Thermal Stability Indicators
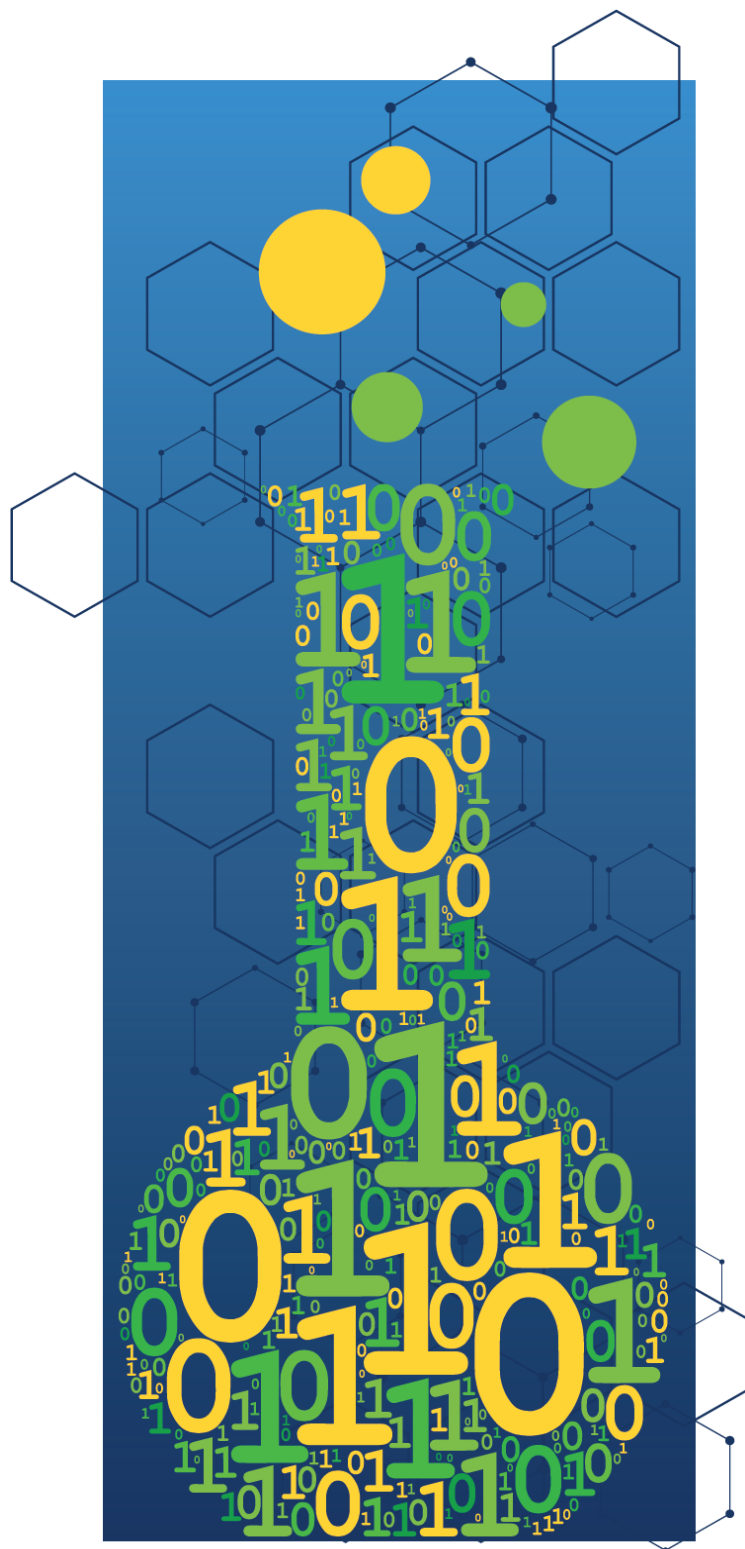
An ioMosaic Corporation White Paper

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Thermal Stability Indicators

Process Safety Management Practices

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August 5, 2020

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1   Introduction

Chemical process hazards cannot be effectively managed if they first cannot be properly identified. This is especially true for reactive chemicals storage, processing, and management. Reaction rates can be significantly influenced by the presence of contaminants, inhibitors, incompatible chemicals, etc. Runaway reactions usually involve undesired reactions although many industrial accidents have occured because of desired chemistry runaway reactions.

Information pertaining to chemical reactivity is required under the Process Safety Information (PSI) element of the Process Safety Management (PSM) standard in the United States. This requirement is rarely satisfied by a safety data sheet. Information about chemical reactivity need to be provided for both desired and undesired chemistries. In addition to regulatory compliance, this information is used to develop safe operating limits for storage and processing.

This paper describes several thermal stability indicators that should be provided as critical PSI for reactive chemicals. This information often requires both laboratory measurements and computer modeling for proper scale-up to plant conditions.

2   Inhibitor Induction Time, L_{ip}

Inhibitors are chemical substances that are used in small amounts to suppress the polymerization reaction of a monomer. An inhibitor has to be completely consumed before a polymerization reaction can proceed at normal rates. The time required to completely consume the inhibitor is often referred to as an "induction" time. Inhibitors react with polymerization initiation radicals to produce products that cannot induce further reaction. Inhibitors are different from reaction "retarders". A retarder does not suppress the reaction but merely slows it down, i.e. the reaction continues to increase at a slower rate until the retarder is consumed. Some impurities in monomers can act as retarders.

Small amounts of inhibitors can substantially prolong the shelf life of a reactive monomer. Common polymerization inhibitors, typically antioxidants, include MEHQ (monomethyl ether hydroquinone) , TBC (4-t-butylcatechol) , HQ (hydroquinone) , PTZ (phenothiazine) , etc. The effectiveness of most commonly used inhibitors depends on the presence of dissolved oxygen to convert free radicals to peroxy radicals that in turn react with the inhibitor to stabilize the monomer. Both inhibitors and oxygen deplete over time. Understanding inhibitor requirements is essential for polymerization reactions safety.

