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Technical Information Sheet No 99

Standard Data and Instrument Performance

Why use a standard sample?

Data from an Adiabatic Safety Calorimeter can be of value for two reasons:

1) To show the fundamental performance of the instrument with a standard sample
2) To show the performance of the instrument with any chosen sample.

Samples chosen by instrument manufacturers usually satisfy two of their criteria

1) Can be tested on their instrument to show good results.
2) Are recognised as samples commonly used.

With an adiabatic safety calorimeter the choice of ‘standard sample’ is limited. Reasons for this are:

1) The sample must be readily available in a pure form at reasonable cost.
2) Thermokinetic reaction data must be known and documented.
3) The sample should be kind to the calorimeter - for example, not explode or destroy sample containers.
4) The exotherm should be relatively simple to give nice, easy to interpret data.

To satisfy these criteria the sample most commonly used is Di-Tertiary Butyl Peroxide (DTBP).

Choice of DTBP as standard sample

DTBP itself is an unsuitable sample - it will undergo runaway reaction from near 100°C and this will result in explosion. This will occur unless the reaction is moderated by heat loss into the sample container or inert diluent. [In this discussion, the concept of thermal inertia or ϕ is assumed to be understood - if not please refer to the THT Technical Information Sheet 23]

Use of a heavy sample container or a diluent of course will increase the thermal inertia, ϕ, and allow heat loss from the sample. This slows down the reaction possibly preventing explosion. Of course in the Accelerating Rate Calorimeter, sample explosion may or may not rupture the sample container - but in other instruments even rapid reaction (pressure rise) can rupture the container.

When using pure undiluted DTBP, to prevent explosion of an Accelerating Rate Calorimeter sample container the ϕ factor must be above 2, to prevent an explosion of the sample within the container the ϕ must be above 3.5. Because of this inherent explosive exothermicity of DTBP all recent published data has been of DTBP/toluene mixtures on usually in the range 15 - 20% DTBP.

No further discussion on the ϕ factor appears here except to say that the true thermal inertia of a DTBP/toluene sample with 15 - 20% DTBP is ϕ = 5 - 9. Do not be confused by claim of ϕ approximately 1 when a 15% sample is used in a very light-weight container!

DTBP/toluene solutions of different DTBP contents are very useful to show performance of an adiabatic calorimeter - if a low percentage of DTBP is used a reaction low energy substance is ‘simulated’, at high percentages are highly energetic substances can be ‘simulated’.

DTBP also has the advantages that (1) its products of decomposition are clean so that sample containers can be re-used and (2) it has significant pressure release on reaction.

It is definitely NOT a challenging sample for any adiabatic calorimeter. A full set of data will show the optimal characteristics of any calorimeter.

Note that the THT Accelerating Rate Calorimeter with a light-weight sample container will allow DTBP/toluene samples in the range 5-50% DTBP to be studied (THT TI Sheet 23). The Thermal Hazard Technology instrument can satisfactory test up to 100% DTBP with either heavier weight sample containers or by use of lower sample mass. Other commercial calorimeters are often restricted to use of 5-15% solutions of DTBP.

Testing of DTBP as the standard sample will show not just the operational performance of the instrument but also reliability, reproducibility and accuracy of the instrument, its ability to determine the thermokinetic parameters.

A key paper detailing the thermokinetic decomposition of DTBP (in toluene) was published by Tou & Whiting (Thermochimica Acta 1981 Vol 41 p21). From this mean thermokinetic values are:.

Order of Reaction	1	
Activation Energy	38 kcal/mole	159 kJ/mole
Heat of reaction	43 kcal/mole	180 kJ/mole

It should be noted in analysis the activation energy is usually determined after fixing the reaction order at 1 and that variation is container material, diluent, even diluent percentage will vary the result. With the THT Accelerating Rate Calorimeter however results within 5% of these values are usually obtained.

Standard sample standard test conditions

The results reported here are for an 15% DTBP solution. This dilution has been selected to compare with results often given by other manufacturers. However THT recommend that the standard sample is 20% DTBP. 20% DTBP results are given in THT TI Sheet 100.

