thermal hazard technology

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Technical Information Sheet No 3

General Application of Accelerating Rate Calorimetry Data

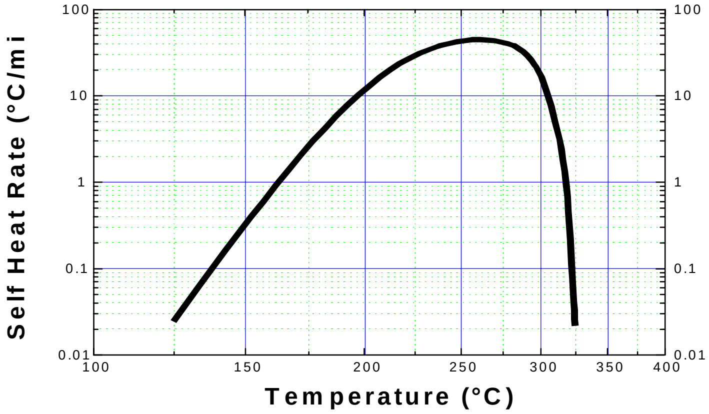
The results of an Accelerating Rate Calorimeter test is a table of time, temperature and pressure values. Data from the Accelerating Rate Calorimeter is given briefly in THT Technical Information Sheet No 2. THT Technical Information Sheet No 100 and higher numbers are examples of specimen data. Kinetic and thermodynamic interpretation of data is detailed in THT Technical Information Sheet No 9 and 10 and THT Technical Information Sheet No 20 discusses the theory of data interpretation. This Technical Information Sheet discusses general interpretation and application of accelerating rate calorimetry data.

Accelerating Rate Calorimeter data can be plotted as raw data graphs or graphs obtained from the calculation for kinetics and thermodynamic analysis, or for application for safety analysis, e.g. the Time to Maximum Rate graph.

The most basic plots are temperature against time and pressure against time. These plots have limited value, the information they contain is better presented in a different form. However the temperature and pressure time plots give an indication of the progress of the exothermic reaction against time and an indication of the acceleration of the reaction.

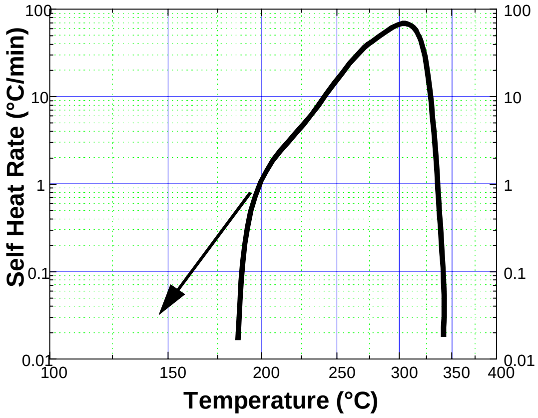
The plot of rate of temperature rise i.e. self-heating rate against temperature is much more informative and one of the most important graphs available from the accelerating rate calorimetry test. An example is shown in Fig. 1. From this graph the onset of reaction can be seen and the self-heating rate at every temperature is also clearly shown. The exothermic profile will indicate

Fig. 1.



whether there is just one simple reaction or several reactions which may or may not overlap. If

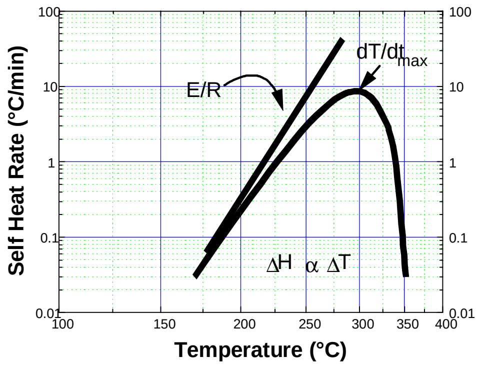
Fig. 2.



there is initial rapid acceleration of the self-heating rate then autocatalysis is likely, Fig. 2. The same sample from a different batch which has experienced a different thermal history may show onset at a lower temperature - at any temperature indicated by the arrow and line. Further study could yield additional information. In this case isothermal ageing for 24 hours at temperatures in the range 90-135°C may be carried out to see if the reaction will begin, after an induction time.

When the reaction is simple, the activation energy may be obtained from the slope of the self-heating rate, and from the temperature rise, the heat of reaction may be obtained. This is illustrated in Fig. 3.

Fig. 3.



Care should be taken when defining the onset temperature. The onset temperature is a function of the sensitivity of the test and perhaps a repeat test would give and onset at the heat step below or above the one at which exothermic necessity was detected here. This may give a variation in onset of +/- 5 °C. See THT Technical Information Sheet No 6. The self-heating rate plot is not usually corrected for heat lost into the bomb, the ϕ correction. Multiple reactions which may not show overlap in the data may overlap in a real situation. Clearly the best way to do a test is to use a ϕ value which is the same as that in the real case.