An inhibitor effectiveness model is usually coupled with polymerization kinetic model(s) in order to properly develop relief requirements and also for accurate hazard assessment. In general, inhibitor effectiveness models correlate the induction time with temperature and initial concentration of inhibitor [1]:

$$L_{ip} \;\; = \;\; \frac{1}{A^\bullet \exp\left[-\frac{E}{T}\right]} C_i^m = \frac{C_i^m}{k^\bullet} \tag{1}$$

where L_{ip} is the polymerization induction time , $A^\bullet$ is the pre-exponential factor, E is the activation

energy [1], C_i is the initial inhibitor concentration, and m is the concentration exponent.

An inhibitor depletion model is more effective when coupled with polymerization kinetic model(s) for dynamic simulation of relief requirements and hazard assessment [2]:

$$\frac{dC}{dt} = -A \exp\left[-\frac{E}{T}\right] C^n = -kC^n \tag{2}$$

where t is time and n is the reaction order [2]. Inhibitor data is provided in the literature or measured as induction time as a function of storage temperature at a specific initial level of inhibitor concentration. If we assume the inhibitor is completely depleted when the concentration reaches a small value, typically 1 ppm, we can develop an expression for induction time and fit the rate parameters from published or measured induction time data.

$$L_{ip} = t_f - t_i = -\frac{1}{k} \int_{C_i}^{C_f} \frac{dC}{C^n} \quad \text{where} \tag{3}$$

$$\int_{C_i}^{C_f} \frac{dC}{C^n} = \frac{C_f^{1-n} - C_i^{1-n}}{1-n} \quad \text{for } n \neq 1 \text{ and } \ln\left(\frac{C_f}{C_i}\right) \quad \text{for } n = 1 \tag{4}$$

For $n = 1$ and $t_i = 0$:

$$L_{ip} = t_f = -\frac{1}{k} \ln\left(\frac{C_f}{C_i}\right) = \frac{\ln\left(C_i/C_f\right)}{k} \tag{5}$$

For $n \neq 1$, $t_i = 0$, and $C_f = 0$:

$$L_{ip} = t_f = -\frac{1}{k}\left(\frac{C_f^{1-n} - C_i^{1-n}}{1-n}\right) = \frac{C_i^{1-n}}{k(1-n)} \tag{6}$$

Table 1 summarizes inhibitor depletion and effectiveness models based on data reported in references [1, 3, 4, 5, 6, 7, 8, 9, 10, 11], and recent work and model development by ioMosaic [2].

3 Induction Time for Autocatalytic Reactions, L_{ac}

Some chemicals exhibit autocatalytic behavior and will be thermally stable at specific storage temperature for only a specific duration. This is also called an induction time and is best established using isothermal aging in adiabatic calorimeters such as the ARC or APTAC or an isothermal calorimeter.

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[1]E is expressed in Kelvin and is equivalent to E/R_g where R_g is the universal gas constant.
[2]If $m \neq 0$ we can show that $n \simeq 1 - m$ and $A \simeq A^{\bullet}/m$ using the same activation energy E.

Table 1: Best fit inhibitor depletion and effectiveness model parameters

Inhibitor	Monomer	Depletion Model			Effectiveness Model		
		A	E, K	n	$A^\bullet$	E, K	m
PTZ	Acrylic Acid	3.284×10^9	11747	0.25	1.975×10^9	11680	0.73
TBC	Styrene	2.400×10^{12}	12615	0	3.644×10^{12}	12615	1.308
MEHQ	Acrylic Acid	1.527×10^{21}	19100	0	1.975×10^{21}	19100	1.19
MEHQ	Ethyl Acrylate	3.992×10^{11}	13419	0.45	2.116×10^{11}	13403	0.55
MEHQ	Butyl Acrylate	3.515×10^{13}	14912	0.55	1.479×10^{13}	14880	0.45
MEHQ	Methyl Methacrylate	1.085×10^{11}	12450	0.1	0.822×10^{11}	12399	0.884
HQ	Vinyl Acetate *	1.733×10^8	10620	0.5	9.341×10^7	10620	0.54
HQ	Vinyl Acetate**	3.869×10^7	10963	0.15	2.981×10^7	10963	0.777

A and $A^\bullet$ are expressed in SI units (s, kmol, m^3). For a 1st order reaction, A and $A^\bullet$ will be in s^{-1}.
* Air atmosphere. ** Low Oxygen atmosphere.

In general, a plot of the ln of induction time vs. isothermal aging temperature should yield a linear behavior as shown to the right. This data set is measured for a reactive residue that exhibits autocatalytic behavior. This data set enabled the plant to determine how long they can safely keep the residue before further processing.
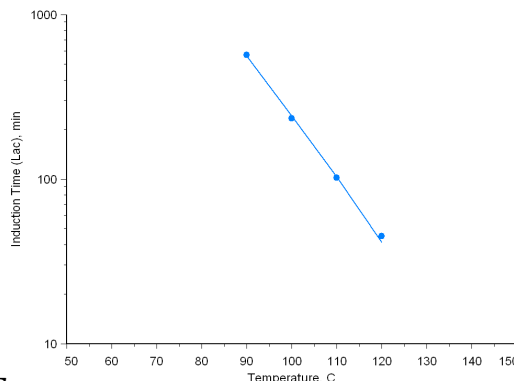
4 Detected Onset Temperature, T_{do}

This is a measured value that indicates that the reaction is producing a sufficient heating rate or gas generation rate or both. The rate is high enough to be detected by a specific instrument or measurement. T_{do} is highly dependent on the instrument used to detect the onset of reaction. It is most useful when it can be used for plant scale equipment. In other words, the heat generation rate by the reaction at T_{do} is just about equal to the heat loss rate by large plant storage or process vessels.

