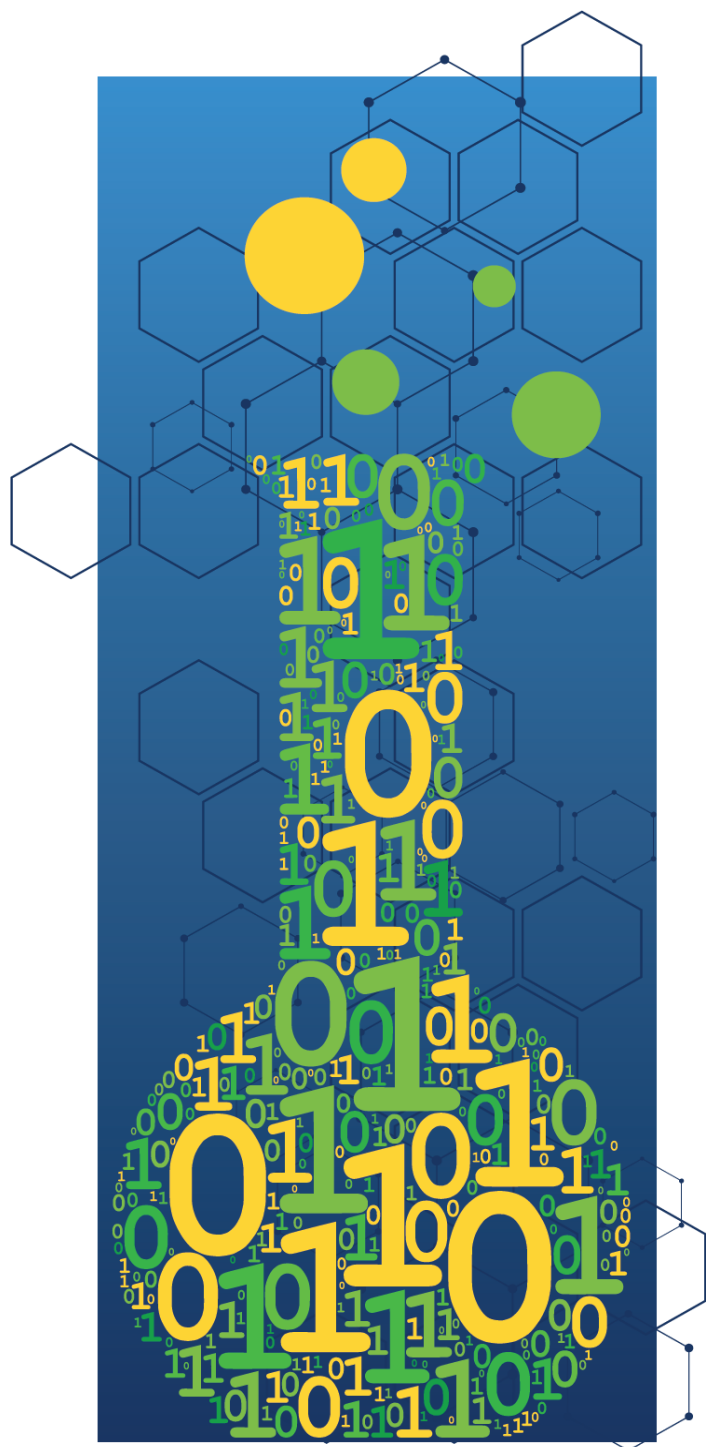


# Development of Kinetic Models - Part I. Thermal Stability



An ioMosaic Corporation White Paper

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IO MOSAIC CORPORATION

# **Development of Kinetic Models - Part I. Thermal Stability**

*Process Safety and Risk Management Practices*

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## 1 Introduction

Safe storage, handling, and transportation of reactive chemicals is challenging. Characterization of both desired and undesired chemistries requires a variety of methods including theoretical and computational screening, testing, and detailed modeling [1]. A multitude of process and environmental conditions can influence reaction rates such as contamination, reactant accumulation, loss of agitation, loss of cooling, etc. Identification and characterization of undesired chemistries are often missed at the development stage and/or not communicated properly to toll manufacturers and production facilities during scale-up. Safety data sheets may not be adequate and cannot be solely relied upon for safe storage, handling, or transportation of reactive chemicals. Exothermic runaway reactions can cause loss of containment, significant loss of property and life, and environmental impact [2].

Adiabatic and isothermal calorimetry are often used to characterize chemical reactions. Calorimetry data can then be reduced and used for direct scale-up or to develop simple and detailed chemical reaction kinetic models. Kinetic models are coupled with fluid dynamics for the assessment of thermal stability, process optimization, and pressure relief systems and vent containment design.

Two types of kinetic models can be developed, (a) simple or isoconversion models, and (b) detailed models [3]. Isoconversion models are easy to develop, do not require information about stoichiometry, phase change, or vapor/liquid equilibrium, but cannot be used for pressure relief design. They are mostly used for thermal stability assessments where phase change can be neglected and where there is no mass exchange with the system boundaries.

Detailed models [3] require the development of reaction stoichiometry, and detailed thermophysical and transport properties. They are mostly used for modeling the dynamics of pressure relief systems and vent containment design, process dynamics, as well as thermal stability assessments. Although they are more complex to develop than isoconversion models, they can be used to extend limited test data to wider ranges of composition, temperature, and pressure. The use of detailed kinetic models is preferred over the use of direct scale-up models because they often result in practical designs and better risk reduction. Once a detailed kinetic model is developed, it can be used over and over again in many process design and modeling applications.

In this paper we provide an overview of how simple kinetic models are developed from calorimetry data and how they are used for the modeling of thermal stability and thermal explosion theory.

## 2 Temperature Based - ARC or APTAC

Simple reaction models, also referred to as isoconversion models, assume that conversion of reactants is only a function of temperature. These models are mostly suitable for the development of thermal explosion theory for solids and for liquid systems without phase changes. In addition to adiabatic calorimetry data from the accelerating rate calorimeter (ARC<sup>TM</sup>) or the automatic pressure tracking adiabatic calorimeter <sup>1</sup> (APTAC<sup>TM</sup>), differential scanning calorimetry (DSC) data can also be used to develop simple models. Depending on the computational tools used, complex

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<sup>1</sup>ARC and APTAC are trademarks of Netzsch

isoconversion models with multiple reaction steps can also be developed.

If the reaction progress is only a function of temperature, we can express the reactant concentration  $C$  as a function of reaction temperature for a single stage simple reaction:

$$\frac{C}{C_0} = \frac{T_{mf} - T}{\underbrace{T_{mf} - T_{do}}_{\Delta T}} \text{ or } C = \left( \frac{T_{mf} - T}{\Delta T} \right) C_0 \quad (1)$$

where  $C_0$  is the starting reactant concentration,  $T_{mf}$  is the measured final temperature and  $T_{do}$  is the detected onset temperature. Differentiating  $C$  with respect to time  $t$  yields the following expression:

$$\frac{dC}{dt} = -\frac{C_0}{\Delta T} \frac{dT}{dt} \quad (2)$$

But the reaction progress can also be expressed as a function of concentration and reaction rate:

$$\frac{dC}{dt} = -KC^n = -A \exp\left(-\frac{E}{T}\right) C^n \quad (3)$$

where  $E$  is the activation energy<sup>2</sup> in Kelvin,  $K$  is the rate constant, and  $n$  is the reaction order. As a result:

$$\frac{dT}{dt} = AC_0^{n-1} \exp\left(-\frac{E}{T}\right) \left[ \frac{(T_{mf} - T)^n}{\Delta T^{n-1}} \right] \quad (4)$$

or

$$\ln \left[ \underbrace{\frac{\Delta T^{n-1}}{(T_{mf} - T)^n} \frac{dT}{dt}}_{K^*} \right] = \ln(AC_0^{n-1}) - \frac{E}{T} \quad (5)$$

For a specific value of  $n$ , a plot of the left hand side of the above equation vs.  $1/T$  yields the activation energy  $E$  of the reaction and the pre-exponential factor  $A$ . With proper regression the reaction order  $n$  can also be determined.

