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Detection of stealthy outliers in thermal-kinetics modeling

Enio Kumpinsky*

Global Technology, Ashland Inc., PO Box 2219, Columbus, OH 43216, USA

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ABSTRACT

A method is presented to uncover outliers in data from small-scale process-safety studies. Points along an adiabatic runaway reaction, especially at the onset and conclusion of the experiment, may be vaguely jittery and difficult to recognize as outliers. Even though they fit well visually, their stealthy misalignment may have a profound impact on the estimate of kinetic parameters, such as reaction order, pre-exponential factor and activation energy. The proposed technique combines temperature and its time derivatives to magnify the effect of hidden outliers. Once identified, these points can be excluded from regression, in order to generate kinetic parameters with minimal distortions. This method is also suited to recognize autocatalysis.

1. Introduction

The safety of exothermic processes has been a fertile topic of research for many decades. It is an interdisciplinary field involving, among others, basic chemistry, kinetics, thermodynamics, transport phenomena, reaction engineering, mathematics and statistics. Advancement is evidenced by the large number of papers in technical journals and meeting proceedings since the work of Townsend and Tou [1] was published. Yet, there are still many opportunities to achieve progress. Kinetics is one area that can benefit from additional research. One key objective of kinetics is the establishment of reliable parameters that allow the practitioner to achieve a good match of self-heating rates between small-scale experimentation and computational modeling, a precondition to simulate large-scale events in industrial chemical reactors.

With good maintenance and calibrations, modern-day adiabatic calorimeters yield reliable experimental data. By means of regression [1] or the simultaneous solution of mass and energy balances [2], these data can then be converted into kinetic parameters for simulations. A topic of discussions between practitioners is the establishment of the initial and final experimental points of self-heating rates. The calorimeter inputs heat to increase the temperature of the sample until it identifies an exotherm. The minimal self-heating rate for which an exotherm can be detected depends on the calorimeter. It is usually 0.02–0.04 °C/min for the best instruments. Even after exceeding this detection limit, the initial data might contain scattering that is difficult to visualize. Similarly, data at the end of the reaction may be jittery, too. It is due, at least in part, to a significant increase in viscosity of the sample.

A key objective of the testing is to generate self-heating rates. Temperatures near the minimally detectable self-heating rate, be it at the onset or at the end of the exotherm, are highly leveraged [3]. Hence, they carry great weight in the calculation of the key parameters, such as reaction order, pre-exponential factor and activation energy. Outliers in the high-leverage zones may have a significant effect on the estimate of these parameters. The emphasis in this paper is the detection of outliers, for the most part at the extremes of the exotherm, because of their high leverage. However, adiabatic data cannot be considered perfect anywhere along a runaway reaction. This technique could be used to detect outliers throughout the entire process.

It may be difficult to identify these outliers when working with traditional Arrhenius plots of logarithm of self-heating rate versus the reciprocal of absolute temperature. The method presented in this work exaggerates the impact of these outliers in different types of plots, making it easy to spot them and deal with them accordingly.

Wagner and Snee [4] discuss the difficulty in detecting autocatalysis in an Arrhenius plot. In her publication on thermal runaway reactions, van Roekel [5] states that just being able to recognize autocatalytic materials is an important component of a hazard evaluation. In addition to providing the means to recognize stealthy outliers, the proposed mathematical treatment also facilitates the identification of autocatalysis in adiabatic experiments.

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* Tel.: +1 614 790 4226; fax: +1 614 790 6503.
E-mail address: ekumpinsky@ashland.com.

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Nomenclature

A	pre-exponential factor ($\mathrm{kg\,mol^{1-m-n}\,m^{3(m+n-1)}\,min^{-1}}$)
c	initial concentration of reactants ($\mathrm{kg\,mol\,m^{-3}}$)
E	activation energy ($\mathrm{J\,kg\,mol^{-1}}$)
k^*	pseudo zero-order rate constant, Eq. (7) ($\mathrm{min^{-1}}$)
m	product order in an autocatalytic reaction, zero for standard power-law kinetics
n	reactant order
R	universal gas constant ($\mathrm{J\,kg\,mol^{-1}\,K^{-1}}$)
R^2	coefficient of determination (%)
t	time (min)
T	thermodynamic temperature (K)
T_f	final temperature (K)
T_0	initial temperature (K)
ΔT_ad	adiabatic temperature rise, $T_\mathrm{f} - T_0$ (K)
Greek letters	
θ	Celsius temperature, $T - 273.16$ (°C)
θ_f	final temperature (°C)
θ_0	initial temperature (°C)
τ_a	term with temperature and its derivatives up to order 2, Eq. (4) (K)
τ_j	term with temperature and its derivatives up to order 3, Eq. (6) (K)

Sreenivas [6] showed that the differentiated and linearized thermal-kinetics equation could be applied to the establishment of parameters for simultaneous runaway reactions. Here, the self-heating rate equation of Townsend and Tou [1] is differentiated with respect to time without further linearization and the derivatives are combined in a way to facilitate the visualization of stealthy outliers and autocatalysis.

Two examples will be discussed: phenol-formaldehyde reaction and free-radical polymerization of acrylates. Uncontrolled reactions between phenol and formaldehyde in acidic or alkaline medium are some of the most hazardous in the chemical industry. The United States Environmental Protection Agency issued a report [7] on a serious incident involving this class of reactive systems. It summarizes the causes and consequences of loss of control and what could be done to prevent such occurrences. The development of an adequate kinetic model is an integral component of a good prevention program. Likewise, acrylate monomers are highly reactive when free-radicals are present, and they can build significant pressure in a vessel during runaway reactions [8].