T_{do} is usually established using DSC , ARC , APTAC , VSP2 , Phi-Tech , or other suitable calorimeters. Most ARCs can produce reliable measurements of T_{do} at a detection sensitivity as low as 0.02 °C/min. This value should be directly applicable to a vessel that is 2000 gal or smaller. However, T_{do} must be first corrected for thermal inertia , ϕ . This correction is needed because in plant scale equipment the thermal capacity of the contents far exceeds that of the container or vessel. In the ARC, for example, the opposite is true depending on how much sample is used and what test cell type/mass is used.

$$\phi = 1 + \frac{m_c c_{p,c}}{m_s c_{p_s}} = \frac{\Delta T_{\text{adiabatic}}}{\Delta T_{\text{measured}}} \tag{7}$$

ϕ values for ARC can range from 1.5 to 5. T_{do} can be corrected for thermal inertia using the following expression:

$$\underbrace{\frac{1}{T_{doc}}}_{\phi=1} \quad = \quad \underbrace{\frac{1}{T_{do}}}_{\phi>1} + \frac{\ln\phi}{E} \tag{8}$$

where E is the reaction activation energy in Kelvin. Note that a detection sensitivity of 0.02 °C/min translates into 29 °C/day. It is recommended that T_{doc} is further reduced by 50 C before applying directly to plant scale equipment [4]. T_{do} data obtained by DSC should be reduced by 75 C [4]. Even with a reduction of 50 or 75 C there can be numerous scenarios that can provide the needed temperature increase to start a runaway reaction including fire exposure, excessive steam or oil heating, contamination, failure of process controls, etc.

The recommended method for correcting calorimetry data for thermal inertia is to simulate the actual test using SuperChems Expert . First, an accurate simulation is performed with representative reaction stoichiometry, reaction energetics, vapor/liquid equilibrium, and volumetric behavior. The test cell mass is then removed or reduced in a subsequent simulation to generate a data set corrected to a specific thermal inertia value. For a single stage, non auto-catalytic, simple reaction, the calorimetry temperature data can be corrected as follows [12]:

1. Correct the measured temperature using the corrected onset temperature T_{doc}:

$$T(t)_{\text{corrected}} \quad = \quad T_{doc} + \phi\left[T(t)_{\text{measured}} - T_{do}\right] \tag{9}$$

2. Correct the measured temperature rise rate, $\frac{dT}{dt}(t)$, data:

$$\frac{dT}{dt}(t)_{\text{corrected}} \quad = \quad \phi\frac{dT}{dt}(t)_{\text{measured}}\exp\left[E\left(\frac{1}{T(t)_{\text{measured}}} - \frac{1}{T(t)_{\text{corrected}}}\right)\right] \tag{10}$$

3. Sequentially update the measured time data:

$$t_{\text{corrected}} \quad = \quad \int_{T_{doc}}^{T(t)_{\text{corrected}}}\left[\frac{1}{\frac{dT}{dt}(t)_{\text{corrected}}}\right]dT \tag{11}$$

where $t_{\text{corrected}}$ is the adjusted reaction time at a thermal inertia of 1.

5   Adiabatic Temperature Rise, $\Delta T_{\text{adiabatic}}$

This is calculated from the thermal inertia multiplied by the difference between the measured final temperature, T_{mf} at the detection sensitivity of the instrument, minus the measured detected onset temperature, T_{do}:

$$\Delta T_{\text{adiabatic}} \quad = \quad \phi\Delta T_{\text{measured}} = \phi\left(T_{mf} - T_{do}\right) \tag{12}$$

6   Heat of Reaction, $\Delta H_{\textbf{rxn}}$

Heat of reaction data are necessary to establish the maximum potential temperature rise due to reaction and cooling requirements. ΔH_{rxn} is typically a weak function of temperature. It is best obtained by measurement although reasonable values can be approximated from group contribution or published literature data. If adiabatic calorimetry data are available, the heat of reaction can be calculated from the measured overall temperature rise:

$$\Delta H_{\text{rxn}} \;=\; \phi c_{p,s} \Delta T_{\text{measured}} \tag{13}$$

7   Maximum Adiabatic Temperature due to Reaction, $T_{\textbf{max}}$

This value can be calculated from the heat of reaction and heat capacity of the reacting mixture. For complex systems where solution effects and temperature dependencies are important, it is better calculated using dynamic simulation using computer software such as SuperChems Expert™ .

$$T_{\text{max}} \;=\; T_0 + \frac{\Delta H_{\text{rxn}}}{c_{p,s}} \tag{14}$$

where T_0 is the starting reaction temperature.

8   Maximum Reaction Pressure, $P_{\textbf{max}}$

The maximum reaction pressure $P_{\text{max}}(T)$ at a specific temperature in a storage or process vessel that is reached due to a runaway reaction can be established by dynamic simulation where cooling and/or venting can be considered during the runaway. Alternatively, P_{max} can be approximated using this simple equation:

$$P_{\text{max}}(T) \;=\; P_{nci}\left(\frac{T}{T_i}\right) + P_{bub}(T) + \kappa R_g T\left(\frac{V_l}{V_v}\right) \tag{15}$$

where T is the temperature of interest, T_i is the starting temperature in K, P_{nci} is initial pressure of non-condensible gases in the vapor space of the vessel in Pa at T_i, $P_{bub}(T)$ is the liquid bubble point or vapor pressure at temperature T, R_g is the universal gas constant, 8314 J/kmol/K, V_l is the liquid volume in m^3, V_v is the vapor space volume in m^3, and κ is the measured moles of gas produced per cubic meter of liquid.

9   Time to Maximum Rate, t_{mr}

The time to maximum rate is used to get an estimate of how much time is available to take action in order to regain control of or to mitigate a chemical reaction. The time to maximum rate can be

calculated for a simple reaction using the following expression:

$$t_{mr} = \frac{T_i^2}{E}\frac{1}{q(T_i)} \tag{16}$$

where t_{mr} is the time to maximum rate in s, T_i is the initial system temperature in K, E is the activation energy in K, and $q(T_i)$ is the self heat rate at T_i in K/s. In general the conversion or reaction rate is expressed as follows:

$$\frac{1}{V_l}\frac{dN}{dt} = -\underbrace{A\exp\left(-\frac{E}{T}\right)}_{k(T)}\Pi_{j=1}^{j=m}C_j^{n_j} \tag{17}$$

where V_l is the liquid volume in m^3, t is time in s, N is the number of moles depleted due to reaction in kmol, C_j is the initial concentration of reactant j in $kmol/m^3$, n_j is the reaction order, m is the total number of reactants, and A is the pre-exponential factor in consistent units.