Isoconversion models relate the reaction progress or conversion  $\alpha$  to concentration as follows:

$$\alpha = 1 - \frac{C}{C_0} \text{ where } 0 \leq \alpha \leq 1 \quad (6)$$

Substitution of  $\alpha$  into the above equations yields the following expression for  $\frac{dT}{dt}$ :

$$\frac{dT}{dt} = \frac{dT}{d\alpha} \frac{d\alpha}{dt} = \Delta T \frac{d\alpha}{dt} \quad (7)$$

---

<sup>2</sup>E is equivalent to  $E/R_g$  and has absolute temperature units

or

$$\frac{d\alpha}{dt} = AC_0^{n-1} \exp\left(-\frac{E}{T}\right) \underbrace{\left[\frac{(T_{mf} - T)}{\Delta T}\right]^n}_{f(\alpha)=(1-\alpha)^n} = AC_0^{n-1} \exp\left(-\frac{E}{T}\right) \underbrace{(1-\alpha)^n}_{f(\alpha)} \quad (8)$$

or

$$\frac{1}{(1-\alpha)^n} \frac{d\alpha}{dt} = AC_0^{n-1} \exp\left(-\frac{E}{T}\right) \quad (9)$$

Equation 8 is always arranged in a similar fashion to Equation 5 such that a plot of the logarithm of left hand side of Equation 9 vs. the inverse of temperature yields the activation energy of the reaction as shown in Equation 10:

$$\ln\left[\frac{1}{f(\alpha)} \frac{d\alpha}{dt}\right] = \ln\left[\frac{1}{(1-\alpha)^n} \frac{d\alpha}{dt}\right] = \ln(AC_0^{n-1}) - \frac{E}{T} \quad (10)$$

When a simple reaction model is developed using  $\alpha$  and  $f(\alpha)$ , the reaction heating rate is expressed as a function of the overall heat of reaction and the change of  $\alpha$  with respect to time:

$$q(T) = \Delta T \frac{d\alpha}{dt} = -\frac{\Delta e_{\text{rxn}}}{c_v} \frac{d\alpha}{dt} \quad (11)$$

where  $\Delta e_{\text{rxn}}$  is the heat of reaction per unit mass<sup>3</sup>,  $c_v$  is the specific heat capacity at constant volume, and  $q(T)$  is the reaction heat generation rate in  $K/s$ . This simple reaction model can be developed directly from ARC, APTAC, Phi-TEC II<sup>TM</sup>, and VSP2<sup>TM</sup> test data because temperature, temperature rise rate, and pressure data are measured as a function of time<sup>4</sup>. The data will first have to be corrected for thermal inertia [4],  $\phi$ , which is a measure of the thermal capacity of the test cell:

$$\phi = 1 + \frac{m_c c_{p_c}}{m_s c_{p_s}} \quad (12)$$

where  $m$  is mass,  $c_p$  is specific heat capacity at constant pressure,  $c$  refers to test cell or container, and  $s$  refers to sample. Equation 12 is commonly used and referenced in the open literature. However, a more fundamental and correct version of Equation 12 should use the heat capacity at constant volume,  $c_v$  because most of the adiabatic test calorimetry data is collected under constant volume conditions.

$$\phi = 1 + \frac{m_c c_{v_c}}{m_s c_{v_s}} \quad (13)$$

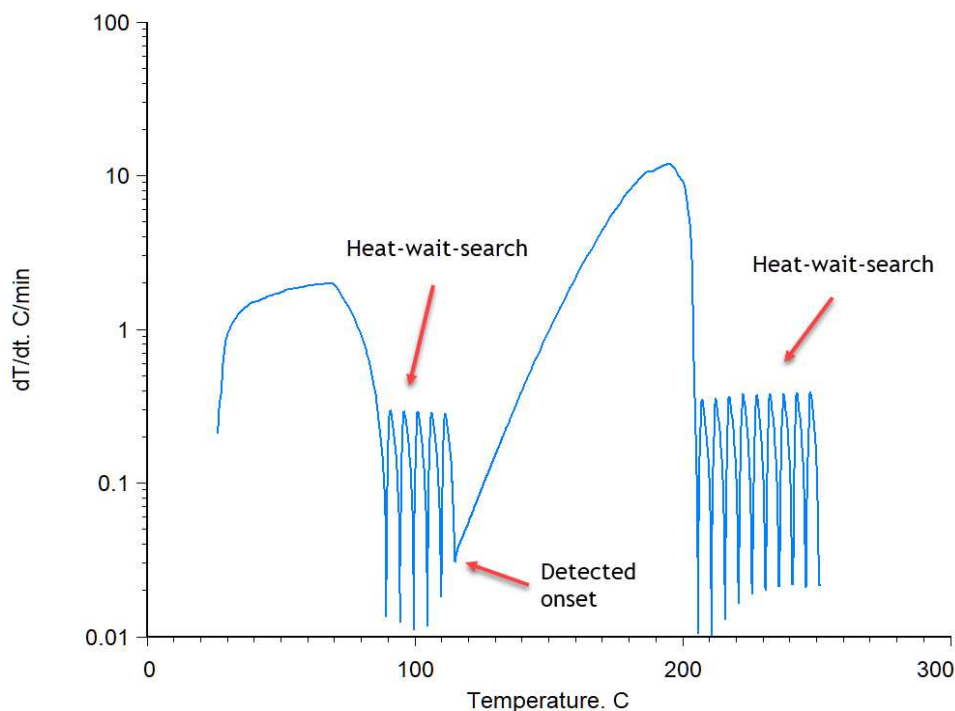
<sup>3</sup> $\Delta e_{\text{rxn}}$  is negative for an exothermic reaction

<sup>4</sup>Phi-TEC II is a trademark of H.E.L Group. VSP2 is a trademark of Fauske and Associates LLC.

While  $c_p$  is approximately equal to  $c_v$  for most liquids and solids, there are numerous liquids where that may not be the case. Similarly, an enthalpy based heat of reaction,  $\Delta h_{rxn}$ , should be  $\Delta e_{rxn}$  where  $e$  is the internal energy as shown in Equation 11.

A measured ARC data set for a 5.8 g sample of 20 % mixture of di-t-butyl peroxide in toluene is shown in Figure 1. The calculated thermal inertia factor excluding the ARC fittings equals to 1.78 assuming a sample average heat capacity of 0.42 cal/g. We note by inspection of Figure 1 that the decomposition reaction is first order,  $n = 1$ .