2. Experimental

All experiments in this work were done in the Automatic Pressure Tracking Adiabatic Calorimeter (APTAC). This is a commercial calorimeter with low thermal inertia. Chippett et al. [9] and Wei et al. [10] describe the instrument in detail. The tests were performed in standard 130 ml titanium thin-walled spherical test cells. A Teflon-coated magnetic stirring bar mixed the reaction mass. Depending on the experiment, 70–80 g of reaction mixture were charged at room temperature, the vapor space of the test cell was evacuated to 70 kPa absolute and then it was sealed. The cell was operated closed until the end of each experiment. The tests initiated with the heat-wait-search mode to identify the onset of the exotherm. Upon detecting an exotherm of 0.04 °C/min, the calorimeter switched to adiabatic mode. When the exotherm subsided, the calorimeter changed from adiabatic to cooling mode after exceeding a preprogrammed temperature. The initial evacuation at room temperature did not cause any significant loss of reactant mass in the systems studied. The APTAC can follow a reaction adiabatically up to about 400 °C/min [9]. The two examples discussed in this work reach maximum self-heating rates well below 400 °C/min.

All raw materials were used as received without further purification. The handling of some chemicals requires especial safety considerations, particularly phenol, paraformaldehyde and acrylic acid. Material Safety Data Sheets should always be consulted prior to working with potentially hazardous materials.

3. Theory

This development starts with an augmented form of the self-heating rate equation of Townsend and Tou [1] that includes autocatalysis. These authors assumed that the temperature rise was proportional to the chemical conversion and that the kinetic parameters were constant. For an adiabatic system,

$$\frac{\mathrm{d}T}{\mathrm{d}t} = kc_0^{m+n-1}\Delta T_\mathrm{ad}\left(\frac{T-T_0}{\Delta T_\mathrm{ad}}\right)^m\left(\frac{T_\mathrm{f}-T}{\Delta T_\mathrm{ad}}\right)^n; \quad k = A\exp\left(-\frac{E}{R}\frac{1}{T}\right) \tag{1}$$

Corrections for the thermal inertia of the experimental apparatus can be taken into account during process simulations. The chemical conversion of the initial charge is represented by $(T-T_0)/\Delta T_\mathrm{ad}$, while one minus the chemical conversion is embodied by $(T_\mathrm{f}-T)/\Delta T_\mathrm{ad}$. Eq. (1) is generic in the sense that it applies to autocatalytic and standard power-law kinetics. If the reaction is autocatalytic, then $m \neq 0$. When it is not autocatalytic, $m = 0$.

Many times, a constant is added to the autocatalytic term, such as (autocatalytic constant) + (conversion)^m, without which the model could not work. The reason is that the conversion is zero in the beginning and autocatalysis cannot initiate. In Eq. (1), the autocatalytic term already has a constant, i.e., $T_0/\Delta T_\mathrm{ad}$. Collinearity issues could arise with the introduction of another constant. One possible solution is to commence simulations with an initial temperature that is a fraction of a degree above T_0. In case of free-radical acrylate polymerizations, the breakdown of the initiator provides the initial exothermic thrust to raise the temperature above T_0.

If Eq. (1) is differentiated with respect to time t, it results in

$$\frac{\mathrm{d}^2T}{\mathrm{d}t^2} = \left(\frac{E}{R}\frac{1}{T^2} + \frac{m}{T-T_0} - \frac{n}{T_\mathrm{f}-T}\right) \times \underbrace{Ac_0^{m+n-1}\Delta T_\mathrm{ad}\left(\frac{T-T_0}{\Delta T_\mathrm{ad}}\right)^m\left(\frac{T_\mathrm{f}-T}{\Delta T_\mathrm{ad}}\right)^n\exp\left(-\frac{E}{R}\frac{1}{T}\right)}_{\frac{\mathrm{d}T}{\mathrm{d}t}}\frac{\mathrm{d}T}{\mathrm{d}t} \tag{2}$$

Eq. (2) can be simplified to

$$\tau_\mathrm{a} = \frac{E}{R} + \frac{mT^2}{T-T_0} - \frac{nT^2}{T_\mathrm{f}-T} \tag{3}$$

where

$$\tau_\mathrm{a} = T^2\frac{\mathrm{d}^2T/\mathrm{d}t^2}{(\mathrm{d}T/\mathrm{d}t)^2} \tag{4}$$

Eq. (4) contains temperature, self-heating rate ($\mathrm{d}T/\mathrm{d}t$) and acceleration ($\mathrm{d}^2T/\mathrm{d}t^2$). Subscript a stands for acceleration, which is the highest-order derivative in this expression. The temperature at which the maximum self-heating rate occurs is obtained by setting τ_a equal to zero. Following the same differentiation procedure on Eq. (2) or (3) results in

$$\tau_j = \frac{E}{R} + \frac{mT^3}{2(T-T_0)^2} - \frac{nT^3}{2(T_f-T)^2} \tag{5}$$

Where

$$\tau_j = -\frac{1}{2}\frac{T^3}{\mathrm{d}T/\mathrm{d}t}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\tau_a}{T^2}\right) = T^3\,\frac{2(\mathrm{d}^2T/\mathrm{d}t^2)^2 - (\mathrm{d}^3T/\mathrm{d}t^3)(\mathrm{d}T/\mathrm{d}t)}{2(\mathrm{d}T/\mathrm{d}t)^4} \tag{6}$$

Eq. (6) contains temperature, self-heating rate ($\mathrm{d}T/\mathrm{d}t$), acceleration ($\mathrm{d}^2T/\mathrm{d}t^2$) and jerk ($\mathrm{d}^3T/\mathrm{d}t^3$), also known as jolt, surge or lurch. Subscript j stands for jerk, the highest-order derivative in Eq. (6). The temperature at which the self-heating rate inflects from acceleration to deceleration is calculated by setting τ_j equal to zero.

