

Chemical Reaction Hazard Evaluation: Initial Calculations

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Abstract:

Reactive chemicals accidents often arise from complex and inter-related physicochemical origins, but most of them could have been foreseen by the use of thermo-kinetic data generated by laboratory tests and hazard analysis. In many instances, an initial elementary hazard evaluation could have forewarned of the potential for subsequent catastrophic events.

For small and mid-sized chemical companies initial hazard identification and reactive chemicals assessment continues to be challenging. Lack of appropriate resources such as experienced personnel, time, and physical resources are usually cited as causes for the difficulties.

In the AIChE Spring 2002 Loss Prevention Symposium we presented 12 hazard assessment tools, many of which could be used within an 8 hour study period, designed to assist in performing an initial hazard assessment. This presentation extends that analysis and details the quantitative tools that can provide clear signals about the potential hazards of the process under consideration. We will show the types of quantitative information that can be gained with and without the need for experimental data. We will also demonstrate the calculations that can be performed to yield valuable information about the target chemical processes and related safety-oriented operating strategies.

These calculation techniques are straightforward to use and provide the information needed to assess the nature and extent of the potential hazards. This information also supports the need and justification for detailed reactive chemical testing and evaluation.

Introduction

Many real-world reaction systems are close to adiabatic if the designed heat removal system (reactor jackets, internal cooling coils, refluxing, etc) fails. At the point of failure the system can cool slowly by natural convection and conduction and by utilizing the heat sink of the now latent cooling system. Under these circumstances vessels containing reactive chemicals, that are thermally active, may begin to self-heat with possibly dire consequences. Process hazard analysis, utilizing the data from appropriate hazards testing, provides information that may be used in the management of a thermal runaway before it reaches thermal explosion. This paper presents some of the techniques that enable the determination of the hazard potential and appropriate strategies for managing a runaway reaction

Thermodynamic, Kinetic and Chemical Background

Thermo Kinetic Considerations

For the majority of hazard assessment calculations involving vessels such as reactors, storage tanks, knockout-pots and still-pots the activation energy, E_a , and the reaction heat, ΔH_R , are needed. The basic equations governing heat generation under adiabatic conditions start with the Arrhenius equation (equation 1 and 2) and end in equations that define useful quantities such as time to maximum rate, t_{MR} , temperature of no return, T_{NR} and the self accelerating decomposition temperature, T_{SADT} (these terms are further defined subsequently in this paper). The equation linking temperature rise in an adiabatic system with reaction heat is also of prime importance.

$$k = A e^{-E_a/RT} \quad k' = C_0^{n-1} A e^{-E_a/RT} \quad (1, 2)$$

Equations 1 and 2 lead, by suitable manipulation, to the practical expressions 3, 4, and 5:

$$\Delta t_{MR} = \frac{RT_o^2}{E_a (dT/dt)_{To} \phi} \quad T_{NR} = \left[-\frac{E_a}{R} \left(\frac{\Delta H_r}{C_v} \right) k_{T_{NR}} \cdot \tau \right]^{1/2} \quad \frac{RT_{NR}^2}{E_a} = (T_{NR} - T_{SADT}) \quad (3-5)$$

Heat conduction in solids and liquids, in stirred or unstirred vessels, may be estimated using the Semenov and Frank-Kamenetskii theories. The area is well covered by Bowes¹. The most straightforward equation for heat conduction in an un-stirred vessel containing a solid is provided by equation 6. It is seen that the equation embodies both kinetic and thermodynamic parameters as well system parameters such as the system's heat conductivity, the material density and the vessel size. The critical parameter, δ , relates to a particular geometric shape (2.53 for a sphere, 3.32 for a cube, etc).

The normal use of the equation is that T_{AMB} (ambient temperature) is adjusted, by iteration, until a value is found such that equation 6 evaluates to the value of δ for the vessel geometry of concern.

$$\delta = \frac{E_a}{RT_{AMB}^2} \cdot \frac{a^2 \Delta H \rho A}{\lambda} \cdot e^{E_a/RT_A} \quad (6)$$

Without delving into the derivations of these equations it is clear that they are very useful in various aspects of hazard evaluation but require that a number of chemical and engineering parameters are known about the system under scrutiny.

¹ P.C Bowes, "Self Heating: Evaluating and Controlling the Hazards", Elsevier, 1984.

Consider the Chemical Reaction

Additional to the qualitative approach of reviewing the molecular structure for high energy groupings² that act as plosophores or auxoploses³ the actual chemical reactions being conducted must be carefully considered. Tables 1,2, and 3 provide (incomplete) lists of a variety of types of reactions and examples of the more common causes for concern for each reaction.

