explosive vapour clouds or a combination of these also. Developing an intrinsically safe process/storage/transportation demands direct monitoring and prevention of the unwanted temperature excursions.

The explosion hazards are governed by the system thermodynamics and kinetics of the thermal process. Theoretical prediction of limiting temperature is difficult due to process complexities. Further, the kinetic data obtained through classical techniques, at conditions far away from runaway situation, are often not valid for assessing the runaway behaviour of exothermic processes. Thermal hazard assessment basically relies on identification of dangerous process conditions, process deviations and thermal sensitivity of reaction mixtures and products. The main focus of this article is to discuss the causes and several contributing factors for thermal runaway and instability and present analyses of the

methodologies of the new instrumental techniques for assessing the thermal hazards of reactive chemicals during processing, storage and transportation.

This article is divided mainly into two sections followed by conclusions. The first section describes the causative factors for thermal runaway which includes unstable chemical structures, endothermicity, decomposition energy and mutual affinity between two chemical compounds. In other words, certain chemical compounds are basically susceptible to thermal runaway and the contributing factors for the same are discussed in this part in detail.

The second part explores the microcalorimetric techniques such as thermal analysis, accelerating rate calorimetry, reaction calorimetry and reactive system screening tool which could be employed for identifying the thermal runaway potential, thus forewarn the process engineers. Further, it also suggests a protocol on how the techniques have to be integrated to evolve an effective way to identify the hazard potential and eliminate the same.

The concluding part emphasizes the need for the profitable application of the thermochemical techniques and the major area of utility in the chemical process industry.

Causes and contributing factors for thermal runaway and instability

Thermal runaway and its consequences

Exothermic chemical reactions tend to accelerate, if the rate of heat removal in a reactor is insufficient to control the temperature rise. While the reaction rate is an exponential function of temperature, the cooling capacity is only a linear function of temperature.

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The possible deviations that can lead to loss of temperature control are either or a combination of:

- ♦ Decrease of heat exchange coefficient U ;
- ♦ Decrease of heat exchange area A ;
- ♦ High temperature for heat exchange fluid T_j .

Figure 1 represents thermal profile of a reaction at steady state, where the rate of heat generation equals the rate of heat removal. This is represented by the straight path along points A and B. Point B represents the metastable region of the reaction. If the system temperature drops lightly, the rate of heat loss exceeds the rate of heat generation and the system steady state is driven to point A. If cooling capacity is lost, steady state can

be restored if cooling is restored, before the reaction temperature exceeds that at point B. Point C or D in Figure 1 is a limiting temperature above which heat rate produced by the reaction is larger than the heat removal rate. Above the temperature at point C or D, the system temperature increases steadily, causing the reaction rate to accelerate exponentially. The temperature at point C or D, where the slope of the heat generation line equals that of the heat removal line, is referred to as the temperature of no return T_{NR} . However, if cooling is restored before the temperature exceeds that at point B, steady state operation can be restored. If the reaction temperature exceeds T_d (partial loss of heat exchange coefficient), the system cannot be restored to steady state and will run away. Therefore, the three distinct regions of the thermal behaviour of an exothermic reactor can be explained as in Figure 2.

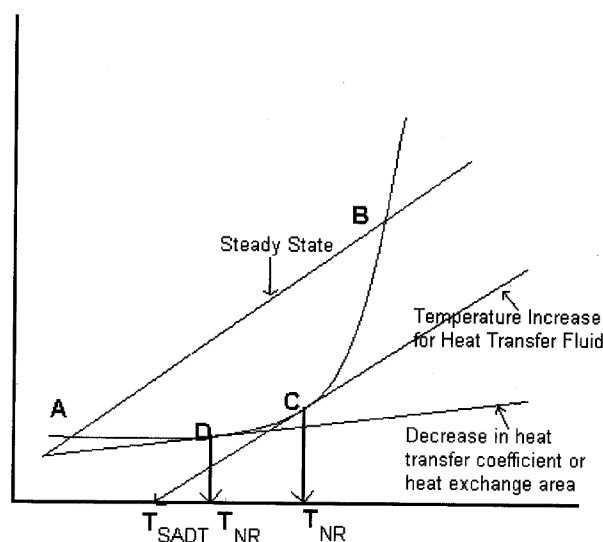


Figure 1. Thermal runaway due to high temperature.

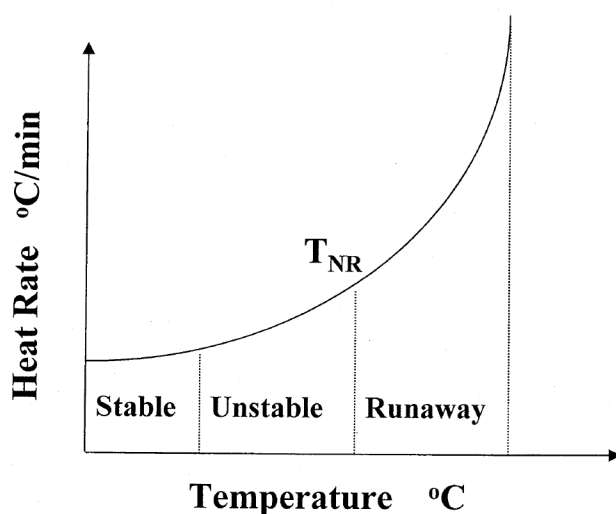


Figure 2. Thermal profile of an exothermic reaction system.