Figure 1: ARC Measured  $\frac{dT}{dt}$  for a 20 % mixture of di-t-butyl peroxide in toluene ( $\phi = 1.78$ )

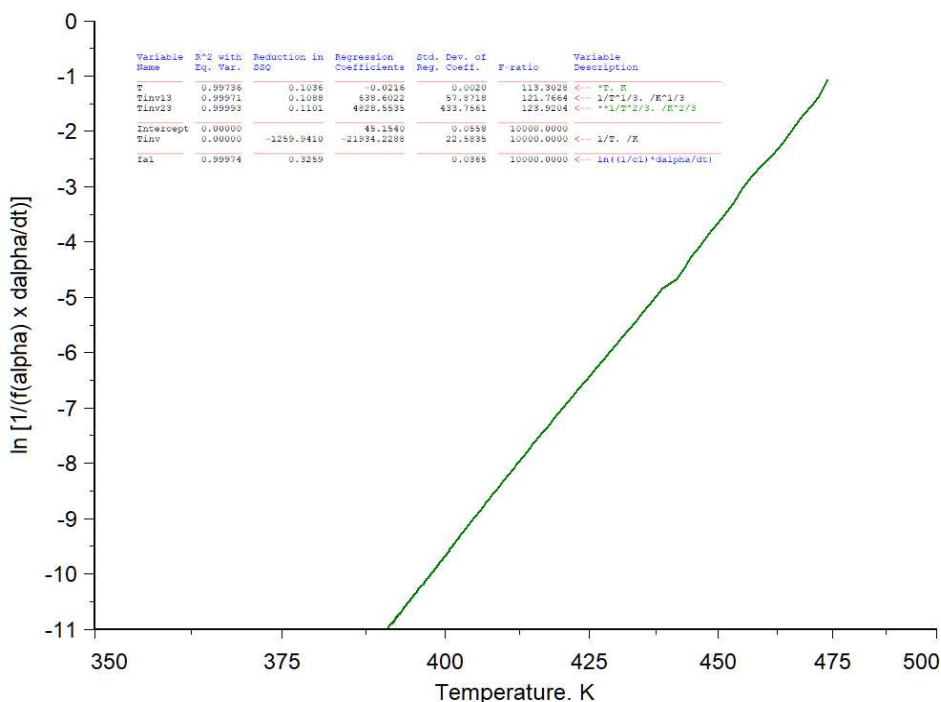


We can use the SuperChems Expert reaction data reduction tools to process the raw ARC data and to develop the isoconversion rate expression for a first order reaction as shown in Figure 2. The first order isoconversion model parameters are shown in Equation 14. The overall heat of decomposition is determined to be -1,416 J/g of di-t-butyl peroxide.

$$\frac{1}{(1-\alpha)^1} \frac{d\alpha}{dt} = \underbrace{4.075 \times 10^{19}}_{A \times C_0^0} \times \exp\left(-\frac{21,934}{T}\right) \quad (14)$$

We note that the initial concentration  $C_0$  is raised to the power  $n - 1 = 0$  and does not influence the pre-exponential factor  $A$ .

Figure 2: ARC data isoconversion best fit model for a 20 % mixture of di-t-butyl peroxide in toluene ( $\phi = 1.78$ ) using SuperChems Expert



### 3 Heat Flow Based - DSC

DSC data<sup>5</sup> can also be used to fit Equation 10. Typically, a combination of isothermal aging tests and tests at different heating rates are used to fit  $A(\alpha)$ ,  $E(\alpha)$ , and  $f(\alpha)$ . If we divide the DSC measured accumulated heat  $Q$  or heat flow  $\dot{Q}$  by the overall measured heat of reaction  $\Delta e_{rxn}$  we can obtain values of  $\alpha$  and  $\frac{d\alpha}{dt}$ :

$$\alpha = \frac{Q}{-\Delta e_{rxn}} \text{ or} \quad (15)$$

$$\frac{d\alpha}{dt} = \frac{\dot{Q}}{-\Delta e_{rxn}} \quad (16)$$

and

$$\ln \left( \frac{1}{f(\alpha)} \frac{d\alpha}{dt} \right) = \ln [A(\alpha)] - \frac{E(\alpha)}{T(t)} \quad (17)$$

$$T(t) = T_0 + \beta t \quad (18)$$

where  $\beta$  is the DSC heating rate. Integration of the conversion rate,  $\frac{d\alpha}{dt}$ , yields the reaction time:

<sup>5</sup>Data is collected using high pressure crucibles



$$t = \int_0^t dt = \int_0^\alpha \left( \frac{1}{\frac{d\alpha}{dt}} \right) d\alpha = \int_0^\alpha \frac{d\alpha}{f(\alpha)A(\alpha) \exp\left(-\frac{E(\alpha)}{T(t)}\right)} \quad (19)$$

Isothermal DSC data can also be used to obtain reaction rates. Several isothermal tests are conducted at different temperatures. Typically three or more tests are required. The heat flow rate,  $\dot{Q}$ , and the partial heats,  $Q$ , are determined from the DSC tests (see Equations 15 and 16). These values are then converted to a fractional conversion,  $\alpha$ , and reaction rate,  $\frac{d\alpha}{dt}$ , using a reference theoretical heat of reaction,  $\Delta e_{\text{rxn}}$ . The calculated values of  $\alpha$  and  $\frac{d\alpha}{dt}$  are regressed using an appropriate kinetics model,  $n^{\text{th}}$  order or autocatalytic, and the best fit kinetic parameters are obtained.

For the special case of a zero order reaction, the maximum heat release rate,  $w(T) = q(T)c_v$  is obtained at each isothermal test temperature. The activation energy is then obtained by regressing the natural logarithm of the maximum heat release rate,  $\ln(w(T))$ , vs.  $\frac{1}{T}$  of all the data points. As also shown by Melhem [4], the activation energy can be directly calculated using two points:

$$E = \frac{\ln \left[ \frac{w(T_2)}{w(T_1)} \right]}{\frac{1}{T_1} - \frac{1}{T_2}} \quad (20)$$

where  $E$  is typically in K,  $w$  is in  $W/kg$ , and  $T$  is in K. To select the proper temperatures for the required isothermal experiments, first heat the material at  $5^\circ\text{C}/\text{min}$ . Then, select isothermal temperatures that lie between a temperature 10 to  $20^\circ\text{C}$  below the onset of reaction and a temperature midway to the maximum. When performing the actual isothermal experiments, the cell is heated to the desired isothermal temperature using an initial temperature program segment. The cell is then rapidly opened, the sample loaded, and the cell re-closed. When the displayed temperature is within  $4^\circ\text{C}$  of the desired isothermal temperature, data collection is initiated [5].

A measured DSC data set for alpha-methylstyrene at a heating rate of  $5^\circ\text{C}/\text{min}$  is shown in Figure 3. The integrated overall heat of reaction is approximately  $-430 \text{ J/g}$ . The best fit isoconversion model parameters (see Figure 4) are shown in Equation 21.

$$\frac{1}{(1 - \alpha^{1/4})^1} \frac{d\alpha}{dt} = 1.722 \times 10^{14} \times \exp\left(-\frac{25,504}{T}\right) \quad (21)$$

Equation 21 is most suitable for thermal stability analysis.