Once the reaction rate is known, the self heat rate $q(T_i)$ is calculated from the following expression:

$$q(T_i) = \frac{\Delta H_{rxn}k(T_i)M_w\Pi_{j=1}^{j=m}C_j^{n_j}}{c_p\rho_l} \tag{18}$$

where ΔH_{rxn} is the heat of reaction in J/kg, M_w is the reactant molecular weight in kg/kmol, c_p is the liquid specific heat capacity in J/kg/K and ρ_l is the liquid density in kg/m^3.

TIME TO EXPLOSION

Note that $k(T_i)[C_i]^n[C_j]^m M_w$ is the reaction rate per unit volume in $kg/m^3/s$ and $\Delta H_{rxn}k(T_i)[C_i]^n[C_j]^m M_w$ is the energy production rate per unit volume in $J/m^3/s$ or W/m^3. For a zero order simple reaction (see figure above to the right), $q(T_i)$ is calculated as:

$$q(T_i) = \frac{\Delta H_{rxn}k(T_i)M_w}{c_p\rho_l} \quad \text{and} \quad t_{mr} = \left(\frac{T_i^2}{E}\right)\left(\frac{c_p\rho_l}{\Delta H_{rxn}k(T_i)M_w}\right) \tag{19}$$

Of practical interest are the temperatures coincident with a time to maximum rate of 24 and 48 hours [13]. For example, if fire proof insulation is to be used to protect a process vessel from fire exposure, special handling is required in order to ensure that after the fire is extinguished, the vessel contents do not reach a temperature that causes a runaway within 48 hours. The 48 hours time limit is selected arbitrarily and should be long enough for most installations to empty the tank contents, inject and circulate additional inhibitor into the tank, cool the tank contents, and/or use the vessel contents in the process. Simple correlations have appeared in the recent literature for thermal stability screening to estimate the temperature value associated with a time to maximum rate of 24 hours [14, 15]:

$$T_{tmr24} = 0.65 \times T_{do} + 50 \tag{20}$$
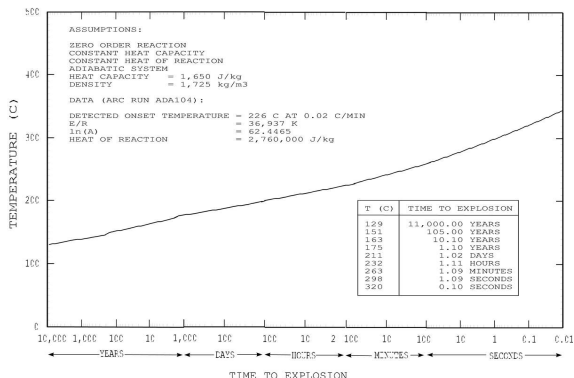
where T_{do} is the detected onset temperature in Klevin, and T_{tmr24} is the temperature coincident with a time to maximum rate of 24 hours in Kelvin.

10   Power Density, W

Another thermal stability indicator is the reaction power density, $W(T)$, which is expressed in energy production rate per volume, $J/s/m^3$ or W/m^3. When the power output of the reaction is expressed per unit mass, it is called specific power, $w(T)$, and has the units of $J/s/kg$ or W/kg. Both indicators are related to $q_(T)$:

$$w(T) \quad = \quad c_p q(T) \tag{21}$$
$$W(T) \quad = \quad c_p \rho q(T) \tag{22}$$

The reaction power density is used for screening and ranking of chemical reactions hazard potential. The national fire protection association (NFPA) recommends a classification of intrinsic thermal instability (see Table 2) based on the instantaneous power density [16], IPD where:

$$\text{IPD} \quad = \quad W(250 \,^{\circ}C) = W(523.15 \text{ K}) \tag{23}$$

Table 2: NFPA 704 Chemical instability rating system based on IPD

| Rating	IPD, W/ml	Description
4	$IPD \geq 1000$	Materials that in themselves are readily capable of detonation or explosive decomposition or explosive reaction at normal temperatures and pressures
3	$100 \leq IPD < 1000$	Materials that in themselves are capable of detonation or explosive decomposition or explosive reaction but that require a strong initiating source or must be heated under confinement before initiation
2	$10 \leq IPD < 100$	Materials that readily undergo violent chemical change at elevated temperatures and pressures
1	$0.01 \leq IPD < 10$	Materials that in themselves are normally stable but that can become unstable at elevated temperatures and pressures
0	$IPD < 0.01$	Materials that in themselves are normally stable, even under fire conditions

For a zero order reaction, the power density measured at two different temperatures can be related to the activation energy using the following equation:

$$E \quad = \quad \frac{T_1 T_2}{T_1 - T_2} \ln \frac{W_1}{W_2} \quad \text{or} \tag{24}$$
$$\ln \frac{W_2}{W_1} \quad = \quad \left(\frac{T_2 - T_1}{T_1 T_2} \right) E = \left(\frac{\Delta H_{\text{rxn}}}{c_p T_1 T_2} \right) E \tag{25}$$