- a) Operating regime I under the control of built-in cooling facility of the reactor;
- b) Operation regime II within which the restabilization of temperature may be feasible with emergency chilling, inhibition or quenching;
- c) Operation regime III in which temperature can no longer be restabilized and where thermal explosion is imminent.

The other pathways capable of causing reaction runaway can be through operational errors, hot spots, reactant accumulation, segregation equipment failure, external heating/fire, extended residence time, spontaneous decomposition and spontaneous bubble collapse. Severity of the exothermicity depends upon material, process control strategy adopted, operation mode and other external factors.

Microcalorimetric techniques play a vital role in establishing the three above thermally sensitive regions and facilitate in evolving an inherently safe process design.

A runaway condition is the direct consequence of the loss of thermal control of any chemical reaction system in an enclosure. The loss of thermal control can subsequently trigger unwanted exothermic secondary reactions, including thermal decompositions. The entire process can lead to excessive gas or vapour generation inside the reactor space leading to abnormal pressure rise, culminating in explosion.

The direct consequence of a thermal explosion is the emission of a single- or two-phase (gas-liquid) mixture into the environment. On contact with atmospheric oxygen, the mixture, if flammable, can catch fire or lead to an unconfined vapour cloud explosion. If the release takes place in an enclosed space, confined explosion can result, leading to the destruction of the building and the surrounding plant installation. There are possibilities of secondary flash fires. The bursting of reaction

vessels can generate metallic projectiles of significant weight and velocity with damage potential. If the released vapour is toxic, it may contribute to instantaneous/long-term toxic effects to the personnel in the neighbourhood. In general, the following are the main contributors to the onset of thermal runaway.

- ◆ More than normal temperature excursions;
- ◆ Unintended introduction of additional reactant or catalyst;
- ◆ Development of high local temperature regions in reaction vessel;
- ◆ Failure of cooling system;
- ◆ Occurrence of auto catalytic reactions;
- ◆ Hazardous reactant accumulation;
- ◆ Generation of gaseous oxidizing compounds, for example nitric oxides;
- ◆ Phase separation of unstable species caused by either lack of mixing or cooling;
- ◆ Over heating of reaction vessel due to external fires.

Notwithstanding these facts, consequences of runaway reactions have not received much attention, compared to the consequences of chemical release from storage and other installations. This may be attributed to the complexity of thermal runaway system behaviour, viz. physics and chemistry of the runaway process and paucity of literature information.

Chemical characteristics contributing to thermal runaway

It is an established fact that the reactivity of chemicals is closely associated with particular groupings of atoms or specific features of their molecular structure or their energy content or their affinity towards other chemicals. Adequate information and data on the potential hazards arising from chemical reactivity for elimination or minimization of such hazards from processing are not readily available. The following data are important for identification of reactive chemicals:

- Chemical structure susceptible to either instability or other undesired reactions;
- Endothermicity;
- Decomposition energy;
- Affinity between two compounds.

Chemical structure

Some specific types of chemical structures lead to instability or unusually high levels of reactivity under appropriate circumstances. Chemical compounds can be classified as self-reacting or mutually reacting (with

other chemicals) depending on their chemical structures. Known self-reacting functional groups are nitro, nitroamino, peroxide, azide, etc. Bond groupings known to confer explosibility are classified as plasophores and explosibility enhancing groups as auxophores (nitrile or oximino).

Certain chemicals (pyrophoric) react very rapidly with air resulting in spontaneous ignition. Finely-divided metals or metal hydrides or fully alkylated metals are typical examples of this class of compounds. Some compounds undergo slow oxidation which may lead to hazardous situations, if susceptible materials are converted into peroxides, hydroperoxides and related groups. Typical chemical structures which undergo autooxidation are given in Table 1.

Many mutually reacting chemical compounds like metallic sodium, aluminium or magnesium, hydrazine and metallic hydrides can participate in reduction reactions with other materials. Several chemical accidents have been reported involving such compounds. Similarly redox compounds like propellants are capable of generating very large reaction rates. Chemical compounds like alkali metals and their hydrides, anhydrous metal and non-metal oxides and halides react vigorously and violently with water to create hazardous situations.

Endothermicity

Chemical compounds that are formed from their elements by absorbing reaction energy into their structures rather than being released are described as endothermic. Because of their high bond energy content, endothermic compounds tend to be less stable than those formed as products of exothermic reactions. The common structural features of endothermic compounds are high degree of unsaturation (double or triple bonds), high proportion/concentration of nitrogen in their molecular structure, presence of nitrogen to halogen bonds, etc. Table 2 lists the heats of formation for typical structures of endothermic compounds. The higher the endothermic heat, greater is the potential energy release per unit weight of the compound. It should be noted that endothermicity discloses the potential for reactivity or explosivity. The real power is determined by the reaction rate.

