Technical Information Sheet No 61

Reprint of paper developed for the IICT Hyderabad on Chemical Reaction Hazards, December 1998.

The Role of Accelerating Rate Calorimetry in the Evaluation of Chemical Reaction Hazards

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The first purpose-designed instruments for the evaluation of reactive chemicals were originally devised in the 1970's. These were required by the major Chemical Processing Industries due to the rapid diversification of chemical species being manufactured - and their reactivity or the hazard that was associated in their processing. The safety issue often arose since the processing reaction was exothermic (i.e. with release of heat) or the chemical itself might decompose exothermically at a rather low temperature.

The Accelerating Rate Calorimeter was originally devised by the Dow Chemical Co to simulate potential runaway reactions or quantify the thermal and pressure hazards of certain chemicals or mixtures. In the 20 years since this technology has been available it has become established throughout the world as the most widely used 'adiabatic safety calorimeter'.

To initiate commercialism a licence was given to Columbia Scientific Industries and the first instruments were manufactured by them in the USA. Recently the technology has been re-engineered by Thermal Hazard Technology in the UK

As an instrument the Accelerating Rate Calorimeter takes a few grams of sample and determines its stability and quantifies any exothermic reaction that can occur. Under conditions of excellent adiabaticity the results can then be extrapolated to any industrial scale. The instrument is simple to use, highly sensitive, can test samples of any physical type or state, samples of any energetic level and its data (which includes pressure data) is easy to interpret and analyse. Such versatility has led to its wide acceptance.

However in today’s environment needs have become both broader and more specialised. In adiabatic safety testing of reactive chemicals a wider range of experiments must be considered. More versatility is demanded. To accommodate this the Thermal Hazard Technology Accelerating Rate Calorimeter has been and is being further developed to extend its applicability well beyond that of the original instrument. In addition ‘thermal safety software’ is now available that links to the Accelerating Rate Calorimeter and allows additional data analysis and interpretation to encompass a full range of scenarios to thermal explosion and vent sizing.

The additional areas for experimentation might be summarised

Low thermal inertia (ϕ) testing
Vent size testing
Safe release of Gas products, gas collection/analysis
Testing below room temperature
Sample testing with stirring at low ϕ
Reagent dosing (under pressure) at low ϕ
Testing of rechargeable batteries under charging/discharging conditions

However this presentation will limit discussion to the instrument and detail main areas of application.

The Accelerating Rate Calorimeter

In any adiabatic calorimeter there is the need to suspend the sample in a container in an environment where the temperature can be programmed to rise (or fall) in parallel to the sample and sample holder. In an adiabatic safety calorimeter the calorimeter itself must be rugged, designed to withstand any explosion of the sample holder caused by explosive decomposition of the sample itself and to allow minimal effort of hot corrosive chemical sprayed onto its surfaces.

Figure 1(a), 1(b) and 1(c) shows the Accelerating Rate Calorimeter its calorimeter assembly and the sample containers. Figure 2 shows a cross-section of the calorimeter assembly.

Fig 1(a)

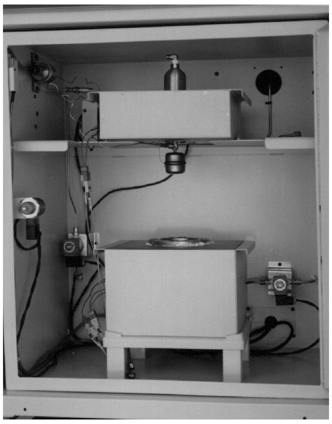


Fig 1(b)

Fig 1(c)