The primary function of Eqs. (3) and (5) in this work is to identify stealthy outliers in the data and to recognize autocatalysis. After all, numerical differentiation tends to amplify noise. In theory, these equations could also be used to determine kinetic parameters. Later, it will be explained that direct regression is not a good application of the method. Note that τ_a and τ_j could be written in dimensionless form by dividing both sides of Eqs. (3) and (5) by T. However, this action would add unnecessary curvatures to graphs, such as $E/(RT)$ instead of a constant E/R, thus hindering the detection of outliers.

Also needed for the calculations are the pseudo zero-order kinetics parameters, calculated as

$$k^* = \frac{\frac{\mathrm{d}T}{\mathrm{d}t}}{\left(\frac{T-T_0}{\Delta T_{ad}}\right)^m \left(\frac{T_f-T}{\Delta T_{ad}}\right)^n \Delta T_{ad}} = c_0^{m+n-1} A \exp\left(-\frac{E}{R}\frac{1}{T}\right) \tag{7}$$

Eq. (7) is very sensitive to the kinetic order. If the order is properly chosen, the plot of $\log(k^*)$ versus $1/T$ should fit approximately a straight line [11].

4. Calculation

The methods for solving Eq. (1) for its parameters are explained elsewhere for linear [12] and non-linear [13] regression forms. The goal is to fit the self-heating rate $\mathrm{d}T/\mathrm{d}t$ as a function of temperature T. The logarithmic version of the equation is used to calculate the reaction order and to estimate the kinetic parameters. Then, the original, non-linear form of Eqs. (1) and (3) are independently regressed for kinetic parameters other than the reaction order. Non-linear regression requires an initial guess for the parameters. Here, their initial values come from the linear regression. The logarithmic transform renders the mathematical treatment very simple and spreadsheet calculations might suffice. The non-linear forms necessitate computational language and careful establishment of an algorithm. As it will be shown through an example, the linearized form of the equation is as good as its non-linear counterpart to estimate the parameters, as long as the outliers are removed from the regression data.

It can be rightfully argued that the kinetic model should be discriminated for different stages of the runaway reaction or even within the same stage. A more sophisticated kinetic model is certainly needed, for example, to establish the composition of vapor-phase evolution and dispersion in the atmosphere after a vessel relief device opens. The scope of this work is not the modeling itself, but to demonstrate how to recognize stealthy outliers.

As mentioned in the theory section, Eqs. (3) and (5) are not good at establishing kinetic parameters. In fact, Eq. (5) may present severe ranking issues, being able to estimate only the activation energy. Eq. (3) is more forgiving. It might be capable of yielding the activation energy and the initial and final temperatures, with the reaction order already pre-calculated by the logarithmic form of Eq. (1). In case Eq. (3) is used to determine kinetic parameters, the pre-exponential term is calculated afterwards by means of least squares:

$$A\left(\frac{c_0}{\Delta T_{ad}}\right)^{m+n-1} = \frac{\sum_{i=1}^{N}(\mathrm{d}T/\mathrm{d}t)_i(T_i-T_0)^m(T_f-T_i)^n \exp\left[-E/(RT_i)\right]}{\sum_{i=1}^{N}\left\{(T_i-T_0)^m(T_f-T_i)^n \exp\left[-E/(RT_i)\right]\right\}^2} \tag{8}$$

For Eq. (3), points at or near the peak exotherm can be exceptionally influential on the values of the parameters. While the regression may be very good at those points, it may be of poor quality elsewhere. For these reason, regression with Eq. (3) should be avoided, even with quality data, as the first example will demonstrate.

Regarding the derivatives of Eqs. (4) and (6), it is essential to consider a good differentiation algorithm. Two or three-point formulas do not work well. Calorimeters usually provide the self-heating rate, $\mathrm{d}T/\mathrm{d}t$. Experience with the APTAC has shown that $\mathrm{d}T/\mathrm{d}t$ calculations are very good and can be trusted. The practitioner is responsible for determining acceleration and jerk. The first step is to match the calculations of first-order derivatives with the self-heating rates that the calorimeter software determined. Only if the match is good should estimates for the second and third derivatives be carried out. All calculations in this work were done using Fortran as programming language. For the computation of derivatives, IMSL subroutine DSPLEZ was employed [14]. This is a double-precision subroutine based on the splines method.

5. Results and discussion

For convenience, temperatures in the graphs will be presented in degrees Celsius, although the calculations have been done in kelvins. The difference between standard power-law and autocatalytic kinetics in the determination of τ_a and τ_j can be better understood in graphic form. In Fig. 1, theoretical curves are traced for a second-order reaction with the given parameters. They tend to E/R as T goes to 0. As T increases, τ_a and τ_j get smaller. As T approaches T_f, τ_a and τ_j go to $-\infty$. Similar curves can be traced for other reaction orders. For a zero-order reaction, however, τ_a and τ_j are constant and equal to E/R. The difference between the standard kinetics of Fig. 1 and the autocatalytic kinetics of Fig. 2 is at lower temperatures. As Fig. 2 demonstrates for autocatalytic reactions, τ_a and τ_j tend to ∞ as T approaches T_0. Figs. 1 and 2 estab-