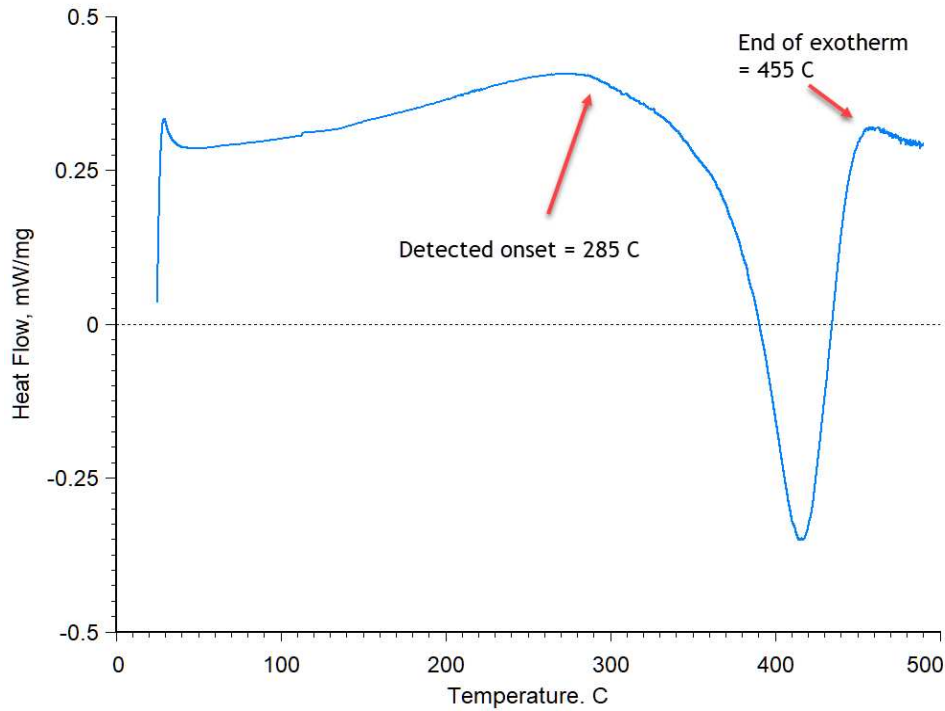
## 4 Mass Loss Based - TGA

Similarly, TGA data can be used to develop simple isoconversion kinetic rate expressions. The degree of conversion is assumed to be proportional to mass loss:

$$\alpha(T) = \frac{m_0 - m(T)}{m_0 - m_f} \quad (22)$$

$$T(t) = T_0 + \beta t \quad (23)$$

Figure 3: Measured DSC heat flow data for alpha-methylstyrene polymerization



where  $m_0$  is the sample mass at  $T_0$ ,  $m_f$  is the sample mass at  $T_f$  and  $m(T)$  is the sample mass at temperature  $T(t)$ . The change of conversion with respect to time is calculated from the change of conversion with respect to temperature and the change of temperature with respect to time:

$$\frac{d\alpha}{dt} = \frac{dT}{dt} \frac{d\alpha}{dT} = \beta \frac{d\alpha}{dT} \quad (24)$$

The change of conversion with respect to temperature can be calculated from the measured data by fitting and differentiating quadratic or cubic splines, or in most applications by using finite difference. If we have  $n$  data points measured, then:

$$\left( \frac{d\alpha}{dT} \right)_0 = \frac{\alpha_1 - \alpha_0}{T_1 - T_0} \quad (25)$$

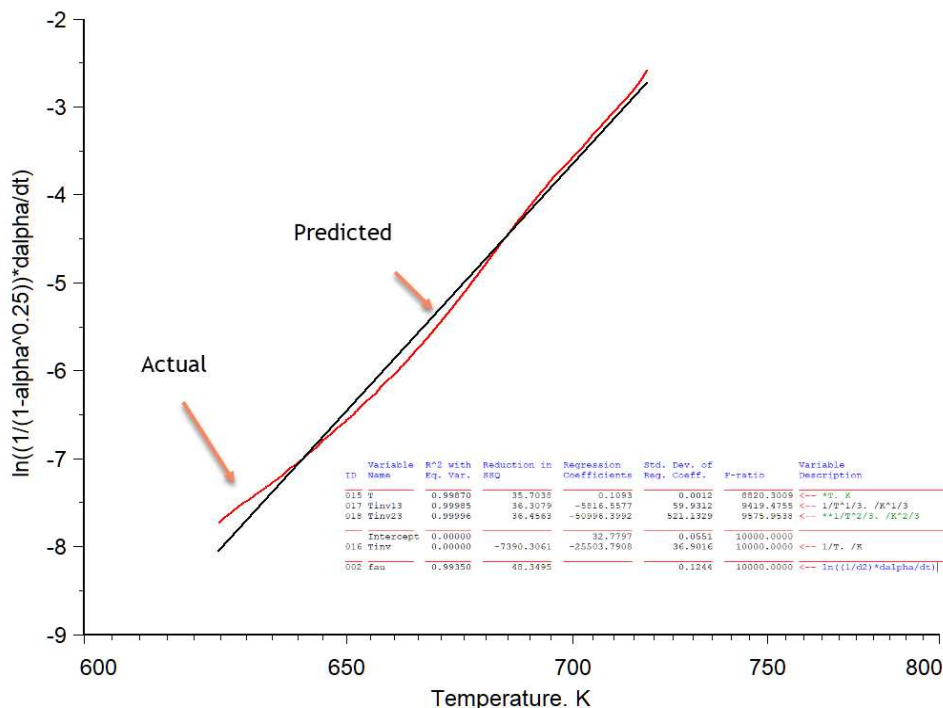
$$\left( \frac{d\alpha}{dT} \right)_i = \frac{1}{2} \left( \frac{\alpha_i - \alpha_{i-1}}{T_i - T_{i-1}} \right) + \frac{1}{2} \left( \frac{\alpha_{i+1} - \alpha_i}{T_{i+1} - T_i} \right) \quad \text{for } i = 1, \dots, n-2 \quad (26)$$

$$\left( \frac{d\alpha}{dT} \right)_{n-1} = \frac{\alpha_{n-1} - \alpha_{n-2}}{T_{n-1} - T_{n-2}} \quad (27)$$

Like DSC data, integration of the TGA conversion rate yields the reaction time (also see [6]):

$$t = \int_0^t dt = \int_0^\alpha \left( \frac{1}{\beta \frac{d\alpha}{dT}} \right) d\alpha = \int_0^\alpha \frac{d\alpha}{A(\alpha) \exp\left(-\frac{E(\alpha)}{T(t)}\right) f(\alpha)} \quad (28)$$

Figure 4: SuperChems Expert best fit DSC isoconversion model parameters for alpha-methylstyrene polymerization



A measured TGA data set for calcium oxalate at a heating rate of 10 °C/min is shown in Figure 5. The data shows three distinct decomposition stages of approximately 12 % weight loss for stage 1 ( $CaC_2O_4 \cdot H_2O(s) \rightarrow CaC_2O_4(s) + H_2O(g)$ ), 19.2 % for stage 2 ( $\rightarrow CaCO_3(s) + CO(g)$ ) and 30.1 % for stage 3 ( $\rightarrow CaO(s) + CO_2(g)$ ).

Simple or isoconversion models can be developed using SuperChems Expert for each of the decomposition stages using reaction progress or conversion,  $\alpha$ , based on mass loss rate (see Equations 17, 22, and 24).