11   Temperature of No Return, T_{NR}

A critical aspect of managing chemical reaction haz-
ards is temperature control as shown to the right. Un-
derstanding and quantification of acceptable temper-
ature safe operating limits are necessary. The safe
temperature operating limits have to be documented
as critical PSI . The temperature of no return, T_{NR}, is
an important indicator and a maximum safe operating
limit. It is the temperature beyond which the reaction
heat generation exceeds the cooling capacity of the
system.
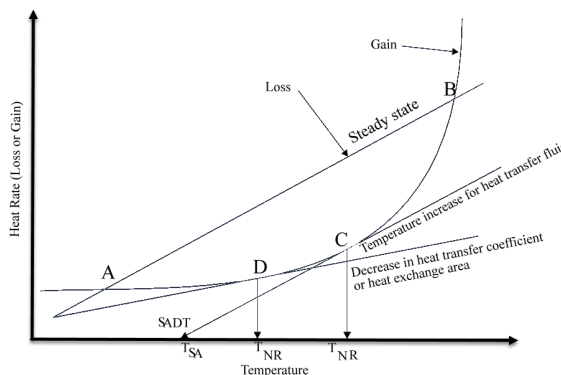
It is not possible to bring the reaction under control if the temperature exceeds T_{NR}. It can be shown
that T_{NR} can be calculated for a simple n order reaction from the following expression [17]:

$$\frac{dT_s}{dT_v} = 1 - \tau(T_{NR})A\left(T_f - T_{NR}\right)^n \exp\left(-\frac{E}{T_{NR}}\right)\left[\frac{E}{T_{NR}^2} - \frac{n}{T_f - T_{NR}} + \frac{d\ln\left[\tau(T_v)\right]}{dT_v}\bigg|_{@T_v=T_{NR}}\right] \quad (26)$$

$$= 0$$

where T_s is the surroundings or heat transfer fluid temperature, T_v is the vessel contents tem-
perature, T_f is the final temperature in the vessel, and τ is a temperature dependent system time
constant defined as follows:

$$\tau(T) = \frac{mc_p}{SU} \quad (27)$$

where m is the liquid mass in the vessel, S is the heat transfer area, U is the overall heat transfer
coefficient, and c_p is the specific liquid heat capacity. Equation 26 must be solved by trial and error.

If we assume that $\frac{n}{T_f - T_{NR}} <<< 1$ and temperature averaged properties over the range of interest,
we can show that T_{NR} will be equal to:

$$T_{NR}^2 = \tau(T_{NR}) \times E \times q(T_{NR}) \quad (28)$$

where $q(T_{NR})$ is defined in Equations 18 or 19. Equation 28 still needs to be solved by trial and
error for T_{NR}. Alternatively, one can plot the time to maximum rate t_{mr} from Equation 16 vs.
temperature and then locate the temperature corresponding to the time value provided by the time
constant $\tau(T)$ as defined in Equation 27.

Estimates of T_{NR} can be improved by obtaining a system specific value of the overall heat transfer
coefficient U from a geometry specific cooling curve [18]. A container specific cooling curve can
be obtained using water (or any suitable liquid) since U is independent of the fluid type. The value
of U can be derived by integrating the cooling curve over a specific duration and temperature drop:

$$U = \frac{m_w c_{p,w}}{S\left(t_f - t_i\right)}\ln\left(\frac{T_{w,i} - T_s}{T_{w,f} - T_s}\right) \quad (29)$$

where t_i is the initial time, t_f is the final time, m_w is the mass of water, $c_{p,w}$ is the specific heat capacity of water, $T_{w,i}$ is the initial water temperature, $T_{w,f}$ is the final water temperature and T_s is the surroundings temperature or ambient air temperature. Once U is established, τ can be calculated from Equation 27 using the actual fluid capacity data [19].

12   Self Accelerating Reaction Temperature, T_{SA} or $SADT$

This is often referred to as the self accelerating decomposition temperature (SADT [3]) or thermal explosion temperature. It is the lowest ambient or heat transfer fluid temperature above which thermal equilibrium is lost. T_{SA} can be approximated using the following equation:

$$T_{SA} \;=\; T_{NR} - \frac{1}{\frac{E}{T_{NR}^2} - \frac{n}{T_f - T_{NR}} + \frac{d\ln[\tau(T_v)]}{dT_v}\big|_{@T_v = T_{NR}}} \tag{30}$$

For a zero order reaction and relatively constant properties, SADT is calculated as:

$$T_{SA} \;=\; T_{NR} - \frac{T_{NR}^2}{E} \tag{31}$$

For complex reactions and vessels geometries, the SuperChems Expert vessel dynamics with detailed wall heat transfer can be used [20] to establish a better value of T_{SA}.

Equations 28, 30 and 31 assume the contents of the storage or process vessel are well mixed with a uniform temperature profile and follow the Semenov concept. For solids and viscous liquids this assumption may lead to an overestimate of the T_{NR} and T_{SA}. A somewhat similar equation can be derived for T_{SA} assuming the reacting material has a distributed temperature profile and follows the Frank-Kamenetskii concept. This is especially important for large liquid vessels and solids storage [4] where significant differences are possible between the two models. We provide a working equation for T_{SA} based on references [18] and [21] and some further mathematical reduction and simplification:

$$T_{SA}^2 \;=\; \underbrace{c_p \rho \left(\frac{r^2}{\lambda \delta_c}\right)}_{\text{time constant}} \times E \times q(T_{SA}) \tag{32}$$

where r is a characteristic length: vessel or container radius or half thickness, λ is the thermal conductivity, and δ_c is the Kamenetskii critical parameter which depends on the geometric shape of the vessel. The construct of Equation 32 is similar to that of Equation 28. Equation 32 has to be solved by trial and error for T_{SA}.

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[3]The minimum ambient air temperature at which a reactive material of specified stability decomposes in a specified commercial package in a period of seven days or less. SADT values are used to determine if a substance should be subject to temperature control during transport.

[4]Instability in solids storage may lead to combustion. It is typical to circulate air at a slow rate during adiabatic calorimetry testing leading to a small loss of adiabaticity. The constant flow of air ensures that the experiment will not be terminated prematurely due to the consumption of oxygen in the experiment.