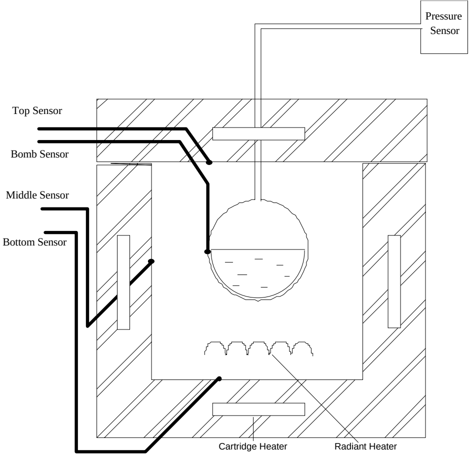


Fig 2

The calorimeter assembly has two parts, a top or lid section and a lower or main section. The main section is a copper pot 2.5cm thick which contains six rod heaters and two thermocouples. The top section has two heaters and one thermocouple and the main section has a side zone with four heaters and one thermocouple and a bottom zone with two heaters and one thermocouple. The calorimeter is surrounded by insulation and contained in a outer aluminium container. The sample container is usually referred to as the bomb since the system is used sealed and pressure tight. The bomb is connected to the top section by a compression fitting, from here tubing leads to the pressure transducer. The pressure line may be varied to allow a burst disk or safety valve or it may be adapted for gas collection or pressurisation. A fourth thermocouple is sited on the outside wall of the bomb. The sample holder is usually spherical and of diameter 2.5cm. Usually it is made from titanium or Hastelloy C.

In use, the calorimeter and pressure transducer are housed in the containment vessel. This is an explosion proof container though it is not a pressure vessel. The control electronics will control the experiment - i.e. the temperature of the calorimeter assembly. There is a PC that is the operator interface. Once the sample is in the bomb, this is connected to the lid and the lid put in place, the containment vessel is shut and the experiment can begin. The experimental conditions will be programmed in via the computer.

A Start Temperature and an End Temperature must be specified, values for Heat Steps, Wait Time and Sensitivity (a self-heating rate above which exothermic reaction is defined) must also be selected. Typically, if nothing is known of the sample, the start and end temperature may be 50°C and 400°C, the heat steps 5°C centigrade the wait time 15 minutes and the sensitivity 0.02 °C/min. Therefore it is not difficult to define the experimental conditions, perhaps the only difficult decision is the amount of samples to use. Too little sample will mean too small reaction but too large sample may cause bomb rupture by a spontaneous explosive decomposition. The sample mass is important, and this should be considered with the type of bomb being used. In the test there will be heat lost to the bomb and this can be corrected by using the ϕ correction. Setting up the test will take about 20 minutes.

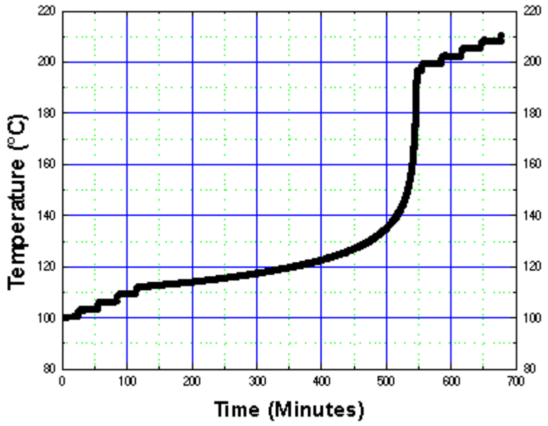
The temperature range of the Accelerating Rate Calorimeter is 0-500°C, the pressure range 0-150 bars, but using other pressure transducers a wider range may be achieved. The samples mass may be up to 10 grams of solid, liquid, slurry or mixture or the sample may be a reactive gas or gas-solid or gas-liquid.

At the start of the test, the temperature will rise to the start temperature. Then during the wait time the system will come to isothermal equilibrium, the temperature differences between the bomb thermocouple and the three jacket thermocouples which control the three heating zones of the calorimeter will be reduced to zero. Then there will be a seek period where should the temperature rise an exothermic reaction will be detected. If there is no temperature rise (greater than the selected sensitivity) the first small heat step will be programmed. After this there will again be a wait time and a seek period. This heat-wait-seek procedure will continue until an exothermic is determined detected, detection is by a temperature rise at a rate greater than the selected sensitivity.