Table 1. Reactions Having a High Hazard Potential

Reaction	Example of Concern
Curtius Rearrangements	Use of acyl azides, nitrous acid or hydrazine.
Decarboxylation:	Removal -COOH with CO ₂ evolution – possible pressure hazard.
Diazotizations	Especially if followed by reduction to the hydrazine (SnCl ₂ reaction); replacement with a -OH or to replace the -NH ₂ with -H
Displacements	Uses oxalyl chloride to displace -OH. (CO ₂ , CO, HCl generated)
Epoxidations	Epoxides are high energy strained rings
Esterification	When using oxalyl chloride
Friedel Crafts (AlCl₃)	Friedel Crafts reactions and their quenches due to use of AlCl ₃ , BCl ₃ , H ₂ SO ₄ , HF.
Grignard Reactions	Reactions require an activation period and are highly exothermic.
Hydrolysis	Hydrolysis of a cyano to an amide oxidatively using H ₂ O ₂
Metallations	Uses n-BuLi, t-BuLi, LDA, NaHMDS
Nitrations	Uses nitric acid and strong acids like sulfuric or triflic acid (trifluoromethane-sulfonic acid). Nitrations are very exothermic. The potential for thermal runaway, initiating violent decompositions and explosions exists.
Oxidations	Use of Jones [chromium based], O ₃ , H ₂ O ₂ , KMnO ₄ (with large exotherms), peroxy acids, cleavage using sodium periodate
Peptide Formations	Use of HOBT (1-hydroxybenzotriazole hydrate).
Quenches	When PCl ₅ or POCl ₃ have been used in a previous step
Reductions	Any nitro compound or high energy functional group reduction. Reductions using LiAlH ₄ , Fe or Zn powder with HCl or acetic acid, hydrazine in caustic; hydrogenations by generating H ₂ <i>in-situ</i> using hydrazine, NaBH ₄ in CH ₃ OH or C ₆ H ₁₂
Sulfonation	Sulfonation of an amine to form sulfonamide

² Bretherick's "Handbook of Reactive Chemical Hazards", 6th Edition, Butterworth-Heinemann 1999.

³ The term *plosophore* refers to a functional group within a molecule that directly confers explosive properties to the molecule when subjected to severe impact (for example, azide, fulminate). An *auxoplose* group tends to increase the plosive nature of the molecule by augmenting the effect of plosophores already present (for example, metals usually increase the plosive nature of a molecule containing a plosophore).

Table 2. Reactions Having a Moderate Hazard Potential

Reaction	Examples of Concern
Acylation	Use of acetic anhydride or acid chloride acylations of amine
Additions	Additions of alkyl metals to ketones or aldehydes, cyano groups, carboxylic acids or esters, or any other functionalities.
Alkylations	Alkyl halide or amine (aromatic or aliphatic) used with a phenol.
BOC protections-deprotections	BOC (t-butoxycarbonyl) used to protect/deprotect amines. Unreacted BOC anhydride in waste streams can liberate CO ₂ and isobutylene.
Condensations	C-C bond or C-N bond formation with elimination of small molecule.
Cross Coupling reactions	These reactions involve the use of a metal to mediate a C-C bond formation, usually a Pd(0) species (Pd tetrakis triphenyl-phosphine); Suzuki coupling; zincate coupling by transmetalating a Grignard or a lithium species with zinc chloride.
Dealkylation	Demethylation of methoxy group using HBr or HCl to generate methyl bromide or methyl chloride. BBr ₃ and BC1 ₃ used at low temperatures.
Displacement	Displacement of -OH with -Cl using PC1 ₅ . Reactions are heated, the distilled PC1 ₅ is a problem to quench due to the delayed water reaction. Use of LiCl in NMP to displace a triflate.
Esterification	Using oxalyl chloride and acid followed by alcohol addition. Reaction liberates CO and HCl - pressure hazard. Also by using acid and SOCl ₂ and then adding the alcohol.
Ether Formations	Ethers formed via Williamson synthesis by alkylating with alkylhalide.
Halogenations	Reactions of alkyl or aryl groups with halogens such as Br ₂ Cl ₂ or I ₂ .
Hydrolysis	Cyano using Lewis acid (e.g. BF ₃). See other categories for other hydrolysis/quench reactions.
Peptide Formations	Coupling of an amine with an acid using PPAA, EDC, EEDQ, or alkyl-chloroformate mediated peptide coupling, or N-hydroxy succinamide.
Reductions	Use of triethylsilane, NaBH ₄ (except with methanol), tri-acetoxyboro-hydride, B ₂ H ₆ generated <i>in situ</i> via BF ₃ / NaBH ₄ . Birch reductions with Na or K is category. Reductions using H ₂ and Pd, Pt, Raney Ni, Ru, Ir
Sulfonation	Use of SO ₂ Cl ₂ with an alcohol (plus base) to form a mesylate or tosylate. Use of triflic anhydride to form a triflate

Table 3. Reactions Having a Low Hazard Potential

Reaction	Examples of Concern
Debenzylations	Involve the removal of benzyl usually via catalytic hydrogenation forming toluene as byproduct is very low energy.
Dehydration	Removal of water (Dean Stark trap). May involve condensations or esterification.
Hydrolysis	Hydrolysis of an ester with an acid or a base; an amide to the acid.
Oxidations	Cryogenic Swern-type oxidations (DMSO & TFAA at -70° C) generate (CH ₃) ₂ and are mildly exothermic. <i>Note in the absence of mediating solvent neat DMSO and TFAA combined is highly exothermic.</i> Tempo oxidations are also mildly exothermic.
Reduction	Cryogenic Birch reduction with liquid NH ₃ (-78 °C) using Li or Ca. Hydrogen generated <i>in-situ</i> using ammonium formate.
Sulfonation	Only the Sulfonation on the oxygen to form a tosylate is category 3.

