

## Technical Information Sheet No 9

### Kinetic Analysis of Accelerating Rate Calorimetry Data

A full mathematical description of kinetic analysis of Accelerating Rate Calorimeter data is given in THT Technical Information Sheet No 20. Here a more general discussion of kinetic analysis aspects of Accelerating Rate Calorimeter data is given.

The kinetics of any reaction describe the speed of the reaction, how it accelerates with temperature and how it decreases in rate as concentration is depleted. The basic starting point is always the Arrhenius equation

$$-\frac{dC}{dt} = Ae^{-E/RT}C^n$$

Where A is the pre-exponential factor, E the activation energy and n the order of reaction.

Only when a fully adiabatic experiment is performed can the assumption be made that

$$-\frac{dC}{dt} \equiv \frac{dT}{dt} \equiv \frac{dp}{dt}$$

As the concentration is depleted so heat is produced and the rates are equivalent

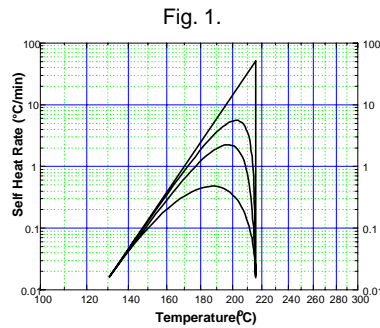
Thus

$$\frac{dT}{dt} \propto Ae^{-E/RT}C^n$$

Or for a zero order reaction

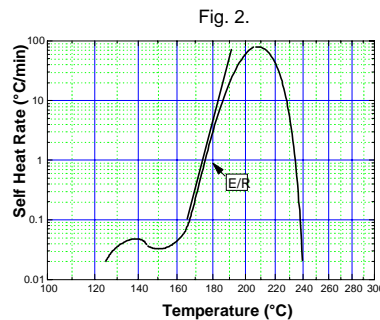
$$\frac{dT}{dt} \propto Ae^{-E/RT}$$

Plotting reaction data for reactions obeying Arrhenius Kinetics should show curves as in Fig. 1.



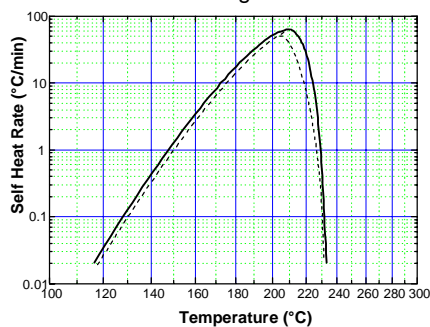
The slopes of the initial part of the self-heat rate curve (or all the curve for a zero order reaction) is  $E/R$  and thus the activation energy is readily obtained. The curvature of the self-heat rate plot is indicative of the order of reaction.

After some experience a fair idea of activation energy can be obtained simply by visual inspection, Fig. 2, even if the reaction is not simple .



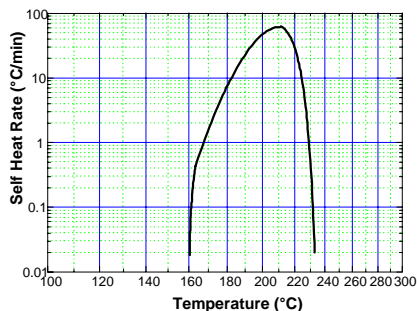
The Accelerating Rate Calorimeter data analysis software has routines built in to determine zero order (worst case) activation energy from portions of self-heat rate curves. By kinetics modeling the activation energy, order of reaction and pre-exponential factor can be determined if a complete set of data showing a simple, single mechanism is available, Fig. 3.

Fig. 3.



There is also the possibility of determining kinetics parameters for autocatalytic reactions. Such a reaction has a self-heat rate curve as shown in Fig. 4.

Fig. 4.

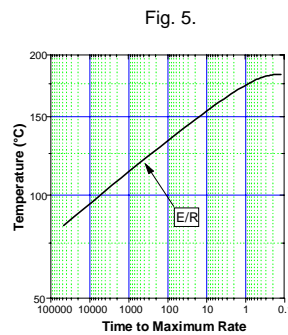


But it may be that this shape curve occurs for a other reasons: endotherm prior to exotherm, loss of inhibitor or build up of accelerator, as well as the classic autocatalysis mechanism.

Ideally kinetics analysis should only be carried out on simple reactions showing a single mechanism, but often in practice "numbers" are demanded from complex data, indicating multiple overlapping reactions. This is usually carried out empirically by selecting Arrhenius portions of data, but this should be done only with great care.

Other methods, outside the scope of this technical information sheet can reliably do this. These methods involve use of more sophisticated software, eg the Thermal Safety Software from Cheminform Ltd

Whilst kinetic analysis is usually carried out with self-heat rate data, the slope of the Time to Maximum Rate curve also yields the activation energy, Fig. 5.



Assuming pressure is generated, the pressure generation rate is itself equivalent to rate of loss of concentration for a single mechanism reaction and therefore this data can also be used.

A key aspect of interpreting accelerating rate calorimetry data is to know how far to proceed in the analysis of test data. As much information as possible should be obtained but unless the validity of kinetic numbers is properly understood it is not just undesirable but dangerous to over interpret the data in this way

To get Accelerating Rate Calorimeter data that will allow kinetic analysis it is necessary to perform the test with significant sample mass. But if there is a reaction mechanism change to give spontaneous exothermic reactions with rates  $100^{\circ}\text{C}/\text{min}$  or higher, the instrument time constant and heat transfer through the sample will have a significant role and cause significant error. Though this may be perceived as a problem, data obtained from such fast reactions is often of no real importance since the time that passes at such rates is so little that it can be considered to be zero.