Table 1. Chemical structures susceptible to autooxidation

Ethers, acetals	—O—C—H
Iso-propyl	—Cme ₂ —H
Allyl compounds	—C=C—C—H
Vinyl compounds	—C=C—H
Styrene	PhCH=C—H

Table 2. Endothermic compounds

Compound	Structure	Endothermic heat, kJ/g
Acetylene	HC≡CH	8.7
Hydrogen azide	HN ₃	6.83
Cynogen	N≡C–CEN	5.9
Allene	H ₂ C=C=CH ₂	4.8
Hydrogen cyanide	HC≡N	4.8
Diazo methane	H ₂ CN ₂	4.6
1,2-Butadiene	H ₂ C=C=CHCH ₂	3.06
Benzotriazone	C ₆ H ₄ NHN=N	2.1
Ethylene	H ₂ C=CH ₂	2.18
Butadiene	H ₂ C=CH–CH=CH ₂	2.1
Nitrogen trichloride	NCL ₃	1.9
Ethylene oxide	CH ₂ –OCH ₂	1.75
Hydrazine	H ₂ NNH ₂	1.57
Styrene	PhCH=CH ₂	1.42
Propylene	H ₂ C=CHCH ₃	0.49

Decomposition energy

A chemical compound can release energy by decomposition or by mutual interaction. In case of the former, rapid energy release can occur when the chemical reacts with the stoichiometric amount of oxygen to give zero oxygen balance. Reactive chemicals such as explosives, contain enough of their own oxygen to give nearly zero oxygen balance on decomposition.

Reaction hazard index

The empirical reaction hazard index (RHI) based on activation energy (E_a ; kcal/mol) and decomposition temperature (T_d ; K) is given as

$$\text{RHI} = \frac{10T_d}{(T_d + 30E_a)}.$$

A number of computer software packages have been developed by various agencies to calculate the equilibrium products and heats of decomposition/combustion. Table 3 presents the decomposition energies of some reactive chemicals.

NFPA ratings for reactivity

NFPA reactivity rating (N_R) is used in conjunction with N_F , the flammability rating. It is a measure of the intrinsic rate of potential energy release from fire or explosion resulting from chemical reaction. N_R can both qualitatively as well as rigorously be estimated. For qualitative evaluation of N_R , the following guidelines based on the chemical characteristics are employed (Table 4).

Table 3. Decomposition energies of some reactive chemicals

Chemical compound	Characteristic bonds	Heat of decomposition kJ/mol
Aromatic nitro	R–NO ₂	220–410
Peroxides	C–O–O–	200–340
Aromatic diazonium	R–N ₂	130–165
Oximes	C=N–OH	110–170
Aromatic azo	R–N=N–C	100–180
Epoxides	–CH–CH ₂ –O	65–100

Table 4. Guidelines for qualitative evaluation of N_R based on chemical characteristics

Value of N_R	Chemical characteristics
0	Completely stable even when heated under fire condition.
1	Mild reactivity upon heating under pressure; reactivity with water accompanied by mild energy release.
2	Unstable and readily undergo violent chemical change, but do not detonate; violent reaction with water accompanied by explosive mixture formation.
3	Themselves capable of detonation; form explosive reaction mixtures but require a strong initiating source; explosive reaction with water.
4	Themselves capable of detonation or explosives capable of detonation or explosive decomposition or reaction at normal temperature and pressure.

Table 5. Relationship between DSC exotherms and N_R

Exotherm, °C	N_R
> 400	0
305–400	1
215–305	2
125–215	3
125	4

The rigorous method of N_R evaluation is based on the exothermic peak temperatures obtained from differential thermal analysis (DTA) or scanning calorimeter (DSC). The principal and operational details of DTA and DSC are covered later in the article. Table 5 gives the relationship between DSC exotherms and N_R .

There are exceptions in case of shock-sensitive substances. For example, these materials must have N_R of 3 or 4 depending on exotherm temperature. For shock-insensitive substances, if the calculated N_R is equal to four it must be reduced to three. On the other hand, if the substance is an oxidizer, N_R should be increased by one, but not for cases where N_R is equal to four. For mixtures, N_R should be determined only through DTA/DSC techniques. However, when the mixtures are noninteracting, engineering approximation can be adopted if the DTA/DSC exotherms of individual constituents are known.

Detonating chemicals

A detonation is defined as an explosive wave traversing a body of the material with a definite front ahead of which the temperature is low. This is in contrast to the uniform pressure build-up occurring during exothermic reactions until the vessel ruptures. It is, however, possible that a material undergoing an exothermic temperature rise of more than 1000°C can be detonated. A detonation wave may be very difficult to set off as in the case of nitromethane or ammonium nitrate. Gas detonations are easy to initiate. Liquids have also very favourable characteristics for detonation. However, liquid concentrations of less than 50% in solvents do not generally encourage detonations. Solids may be very sensitive or insensitive to detonations. In chemical practice, detonation can be avoided if gases are kept out of the explosive range and hazardous liquids and solids are kept in solution.