The DTBP used is 98% DTBP, there are several manufacturers of this standard grade. Though different tin-based stabilisers may be used, experience in THT indicates that fresh 98% DTBP from any source may be used. Toluene was of Analytical Reagent Grade. The mixture was made by weight and to within 0.05%.

A standard 8.75ml lightweight titanium bomb was used - its weight 5.140g. The sample mass was 6.696g. Using a specific heat of 2.095J/g°C for both DTBP and toluene the ϕ value for the mixture was $\phi = 1.19$ - but for DTBP alone $\phi = 8.00$.

Sample conditions were:

Start temperature	50°C	
End temperature	275°C	(Note 1)
Pressure Stop	135bar	(Note 1)
Detection Sensitivity	0.02°C/min	(Note 2)
Heat Step	3°C	
Wait Time	15 min	

Note 1	Whichever occurs sooner
Note 2	Sensitivities down to 0.005°C/min are possible.

Sample tests results

Fig 1 shows the temperature - time profile for the experiment. Note the precise, short time 3°C heat steps that lead in to the exotherm above 110°C. After the exotherm further heat - wait - seek periods are shown - again (and until 275°C) the stability of the instrument is evident. Fig 2 and Fig 3 magnify the scale of this data.

In Fig 2, the heat steps before the exotherm show an initial overshoot and settling. This is during the ‘wait period’. At 101°C after settling the temperature is essentially constant – i.e. isothermal, there is no indication of an exotherm. This is during the ‘seek period’. At successively higher temperatures (3°C increments) it can be seen that the temperature line slopes upwards (there is continuous increase at a rate which increases with temperature).

At the 113°C step the rate is exceeding the selected sensitivity (0.02°C/min) and the instrument automatically enters the exotherm mode and tracks the exothermic reaction. At the temperature steps 104°C, 107°C and 110°C, exothermicity is apparent (by the continuous temperature rise) but the rate is below the selected sensitivity. If a sensitivity threshold of 0.005°C/min was for example selected the exotherm would be detected (and recorded) from a lower temperature (107°C). However since at this rate a 1°C temperature rise would occur over 200 minutes the length of time of test would be very much longer.

In Fig 3 the heat steps after the exotherm are shown, it is clear that the reaction has finished, the Accelerating Rate Calorimeter indicates (correctly) no exothermicity or endothermicity. This is not the case with other technologies - these instruments show significant continuous temperature decrease. This is caused by reflux condensation - usually on the lid part of the sample container. In these two zoomed figures the temperature of the sample is clearly in an exceptionally stable and adiabatic environment.

Fig 4 shows pressure data. This is an enlarged portion of the real time data at high temperature. This curve shows the ability of the instrument to record pressure when at high pressures and temperatures. Note the stability of the pressure data.

The figures shown below detail the exotherm data. The first figures show raw data, later ones are the result of calculation.