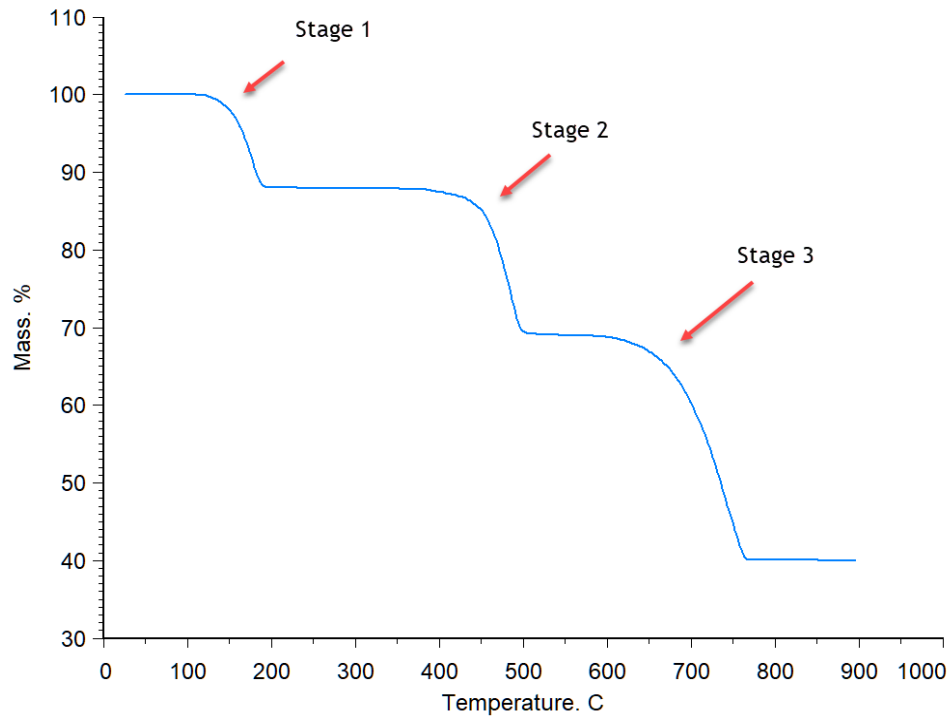
## 5 Pressure Based - ARC or APTAC

In some instances, simple kinetic expressions can be developed from pressure data. This can be useful for combustion or oxidation reactions and liquid phase endothermic reactions that produce non condensable reaction products. Assuming a linear dependence of degree of conversion  $\alpha$  on pressure, we can write the following expression for  $\alpha$ :

$$\alpha = \frac{P - P_0}{P_{mf} - P_0} \quad (29)$$

where  $P_{mf}$  is the measured maximum constant volume pressure, and  $P_0$  is the initial starting pressure. The differential change of reaction conversion  $\alpha$  with respect to time is simply proportional

Figure 5: Measured TGA mass loss data for calcium oxalate



to change in pressure:

$$\frac{d\alpha}{dt} = \left( \frac{1}{P_{mf} - P_0} \right) \frac{dP}{dt} \quad (30)$$

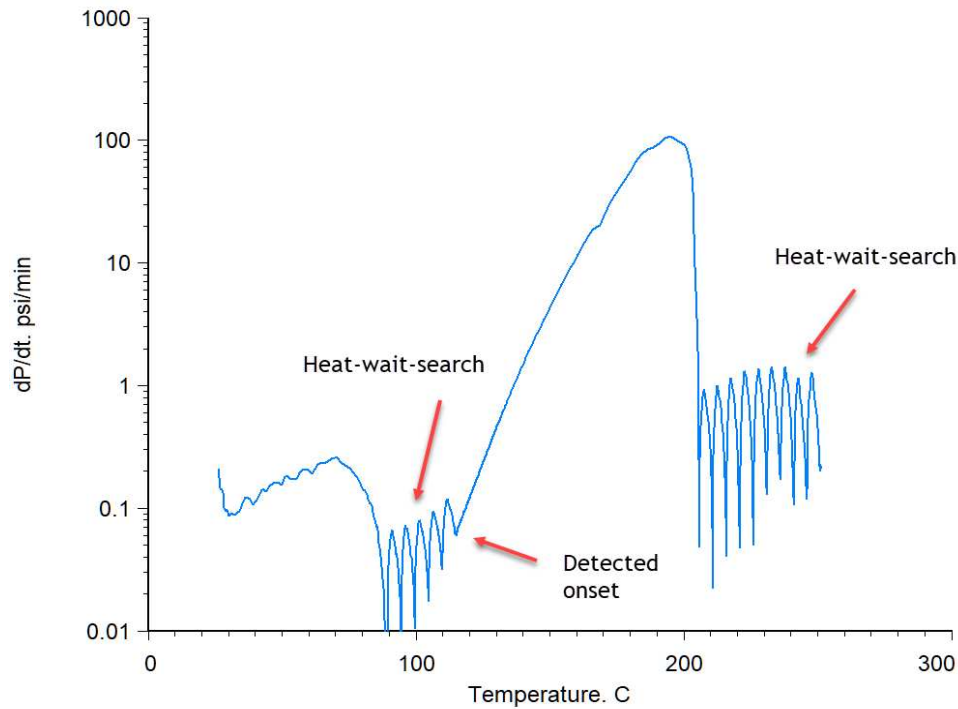
The same measured ARC data set for a 5.8 g sample of 20 % mixture of di-*t*-butyl peroxide in toluene is shown in Figure 6. The calculated thermal inertia factor excluding the ARC fittings equals to 1.78 assuming a sample average heat capacity of 0.42 cal/g. We also note by inspection of Figure 6 that the decomposition reaction is first order.

A similar model to that shown in Equation 14 can be developed using SuperChems Expert but using reaction progress or conversion,  $\alpha$ , based on pressure as shown by Equations 29 and 30.

## 6 Isoconversion $f(\alpha)$ Forms

More complex formulations of Equation 10 have been developed to represent multi-step reactions and reactions with autocatalytic behavior. It is common to represent a multi-step reaction using the following expression:

$$\frac{d\alpha}{dt} = \sum_{i=1}^{i=N_{\text{steps}}} K_i (1 - \alpha^{n_i}) \alpha^{m_i} \quad (31)$$

Figure 6: ARC measured  $\frac{dP}{dt}$  for a 20 % mixture of di-t-butyl peroxide in toluene ( $\phi = 1.78$ )

If the number of steps is two and we set  $n_1 = 1, m_1 = 0, n_2 = 1, m_2 = 1$  then:

$$\frac{d\alpha}{dt} = K_2 (1 - \alpha) \left( \frac{K_1}{K_2} + \alpha \right) \quad (32)$$

When  $K_1 \ll K_2$  the implied reaction become autocatalytic:

$$\frac{1}{(1 - \alpha) \alpha} \frac{d\alpha}{dt} \simeq K_2 \quad (33)$$

When  $K_1 \gg K_2$ :

$$\frac{1}{(1 - \alpha)} \frac{d\alpha}{dt} \simeq K_1 \quad (34)$$

SuperChems Expert enables the user to select a more complete and flexible representation of  $f(\alpha)$ :

$$\frac{1}{f(\alpha)} \frac{d\alpha}{dt} = K \quad (35)$$

$$f(\alpha) = (a - b\alpha^c)^n (d + \alpha^m) \quad (36)$$

where  $a, b, c, n, d,$  and  $m$  are user defined constant parameters. The constant parameters  $d$  and  $m$  are typically used when considering autocatalytic reactions.

A complex reaction system can be divided into multiple reaction segments such that:

$$\frac{d\alpha}{dt} = \sum_i f(\alpha_i) K_i \quad \text{where } i = 1, \dots, \text{Number of reaction segments} \quad (37)$$

## 7 Thermal Explosion Theory

SuperChems Expert implements multiphase detailed mass, energy, phase equilibria, and chemical reaction dynamics. The SuperChems Expert dynamic models allow for phase change and a variety of boundary conditions for mass and heat transfer. These models are used to develop thermal stability estimates such as time to maximum rate, pressure relief requirements, multiphase flow, etc. Isoconversion kinetic models cannot be used to establish relief requirements or thermal stability where phase change and/or phase equilibria is required.