Caution should be exercised while separating solids or liquids from mixtures containing free oxygen, hydrogen peroxide, halogens, acetylene, nitric acid and oxides, chromates, permanganates or heavy metals. Mixtures of finely-powdered active metals like sodium, magnesium and aluminium with chlorinated solvents or oxygenated compounds can detonate.

Analysis and the methodologies of instrumental techniques*Microcalorimetry*

The experimental methods to assess the thermal instability/runaway potential are primarily based on micro calorimetry. Adiabatic calorimetry is one of the main experimental tools available to study the self-propagating and thermally-sensitive reactions. A systematic thermal hazard assessment includes procedures and techniques in the following:

- Avoiding the hazard course of reactions;
- Assessing the temperature dependency of an undesirable thermal event and its distance from the process conditions;
- Assessing the sensitivity of critical operating parameters.

Microcalorimetric techniques have been successfully employed to achieve the above requirements. The basic parameters that have to be considered for assessing the chemical reaction system are given in Table 6.

In addition to the above parameters the safe limits of temperature, feed rate and concentration have to be defined as a function of operating conditions. Assessing the true destructive potential of an undesirable chemical

activity not only involves thermal analysis of the desired chemical reaction, but also that of unwanted chemical reactions occurring in series or parallel mode or both. The most critical factor in assessing the intrinsic safety of a chemical process is to estimate the most probable thermal energy release under runaway conditions.

Microcalorimetric techniques are excellent tools for evaluating thermal explosion hazards of chemicals/chemical processes. They measure the thermal instability of a compound which is the root cause for runaway and decomposition reactions. Smaller sample size, accuracy of measurement and robustness of facility to withstand explosion are the chief advantages of these techniques. Using this, the total heat produced by all chemical reactions (primary or secondary) occurring under runaway conditions can be measured as a thermal parameter. Complex runaway reactions have been thus simplified by employing Arrhenius type equations to represent their thermal energy as a function of temperature/pressure/time under near adiabatic conditions.

The following microcalorimetric techniques have attained scientific importance due to their novelty in determining the instability or thermal runaway potential of a chemical compound.

- Thermal analysis (DSC, HPDS, DTA and TGA);
- Accelerated rate calorimetry (ARC);
- Reaction calorimetry (RC);
- Reactive system screening tool (RSST).

Thermal analyser

The major tools for thermal analysis are high pressure differential scanning calorimeter (HPDSC), differential thermal analyser (DTA) and thermo gravimetric analyser (TGA). They have been widely used for first-level thermal hazard evaluation in view of their simplicity of operation and approach. They yield quantitative data on sensitivity (exothermic onset temperature) as well as severity (heat of decomposition). However their intrinsic drawbacks are attributed to the uncertainties associated with the very small quantity of samples (5–10 mg)

Table 6. Components of intrinsic safety parameters

Thermodynamic	Kinetic	Physical
Reaction energy	Activation energy	Heat capacity
Adiabatic temperature and pressure rise	Reaction rate	Thermal conductivity
Quantum of gas generated	Rate of heat generation	
	Rate of vessel pressure rise	
	Time to maximum rate	
	Apparent activation energy	
	Onset of exothermicity	

used in the experiments, poor reproducibility of results and nonadiabatic experimental conditions. Due to this, their application in assessing the safe reaction or storage temperatures of chemical compounds and in the evaluation of heats of decomposition can result in experimental errors of the order of 5 to 10%. In spite of these drawbacks, DSC is regarded as a useful tool for the evaluation of thermal hazards and for evaluating the investigation of decomposition mechanisms of reactive chemicals. The basic principle of the DSC is to measure the heat flow as a function of temperature or time, particularly at the temperature of phase transitions. This is achieved by measuring the difference in power required to maintain the temperatures of reference and test samples.

The DSC facility consists of a furnace which is internally equipped with aluminium pans of diameter not more than 3 mm, placed beneath two thermocouples. One of these pans is loaded, filled with typically 5 mg of sample, while the other is empty. The pans are then sealed and a pinhole is provided (in case of HPDSC experiments) on the lid. An on-line PC is connected to control and monitor the DSC. The pans are kept in a chamber of approximately 250 ml capacity and purged with N_2 gas. The DSC heats the pans at a constant heating rate. From the generated thermal responses, the heats of transition, onset of endothermicity or exothermicity, etc. can be evaluated. HPDSC is used for volatile samples like acrylonitrile monomer to carry out experiments at relatively high pressures to suppress vaporization and to ensure that the decomposition (T_d) is lower than the corresponding boiling point of the sample. The data obtained are then treated conventionally as stated above.

The differential thermal analyser operates on a similar principle as that of the DSC with the exception that pure aluminum oxide powder is used as the reference substance. The output information will be in the form of temperature difference as a function of temperature or time. DTA is used for assessing thermal behaviour of chemicals/compounds at elevated temperatures ($> 600^\circ\text{C}$).