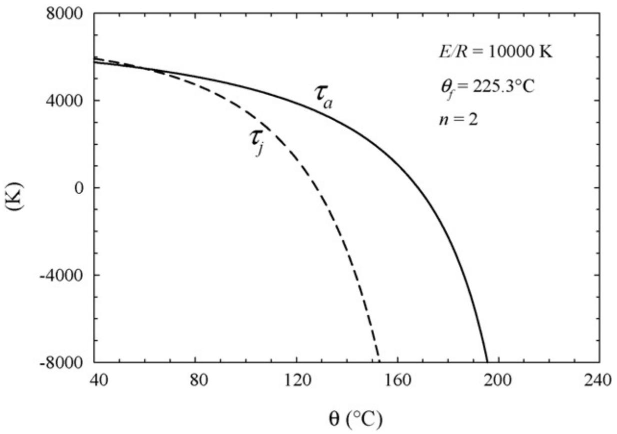

Fig. 1. Typical τ_a and τ_j profiles for a standard power-law second-order reaction.

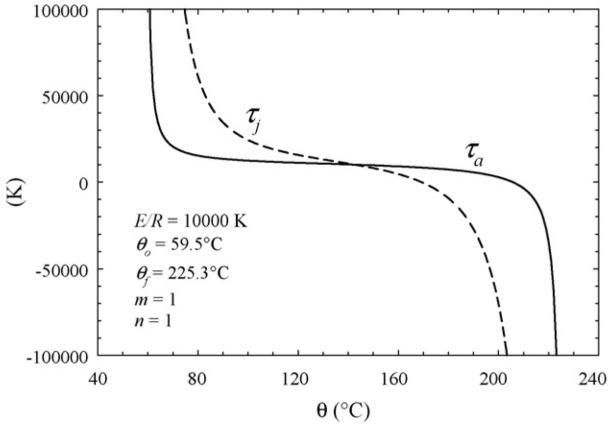

Fig. 2. Typical τ_a and τ_j profiles for an autocatalytic second-order reaction.

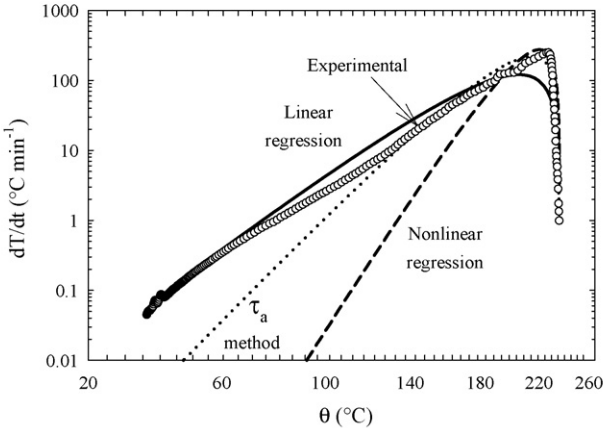

Fig. 4. Resole runaway reaction. Kinetic modeling with all experimental points.

lish a foundation for the interpretation of experimental results that follow.

Fig. 3 shows self-heating rates in the APTAC for a resole, i.e., a phenol-formaldehyde resin catalyzed by an alkali. This is a reaction of great commercial value. The experimental points seem to fit a standard *n*th order kinetics, i.e., $m = 0$ in Eq. (1). Note that Fig. 3 is a reverse Arrhenius plot having the ticks in the abscissa valued at $1-273.16/T$, with labels set at the respective θ values.

It is known that phenol–formaldehyde reactions consist of at least two consecutive stages with some overlap, i.e., addition and condensation. This can be verified through a careful examination of Fig. 3. Nevertheless, a simple one-stage model is applied for data treatment in this work. The complexity of this system cannot be underestimated. Atthajariyakul and Vanichseni [15] developed kinetics for seven different addition reactions at 30 and 57 °C. These temperatures are much lower than those of typical phenol-formaldehyde runaway reactions, but this is a clear demonstration of the associated intricacies. With the initial species identified by these authors, the possibilities for the ensuing condensation reactions are virtually unlimited. Furthermore, the formation of methylene glycol, polyoxymethylene glycols, hemiformals and polyoxymethylene hemiformals adds to complexity. Kossoy and Akhmetshin [16] indicate that, with lack of detailed information about the process, it may be necessary to apply a simple kinetic model. In other words, even if the model does not describe a detailed mechanism, at least it should satisfactorily explain the main characteristics of the reactive system for the intended purpose.

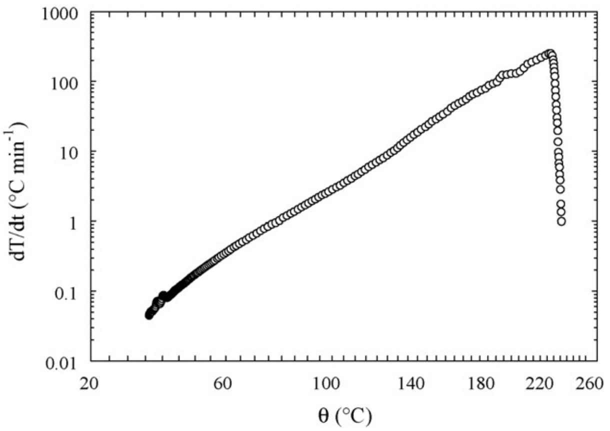

Fig. 3. Self-heating rate of a resole in the APTAC in a reverse Arrhenius plot.

The one-stage model presented here was based on this specific experimental data and cannot be generalized. It was oriented towards producing a reasonable prediction of temperature and pressure profiles inside a chemical reactor equipped with a relief device, such as a rupture disc or a relief valve. This particular one-step global kinetics mechanism cannot be used to predict the flow rates and total amounts of phenol, formaldehyde or other vapors that might be released to the atmosphere after opening the relief device.