If the self-heat rate plot shows multiple overlapping reactions these may be reactions in series A → B → C or parallel reactions of the type A → B, A → C. These types of multiple reactions have to be studied further to decide which type they are. A test with a lower mass, higher ϕ (see THT Technical Information Sheet No 22) may separate the reactions since their heat output would be smaller. Thus they may be analysed singly, Fig. 4 and Fig. 5.

Fig. 4.

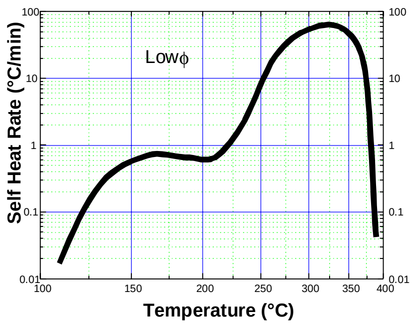
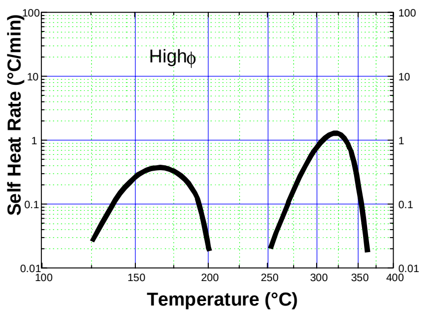


Fig. 5.



Parallel reactions may be studied by varying the mass or by isothermal ageing. Also the separate reactions may be studied by their pressure data, Fig. 6 and Fig. 7.

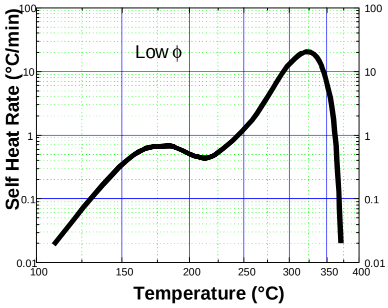


Fig. 6.

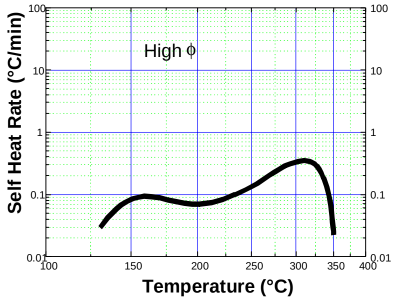


Fig. 7.

The two reactions may be of similar energy release or one may dominate, Fig. 8 and Fig. 9. There may be initial low energy reactions, perhaps caused by impurities, that lead in to the main

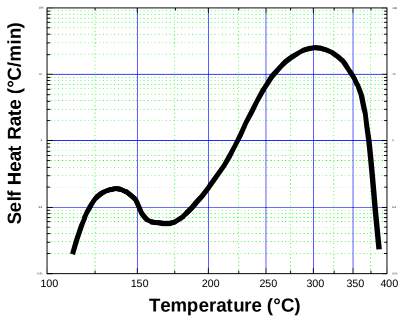


Fig. 8.

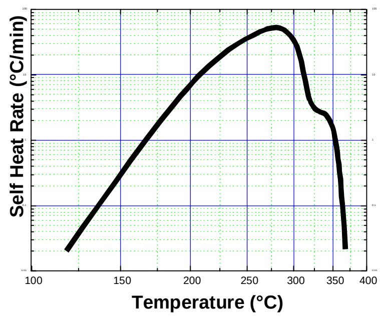


Fig. 9.

reaction and make the sample less stable, Fig. 10. Initial low temperature reactions may not be observed in tests with lower sensitivity instruments, Fig. 11.

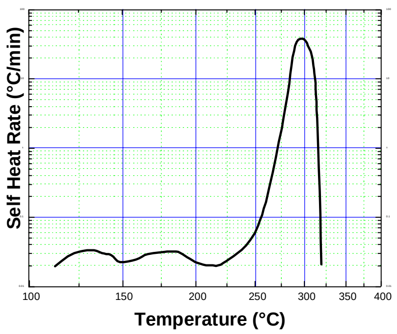


Fig. 10.