The thermo-gravimetric analyser (TGA) is based on the weight loss undergone by a chemical on receiving thermal inputs, as a function of temperature/time. Measurement of changes in sample mass as a function of temperature is made using a thermobalance. In TGA, an electronic microbalance is equipped with a furnace and a temperature-programming device. The balance is placed in a closed system so that the experiments can be conducted under different atmospheres, viz. oxygen, nitrogen and others. Temperature measurements are made through a thermocouple located nearer to the sample holder.

Several research papers¹⁻⁷ have appeared on thermal analysis of hazardous chemicals. This field has also

generated significant academic interest. The thermal decomposition reactions studied are mostly heterogeneous reactions and the rate of thermal energy release has been the subject of recent studies. The developed thermokinetic models are based on Arrhenius temperature dependency. Their validity for heterogeneous reactions is yet to be fully established. The Arrhenius parameters, viz. E and A do have practical significance, even though their theoretical interpretation is difficult in thermal analysis. Several other kinetic models have been proposed in the literature for interpreting the isothermal and non-isothermal data from thermal analysis. Among them the models proposed by Flynn and Wall² and Borchard and Daniel⁵ are important.

The complications in thermal analysis arise out of:

- Base line determination;
- Heating rate effect;
- Pressure effect;
- Time to maximum rate based on E_a ;
- Melting followed by decomposition;
- Auto catalytic reactions.

During the year 1979, the American Society for Testing and Materials (ASTM) proposed a method for determining reaction kinetics by DSC. The dependence of reaction rate constant is described by a modified Arrhenius relationship,

$$K = T^2 \exp[-E_a/RT], \quad (1)$$

which is valid for first-order reactions. The ASTM method⁸ is based on the assumption that the frequency factor A is a function of T^2 and can be used to evaluate the activation energy. The half-life, i.e. the time required for the initial concentration of the chemical species to reach half of its original value, can be expressed as

$$t^{0.5} = 0.693/k. \quad (2)$$

The calculated kinetic parameters can be checked by making a half-life estimation by DSC.

Accelerating rate calorimetry

ARC has gained importance in the 1980s for studying the self-heating reactions that cause thermal runaway. The ARC was developed by the Dow Chemical Co and was licensed to Columbia Scientific Industries (now known as Thermal Hazard Technology) of Austin, Texas which currently markets the instrument as CSI-ARCTM. It is reported in the literature for studying the runaway characteristics of chemical reactions.

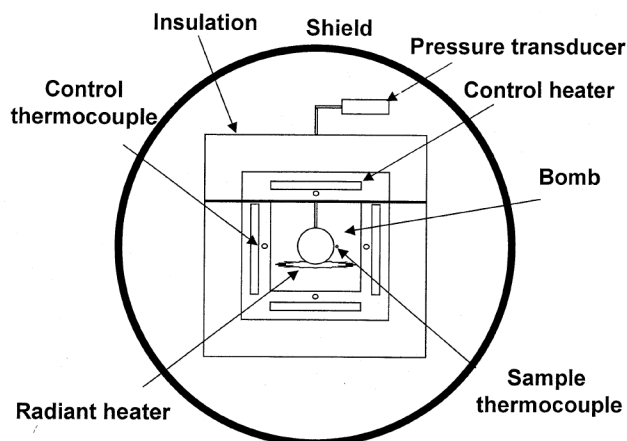


Figure 3. Accelerating rate calorimeter.

Figure 3 illustrates the calorimeter part of ARC. It is a container with its contents maintained at adiabatic conditions with respect to its environment. This is accomplished by constant monitoring of its temperature and suitably adjusting the surrounding temperature to minimize the heat gains/or losses from the container. In order to achieve an adiabatic environment over a temperature range of ambient to 425°C, the ARC is equipped with a sophisticated digital control for the heater system. The calorimeter can be divided into three temperature-control zones, viz. top, middle and bottom, with each of them equipped with their own control instrumentation. The sample container or 'bomb' is attached to a pressure transducer on the top of the chamber for close monitoring of pressure responses. The radiant heater located at the bottom of the adiabatic chamber is meant for heating the sample container at the start of the experiment.

ARC operates on the heat-wait-search principle to identify the initiation and progress of exothermic self-heating. It follows the thermal process under the adiabatic mode right from the point of onset. Figure 4 provides a typical temperature profile for an ARC experiment. An ARC experiment is initiated under the 'heat' mode and to enhance the sample and container temperatures from ambient to 50°C. It is then kept under 'wait' mode for a minimum of 10 min. This is followed by the search mode, wherein the rate of temperature rise of the sample container is monitored. If the self-heat rate is below, say 0.02°C/min, the calorimeter re-enters heat mode to further enhance the sample temperature by a prefixed increment (usually 5°C). This process of 'heat-wait-search' is repeated until the system experiences a self-heat rate above the set threshold. When the self-accelerating exothermicity is detected, the sample container is maintained under adiabatic condition as explained earlier. Under these conditions, any increase in sample temperature can be attributed totally to the exothermicity of chemical transformation. When the