Note: Processes such as crystallizations, optical isomer resolution, salt formation, polymorph conversions generally are low level exothermic reactions or thermally neutral

Any time that a high hazard reaction (Table 1) is contemplated both adiabatic and isothermal calorimetry should be performed to evaluate the nature and extent of the

hazards that could arise from the desired or undesired reactions. Determination of the principle thermo-kinetic parameters (E_a , A , and ΔH) should be considered as the minimum level of hazard evaluation in these situations.

The preferred approach is to conduct process hazard evaluations during the development and design phase of the manufacturing process. These studies dictate the need to generate hazards test data that will be required to provide guidance for the design of appropriate lines of defense and safety interlock systems.

The less-preferred approach, but sometimes necessary, is having to use the data during the management of a thermal runaway. The second part of the paper provides some simple calculation tools that can provide guidance quickly using a variety of thermal information, including how to operate without the needed data.

Applying Test Data to Designing Lines of Defense

Initial Screening Calculations

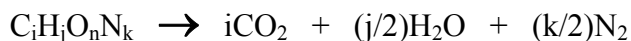
In the absence of real hazards test data there are a number of numerical, semi-quantitative methods available to assist in the assessment of chemical stability. The information provided by these methods should be used to determine the severity of the risk that might be incurred by proceeding without knowledge of reliable values of E_a , A , and ΔH .

Oxygen balance

The oxygen balance of a compound is the difference between the oxygen content of the compound and that required fully to oxidize the carbon, hydrogen and other oxidizable elements present to carbon dioxide, water, etc. It is normally expressed as a percentage.

It is known empirically that explosives with an oxygen balance close to zero are the most powerful having maximum energy release at this equivalence point. If there is a deficiency of oxygen present, the balance is negative, and deficient amount of oxygen needed for the oxidation is reported with a negative sign. An excess of oxygen gives a positive balance, means that there is more than sufficient oxygen present in the molecule for complete conversion to the simple molecules. Clearly, such a methodology that estimates the possibility that a particular compound, defined only by its molecular formula, might be a good explosive is of value to the task of assessing the hazard potential of a molecule.

For substances containing only carbon, hydrogen, nitrogen and oxygen, the balanced reaction is given by:



The reaction implies that sufficient oxygen exists within the molecule for complete oxidation of carbon and hydrogen that is the oxygen balance is zero.

The oxygen balance, OB, is defined by the equation:

$$OB = \frac{-1600 \times [2i + (j/2) - n]}{MWt}$$

Methyl nitrite (CH₃ONO), for example, has an OB of +39.3% and therefore should be considered as thermally unstable and possibly explosive. The known data for the compound supports this simple paper evaluation. There are several examples of well-known chemicals that are not explosive yet have an OB \approx zero. The evaluation of the hazard potential based on the oxygen balance is not absolute, but only an indicator. The actual significance of the rating depends on how the oxygen is bonded in the molecule.

Several compounds that are known explosives have a negative oxygen balance, for example, TNT has OB = -79%. A conservative use of this approach is to be concerned about molecules that show a positive OB but do not be unconcerned about molecules that have a negative OB.

Rules of Thumb

There are several rules-of-thumb that pertain to hazard assessment. One of them is the 100 degree rule. This rule states that if the experimentally determined T_{ONSET}, measured by a differential scanning calorimetry (DSC) experiment, is 100 °C away from the process temperature then the process will not experience that thermal activity. Unfortunately, this rule, although simple to use, makes many assumptions that are not valid. The main problem is that the rule significantly underestimates the hazard potential because the temperature at which a runaway reaction may become hazardous is tied to E_a and the size and type of vessel. A better approach would be to determine qualitatively the nature of the potential hazard using the techniques described in this paper. If it is believed that there is a reasonably high hazard potential then the appropriate thermal data should be obtained in order to make sound hazard assessment decisions.

Reaction Heat Estimation

The energy that is involved in a reaction can be estimated by Hess's Law if the enthalpies of formation of the reactants and products are known. The enthalpy of formation, ΔH_f , is defined as the heat released during the formation of a substance from its elements at 20 °C (or 25 °C) and 1 bar. It can be determined theoretically and experimentally measured. The theoretical methods include those that use bond contributions, for example average bond summation methods, and ones that use group contributions, (e.g., CHETAH). A comparative evaluation of various methods for predicting thermodynamic properties and enthalpies of combustion was made under the DIPPR program. CHETAH was deemed, in general, the most accurate program and also the most broadly applicable.

Once $\Delta H_{\text{reactants}}$ and $\Delta H_{\text{products}}$ are known, the enthalpy of reaction or decomposition can be calculated. Most of the decomposition products are small molecules such as H_2O , CO_2 , CO , C , N_2 , NO , NO_2 , SO_2 , and CH_4 . Enthalpies of decomposition, which are estimated on the basis of these products, usually result in a conservative prediction. In practice, decomposition is nearly always incomplete due to the evaporation of volatile reaction products and polymerization or tar formation by heavier molecules. Only in the case of very high efficiency explosives do the products defined by CHETAH approximate the experimental values. Computations via CHETAH indicate the maximum energy yield as constrained by stoichiometry alone, which is used as a parameter for predicting impact sensitivity.