A variety of vessel shapes (cylindrical, spherical, rectangular, cone frustum, composite) and vessel heads (flat, elliptical, torispherical, hemispherical, dished, conical) can be used with and without insulation. Heat transfer modes considered by SuperChems Expert include convection, conduction, and radiation. SuperChems Expert divides the vessel walls into multiple segments and enables heat transfer in and out of the segments and also between the segments. Under external heating from fire exposure or internal heating from runaway chemical reactions or both, SuperChems Expert can be used to determine expected vessel time to failure, *ettf*, or expected vessel time to yield, *etty*.

The SuperChems Expert dynamic models are complex in nature primarily due to multiphase and phase equilibrium considerations. Because of these complexities, it is assumed that the temperature in the vessel contents is uniform while the temperature in the vessel wall segments is not. SuperChems Expert is the preferred method of establishing thermal stability for reacting systems where phase change can occur during chemical reactions, venting, mass and/or heat transfer.

It is possible to simplify these models to enable the use of isoconversion kinetic model rate expressions. Let  $m_T$  be the total reacting mass which consists of the reactant and products, and  $c_{v_T}$  be the heat capacity of the reactant and products:

$$m_T = m_r + m_p \quad (38)$$

$$m_r = (1 - \alpha) m_T \quad (39)$$

$$m_p = \alpha m_T \quad (40)$$

$$m_T c_{v_T} = m_r c_{v_r} + m_p c_{v_p} \quad \text{or} \quad c_{v_T} = (1 - \alpha) c_{v_r} + \alpha c_{v_p} \quad (41)$$

If we assume that there is no phase change and a uniform vessel contents temperature (Semenov assumption), we can write a single energy equation to represent the vessel contents temperature.

$$\underbrace{m_T c_{v_T} \frac{dT}{dt} + m_c c_{v_c} \frac{dT_c}{dt}}_{\text{Heat Accumulation}} = \underbrace{US (T_a - T_c)}_{\text{Heat Transfer}} - \underbrace{\frac{dm_p}{dt} \Delta e_{\text{rxn}}}_{\text{Heat Generation}} \quad (42)$$

where  $\Delta e_{\text{rxn}}$  is the heat of reaction per unit mass and is negative for an exothermic reaction. We note that  $\frac{dm_p}{dt} = m_T \frac{d\alpha}{dt}$ . Therefore:

$$m_T c_{vT} \frac{dT}{dt} + m_c c_{vc} \frac{dT_c}{dt} = US (T_a - T_c) - m_T \frac{d\alpha}{dt} \Delta e_{\text{rxn}} \quad (43)$$

If we also assume that the container temperature is equal to the contents temperature, we can further simplify the above equation:

$$m_T c_{vT} \frac{dT}{dt} + m_c c_{vc} \frac{dT}{dt} = US (T_a - T) - m_T \frac{d\alpha}{dt} \Delta e_{\text{rxn}} \quad \text{or} \quad (44)$$

$$\underbrace{\left(1 + \frac{m_c c_{vc}}{m_T c_{vT}}\right)}_{\phi = \text{Thermal Inertia}} \frac{dT}{dt} = \frac{US}{m_T c_{vT}} (T_a - T) - \frac{\Delta e_{\text{rxn}}}{c_{vT}} \frac{d\alpha}{dt} \quad \text{or} \quad (45)$$

$$\phi \frac{dT}{dt} = \frac{US}{m_T c_{vT}} (T_a - T) + q(T) \quad \text{and} \quad (46)$$

$$\phi \frac{dT}{dt} = \frac{U}{\rho_T c_{vT}} \frac{S}{V_T} (T_a - T) + q(T) \quad (47)$$

$$(48)$$

where  $\frac{S}{V_T}$  is the surface to volume ratio,  $V_T$  is the total volume of reactant and products, and  $\rho_T$  is the mass density of reactant and products. It is easy to recognize that larger values of surface to volume ratios enhance heat exchange with the surroundings while smaller values of surface to volume ratio reduce heat exchange with the surroundings. The rate of temperature change of the vessel contents is therefore a function of the vessel thermal inertia,  $\phi$ , heat exchange with the surroundings, and reaction heat generation:

$$\frac{d\alpha}{dt} = A(\alpha) f(\alpha) \exp\left(-\frac{E(\alpha)}{T}\right) \quad \text{and} \quad (49)$$

$$q(T) = -\frac{\Delta e_{\text{rxn}}}{c_{vT}} \frac{d\alpha}{dt} \quad \text{and} \quad (50)$$

$$\tau(T) = \frac{m_T c_{vT}}{US} \quad \text{and} \quad (51)$$

$$\frac{dT}{dt} = \frac{1}{\phi} \left[ \frac{1}{\tau(T)} (T_a - T) + q(T) \right] \quad (52)$$

where  $\tau(T)$  is the system time constant. The above three differential equations can be integrated readily to yield the time to maximum rate,  $t_{MR}(T)$ , the temperature of no return,  $T_{NR}$ , and the self accelerating temperature  $T_{SA}$  also commonly known as self accelerating decomposition temperature  $T_{SADT}$ .

Melhem [4] recently demonstrated that the above equations can be further simplified to calculate  $t_{MR}$ ,  $T_{NR}$ , and  $T_{SA}$  using the following equations and a straight forward trial and error calculation of a single nonlinear equation in one variable <sup>6</sup>,  $T$ :

<sup>6</sup>The simplified equations assume zero reactant consumption. Also note that  $\frac{T_{NR}^2}{E} = \frac{d\alpha/dT}{d^2\alpha/dT^2}$

**Semenov:**

$$T^2 = t_{MR}(T) \times E \times q(T) \text{ or } t_{MR}(T) = \frac{T^2}{E} \frac{1}{q(T)} \quad (53)$$

$$T_{NR}^2 = \tau(T_{NR}) \times E \times q(T_{NR}) \quad (54)$$

$$T_{SA} = T_{NR} - \frac{T_{NR}^2}{E} \quad (55)$$

**Kamenetskii:**

$$T_{SA}^2 = \underbrace{c_{vT} \rho_T \frac{r^2}{\lambda_T \delta_c}}_{\text{Time Constant}} \times E \times q(T_{SA}) \quad (56)$$

$$(57)$$

where  $\delta_c$  is the geometric shape Kamenetskii critical parameter,  $\lambda_T$  is the thermal conductivity of the reactant and product mixture, and  $r$  is the characteristic length or vessel radius or container half thickness.