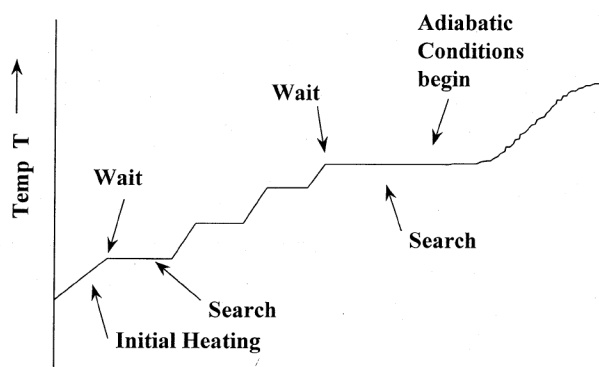


Figure 4. ARC experimental procedure.

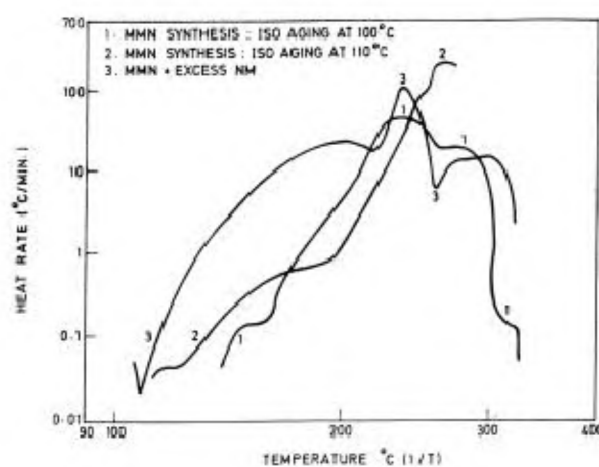


Figure 5. ARC self-heat rates for an organic synthetic reaction.

sample temperature exceeds the preset maximum attainable temperature, the ARC run is terminated.

The following data plots can be obtained from a ARC experiment.

Self-heat rate vs temperature: This plot provides information on the onset temperature of the exothermic activity and qualitative indication of the rate of energy liberation. The adiabatic temperature rise is given by $\Delta T_{ad} = [T_f - T_o]$, where T_o and T_f are the initial and final temperatures of the exotherm. A typical ARC self-heat rate plot for a synthetic mixture of an organic reaction is shown in Figure 5.

Temperature vs time: It provides information on the vigour of the exothermic reaction and also the available time span from the onset of exothermic activity to the end of the reaction.

Pressure vs time/temperature: Information on the rate of pressure and temperature rise will be most useful for estimating the vent area required for the safe operation of a reactor. The above information can be further proc-

essed employing adiabatic kinetics to generate following characteristic parameters.

- Time to maximum rate (T_{MR});
- Temperature of no return (T_{NR});
- Activation energy (E_a);
- Order of reaction (n);
- Heat of decomposition (ΔH_d).

Reaction calorimetry

Reaction calorimeter (Mettler RC1) is a computer-controlled stirred tank reactor which can be operated in batch or semi-batch mode under isothermal and adiabatic conditions. It is equipped with sophisticated instrumentation to measure and control process parameters like pH, temperature, stirring speed and the heat generation or absorption. The other information that can be obtained from a reaction calorimeter includes the heat of reaction, the specific heat of the reaction mixture, reactant accumulation as a function of process temperature and the cooling load required to maintain the process temperature within the desired limits. Reaction calorimeters are not suitable for the measurement of rate of energy release in a reaction under runaway conditions.

The reaction calorimetry is based on the principle of continuous measurement of the temperature difference between the reactor contents (T_r) and the coolant on the jacket. The quantum of energy transfer is given by equation

$$Q_r = Q_{\text{flow}} = UA [T_r - T_i], \quad (3)$$

where U is the heat transfer coefficient and A is the heat exchange area. The proportionality factor UA is determined through the calibration of RC by providing a known amount of energy to the reactor.

Heat or mass balance around the reactor is given by,

$$\begin{aligned} \text{Input} &= \text{Output} + \text{accumulation,} \\ \text{Balance area} &= \text{Inner surface of wall.} \end{aligned}$$

Heat balance, specifically, is given by

$$Q_r + Q_c = Q_{\text{flow}} + Q_{\text{dos}} + Q_{\text{loss}} + Q_{\text{accum}}, \quad (4)$$

where Q_r is the total heat flow in the reactor; Q_c is the heat supplied by the calibration heating; Q_{flow} is the heat flow across the wall; Q_{dos} is the heat due to dosing; Q_{loss} is the heat dissipated due to the internal fittings and Q_{accum} is the heat accumulation in the mass through temperature increase.