The CHETAH program, first issued by the American Society for Testing and Materials in 1974, was used to screen organic and organo-metallic chemicals and mixtures for their potential to undergo a violent decomposition leading to a deflagration or detonation. While it is still extremely useful for this application, industrial experience has shown that it is also a valuable tool for the estimation of thermodynamic data. The program also estimates enthalpy, entropy, heat capacity, and Gibbs free energy data for specified chemical reactions, including inorganic salts.

CHETAH classifies the energy hazard potential of a composition by a pattern recognition interpretation of the four internally generated criteria listed below:

1. *Chemical Energy Density* For the first criterion, substances are placed in four different hazard classes based on enthalpy of reaction/enthalpy of decomposition. In practice, classes C and D (lower energy primary decompositions) do not recognize the fact that the chemicals under consideration still may have the potential to show rises in temperature of more than 600 °C, which can result in significant and severe gas production and high pressures.

2. *Probability Correlation*. The second criterion is based on the difference between the combustion enthalpy in excess oxygen and the maximum decomposition enthalpy. This second criterion assumes that a substance with sufficient oxidizer within its own structure to convert fully to normal oxidation products ($\text{OB} \sim 0$) presents a larger energy hazard potential than a substance that does not have sufficient oxygen. This hazard classification is based on a combination of criterion 1 and criterion 2.

Substances with a *high* hazard potential according to the first criterion are classified as such only if a difference between the enthalpy of combustion in excess oxygen and the maximum enthalpy of decomposition is less than 3 kcal/g; *medium* if the difference is between 3 and 5 kcal/g, and *low* if the difference exceeds 5 kcal/g.

3. *The Oxygen Balance*. The oxygen balance related to oxygen available in the molecule, as defined earlier, is calculated as the third criterion for hazard potential ranking in CHETAH. As discussed previously, it is known empirically that explosives with an oxygen balance close to zero are the most powerful.

4. *The "Y" Criterion.* The fourth criterion for hazard potential classification in the CHETAH program takes into account the number of atoms in a molecule of the substance involved, and is called the "Y" criterion.

The four criteria provide a conservative hazard rating for the molecules under study.

Using Thermo-Kinetic Hazard Test Data to Generate Hazard Indicators

Background

Figures of Merit, a term coined by the ASTM, are a group of numerical indicators that together provide an indication of the potential hazards of a molecule or chemical reaction, from a thermal stability viewpoint. Details are presented in the ASTM standard.⁴

This approach evaluates a number of parameters derived from an exothermic reaction (E_a , A , ΔH and T_{ONSET}), and some engineering quantities that relate to the system (density, thermal conductivity, and mass of material) to derive the set of eight Figures of Merit.

- **A d i a b a t i c d e c o m p o s i t i o n
t e m p e r a t u r e r i s e , $\Delta T_{AD I A B}$**

This parameter provides an estimation of the computed temperature at which a specimen would attain if all of the enthalpy (heat) of decomposition reaction were to be absorbed by the sample itself. High values represent high hazard potential.

$$\Delta T_{AD I A B} = \frac{Q_{RXN}}{m \cdot C_p}$$

- **C r i t i c a l h a l f t h i c k n e s s , a**
An integral part of the heat balance evaluation is the mass of material present and the geometry of the containment vessel. These data may be expressed as the half thickness of a sample in an *unstirred container*. The critical half thickness relates to the mass of material present in the particular vessel above which a runaway reaction will occur unless the heat removal of the system is increased in some manner.

- **C r i t i c a l t e m p e r a t u r e , T_c**
The critical temperature estimation of the lowest temperature of an *unstirred container* at which the heat losses to the environment are less than the retained heat leading to a buildup of internal temperature which can lead to a thermal-runaway reaction.

⁴ ASTM E1231-01 Standard Practice for Calculation of hazard Potential Figures-of-Merit for Thermally Unstable Materials, 2001.

- I m p a c t s e n s i t i v i t y , S S

This empirical parameter provides an estimation of the sensitivity of a material to an impact-induced stimulus relative to *m*-dinitrobenzene used as a reference material. A positive value indicates greater sensitivity; a negative value less sensitivity. The reliability of this go-no-go indication is provided by the magnitude of the numerical value. ASTM use the term *shock* sensitivity, which is misleading because “shock” could imply *shock*-wave sensitive or electrically *shock* sensitive – neither of which are meant by this parameter.

- E x p l o s i o n p o t e n t i a l , E P

The magnitude and sign of the explosion potential are used to estimate the potential for a rapid energy release that may result in an explosion. Positive values indicate likelihood.

- T i m e - t o - t h e r m a l - r u n a w a y ,
t_{NR}

This parameter is an estimation of the time required for an exothermic reaction, in an adiabatic container, to reach the point of thermal runaway as defined by $q_{\text{reaction}} > q_{\text{removal}}$.