Linear regression shows an overall, one-stage reaction order $n = 1.154$. Problems arise when fitting Eqs. (1) and (3) to the data, as Fig. 4 shows. Linear regression comes from the logarithmic transform of Eq. (1). Non-linear regression is done with Eq. (1) as is [17]. Regression with the τ_a formula is done in non-linear form by means of Eq. (3), with τ_a obtained from Eq. (4) based on experimental data and numerical differentiation. Linear regression seems to be the least sensitive to outliers, but this can be deceiving. The other two lines, obtained by non-linear regression, differ significantly from the experimental data. In practice, the non-linear Eq. (1) works as an excellent indicator of the quality of the data.

Figs. 5 and 6 plot Eqs. (4) and (6), respectively. The hidden outliers from Fig. 3 are revealed in Figs. 5 and 6 as star points. The curves should have shapes similar to those of Fig. 1. Figs. 5 and 6 confirm that most points do fit the model, but there are some that do not belong to the data set. For best results, they should be excluded from the regression. It is advantageous to generate plots for both τ_a and τ_j, because one of them discloses outliers better than the other. In this particular case, it was difficult to discern the higher-

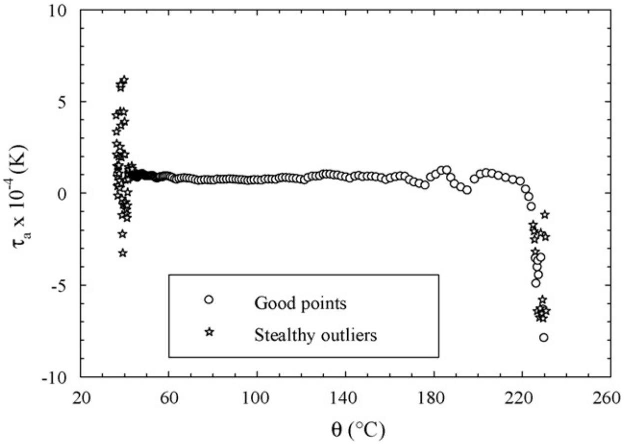

Fig. 5. τ_a plot for a resole runaway reaction showing outliers.

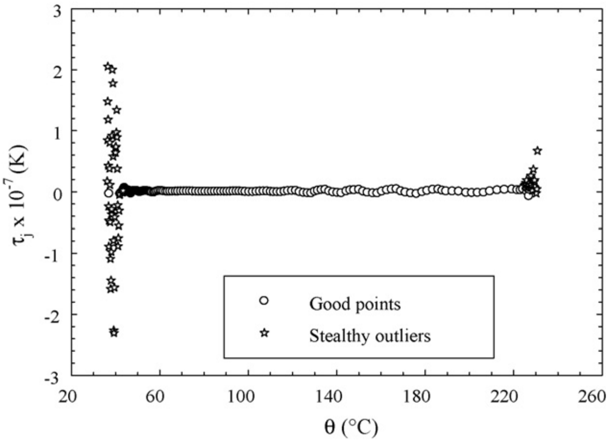

Fig. 6. τ_j plot for a resole runaway reaction showing outliers.

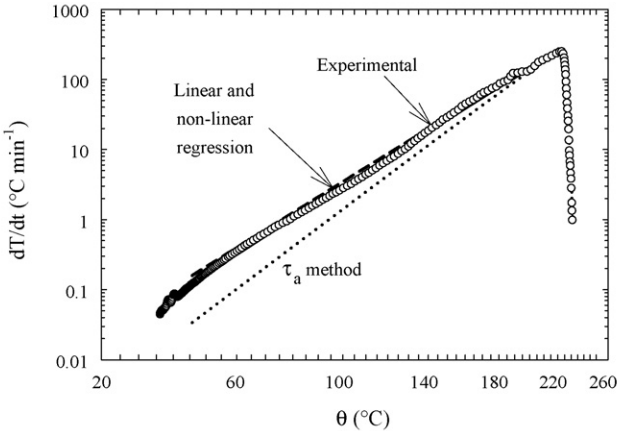

Fig. 7. Resole runaway reaction. Kinetic modeling with outliers removed.

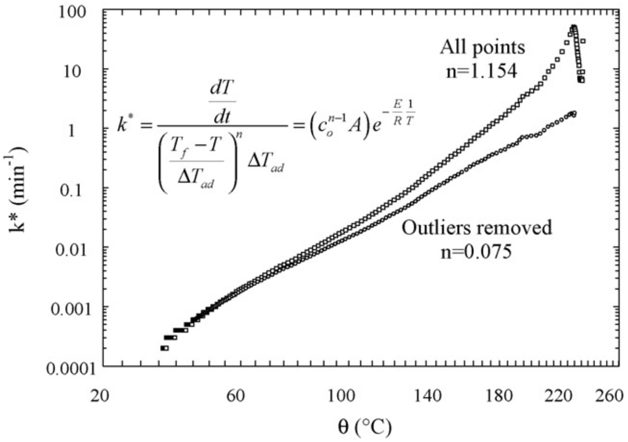

Fig. 8. Resole runaway reaction. Pseudo zero-order kinetic constant versus reaction temperature in a reverse Arrhenius plot.

temperature outliers in the τ_a graph, but they became apparent in the τ_j plot.