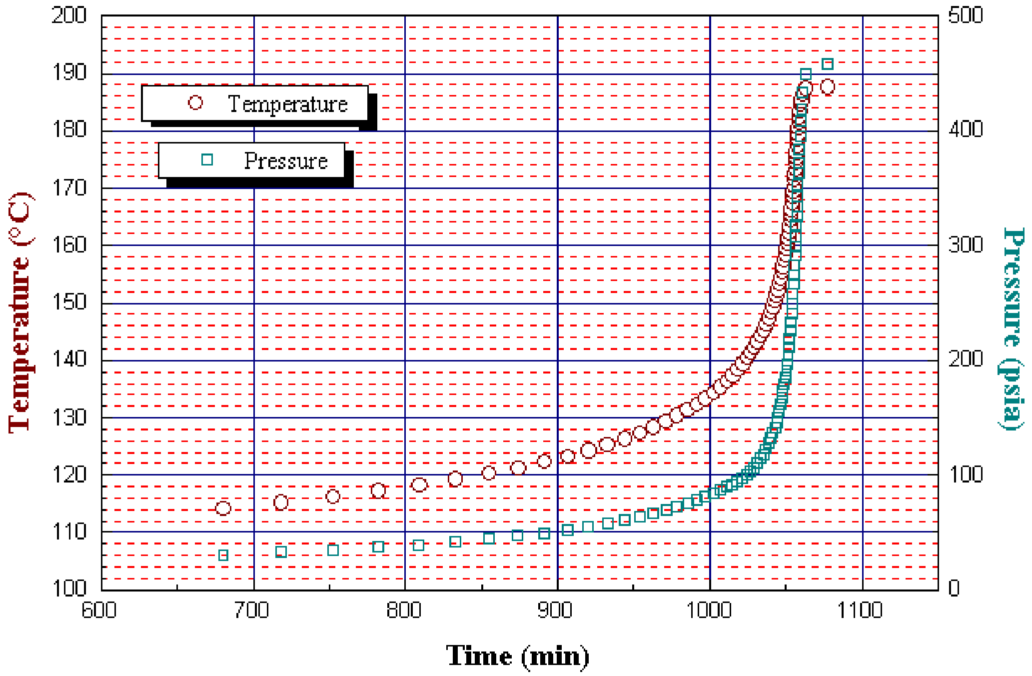


Fig 5

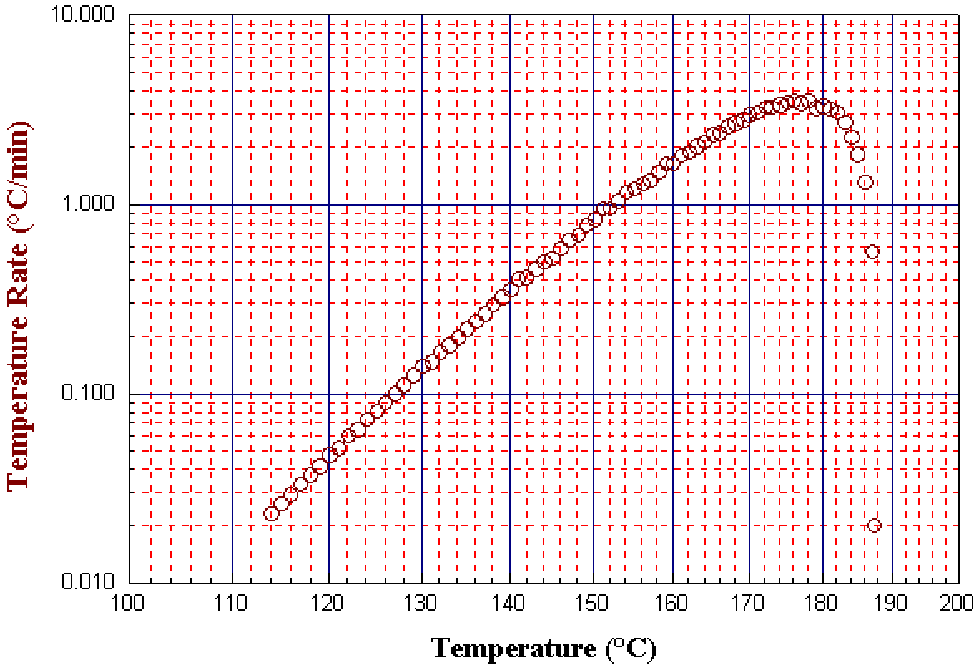


Fig 6

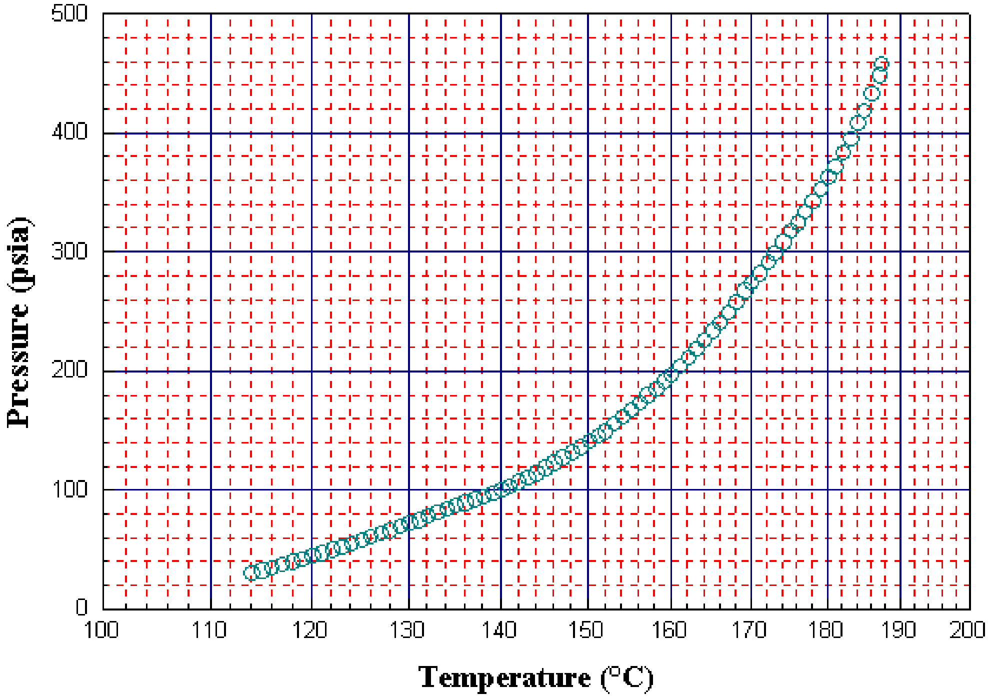


Fig 7

Fig 5 shows the real time integral response, the temperature and pressure increase with time. Fig 6 shows the derivative response for the temperature increase. These basic data plots show a simple single reaction. The Self-heat Rate data is plotted as a logarithmic value and the temperature is reciprocal Kelvin. These are 'kinetic axes', the shape of this self-heat rate curve shows that the reaction obeys Arrhenius Kinetics, the slope of the initial part of the curve (being a straight line) directly relates to the activation energy and the total temperature rise is directly proportional to the heat of reaction. The data plots show the clarity of presentation of Accelerating Rate Calorimeter data and indicate its ease of interpretation

Fig 7 and Fig 8 show the pressure data plotted against temperature.