Mass balance is given by:

$$\begin{aligned} \text{Mass} &= \text{Initial feed} + \text{sum of all dosings} + \text{weight} \\ &\quad \text{of samples drawn from} \\ &\quad \text{the start to end of operation.} \end{aligned} \quad (5)$$

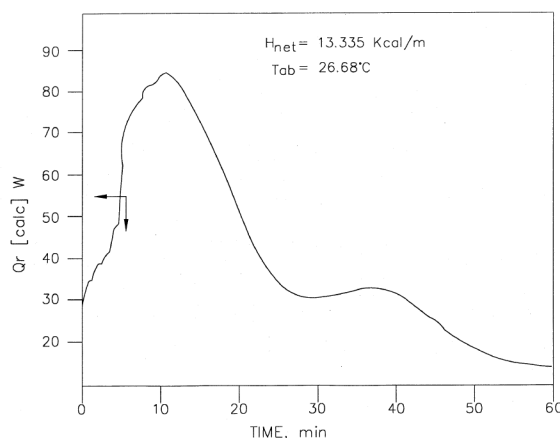


Figure 6. Exothermic heat of acrylonitrile polymerization: Reaction calorimetric studies.

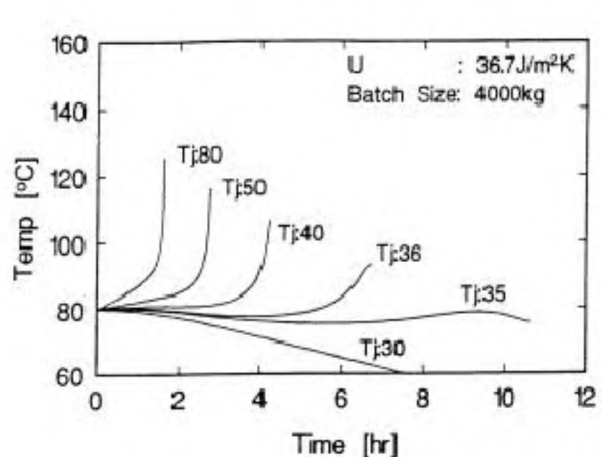


Figure 7. Heat removal profiles for styrene suspension polymerization.

A RC heat flow curve recorded for a polymerization reaction and the heat removal curve calculated from heat flow curves at various monomer, initiator and process temperatures are shown in Figures 6 and 7.

Reactive system screening tool

The RSST consists of a small glass test cell (10 cc) mounted inside a large (350 cc) containment vessel. The small glass test cell is open to the containment throughout the test. During a test, the liquid in the test can become very hot, however the containment walls remain relatively cool. The containment is pressurized to the desired level and sealed at the start of the test. Each system type (vapour, hybrid or gassy) is easily distinguished by its behaviour in the RSST.

System characterization data are obtained by first setting the RSST containment pressure equal to the maximum allowable pressure (MAP) of the process vessel and letting the reaction to run to completion. If the system behaves like a vapour system, vapour condensa-

tion will occur in the containment vessel with no significant change in pressure. In this case, the test is repeated with a back pressure equal to the relief set pressure (generally well below the MAP to minimize the energy release rate) in order to establish the boiling temperature. A good measure of the corresponding self-heating rate, \dot{T} , is then obtained from the temperature-time plot of the first test, where boiling is suppressed. With this information (no other information related to kinetics or thermophysical properties is required) a vent size can be assessed by using the relationship accounting for DIERS methodology⁹ (flashing two-phase flow and allowing for 20% overpressure relative to the relief set pressure during the removal of the reactants from the reactor vessel).

If the system is gassy in nature, the rate of pressure change \dot{P} , in the RSST containment vessel will be significant, i.e. $\dot{P} \gg 0$; a safe vent size can be obtained by conducting a single RSST test (initial containment pressure equal to P_{MAP}) and using a simple expression¹⁰, which results from assuming no early loss of reactant and homogenous two-phase conditions at the peak gas generation rate. RSST is an inexpensive calorimeter widely used to characterize the reaction system for reactor vent sizing.

Protocol of microcalorimetry in thermal hazard quantification

The conventional hazard assessment methods¹¹, viz. HAZOP (hazard and operability studies), FMEA (fail-

ure mode and effect analysis), FTA (fault tree analysis), etc. operate on the premise of thermally stable behaviour of chemicals and are directly unsuitable for assessing thermal hazards of chemical reactions. They have to be integrated with microcalorimetric studies at the front end. Furthermore, no single technique will be adequate to study all aspects of thermal hazards in the process. Keeping these in view, the Cell for Industrial Safety and Risk Analysis (CISRA) at CLRI, Chennai has formulated an integrated method to assess the thermal hazards of chemical reaction systems (Figure 8) in which microcalorimetric studies are highlighted in the front end. The exothermicity during the desired chemical process can be effectively quantified in a reaction calorimeter and the cooling requirements for a process can be estimated from RC's heat flow data. Thus, RC testing has been put in the top of the protocol to identify and control the process thermal hazards under normal operating conditions. The next stage of undesired activity/thermal instability of reactants and products for their influence on the process is analysed using DSC/DTA. It is recommended that once an exotherm is detected, further investigation under adiabatic conditions is required. A preliminary estimates for ARC onset temperature can be obtained using activation energy calculated using DSC data. When the predicted ARC onset data are within 50°C of the process temperature, ARC run is required. A thermally safe range of 50–75°C between the operating and ARC exothermic onset has been arrived at after examining 350 ARC runs from the literature¹² and comparing the results under various conditions. The margin