- I n s t a n t a n e o u s p o w e r
d e n s i t y , I P D

This parameter is the amount of energy per unit time per unit volume initially released by an exothermic reaction. This parameter attempts to link both kinetics and thermodynamics to hazard potential. The parameter provides a key to the amount of energy released at 250° C. The energy of activation, reaction heat at 250° C and the pre-exponential factor must be known for this parameter to be calculated.

$$IPD = \Delta H_{RXN} \cdot A \cdot \rho \cdot e^{-E_a/523R}$$

- N F P A i n s t a b i l i t y r a t i n g , I R

The instability rating is an index value for ranking, on a scale of 0 to 4, the instantaneous power density of materials. The greater the value, the more unstable the material.

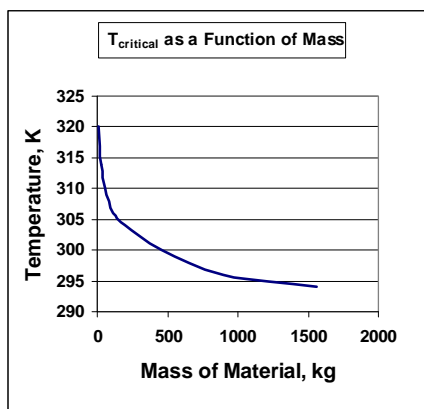
Example of Use of Figures of Merit

The kinetic parameters needed in this calculation may be obtained from DSC data. This technique is best applicable to simple, single reactions whose behavior can be described by the Arrhenius equation and the general rate law. For reactions that do not meet these conditions, this technique may, with caution, serve as an approximation of the relative thermal hazard potential of a system. Table 4 shows the results of the calculation of eight parameters for a hypothetical molecule with the experimentally determined values shown in the first part of Table 4.

Table 4. Inputs for and Figures Merit of a Hypothetical Molecule

Experimentally Determined		
Activation Energy	26.50	kcal/mol
Initial Temperature, T_{INIT}	300	K
Environmental Temperature, T_{AMB}	300	K
Frequency Factor	2.00E+11	1/s
Enthalpy of reaction	1.26	kJ/g
Calculated Thermal Stability Indicators		
Time to Thermal Runaway from T_{INIT}	11.1	days
Adiabatic Decomposition Temperature Rise	697	K
T_{CRIT} for Specific Mass and Shape	298	K
Critical Half-Thickness at T_{AMB}	0.39	meters
Explosion Potential, EP	0.16	
Shock Sensitivity, SS	0.26	
Instantaneous Power Density, IPD	1942.3	W/ml
Instability Rating (NFPA 704)	4	

An example of this screening tool involves a hypothetical molecule having values of E_a , A , and ΔH (Table 4). Storage of the material could pose a problem if delivered to the



plant site in a 1,000 kg Flexible Intermediate Bulk Container (FIBC). The calculated T_{CRIT} is 296 K which is four degrees below the current storage temperature ($T_{AMB} = 300$ K). The time to runaway at 300 K is 11 days. The graph of T_{CRIT} vs. mass stored, at 300 K however shows that if the package size is reduced to 25 kg containers T_{CRIT} increases to 314 K. If only FIBCs can be used then refrigerated storage (273 K) would be used to increase the time to runaway reaction to nearly 750 days and increase the critical package size to well over the 10,000 kg.

Using Adiabatic Information to Derive Specific Engineering Quantities

Time to Maximum Rate (t_{MR})

This is an approximate measure of the time available before the chemical self-heats from the selected storage temperature, T_{INIT} , to a higher temperature where the reaction is much faster. Mathematically, by selecting the higher temperature as that temperature at which the runaway rate is the maximum provides a straightforward route to Δt_{MR} . It is an idealized measure of the time to the maximum rate of the runaway reaction if there is no action taken and the reaction proceeded adiabatically.

In a practical sense this time is related to the actual time that may be available to initiate measures that could allow control of the reaction to be recovered. Time-to-Maximum-Rate is an intrinsic parameter, related only to the properties of the molecule or reaction and independent of the state of the system.

Table 5. Time to Maximum Rate (t_{MR}) as a Function of Reactant Temperature

Storage Temperature, T_o		Time to Maximum Rate, t_{MR}		
(°C)	(K)	(days)	(hours)	(minutes)
80	353	55.9	-	-
100	373	2.03	-	-
120	393	0.10437	2.5	-
140	413	-	0.172	10.3

Temperature of No Return, T_{NR}

Consider an exothermically reacting mixture, or pure substance (such as a monomer) stored in a vessel. It is clear that either the system will come to equilibrium with its surroundings or a thermal explosion will result. The actual outcome depends on heat generation rate vs. heat loss. In other words, this T_{NR} is the maximum temperature above which the heat generated by the reaction exceeds the cooling capacity available. Therefore T_{NR} is an extrinsic property - not solely a fundamental property of the reaction chemistry - depending on the state and properties of the vessel such as the cooling capacity of the vessel, its size and geometry, fill level, rate of agitation, etc. This variable is frequently used to assess the safety of storage tanks and drums where cooling is by natural convection to air.

Since the use of T_{NR} requires that the heat loss characteristics of the vessel are known it is usually too late to obtain reliable estimates of the heat characteristics of a vessel containing a reactive monomer that is self heating. Therefore the vessel's time constant, τ , needs to be estimated⁵ in anticipation of runaways in order that reliable estimates of T_{NR} may be made as part of a runaway management strategy.