δ_c can be approximated using the following equation for different geometries:

$$\delta_c = \frac{K+1}{e\left[\frac{1}{B_{i\infty}} + \frac{1}{B_i}\right]} \quad \text{where} \tag{33}$$

$$B_i = \frac{rU}{\lambda} \quad \text{Biot Number with thermal resistance or insulation} \tag{34}$$

$$B_{i,\infty} = \quad \text{Biot Number without thermal resistance or insulation} \tag{35}$$

$$e = 2.7183 \tag{36}$$

Values of K and $B_{i,\infty}$ can be obtained from Table 3.

Table 3: $\delta_c = \frac{K+1}{2.72\left[\frac{1}{B_{i\infty}} + \frac{1}{B_i}\right]}$ geometry parameters

Geometry or shape	K	$B_{i,\infty}$
Infinite slab	0	2.39
Infinite cylinder	1	2.72
Sphere	2	3.01
Right cylinder $(l = d)$	1.78	2.72
Finite cylinder $(l > d)$ with heat loss at both ends	$1 + 0.78(d/l)^2$	2.72
Finite cylinder $(l > d)$ with heat loss at one end	$1 + 0.195(d/l)^2$	2.72
Finite cylinder $(d > l)$ with heat loss at both ends	$-0.12 + 1.9(l/d)^2$	2.72
Cube	1.52	2.72
Box	$0.825\left[1.067 + (x/y)^2 + (x/z)^2\right] - 1$	2.72

l is length, d is diameter, x is shortest dimension, y and z are linear dimensions. When insulation or surface resistance is not used, $B_i = \infty$.

δ_c can be corrected for reactant consumption usually experienced in slow reactions before criticality is reached. The is accomplished by multiplying δ_c by a correction factor [21]:

$$\delta_c^*(T) = \delta_c \times \frac{1}{1 - 2.52\left(\frac{n}{B(T)}\right)^{2/3}} \tag{37}$$

$$B(T) = \left(\frac{E}{T^2}\right)\left(\frac{\Delta H_{\text{rxn}}}{c_p}\right) \tag{38}$$

As a result, Equation 32 can be used with δ_c^* to determine a more realistic T_{SA} value:

$$T_{SA}^2 = \underbrace{c_p\rho\left(\frac{r^2}{\lambda\delta_c^*(T_{SA})}\right)}_{\text{time constant}} \times E \times q(T_{SA}) \tag{39}$$

13   Case Study - Styrene Thermal Stability Indicators

Styrene monomer can thermally polymerize to form polystyrene. Styrene polymerization is highly exothermic and can result in elevated pressures and temperatures in storage and process vessels. This can cause a potential loss of containment without proper safeguards. The use of inhibitors and/or cooling can increase the shelf life of the styrene monomer. This case study aims to calculate simple styrene thermal stability indicators by using calorimetry test data, as well as chemical reaction rate kinetic parameters.

Using the effectiveness model generated and shown in Table 1, $A^\bullet$ is equivalent to 3.644×10^{12}, the activation energy is $12,615$, the reaction exponent is 1.306, the initial concentration of 4-Tertiary Butylcatechol (TBC) is 15 ppm, and the temperature of evaluation is 85 °C.

$$L_{ip} = \frac{1}{A^\bullet \exp\left[-\frac{E}{T}\right]}C_i^m = \frac{1}{3.644 \times 10^{12} \exp\left[-\frac{12615}{358.15}\right]}15^{1.306} = 18,782 \text{ s or } 5.21 \text{ hr} \qquad (40)$$

Isothermal aging ARC tests were run to measure the polymerization induction time at specific temperatures. The induction time can be seen for styrene at 85 °Cin the figure to the right.
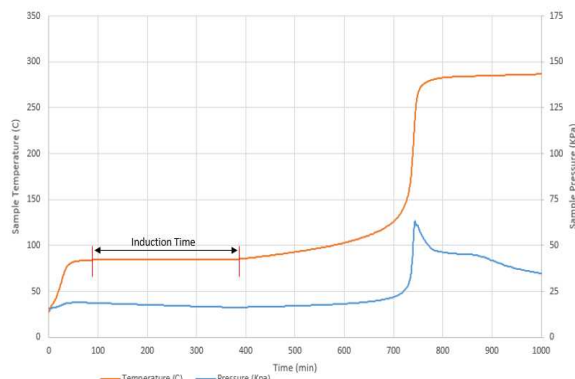
Several additional tests were conducted at temperatures up to 95 °Cat 5 °Cintervals. As the aging temperature increases, the induction time decreases.

Isothermal Aging Temperature	Induction Time
80ºC	437.74 min
85ºC	223.41 min
90ºC	56.55 min
95ºC	16 min

The figure to the right shows the induction time in minutes plotted on a logarithmic scale against the isothermal aging temperature. As expected, this results in a linear relationship.
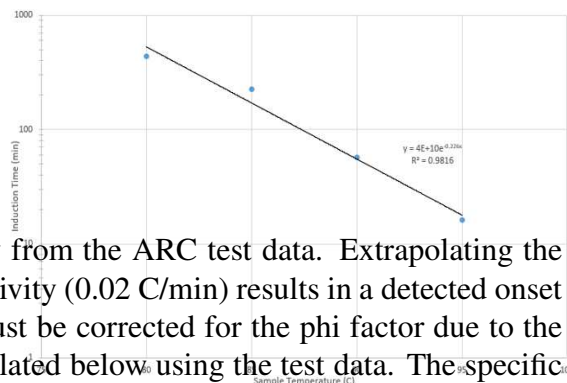

The detected onset temperature can be taken directly from the ARC test data. Extrapolating the detected exotherm down to the device detection sensitivity (0.02 C/min) results in a detected onset temperature of 65.5 °C. As described earlier, this must be corrected for the phi factor due to the thermal inertia of the test cell. The phi factor is calculated below using the test data. The specific

heat of both the styrene and the titanium cell were taken at room temperature.

$$\phi \;=\; 1 + \frac{m_c c_{p,c}}{m_s c_{p_s}} = 1 + \frac{11.63}{10.47} = 2.11 \tag{41}$$