For solid systems or liquid systems where fluid convection can be ignored, we can extend the thermal explosion theory to account for conduction in two or three dimensions. For three dimensional systems and using Cartesian coordinates:

$$\begin{aligned} \frac{\partial T}{\partial t} = & \underbrace{\frac{\lambda_T}{\rho_T c_{vT}}}_{\text{Thermal Diffusivity}} \left[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right] - \frac{\Delta e_{\text{rxn}}}{c_{vT}} \frac{\partial \alpha}{\partial t} \\ & + \frac{1}{\rho_T c_{vT}} \left[ \frac{\partial \lambda}{\partial x} \frac{\partial T}{\partial x} + \frac{\partial \lambda}{\partial y} \frac{\partial T}{\partial y} + \frac{\partial \lambda}{\partial z} \frac{\partial T}{\partial z} \right] \end{aligned} \quad (58)$$

For two dimensional cylindrical coordinates where  $\lambda$  does not change with location, the heat conduction equation can be written as:

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho_T c_{vT}} \left[ \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right] - \frac{\Delta e_{\text{rxn}}}{c_{vT}} \frac{\partial \alpha}{\partial t} \quad (59)$$

For one dimensional problems, we can rewrite the conduction equation as follows:

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho_T c_{vT}} \left[ \frac{\partial^2 T}{\partial r^2} + \frac{J}{r} \frac{\partial T}{\partial r} \right] - \frac{\Delta e_{\text{rxn}}}{c_{vT}} \frac{\partial \alpha}{\partial t} \quad (60)$$

where  $q(T)$  is defined by Equation 11,  $J = 0$  for an infinite plate,  $J = 1$  for an infinite cylinder, and  $J = 2$  for a sphere. Equation 60 can be extended to represent finite geometries in two dimensions and to also represent reactant depletion and diffusion with different boundary conditions.



Boundary conditions can include a perfectly insulated boundary, a constant or time dependent surface temperature boundary, a heat exchange boundary, and a heat conduction boundary with two solids in contact, to name a few:

$$\frac{\partial T}{\partial x} = 0 \quad \text{Insulated boundary} \quad (61)$$

$$T = T(t) \quad \text{Time dependent surface temperature boundary} \quad (62)$$

$$\lambda \frac{\partial T}{\partial x} = U(T_a - T) + C(T_a^4 - T^4) \quad \text{Heat exchange boundary} \quad (63)$$

$$\lambda \frac{\partial T}{\partial x} = \lambda_2 \frac{\partial T_2}{\partial x_2} \quad \text{Two solids in contact boundary} \quad (64)$$

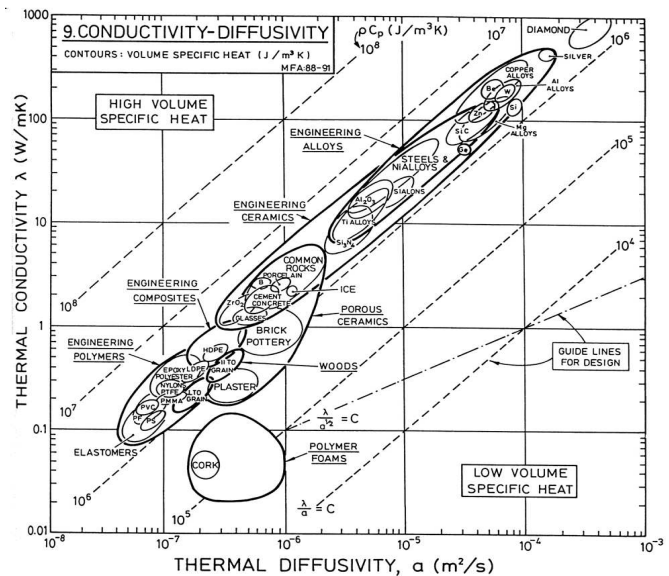
For a shape that is not planar, cylindrical, or spherical, we can use an equivalent spherical shape where:

$$r_{\text{sphere}} = \left( \frac{3V}{4\pi} \right)^{1/3} \quad (65)$$

where  $r_{\text{sphere}}$  is the equivalent spherical radius and  $V$  is the total volume of the shape.

We note that the partial differential equations in one, two, or three dimensions have to be solved for both temperature,  $T$ , and degree of conversion  $\alpha$ . It is critical to have measured values of the thermal conductivity, heat capacity, and density as a function of temperature as shown to the right <sup>a</sup>.

<sup>a</sup><https://www.lehigh.edu/~intribos/Resources/chart9.jpg>



## 8 Chemical Reactions Heat Generation Rates

Simple reaction rate expressions can be used to provide heat generation rates in K/s,  $q(T)$ , for use in dynamic modeling of thermal explosion theory or in dynamic modeling of runaway reactions and pressure relief. For isoconversion kinetic models, we can relate conversion,  $\alpha$ , to reactant mass or moles using the following equations:

$$m_p = \alpha m_T \quad (66)$$

$$\frac{dm_p}{dt} = m_T \frac{d\alpha}{dt} \quad \text{where} \quad \frac{d\alpha}{dt} = A(\alpha) \underbrace{(1-\alpha)^n}_{f(\alpha)} \exp\left(-\frac{E(\alpha)}{T}\right) \quad (67)$$

$m_T$  is the total reactant and products mass. Note that  $f(\alpha)$  can be different depending on the complexity of the reaction system.  $(1 - \alpha)^n$  usually works well for a simple reaction. The reaction heat generation rate becomes:

$$q(T) = -\frac{1}{m_T} \frac{dm_p}{dt} \frac{\Delta e_{\text{rxn}}}{c_{vT}} \quad (68)$$

where  $q(T)$  is in K/s and is positive for an exothermic reaction where the heat of reaction is negative by convention. Substituting rate of conversion instead of rate of mass change yields the following:

$$q(T) = -\frac{1}{m_T} m_T \frac{d\alpha}{dt} \frac{\Delta e_{\text{rxn}}}{c_v} \quad (69)$$

As a result, the heat generation rate  $q(T)$  is normally expressed without the use of reactant and product mass:

$$q(T) = -\frac{d\alpha}{dt} \frac{\Delta e_{\text{rxn}}}{c_{vT}} \quad (70)$$

The SuperChems Expert reaction rates used in detailed dynamics modeling of multiphase vessels require a volume based rate expression. For a decomposition reaction, this can be written as follows:

$$\dot{R} = \frac{1}{V_T} \frac{dn_p}{dt} = -k(T) \left( \frac{n_p}{V_T} \right)^n \quad \text{where } k(T) = A \exp \left( -\frac{E}{T} \right) \quad (71)$$

where  $V_T$  is the total liquid volume in  $\text{m}^3$ ,  $k(T)$  is the reaction rate in SI units,  $n_p$  is the number of moles in kmol,  $n$  is the reaction order, and  $\dot{R}$  is the reaction rate in  $\text{kmol}/\text{m}^3/\text{s}$ . As a result, the reaction heat generation rate  $q(T)$  becomes:

$$q(T) = -\frac{1}{V_T} \frac{dn_p}{dt} \frac{m_w}{\rho_T} \frac{\Delta e_{\text{rxn}}}{c_{vT}} = -\frac{1}{m_T} \frac{dm_p}{dt} \frac{\Delta e_{\text{rxn}}}{c_{vT}} \quad (72)$$

We can show that the above reaction reduces to the same expression for heat generation using an isoconversion reaction rate if  $\frac{dm_p}{dt}$  is replaced with  $m_T \frac{d\alpha}{dt}$ :

$$q(T) = -\frac{1}{m_T} m_T \frac{d\alpha}{dt} \frac{\Delta e_{\text{rxn}}}{c_{vT}} = -\frac{d\alpha}{dt} \frac{\Delta e_{\text{rxn}}}{c_{vT}} \quad (73)$$