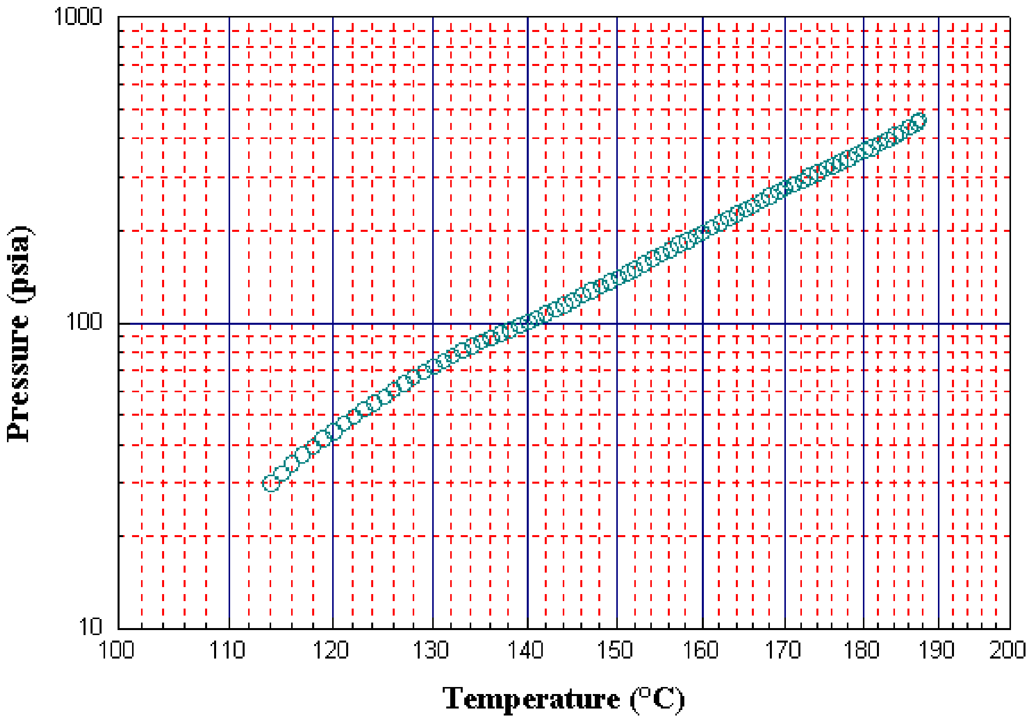


Fig 8

The pressure data plotted on linear axes would, if a straight line, indicate pressure rise of a non-condensible gas. The pressure data plotted on log-reciprocal axes would, if a straight line, indicate pressure rise of a condensible gas.

Fig 9 shows the real data (raw) Time to Maximum Rate curve. This curve is obtained by plotting back the data in time from the data point that occurs at the maximum self heat rate. The TMR curve is used to determine safety time and temperature limits and is always ϕ-corrected – and normally has to be extrapolated. In this example the ϕ value is low (ϕ=1.19) and therefore in the figure the corrected and uncorrected curves are not easily distinguished. However note that this ϕ value is for the mixture - considering DTBP alone and toluene absorbing heat then ϕ would be 8.0 (See THT TI Sheet 23).

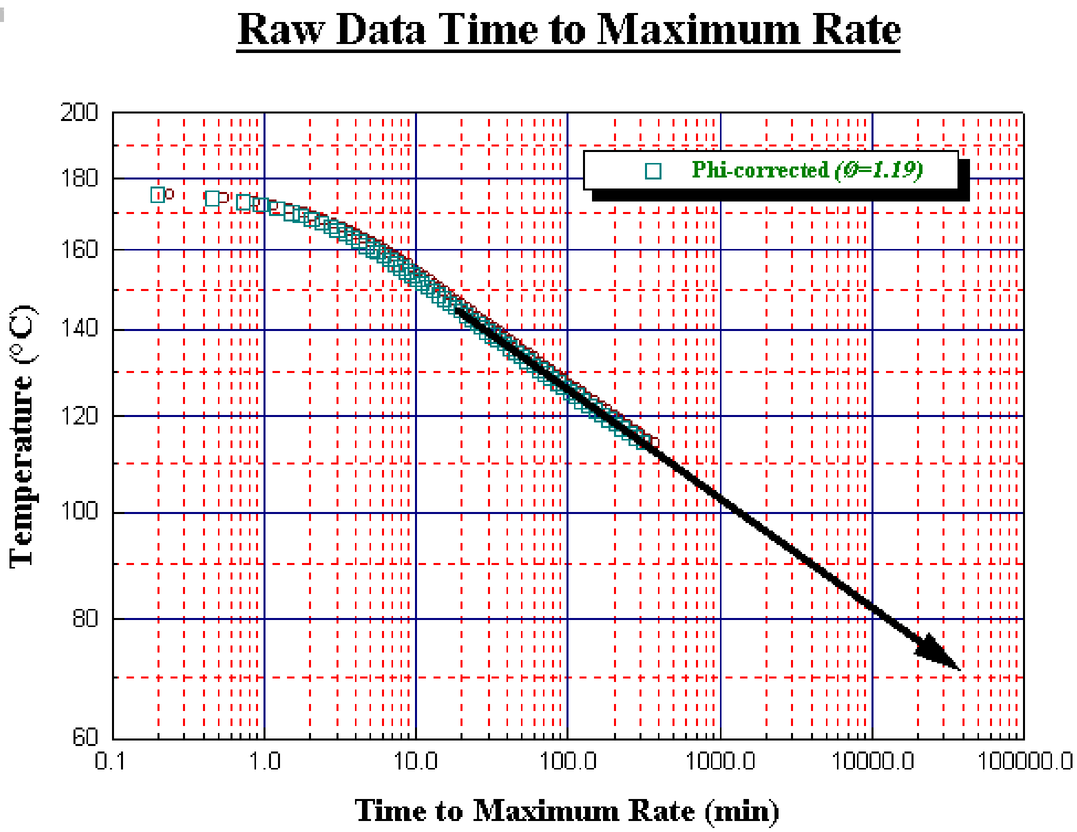
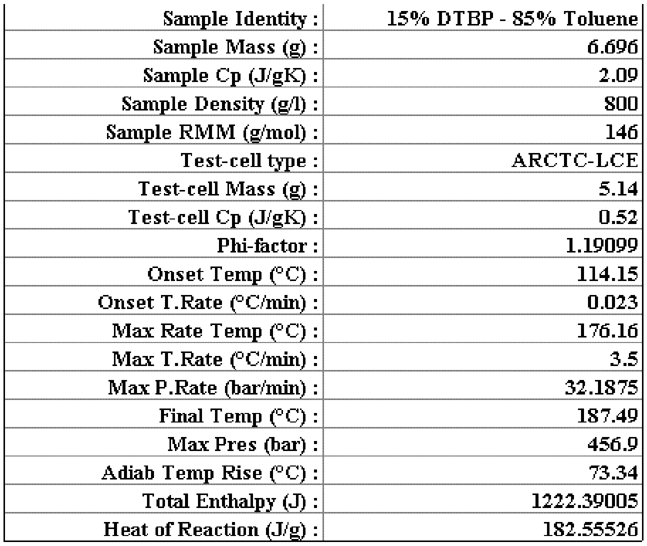