The system will then enter the exothermic mode automatically and as the temperature of the bomb increases the calorimeter temperature will also increase, the system keeping the temperature differences between the sample bomb and a three separate calorimeter zones as small as possible. The system will continue in the exothermic mode until the self-heating rate decreases below the selective sensitivity, then the heat wait seek process will commence again. When the temperature reaches the end temperature the system will automatically switch off. There is an automatic cooling procedure whereby compressed air will cool the calorimeter to the chosen ‘Cool Temperature’. Throughout the test and until cool down the containment door cannot be opened.

During the test, data comprising time temperature and pressure and indicating the mode of the instrument will be stored. Of most use is the time temperature and pressure data relating to the exothermic reactions. However other data is useful, even the cooling data. Figure 3 shows typical real time experimental data.

Fig. 3.



Accelerating Rate Calorimeter Data.

The raw data plots are :

Temperature against time

Pressure against time

Self-heating rate against time

Pressure against temperature

Self-heating rate against temperature

Pressure rate against temperature

Self-heating rate against pressure rate

Calculated plots are available for

Time to maximum rate against temperature

Activation energy determination

Kinetic modelling

Thermodynamic heat of reaction determination

Di-Tertiary Butyl Peroxide is a ‘standard sample’ and a set of data plots is shown. The temperature and pressure plotted against time are shown in Figure 4 and Figure 5. They show the course of the reaction in real time.

Fig. 4.

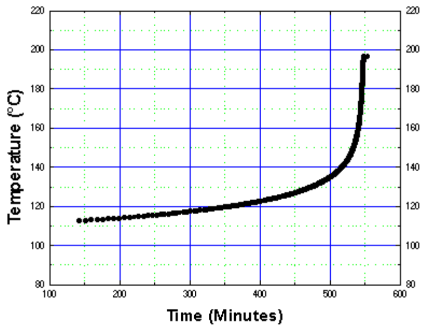
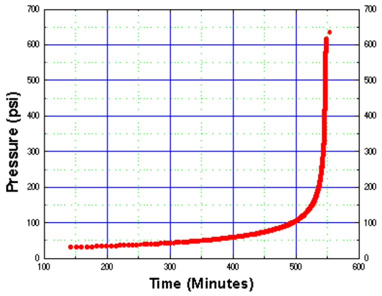


Fig. 5.



The onset of reaction, the end of reaction and the final pressure may be observed. However data presented this way does not reveal as clearly and as usefully as data presented in terms of self-heat rate and pressure rate plotted against temperature, Figure 6 and Figure 7.

Fig. 6.

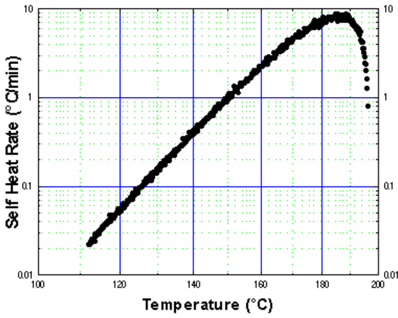
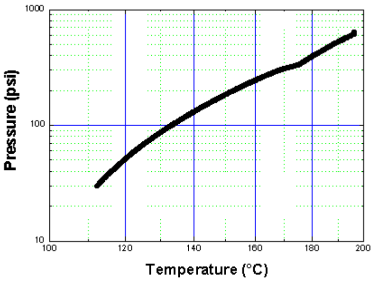


Fig. 7.

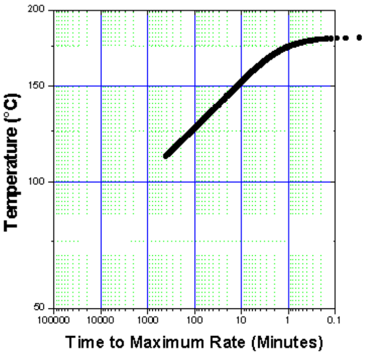


From the self-heat rate plot the onset is seen clearly, the heat rate at any temperature, the temperature of maximum rate and the type and number of reactions can be observed. Perhaps there are several overlapping reactions. The pressure rate plot clearly shows how the pressure develops.

The Time to Maximum Rate plot, Fig. 8, is a plot of temperature against the time that must elapse to get to the time when the self-heating rate is a maximum. This shows the 'Time to Explosion' at all temperature.