Regression was done with and without the stealthy outliers, and the numerical results are reported in Table 1. Some few influential outliers caused significant distortions to the non-linear regression. The logarithmic transform tends to level the influence of points that are orders of magnitude apart, so it is less prone to show visible distortions. Yet, the regression is flawed. Indeed, the order of the reaction estimated with the entire set of experimental points was 1.154. This is a deviation from practical experience, as the order of this reaction tends to be closer to zero. If the calculation is repeated excluding the outliers identified in Figs. 5 and 6, the value obtained for n becomes 0.075, which is much closer to zero. Table 1 confirms that the stealthy outliers affect all kinetic parameters.

Fig. 7 corroborates the numbers of Table 1. The exclusion of outliers greatly improves the outcome. In fact, the lines of the linear and non-linear regressions overlap almost perfectly. However, the τ_a method still yields inadequate results. The regression of Eq. (3) is highly influenced by the points around the peak exotherm, and the parameters it determines undervalues self-heating rates away from the top. For this reason, it is suggested that Eqs. (3) and (5) be used only to identify stealthy outliers. Parameters are best estimated with Eq. (1).

As Snee et al. [11] explain for power-law kinetics, the best estimate of n yields a straight line in the graph of the logarithm of k^* versus the inverse of the temperature. Fig. 8 shows the results for Eq. (7) based on the original regression ($n = 1.154$) and the regression with the outliers removed ($n = 0.075$). $\mathrm{d}T/\mathrm{d}t$ is experimental, while ΔT_ad, T_f and n are calculated. Clearly, Eq. (1) predicts a better reaction order once the stealthy outliers are excluded from the regression. The outcome for $n = 0.075$ is far from perfect because of model simplifications, but it is much better than that of $n = 1.154$. We might be tempted to round the reaction order n to zero, but it is important to remember that the nature of the kinetic model of this work is empirical. Mathematically, the parameters are simple expressions of the regressed experimental data.

Another reaction of great commercial interest is a mixture of different acrylate monomers, a thermal initiator and solvents. The monomer composition targets desired end-use properties. As per Fig. 9, the data the APTAC generated for this reaction seems to be of very high quality. Still, outliers may exist. This point can be explored with the use of Eqs. (4) and (6). Comparing Figs. 2 and 10, the reaction of Fig. 10 clearly exhibits consecutive autocatalysis.

Wagner and Snee [4] commented on the difficulty to identify autocatalysis with the simple interpretation of adiabatic data. Indeed, the detection of autocatalytic behavior in a plot of self-heating rates versus temperature may not be a straightforward task. The present work offers two expressions, τ_a and τ_j, to assist in the recognition of autocatalysis. As emphasized in the Calculations section, it is of paramount importance to have a good differentiation algorithm for the method to work.

Table 1
Regression results for the phenol-formaldehyde runaway reaction

Parameter	Linear regression		Non-linear regression		τ_a method, Eq. (3)	
	All points	Good points	All points	Good points	All points	Good points
$A(c_0/\Delta T_\mathrm{ad})^{n-1}$ ($\mathrm{K}^{1-n}\,\mathrm{min}^{-1}$)	2.64×10^{13}	3.16×10^{8}	1.49×10^{17}	2.01×10^{8}	2.71×10^{11}	3.57×10^{9}
E/R (K)	8770	7030	18130	6810	11950	8220
θ_f (°C)	231.7	225.3	231.3	225.3	233.2	225.8
n	1.154	0.075	1.154	0.075	1.154	0.075
R^2 (%)	97.7	99.9	76.6	99.7	69.4	91.0

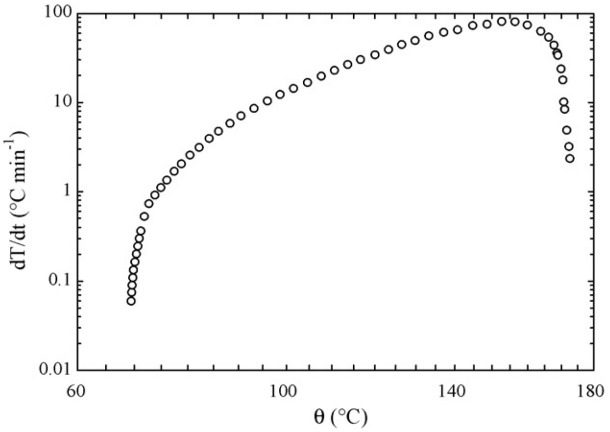

Fig. 9. Self-heating rates of a product consisting of a mixture of acrylates, a thermal initiator and solvents.

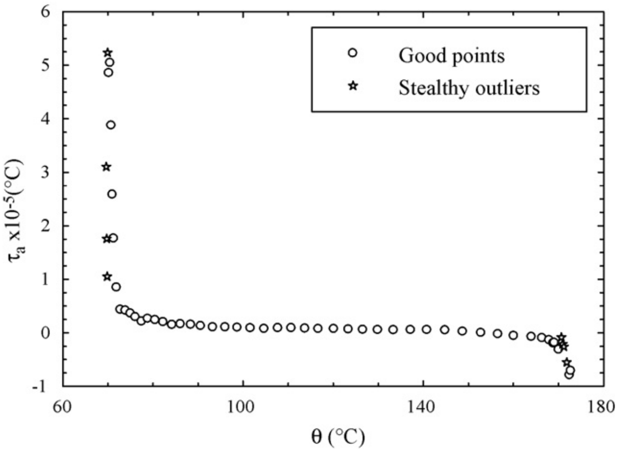

Fig. 10. τ_a plot for a runaway reaction of acrylates showing outliers.

Fig. 10 shows the outliers as star symbols in a τ_a plot. While outliers at the high end of temperature can be more easily spotted, especially if the ordinate scale is magnified, it is difficult to discern them at lower temperatures. However, τ_j reveals these outliers with no difficulty in Fig. 11. None of these outliers could have been identified by simply looking at the near-perfect plot of Fig. 9. Figs. 10 and 11 prove that it is best to generate graphs for both τ_a and τ_j, because one of them tends to expose some outliers more effectively than the other.