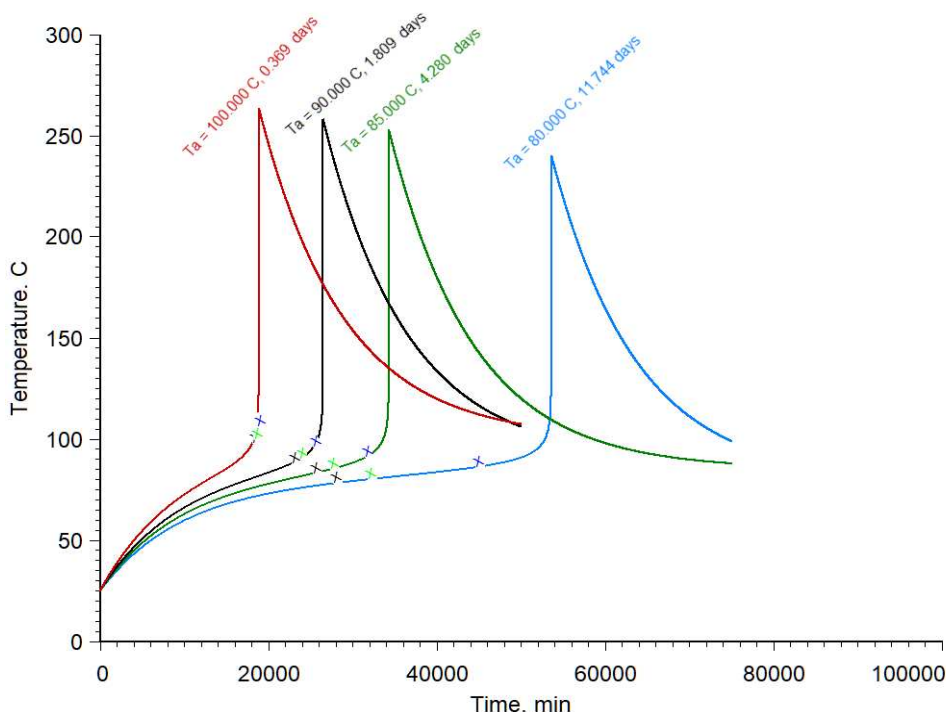
$q(T)$  can also be expressed as a sum of multiple individual reaction steps for complex systems.

## 9 $T_{SADT}$ for di-t-Butyl Peroxide

Using the first order isoconversion model developed for di-t-butyl peroxide (see Equation 14), we can easily calculate  $T_{SADT}$  using the Semenov approach outlined earlier (see Equations 49, 50, 51, and 52) which is implemented in SuperChems Expert . The 20 % mixture is stored in a 10 m<sup>3</sup> spherical vessel at 25 °C and is not exposed to solar heating. The overall heat transfer coefficient is assumed to be 5 W/m<sup>2</sup>/K.

$T_{SADT}$  is defined by the United Nations SADT test H.1 as the lowest ambient temperature at which the center of the material within the package heats to a temperature 6 °C higher than the environmental temperature,  $T_a$ , after seven days or less [7]. This duration is measured from the time when the temperature in the center of the packaging reaches 2 °C below the ambient temperature.  $T_{SADT}$  is the critical ambient temperature rounded to the next higher multiple of 5 °C.

Figure 7: SuperChems Expert  $T_{SADT}$  estimates for 20 % di-t-butyl peroxide in toluene



The SuperChems Expert simulations in Figure 7 show that  $T_{SADT}$  is between 85 °C (4.28 days) and 80 °C (11.74 days). The x marks on the curves shown in Figure 7 locate the 2 °C point below  $T_a$ , the point where the reaction temperature reaches  $T_a$ , and the point where the reaction temperature reaches 6 °C above  $T_a$ .

The simple Semenov models in SuperChems Expert also allow the user to select a variety of vessel shapes and to add simulation options including solar heating and transient meteorological data sets. SuperChems Expert also includes options for 1D and 2D thermal explosion theory models as discussed earlier (see Equations 58, 59 and 60). SuperChems Expert provides dynamic simulation options for reaction systems where phase change and venting can occur with extensive options for

multiphase flow, wall segmentation, multiphase reactions, etc.

## 10 Quick estimates for $t_{MR}$ , $T_{NR}$ , and $T_{SA}$

Quick estimates for  $t_{MR}$ ,  $T_{NR}$ , and  $T_{SA}$  can be obtained using SuperChems Expert from the simplified equations developed by Melhem [4] and shown by Equations 53, 54, 55, and 56. Note that Equation 56 will require information about liquid thermal conductivity and shape factor.

Figure 8: Quick estimates for  $t_{MR}$ ,  $T_{NR}$ , and  $T_{SA}$  for 20 % di-t-butyl peroxide in toluene using SuperChems Expert

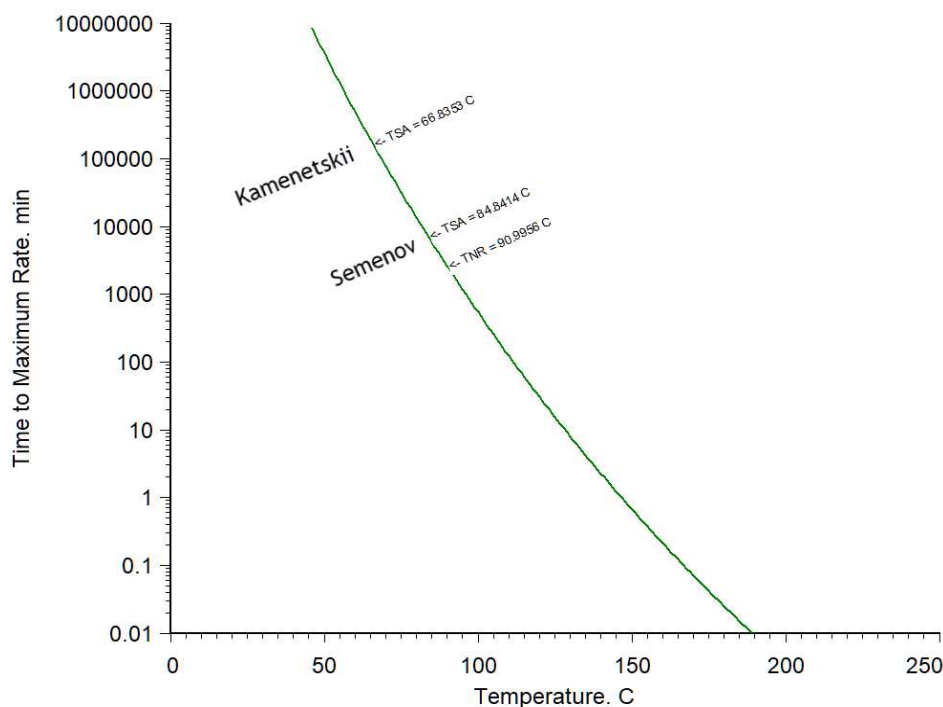


Figure 8 shows  $T_{SA}$  estimates for the same  $10 \text{ m}^3$  spherical vessel used in previous examples with an average thermal conductivity of  $0.1 \text{ W/m/K}$ .

## 11 Conclusions

Simple or isoconversion kinetic rate expressions are easy to construct and have been incorporated in SuperChems Expert versions 11.5 and later. They are useful for calculating thermal stability in systems without phase change and/or mass exchange.

Most importantly, they can be used in detailed thermal explosion theory computer codes and SuperChems Expert to evaluate thermal stability for storage and transportation of chemicals and

chemical mixtures for simple and complex packaging geometries under a variety of ambient and heating/cooling conditions.

As shown by this work, the use of isoconversion kinetic rate expressions can simplify the calculation of time to maximum rate, self accelerating reaction temperature, temperature of no return, and self accelerating decomposition temperature.

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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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