Analysis of self heat rate data and modelling the curve (if possible) will allow a full thermokinetic evaluation. However it is clear that a single Accelerating Rate Calorimeter test produces data that in full analysis aims to answer many questions...................

Fig. 8.



Is there a thermal hazard?
At what temperature does it begin?
Are there small low temperature reactions?
At each temperature, what is the self-heating rate?
What is the temperature of maximum self-heating?
What is the temperature of no return?
What is the time of explosion?
How many reactions (simple or complex)?
How fast is the reaction (kinetics)?
How big is the reaction (thermodynamics)?
What pressure develops?
How rapid is the pressure rise?

Is pressure associated with particular reactions?

Therefore

How to optimise the process
How to keep control of the process
How to maximise process yields

How to regain control, if this is lost
How much time for corrective action
How much time for evacuation
Temperature to set alarms
Reaction rate, order, mechanism
Impurity catalyst inhibitor evaluation
Reactor design, heat exchanger info
Relief vent sizing

Time to Explosion, Temperature of No Return, Maximum Safe Temperature

Should a runaway reaction commence, unless control is regained, the reaction will often go to explosion with devastating results. The reaction proceeds with rate increasing exponentially with temperature. This is described by the well-known Arrhenius Equation:

$$\frac{dT}{dt} \equiv -\frac{dc}{dt} = Ae^{-E/RT}c^{n}$$

But heat loss from vessels is known to increase only linearly with temperature. Therefore it is likely that at low temperatures where heat release from exothermic reactions is small, then the heat generated may be lost to the surroundings - but at higher temperatures where the heat release is rapid - then the heat will accumulate. Clearly there is a critical temperature, the ‘temperature of no return’.

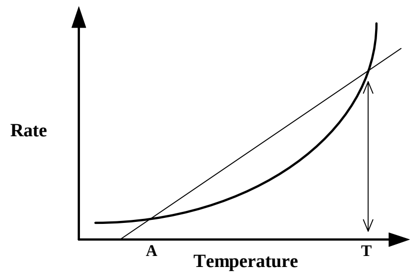
As indicated, a feature of the Accelerating Rate Calorimeter is its ability to determine directly the time to explosion or maximum rate of the material under investigation. The *time to maximum rate* must not be confused with the *temperature of no return*.

The *time to maximum rate* is the time period available prior to the incident from any specific temperature in the worst case. A knowledge time to maximum rate at all temperatures therefore allows alarm temperatures to be set, and time available for remedial measures or for evacuation. The time to maximum rate measured determined by accelerating rate calorimetry gives the time available at all temperatures under the worst case, fully adiabatic, conditions. The time to maximum rate is usually written tmr.

The *temperature of no return* is a temperature above which it is not possible to control a reaction or material in the vessel in which it is contained. The temperature of no returned is therefore dependent on the vessel size and shape and the ambient environment. The temperature of no return is usually written Tnr.

To illustrate this in the simplest case the heat generated and lost from a material held in a vessel is shown in Figure 9.

Fig. 9.



Self-heating of a reaction and heat loss from a vessel . Temp A is the equilibrium temperature, temp T is the max safe temperature.

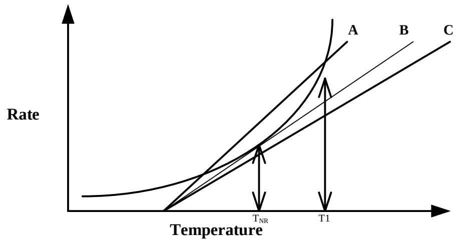
The basis of stability of a material in a vessel is
heat loss capability > heat production

This situation exists below the temperature marked ‘a’. Since the heat produced by a reaction increases exponentially with temperature whereas the heat loss from a vessel will increase linearly, the Temperature of No Return is shown at temperature T where
heat loss capability = heat production

And of course at higher temperatures the reaction will then go to completion as a runway reaction.