The figure to the right shows the detected onset temperature of 65.5 °Ctaken directly from the test data. The extrapolation is performed to adjust for the detection sensitivity of the equipment and to correctly predict the onset temperature as seen in the ARC test cell. This should also be corrected for the thermal inertia of the test cell.
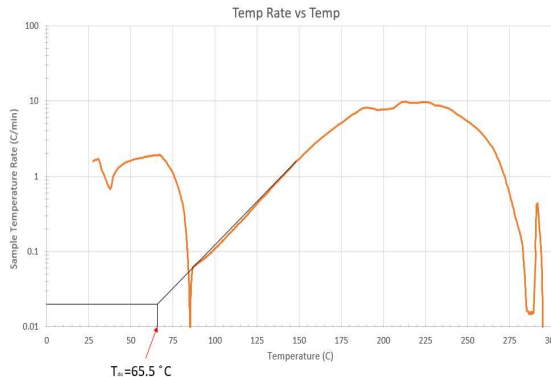
$$\underbrace{\frac{1}{T_{doc}}}_{\phi=1} \;=\; \underbrace{\frac{1}{T_{do}}}_{\phi>1} + \frac{\ln \phi}{E} \tag{42}$$

$$T_{doc} \;=\; \left(\frac{1}{338.65} + \frac{\ln 2.11}{10,040} \right)^{-1} = 330.33K = 57.2 \text{ °C} \tag{43}$$

The adiabatic temperature rise is corrected for the thermal inertia by multiplying the phi factor by the measured temperature rise in the experimental data:

$$\Delta T_{\text{adiabatic}} \;=\; \phi \Delta T_{\text{measured}} = \phi \left(T_{mf} - T_{do} \right) \tag{44}$$
$$=\; 2.11 \times (553.15 - 358.65K) = 411.5 \text{ or } 411.5 \text{ °C} \tag{45}$$

Additionally, using the phi factor the heat of reaction is calculated using the equation below:

$$\Delta H_{\text{rxn}} \;=\; \phi c_{p,s} \Delta T_{\text{measured}} \tag{46}$$
$$=\; 411.5 \times 183.2 = 75,391 \text{ kJ/kmol} \tag{47}$$

Using the calculated heat of reaction, a simple estimate for the maximum adiabatic temperature due to reaction can be performed:

$$T_{\text{max}} \;=\; T_0 + \frac{\Delta H_{\text{rxn}}}{c_{p,s}} = 358.15 + \frac{75,391}{183.2} = 769.67 \ K = 496.5 \text{ °C} \tag{48}$$

The time to maximum rate is a parameter that estimates the amount of time available to regain control over the reaction. First, the self-heat rate needs to be estimated at the temperature of

interest (85 °C).

$$q(T_i) = \frac{\Delta H_{\mathrm{rxn}} k(T_i) M_w \Pi_{j=1}^{j=m} C_j^{n_j}}{c_p \rho_l} \tag{49}$$

$$= \frac{723,856 \times 1.31 \times 10^{-7} \times 104.152 \times 8.15^{2.5}}{848.84 \times 183.2} = 0.012 \text{ K/s} \tag{50}$$

Using this, the time to maximum rate at 85 °C can be estimated.

$$t_{mr} = \frac{T_i^2}{E} \frac{1}{q(T_i)} = \frac{358.15^2}{10,040} \times \frac{1}{0.012} = 1,057 \text{ s or } 17.61 \text{ min} \tag{51}$$

The power density of styrene can be estimated and ranked based on the NFPA rankings (see Table 2) of the instantaneous power density. Solving for the power density at 250 °C gives the IPD of the chemical. As shown below, styrene falls into the NFPA ranking of 2, material that will readily undergo violent chemical change at elevated temperatures and pressures.

$$\text{IPD} = W(250 \text{ °C}) = W(523.15 \text{ K}) \tag{52}$$

$$= c_p \rho q(523.15) = 183.2 \times 8.15 \times 15,840 = 23.65 \times 10^6 \text{ W/m}^3 = 23.65 \text{ W/ml} \tag{53}$$

14 Case Study - Butyl Acrylate Thermal Stability Indicators

The polymerizations of methyl, ethyl, and butyl acrylate are described by Melhem [8]. Kinetic expressions for thermally and for free radical initiated polymerization reactions of acrylates are developed in [8]. The rate expressions are developed based on ARC measurements. We use that data here to develop simple thermal stability indicators for butyl acrylate.
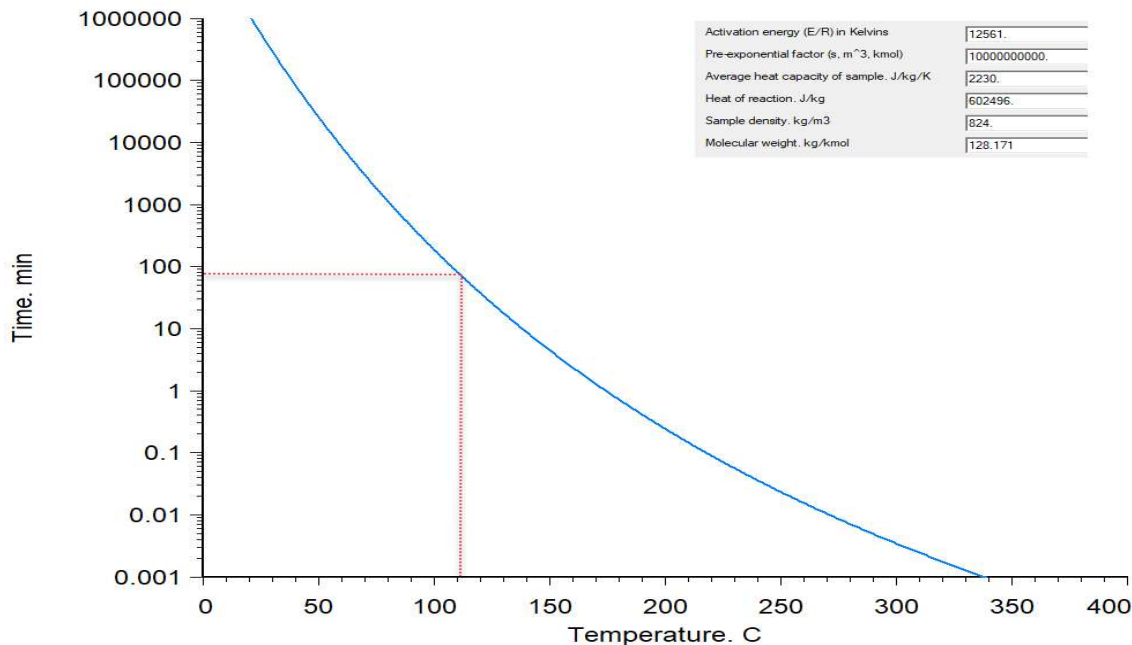
14.1 Time to Maximum Rate, t_{mr}