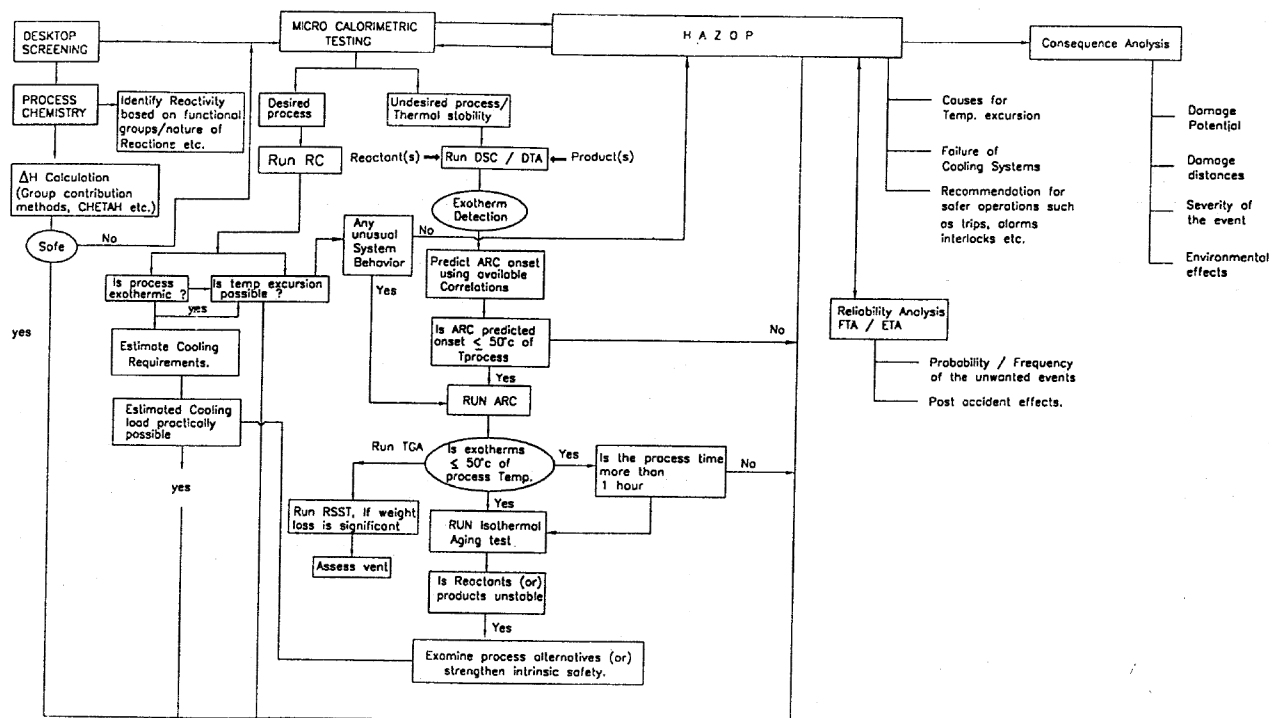


Figure 8. Integrated approach for thermal hazard assessment.

can be still reduced if possible routes through which the temperature rises are identified and modelled to obtain the exact safe temperature. The decision required at this stage is dependent on a number of factors for processes, where the safety margin is less than 50°C. Further ARC tests should be done in an isothermal mode to detect any delayed exotherm occurring between the process temperature and the ARC onset temperature. If significant pressure rise is detected during process or decomposition, independent of safety/pressure relief system, emergency vent has to be designed to dump the materials. The sizing estimations can be done using RSST. Finally, if results are positive in all the above tests, a careful review of process chemistry is recommended.

A grey area in risk assessment is the exact identification and quantification of runaway reactions or degradation of highly unstable intermediates independently or in the presence of impurities. This could be properly identified only by thermochemical strategies which follow the protocols suggested in Figure 8. It is gratifying to note that this protocol has been effectively applied in the risk assessment studies carried out by CISRA. Thus risk analysis becomes complete with such results of thermal studies which recommend safe operating temperature with appropriate justification. The recommendations emanating from these studies are useful in designing trips, alarms, alternate/standby cooling systems or to devise a different method to avoid any thermal hazard in the process.

Conclusions

With the growing awareness for safety in chemical process industries, the new and most sophisticated tech-

niques like microcalorimetry have opened the scope for better sensitivity, effective application and precise determination of safe process conditions and handling. CISRA has established its expertise in this area with several assignments to its credit, especially in the field of agrochemicals, bulk drugs and polymers. It is, indeed, a special achievement in the scientific advancement that even the most unpredictable and uncontrolled reactions also could be predicted and modelled. Needless to emphasize that these techniques enjoy a place of pride and privilege in developing an intrinsically safe process.

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