Fig 9



Sample Identity :	15% DTBP - 85% Toluene
Sample Mass (g) :	6.696
Sample Cp (J/gK) :	2.09
Sample Density (g/l) :	800
Sample RMM (g/mol) :	146
Test-cell type :	ARCTC-LCE
Test-cell Mass (g) :	5.14
Test-cell Cp (J/gK) :	0.52
Phi-factor :	1.19099
Onset Temp (°C) :	114.15
Onset T.Rate (°C/min) :	0.023
Max Rate Temp (°C) :	176.16
Max T.Rate (°C/min) :	3.5
Max P.Rate (bar/min) :	32.1875
Final Temp (°C) :	187.49
Max Pres (bar) :	456.9
Adiab Temp Rise (°C) :	73.34
Total Enthalpy (J) :	1222.39005
Heat of Reaction (J/g) :	182.55526

Fig 10

Other graphs are the result of data analysis by calculation and statistical fitting. The tabulated results are shown in Fig 10. In this example the reaction order was held at 1. The activation energy was determined (not shown) as 162kJ/mol and the heat of reaction calculated from the value shown as 178kJ/mol. Both agree well with the reported values discussed earlier.

From the Heat of Reaction, no other result should be obtained! A lower value would imply heat lost from the sample during the test, a higher value would indicate heat gain, which is only possible by the calorimeter being hotter then the sample. This is the perfect test to determine the adiabaticity of an adiabatic calorimeter.

The activation energy can be somewhat more variable and errors will be seen if the calculated result differs from the real time data. To show this, two graphs are available. The ‘psuedo-zero order plot’ which is a plot of the data at the chosen reaction order. This must be a good straight line fit if the order has been chosen correctly. This is shown in Fig 11. The second plot, as shown in Fig 12, is the fit of the modelled Self-heat Rate with the raw data. This is the final test to see the goodness of fit of the model.