We first convert the reaction rate model developed in [8] from a first order to a zero order model in concentration and use the simple expression for t_{mr} shown in equation 19 to generate the time to maximum rate plot shown in Figure 1. At a temperature of 100 °C, the time to maximum rate is approximately 200 minutes or 3.3 hours. Note that t_{mr} values are less accurate at high temperatures when assuming a zero order reaction model. Actual t_{mr} values should be computed using detailed runaway reaction dynamics at a thermal inertia of 1 with SuperChems Expert .

14.2 Temperature of No Return, T_{NR}

If we consider a vessel that contains 1000 kg of butyl acrylate with a heat transfer area of 100 m^2 and an overall heat transfer coefficient of 5 $W/m^2/K$, we calculate a system time constant of 74.3

Figure 1: Butyl acrylate thermal polymerization time to maximum rate as a function of temperature

Activation energy (E/R) in Kelvins	12561.
Pre-exponential factor (s, m^3, kmol)	10000000000.
Average heat capacity of sample. J/kg/K	2230.
Heat of reaction. J/kg	602496.
Sample density. kg/m3	824.
Molecular weight. kg/kmol	128.171

minutes using constant temperature properties:

$$\tau(T) \quad = \quad \frac{1,000 \times 2,230}{100 \times 5} = 4,460 \text{ s or } 74.3 \text{ min} \tag{54}$$

T_{NR} is then read directly from Figure 1 to be approximately 111 °C.

14.3   Self Accelerating Reaction Temperature, T_{SA} or $SADT$

Knowing T_{NR}, for a zero reaction order , T_{SA} is calculated from:

$$T_{SA} \quad = \quad T_{NR} - \frac{T_{NR}^2}{E} = 384.15 - \frac{384.15^2}{12,561} = 372.4 \text{ K or } 99.25 \text{ °C} \tag{55}$$

This estimate of T_{SA} assumes the contents of the storage or process vessel are well mixed with a uniform temperature profile following the Semenov concept.

15   Conclusions

Thermal stability information including time to maximum rate, temperature of no return, and self acceleration reaction temperature should be established. Measurements using small scale calorimetry testing coupled with practical dynamic modeling using SuperChems Expert or other suitable

tools can provide a wealth of process and safety critical data and information. This information is required for PSM regulated chemical facilities in the USA in order to establish proper safe operating limits as required by the PSI element.

16   How can we help?

In addition to our deep experience in process safety management (PSM) and the conduct of large-scale site wide relief systems evaluations by both static and dynamic methods, we understand the many non-technical and subtle aspects of regulatory compliance and legal requirements. When you work with ioMosaic you have a trusted ISO certified partner that you can rely on for assistance and support with the lifecycle costs of relief systems to achieve optimal risk reduction and PSM compliance that you can evergreen. We invite you to connect the dots with ioMosaic.

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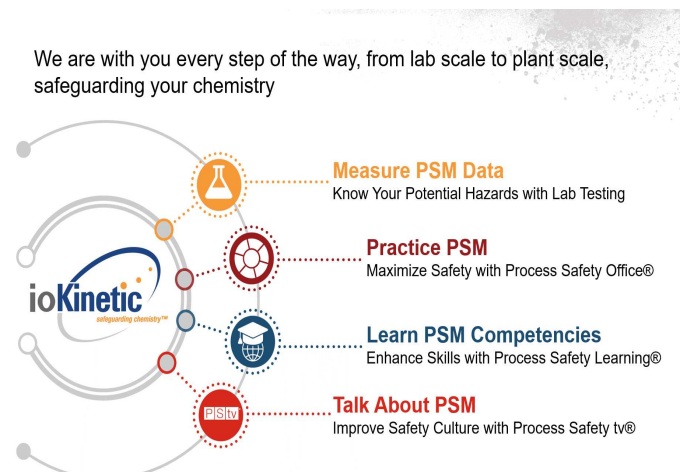
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About the Author

Dr. Melhem is an internationally known pressure relief and flare systems, chemical reaction systems, process safety, and risk analysis expert. In this regard he has provided consulting, design services, expert testimony, incident investigation, and incident reconstruction for a large number of clients. Since 1988, he has conducted and participated in numerous studies focused on the risks associated with process industries fixed facilities, facility siting, business interruption, and transportation.

Prior to founding ioMosaic Corporation, Dr. Melhem was president of Pyxsys Corporation; a technology subsidiary of Arthur D. Little Inc. Prior to Pyxsys and during his twelve years tenure at Arthur D. Little, Dr. Melhem was a vice president of Arthur D. Little and managing director of its Global Safety and Risk Management Practice and Process Safety and Reaction Engineering Laboratories.

Dr. Melhem holds a Ph.D. and an M.S. in Chemical Engineering, as well as a B.S. in Chemical Engineering with a minor in Industrial Engineering, all from Northeastern University. In addition, he has completed executive training in the areas of Finance and Strategic Sales Management at the Harvard Business School. Dr. Melhem is a Fellow of the American Institute of Chemical Engineers (AIChE) and Vice Chair of the AIChE Design Institute for Emergency Relief Systems (DiERS).

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