In the event of unexpected self-heating plausible guesses can be made to help in understanding the time available to remediate or reverse the course of the self-heating. Table 6 provides a set of commonly accepted typical values for a variety of containers.

⁵ The thermal time constant, τ , of a vessel relates to the thermal mass of the vessel. The higher the time constant the longer the vessel takes to cool down. The exact definition is "the time it takes for the temperature to reduce by $1/e$ ". A value for τ may be determined by filling the vessel with hot water and measuring the water temperature vs. time as the vessel cools. A plot of $\ln(T_{WATER} - T_{AMB})_{time}$ vs. time gives τ as the slope of the line. A straightforward explanation of the math involved is given on the web page <http://scienceworld.wolfram.com/physics/NewtonsLawofCooling.html>

Table 6. Time Constants for Various Vessels

<u>Container</u>	<u>Content</u>	<u>Time Constant (min)</u>
1 liter Polythene bottle	Liquid	15
1 liter Polythene bottle	Solid	100
4.5 liter Metal can	Liquid	200
4.5 liter Metal can	Solid	250-300
25 kg Paste bucket	Solid	500
210 liter Drum	Liquid	1,000
210 liter Drum	Solid	1,500
1 ton tank	Liquid	2,200 (~1.5d)
10m ³ tank (~2,640 gal)	Liquid	4,400 (~3d)
100m ³ tank (~26,400 gal)	Liquid	9,600 (~6 ² / ₃ d)
1000m ³ tank	Liquid	22,300 (~15 d)
10,000m ³ tank	Liquid	49,000 (~34 d)

However, if no hazards testing has been performed on the vessel contents none of these calculations can be performed with the result that “fire-fighting” efforts will be largely a matter of guesswork.

Self-Accelerating Decomposition Temperature, T_{SADT}

This parameter is a measure of the maximum ambient (air) temperature that can be tolerated without thermal runaway, for a selected operating temperature. SADT is influenced by the size of the storage container similar to T_{NR}. It is a parameter that specifically addresses the storage of potentially thermally unstable materials.

At the critical temperature, T_{NR} or T_{SADT}, heat generation caused by an internal runaway reaction is equal to the heat loss of the system vessel. This implies mathematically that the slopes of the heat loss and heat generation curves are equal. Therefore, equating the differentials of the heat gain and heat loss and rearranging gives the useful expression, shown earlier:

$$\frac{RT_{NR}^2}{E_a} = (T_{NR} - T_{SADT})$$

If T_{NR} is known T_{SADT} can be calculated by a straightforward trial and error series of calculations (Excel Goal Seek works very well for this). Steps to determine SADT are:

1. Determine time constant for vessel
2. Determine ΔH_{RXN} and E_a from adiabatic calorimetry
3. Pick T_{NR} by estimating k_{T(NR)} from experimental data
4. Calculate T_{NR} by iteration
5. Evaluate T_{SADT}

Compared to the full scale UN test protocol⁶ there is a much to recommend this method for estimating T_{SADT} using data from a lab-scale adiabatic calorimeter. Fisher⁷ illustrates the principle of using adiabatic calorimetry data and provides experimental verification of T_{SADT} by this technique together with comparisons of the classical UN experimental method. The agreement shows that T_{SADT} values derived from adiabatic data are usually within 3-4 °C and, by statistical analysis of the ARC and UN test data, are shown to be lower (more conservative) than the UN test data. These results substantiate the position that a very good estimate of T_{SADT} , certainly from the point of view of assessing process safety, may be obtained from adiabatic calorimetry.

Developing Intervention Strategies During Runaway Reactions

Case 1: No Hazard Test Data is Available

This estimation procedure provides a means of estimating a value of the activation energy from the data of the runaway reaction.⁸

Imagine that a storage tank has just been discovered to be self-heating. The calculations required to develop an effective intervention strategy are based on the time to maximum rate, t_{MR} and therefore require knowledge of E_a . Unfortunately, the plant has not done a good job of hazard evaluation and there is no data available for E_a . This calculation shows how to work around this apparent difficulty to obtain a reasonable estimate of t_{MR} . Recalling the equation for t_{MR} it is noted that energy of activation and temperature rise rates are required in order to solve for t_{MR} .

$$\Delta t_{MR} = \frac{RT_o^2}{E_a (dT/dt)_{T_o} \phi}$$

In one hour the temperature of the contents (liquid) of the large insulated vessel has increased from 35 to 36 °C. At this point in the exotherm the assumption of zero-order kinetics is valid.

$$dT/dt = (36 - 35)/60 \text{ min} = 0.01667 \text{ °C min}^{-1}.$$

Therefore

$$t_{MR,1} = 1.14 \times 10^7 / (E_a) \text{ minutes}$$

⁶ Recommendation on the Transportation of Dangerous Goods. Manual of Test and Criteria, 3rd Revised Edition, (ST/SG/AC.10/11/Rev. 3, United Nations 1999), Section 28.4.2, Test H2.