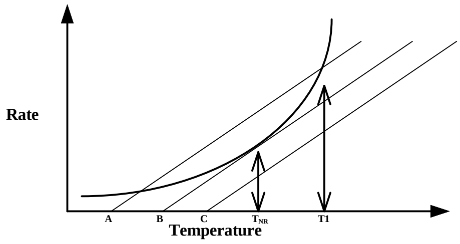
Therefore from such an analysis there is the possibility to determine;
Temperature of no return
Maximum pack size
Maximum safe operating temperature
Self- accelerating decomposition temperature, SADT

But from this simple visual illustration we can also see if for example there is less heat loss from the vessel (Figure 10) caused by using a larger vessel or if the ambient temperature increases (Figure 11). These figures show what happens to the Temperature of No Return!



Self-heating of a reaction and heat loss from 3 vessels, A, B and C. A can control the sample to temp T1, B is at the critical temperature T_{NR} and C cannot control the thermal runaway.

Fig. 10.



Self-heating of a reaction and heat loss from a vessel, at 3 ambient temps, A, B and C. A can control the sample to temp T1, B is at the critical temperature T_{NR} and C cannot control the thermal runaway.

Fig. 11.

but to do such an analysis the heat loss characteristics of the vessel must be known. It is these heat loss characteristics that describe the adiabaticity of the vessel.

To determine the heat loss from a vessel the overall heat transfer deficient, U, must be calculated or measured. This may be calculated using standard chemical engineering protocol (assuming the system is not too complex). Measurement involves filling the vessel with hot liquid (either water or a liquid of heat capacity matching that to be used) and determining the experimental cooling curve.

From this the "time constant" (τ) of the vessel can be determined

$$\tau = \frac{Mc_p}{UA}$$

Where M = mass and C_p = specific heat of the material and A is the surface area. And for any vessel

$$\tau = t_{mr}$$

The time constant represents the vessels adiabaticity and is the time from start of runaway to maximum rate or explosion. Typical values are shown below

Vessel	τ (minutes)
1 litre	30
25 litre	500
1 tonne	2200
10 tonne	4500
100 tonne	22000
1000 tonne	50000

A major advantage of the Accelerating Rate Calorimeter is that the t_{mr} curve is readily available. And from this curves therefore maximum safe temperatures can therefore be read directly.

This is shown in Figure 12 below.

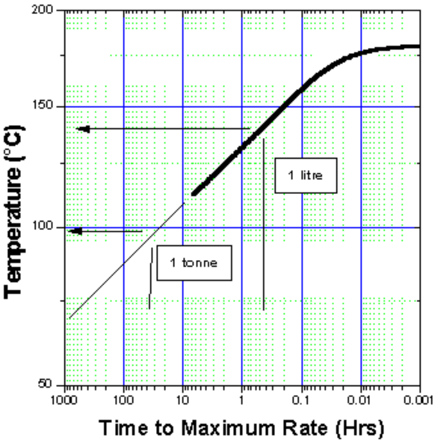


Fig. 12.

Kinetics, Thermodynamics and Real Samples.

An initial piece of information often considered is the onset temperature. Whilst the onset temperature is important, it is very important that it is understood that the onset temperature is not a simple number and should be quoted with further information describing the experiment. Clearly instruments that are more sensitive than the

Accelerating Rate Calorimeter will give onsets at lower temperature (eg isothermal micro-calorimeters) and instruments of lower sensitivity (eg vent size devices and DSC) will give onset at higher temperatures. This is illustrated in Figure 13.

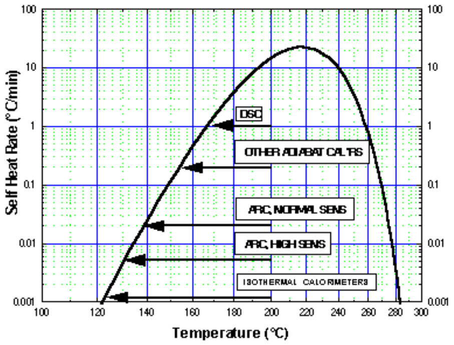


Fig. 13.

But in conjunction with the knowledge of the onset temperature there is usually applied a safety margin. A "safety margin rule of thumb" is still very regularly applied based on purely empirical views. Commonly there is a 50°C rule, a 60°C rule, even a 100°C rule.