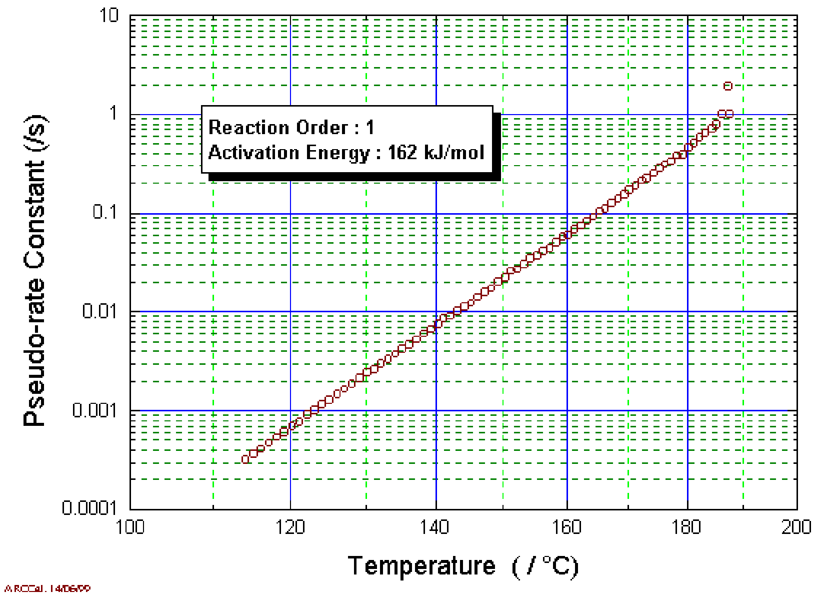


Fig 11

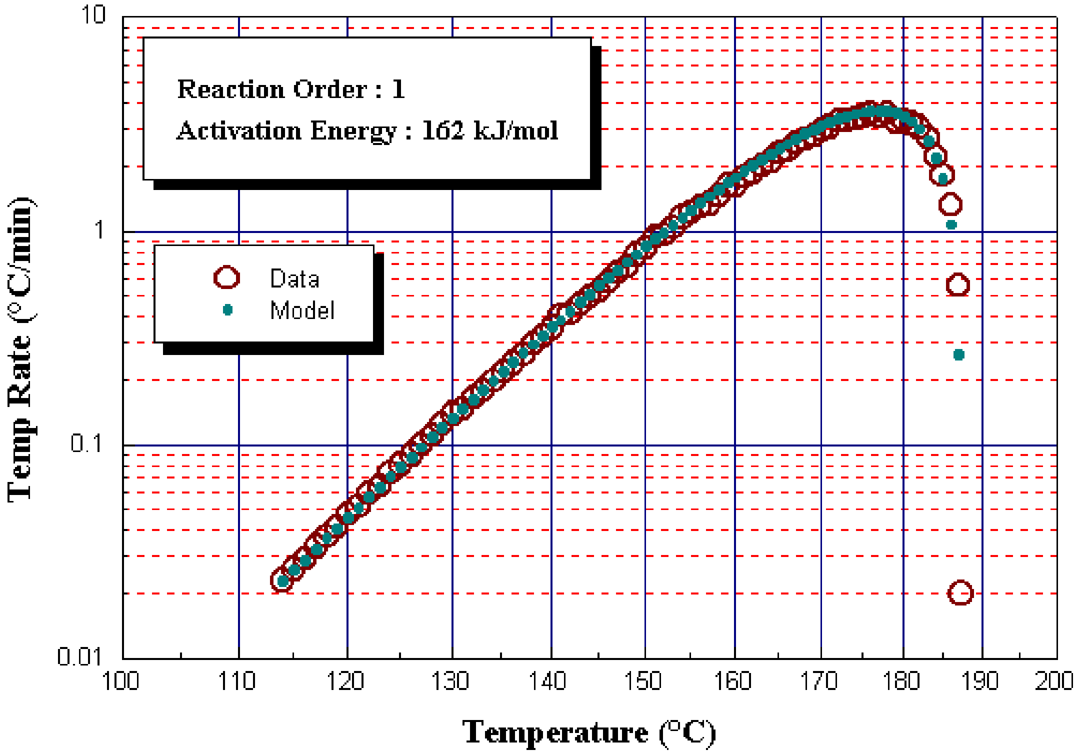


Fig 12

Both plots show an excellent fit. However true instrument performance is not fully described by data from an experiment carried out with a 'nice & easy' sample!

Reproducibility should be considered, range of sample type (solids, liquids, slurries, residues), range of sample energetics (detergents to explosives) and amount of sample available (mg to tonnes). Ability to work under varying pressure, vacuum, reactive or inert gas is also important as is operation at low and high temperature.

Uniquely the Accelerating Rate Calorimeter will cover this vast range of possibilities. It is not appropriate to go further here but we invite you to either: **Contact us to learn what the Accelerating Rate Calorimeter will do with your samples or send us a sample for no-obligation testing.**