⁷ H.G. Fisher and D.D. Goertz, J Loss Prev. Proc. Ind., **4**, 305-316 (1991)

⁸ D.I. Townsend, H.D. Ferguson and H. T. Kohlbrand, Proc. Safety Prog., **14**, 71-76 (1995).

In order to estimate t_{MR} at 35.5 °C requires knowledge of E_a . The best we can do is to use a range for E_a , which for a normal reaction is between 10 and 40 kcal mole⁻¹. Using this range of values we can estimate t_{MR} as 18.9 > t_{MR} > 4.7 hours.

However, the temperature in the vessel is still rising and after another hour the temperature has reached 37.2 °C.

$$\frac{dT}{dt} = (37.2 - 36)/60 \text{ min} = 0.02 \text{ } ^\circ\text{C min}^{-1}.$$

Therefore,

$$t_{MR,2} = 0.953 \times 10^7 / (E_a) \text{ minutes}$$

With two value of t_{MR} we can now obtain an estimate of E_a :

$$t_{MR,1} - t_{MR,2} = [1.14 \times 10^7 / (E_a)] - [0.953 \times 10^7 / (E_a)] = 60 \text{ minutes}$$

Solving for activation energy gives $E_a \approx 30.4 \text{ kcal mole}^{-1}$ therefore $t_{MR, 37.2} \approx 5 \text{ hours}$.

These estimates for E_a and hence t_{MR} will become refined as the exotherm progresses. At this stage in the exotherm it is clear that there is not a lot of time to attempt to turn the runaway around before the maximum runaway rate is experienced.

Case 2: Hazard Evaluation Test Data is Available

This situation involves a monomer storage tank that is being pumped into a reactor for polymerization at a controlled rate. Test data have been obtained for the reaction heat. The complete set of data, pertinent to the polymerization reaction, is shown in Table 7.

Table 7. Monomer Storage Tank Basic Data

Parameter	Quantity
Volume of un-cooled monomer storage tank	7 m ³
Planned addition rate to reactor	6 hours
Mass of monomer in storage tank	2,500 kg, 40% Fill
Maximum monomer transfer time	1 hr
Maximum water addition rate	100 kg min ⁻¹
Reaction heat for polymerization reaction	145 cal g ⁻¹
Adiabatic temperature rise, ΔT_{AB}	363 °C
Effective specific heat of reaction mass	0.4 cal C ⁻¹ g ⁻¹
Viscosity at 40% conversion	< 100 cP
Minimum temperature of heat transfer fluid	20 °C
Effective heat transfer (minimum)	1 x 10 ⁵ cal hr ⁻¹ m ² °C ⁻¹
Effective heat transfer area at 40% fill (minimum)	8 m ²

The data shown in Table 8, were obtained from an adiabatic calorimetry run for the polymerization, give the temperature rise rates as a function of reaction temperature.

Table 8. Experimentally Determined Temperature Rise Rate Data for Monomer

Temperature (°C)	dT/dt (°C min ⁻¹)
45	0.012
55	0.025
65	0.065
75	0.15
85	0.34
90	0.6
95	0.9
100	1.4
105	2.5

The monomer tank is self-heating and, at this point, a couple of strategies are available to mitigate the situation:

1. Allow the material to polymerize in the storage tank.
2. Add water to the monomer tank to cool the contents

Strategy 1: *Can the material be allowed to polymerize in the storage tank?*

The available data may be used to evaluate how reasonable this strategy may be. Consider the heat balance of the storage tank vessel:

$$q_{reaction} = q_{removal} \quad (9)$$

Each side of the equation may be evaluated using the available experimental data. For $q_{reaction}$ the following holds for dT/dt at T_{RXN} , the temperature of the vessel's contents:

$$\begin{aligned} q_{reaction} &= \frac{dT}{dt} (\text{°C} \cdot \text{min}^{-1}) \cdot C_p (\text{cal} \cdot \text{°C}^{-1} \cdot \text{g}^{-1}) \cdot 60 (\text{min} \cdot \text{hr}^{-1}) \\ &= 8.74 \times 10^7 \frac{dT}{dt} (\text{°C} \cdot \text{min}^{-1}) \text{ cal} \cdot \text{hr}^{-1} \end{aligned} \quad (10)$$

For $q_{removal}$ the following holds:

$$(11)$$

$$q_{removal} = U(\text{cal} \cdot \text{hr}^{-1} \text{m}^{-2} \text{°C}^{-1}) \cdot A(\text{m}^2) \cdot (T_{RXN} - T_{AMB})(\text{°C})$$

$$= 8 \times 10^5 \cdot (T_{RXN} - T_{AMB}) \quad \text{cal} \cdot \text{hr}^{-1}$$

Equating $q_{reaction}$ and $q_{removal}$ and evaluating yields the equation:

$$T_{RXN} - T_{AMB} = 108 \text{ dT/dt}$$

This equation is solved by assuming a particular value for T_{RXN} and evaluating T_{AMB} , needed to hold the reaction at the thermal balance point. This approach assumes a number of important things. First, that all the data shown earlier are available and correct. Second that the effective heat transfer of the vessel does not decrease due to possible build-up of polymer on the walls.