It would seem more sensible that the safety margin need reflect certain aspects of the actual experimental data and real life scenario.

The data considerations may be:

Kinetic parameters
Activation energy
Order of reaction
Autocatalytic behaviour
Low temperature impurity reactions

The real life considerations may be:

Storage or processing
Storage ambient conditions
Cooling capacity
HAZOP findings
Mis-charging factors

These lists could be extended considerably.

The heat release from a material when it undergoes a self heating runaway reaction will raise the temperature of the sample. In an adiabatic system there is no heat loss and therefore the temperature rise is directly proportional to the heat of reaction. So simply measuring the temperature rise and then calculating to include the sample's specific heat, any heat loss correction, the sample's molecular weight and its purity the Heat of Reaction is obtained and the sample thus thermodynamically characterised. This may be simple for a simple reaction but for a complex decomposition, various the heat release from the components can be obtained. Figure 14 illustrates the determination of Heat of Reaction for a simple sample.

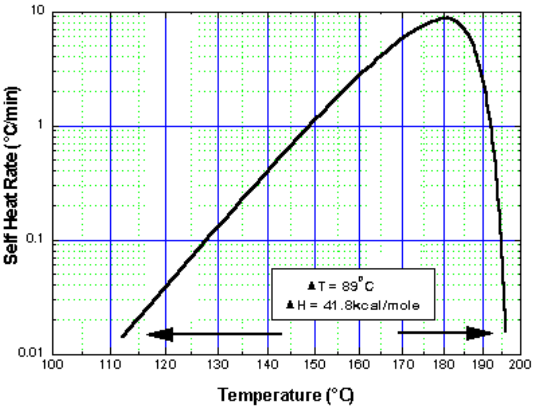


Fig. 14.

Determination of kinetic parameters is similarly easy - if the self-heat rate curve indicates a single reaction. Should the curve indicate more than one reaction or be of unusual shape part of the data may be used or it may be difficult to make a kinetic analysis.

Essentially in an adiabatic test, when the sample reacts or decomposes it gives out heat. The amount of heat is a quantitative indication of the amount of reaction. More specifically the rate of self-heating is directly proportional to the loss of concentration of reactant. The self heat rate curves are shown on scale which is logarithmic against reciprocal temperature in degrees Kelvin. This is deliberate since the axes are thus ‘kinetic’, the slope of the initial part of the curve gives the activation energy directly. Indeed from simply looking at a self-heat rate curve it is possible to get an estimate of the activation energy and the order of reaction. The higher the activation energy, the steeper the slope. The higher the order, the more curved is the data. Kinetic analysis however is carried out by a curve fitting procedure, this allows a best fit analysis to be done to get all kinetic parameters - and the analysis can be carried out with any chosen part of the data.

Figure 15 illustrates theoretical self-heat rate curves with Reaction order 0 to 3. Figure 16 shows the result of a curve fitting analysis - here the fit data has been offset since it would have been difficult to see both the fit and the real data since the two curves are very similar.

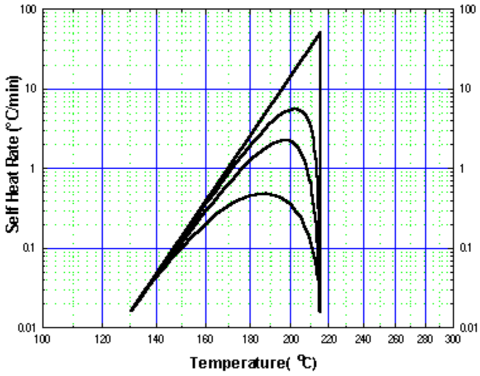


Fig. 15.