Four regressions were performed with the data, i.e., *n*th order and autocatalytic kinetics, including and excluding the outliers. The results are summarized in Table 2. In all cases, the overall order of reaction approaches 2, as expected for this type of system. The coefficients of determination R^2 for all instances are high, which is usually regarded as an indication of good regression. Fig. 12, however, tells a different story. The simple power-law kinetics is not a good fit, overall. It shows that a value of R^2 generally regarded as high, such as 97%, is not necessarily an indication of good regression. The reason why all coefficients of determination are so high in Table 2 is the same as described for Table 1. All regressions made good predictions around the peak exotherms, where the points are very influential and have the highest effect on R^2.

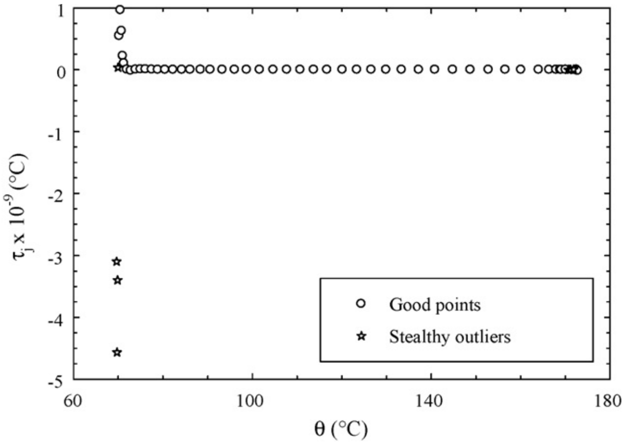

Fig. 11. τ_j plot for a runaway reaction of acrylates showing outliers.

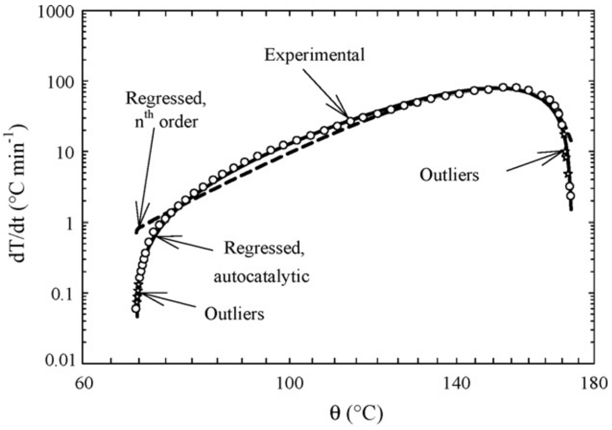

Fig. 12. Experimental self-heating rates compared to *n*th power and autocatalytic models. Regressions done with the outliers removed.

Most industrial vessels carrying out exothermic processes that may potentially release vapors and gases are equipped with relief devices. These are usually set to open at much lower temperatures than those achieved near the peak exotherm of most closed-cell lab experiments. Under these conditions, the kinetic model may

Table 2
Regression results for the acrylate runaway reaction

Parameter	*n*th order reaction		Autocatalytic reaction	
	All points	Good points	All points	Good points
$A(c_0/\Delta T_{\mathrm{ad}})^{m+n-1}$ (K^{1-m-n} min^{-1})	2.64×10^{13}	3.47×10^{12}	3.91×10^{7}	1.08×10^{6}
E/*R* (K)	14380	13180	8520	7150
θ_0 (°C)	26.2	41.3	68.5	69.2
θ_f (°C)	178.2	178.1	173.0	173.0
m	–	–	0.760	0.879
n	2.242	1.999	1.196	1.119
m + *n*	2.242	1.999	1.957	1.998
R^2 (%)	96.2	97.4	97.6	99.6

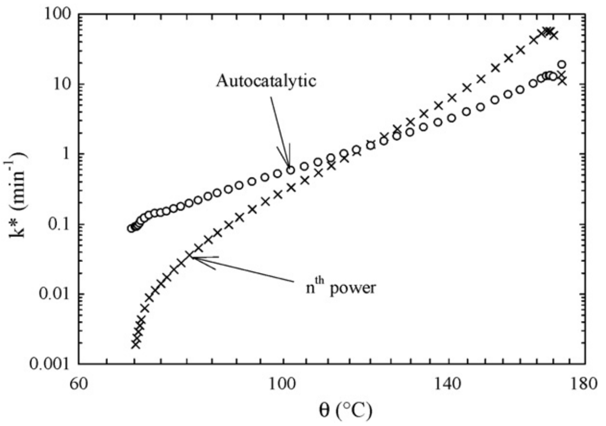

Fig. 13. Pseudo zero-order rate constant versus temperature for *n*th order and autocatalytic kinetics in a reverse Arrhenius plot based on regressions that exclude outliers.