Taking a couple of reaction temperatures we note that provided heat generation and heat removal remain as expected the reaction may be safely held in the vessel up to about 90 to 95 °C given that the ambient temperature is not less than 25 °C.

T_{RXN} (°C)	dT/dt (°C min ⁻¹)	T_{AMB} (°C)
90	0.34	48.28
95	0.6	25.2
100	0.9	-2.2

Strategy 2: *Can a water dump into the vessel be used to control the reaction?*

The temperature of the vessel's contents rises to the range of 70 – 85 °C. The vessel can hold at least 2.5 m³ of water.

It is well known that water can often be used to successfully reduce a vessel's temperature and often reverse a runaway reaction. Obviously this is a course that can only be used if the reaction mass is below 100 °C.

The reaction heat is 363 cal g⁻¹. The addition of 2,500 kg cold water (30 °C) will raise the effective heat capacity of the emulsion to about 3.5 [=1+(1.0x2,500)/(0.4x2,500)]. Even at the reduced addition rate of water of 20 kg min⁻¹ the results indicate that up to about 95 °C the heat removal is ahead of heat generation.

However, since the reactor has been filled with water the contents must be removed. This strategy buys time for mitigation activities but does not ultimately turn the runaway reaction around. Again, a number of simplifying assumptions are being made.

T_{RXN}	$(dT/dt)_{T_{RXN}}$	Heat Absorbed	Heat Generation
(°C)	(°C min ⁻¹)	(cal min ⁻¹)	(cal min ⁻¹)
75	0.15	900,000	150,000
80	0.22	1,000,000	220,000
85	0.35	1,100,000	350,000
90	0.6	1,200,000	600,000
95	0.9	1,300,000	900,000
100	1.4	1,400,000	1,400,000

Data derived for $T_{WATER} = 30$ °C; $q_{REACTION} = C_{V,MONOMER} \bullet (dT/dt)_{T_{RXN}} \bullet M_{MONOMER}$; $q_{REMOVAL} = (T_{RXN} - T_{WATER}) \bullet C_{V,WATER} \bullet \text{Water Add Rate}$

Summary

Hazard evaluation and assessment of a chemical process is based, in large part, on the thermodynamics and kinetic properties of the system and on the explicit nature of the chemical reaction(s) involved. This paper has shown that oxygen balance and reaction heat estimations may be used, in the absence of experimental values for E_a , A , and ΔH , to provide initial guidance about the potential hazards of a particular chemical process.

It has been illustrated that, with reliable values for E_a , A , and ΔH , valuable information about the actual processing hazard may be gained from the Figures of Merit and from evaluation of t_{MR} , T_{NR} and T_{SADT} . This paper has also presented calculation strategies that may be used to determine the best course of action in the event of a runaway reaction.

Symbol	Meaning	Units
$(dT/dt)_{T_0}$	Temperature rise rate at T_0	deg K .min ⁻¹
A	Pre-exponential factor in Arrhenius equation	min ⁻¹
a	The half-thickness, for example radius of a right cylinder, for which heat losses are exceeded by the heat gains. Related to T_{CRIT} .	m
ARC	Accelerating Rate Calorimeter, an adiabatic calorimeter	
C_O	Initial Concentration	mol
C_P	heat capacity at constant pressure	J K ⁻¹ g ⁰
C_V	heat capacity at constant volume	J K ⁻¹ g ⁻¹
ΔH	Heat of reaction. Units are variously, cal(joules) g ⁻¹ or (k)cal(joules) mol ⁻¹	J mol ⁻¹ or J g ⁻¹
DSC	Differential Scanning Calorimeter, a heat flow calorimeter	
Ea	Activation Energy	J mol ⁻¹
IPD	Instantaneous Power Density	W ml ⁻¹
k, k'	rate constant	mol s ⁻¹
$k_{T(NR)}$	rate constant at TNR	mol s ⁻²
m	Mass of material	g
Q_{RXN}	Reaction Heat	J g ⁻¹
$Q_{reaction}$	heat generated by (runaway) reaction	J
$Q_{removal}$	heat removed from system by all routes	J
R	Gas constant = 8.31441	J K ⁻¹ mol ⁻¹
T	Temperature	K
T_{ADIAB}	Adiabatic temperature rise (= DH / C_V)	K
T_{AMB}	Temperature of the ambient air or of the environment	K
T_{CRIT}	The critical temperature at which heat losses are exceeded by the heat gains. Related to critical half thickness, a.	K
T_{INIT}	Initial temperature of the vessel or vessel contents	K
T_{NR}	Temperature of no-return, the point where heat gain has exceeded heat removal for the system	K
T_{ONSET}	Onset of thermal activity, determined experimentally by a calorimeter	K
T_{SADT}	Self accelerating decomposition temperature	K
t_{MR}	time to the maximum rate of a runaway reaction	s
t_{NR}	time taken to advance from some temperature, usually ambient, to T_{NR}	s
Greek Symbols		
δ	Frank Kamenetskii critical parameter	Dimensionless
ϕ	Thermal inertia or effective heat capacity	Dimensionless
λ	Thermal conductivity	cal hr ⁻¹ m ⁻² C ⁻¹
ρ	Density	kg m ³
τ	Time constant	sec ⁻¹