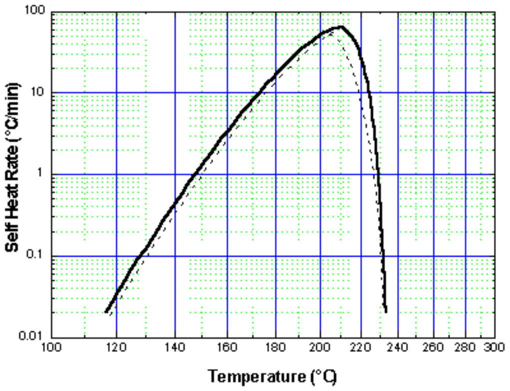


Fig. 16.

But real samples may contain impurities, may show complex reactions or the kinetics may not be simple. Figure 17 shows the result that might be expected from an autocatalytic sample - an initial very rapid rise in the self heating after perhaps an induction period. Figure 18 shows how impurities with low temperature decomposition might bring down the onset of decomposition. Note that this sample tested in an instrument of lower sensitivity may not observe such reactions. Therefore such a test may not pick up a problem caused by impurities

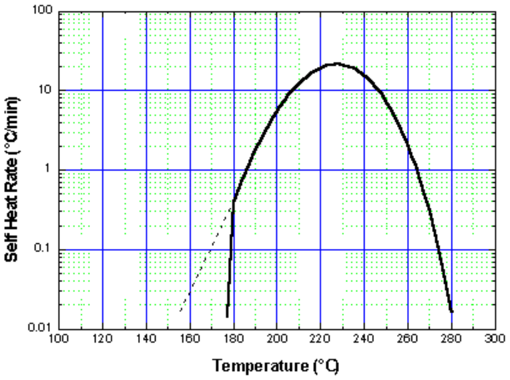


Fig. 17.

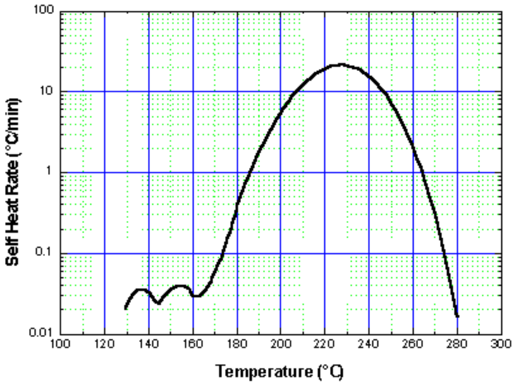


Fig. 18.

Of course samples may have a similar onset of reaction but differing activation energy. Figure 19 shows that extrapolation will give differing proposed safety margins.

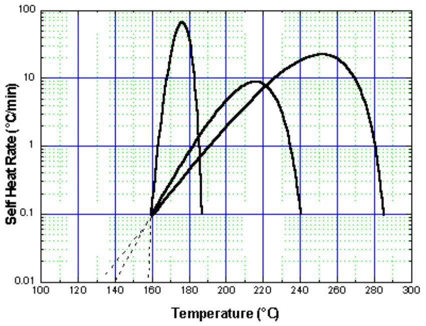


Fig. 19.

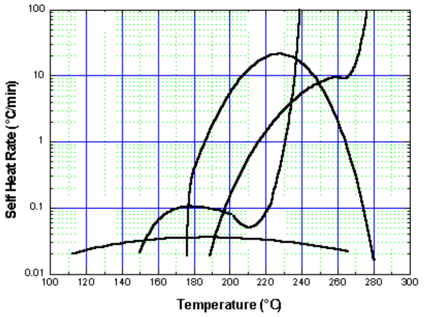


Fig. 20.

There is no simple answer to what safety margin ought to be allowed from any set of data. However the final figure, Figure 20, simply poses the question - which is the most dangerous sample? Of course the answer will depend upon what real life scenario is being simulated!

This article has attempted to introduce the Accelerating Rate Calorimeter and show how the data obtained is useful and how it should or should not be applied. How far interpretation of data can be carried does depend on the complexity or simplicity of the data itself, how much is know of the process or operation for which the testing is being carried out - and the experience of the interpreter. It is not difficult. There have been very many publications relating to the Accelerating Rate Calorimeter and its data. Much of what is written here is taken from Technical Information Sheets issued by Thermal Hazard Technology. These are freely available from Thermal Hazard Technology at the address of the authors and can be consulted for more detailed information.