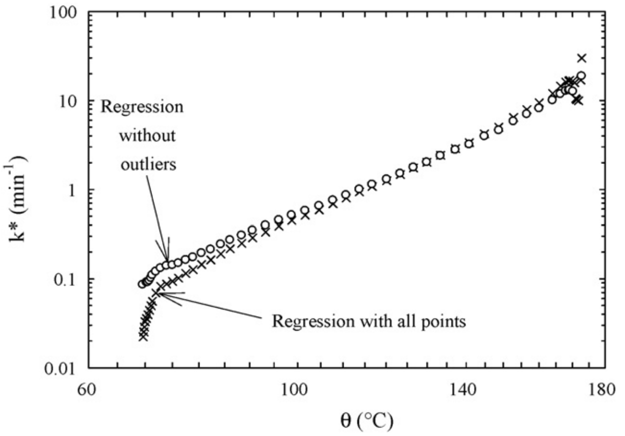

Fig. 14. Pseudo zero-order rate constant versus temperature for autocatalytic kinetics in a reverse Arrhenius plot based on regressions that include and exclude outliers.

not be a good representation of the reaction at temperatures in which the relief device opens. The effect of inadequate kinetics can be significant when simulating commercial-scale runaway reactions with programs such as SuperChems Expert [18]. It is most desirable to have R^2 as high as possible to ensure that the match of regressed kinetics with experimental data extends to temperatures well below the peak exotherm of the closed-cell tests. It is also worth noticing that the pre-exponential factor and the activation energy of autocatalytic kinetics are usually lower than those of *n*th-order kinetics.

For good kinetic representation of autocatalytic reactions, the logarithm of the pseudo zero-order rate constant, Eq. (7), should approach a straight line when plotted against the inverse of the temperature. Fig. 13 compares k* values for nth order and autocatalytic kinetics. Undoubtedly, the near straight line of the autocatalytic line is far superior to the *n*th-power profile. dT/dt is experimental, whereas ΔT_{ad}, T_0, T_f, m and n are determined mathematically.

Fig. 14 illustrates the importance of eliminating outliers from the data to be regressed. This plot was built using experimental self-heating rates and regression results from the last two columns of Table 2. Parameters estimated with all points yield curvature at lower temperatures and scattering at higher temperatures. Parameters determined without stealthy outliers generate a straight line with negligible scattering. The latter is the same line that appeared in Fig. 13.

6. Conclusions

A technique based on time differentiation of temperatures or self-heating rates of adiabatic runaway reactions was shown to facilitate the detection of outliers that otherwise would go unnoticed. These seemingly ordinary data points may cause considerable distortions to the estimate of kinetic parameters. Their exclusion from the calculations improves the quality of the regression, thus enhancing the match between experiments and modeling. The method can also be used to recognize autocatalysis. The technique was validated by means of two examples of commercial interest.

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References

[1] D.I. Townsend, J.C. Tou, Thermal hazard evaluation by an accelerating rate calorimeter, Thermochim. Acta 37 (1980) 1–30.
[2] Y. Iizuka, M. Surianarayanan, Comprehensive kinetic model for adiabatic decomposition of di-*tert*-butyl peroxide using BatchCAD, Ind. Eng. Chem. Res. 42 (2003) 2987–2995.
[3] D.H. Hildebrand, R.L. Ott, Statistical Thinking for Managers, 4th ed., Duxbury Press, Belmont, California, 1998, pp. 506–514.
[4] S. Wagner, T.J. Snee, Determination of kinetic parameters by calorimetric measurements, Prax. Sicherheitstech. 4 (1997) 231–247.
[5] L. van Roekel, Thermal runaway reactions: hazard evaluation, ACS Symp. Ser. Chem. Proc. Hazard. Rev. 274 (1985) 69–80.
[6] V. Sreenivas, Nonlinear concentration depletion effects on modeling runaway reactions, DIERS Users Gr. Mtg., http://www.ioxpress.com/diers, DUG 40-840-1, Fall 2007, Manchester, New Hampshire.
[7] EPA Report 550-F99-004. How to Prevent Runaway Reactions. Case Study: Phenol–Formaldehyde Reaction Hazards, August 1999.
[8] L.S. Kirch, J.W. Magee, W.W. Stuper, Applying calorimetry to polymerization, Chem. Eng. Prog. 83 (1987) 22–24.
[9] S. Chippett, P. Ralbovsky, R. Granville, The APTAC: a high pressure, low thermal inertia, adiabatic calorimeter, in: Proc. Int. Symp. Runaway Reaction, Pressure Relief Design and Effluent Handling, New Orleans, 1998, pp. 81–108.
[10] C. Wei, S.R. Saraf, W.J. Rogers, M.S. Mannan, Thermal runaway reaction hazards and mechanisms of hydroxylamine with acid/base contaminants, Thermochim. Acta 421 (2004) 1–9.
[11] T.J. Snee, C. Barcons, H. Hernandez, J.M. Zaldivar, Characterization of an exothermic reaction using adiabatic and isothermal calorimetry, J. Therm. Anal. 38 (1992) 2729–2747.
[12] D.C. Montgomery, E.A. Peck, Introduction to Linear Regression Analysis, 2nd ed., Wiley-Interscience, New York, 1992, Chapter 2.
[13] M.N. Ediger, A Gauss–Newton method for regression, The Mathem. J. 1 (1990) 42–44.
[14] IMSL Fortran Numerical Library, Subroutines for Mathematical Applications, Visual Numerics Inc., Houston, Texas.
[15] S. Atthajariyakul, S. Vanichseni, Development of a kinetic model for resole type phenolic resin formation, Thammasat Int. J. Sc. Tech. 6 (2001) 13–18.
[16] A. Kossoy, Y. Akhmetshin, Identification of kinetic models for the assessment of reaction hazards, Process Saf. Prog. 26 (2007) 209–220.
[17] E. Kumpinsky, Lumped kinetics of self-heating runaway reactions: a statistical treatment, Ind. Eng. Chem. Res., in press.
[18] SuperChems Expert, Software for pressure relief design, chemical reactivity assessment and management, consequence analysis and quantitative risk analysis; ioMosaic Corp: Salem, NH, v.5.98mp, 2008, Georges Melhem, President.