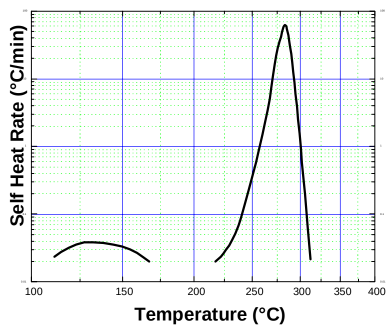
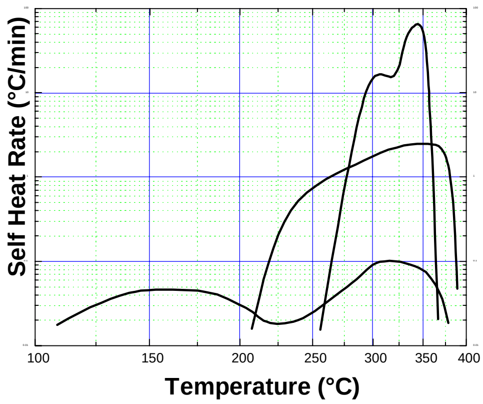


Fig. 11.

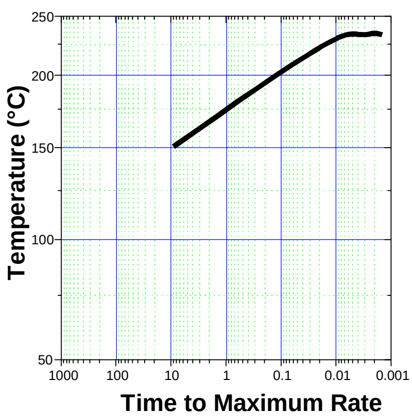
However as Fig. 12 shows it may not be easy to determine which is the most hazardous material!

Fig. 12.



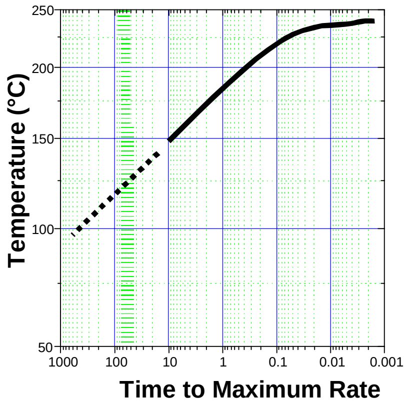
It is possible to present the temperature and time data in another form which is allows for additional analysis. This is the 'time to maximum rate' or 'time to explosion' plot. There will be a temperature at which the self-heating rate is a maximum and at this temperature the 'time to maximum rate' is by definition zero. However at all temperatures below this 'temperature of maximum rate' there will be a *time to the temperature of maximum rate*. Going down in temperature from the 'temperature of maximum rate', the 'time to maximum rate' will get longer and the longest 'time to maximum rate' will be at the very first data point. It is possible to plot this 'time to maximum rate' against temperature. This is shown in Fig. 13. There is a simple correction for the heat lost into the bomb, the ϕ correction and data from this plot is usually corrected.

Fig. 13.



After correction the time to maximum rate plot is a worst-case representation of the time from any temperature to the maximum rate or (in the real case) possibly explosion. It is important that this has been obtained directly by experiment. From this plot one can see how much time there is from any temperature to a disaster and as shown in THT Technical Information Sheet No 4 this can quantitatively be readily applied to give 'temperature of no return' in any vessel , Fig. 14.

Fig. 14.



But care should be taken when the exothermic reaction does not indicate a simple single mechanism. The data from this curve often needs extrapolation to get times appropriate for real-life scenarios. Only a worst-case extrapolation should be done. Fig. 15 and Fig. 16 show extrapolations from autocatalytic and multiple reactions 'time to maximum rate' plots.

Fig. 15.

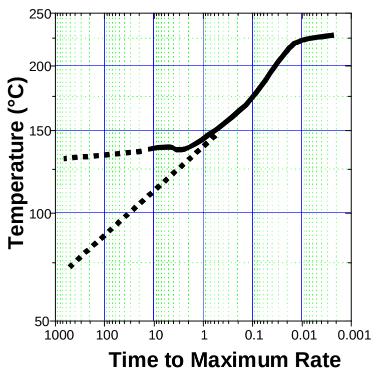
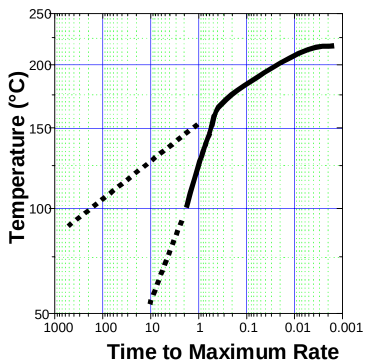
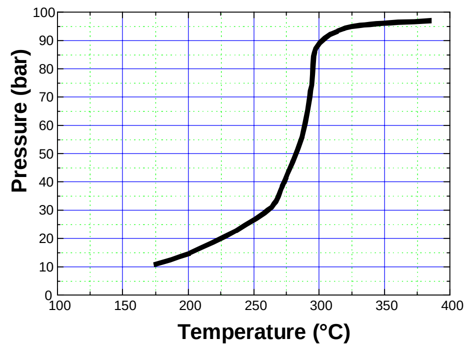


Fig. 16.



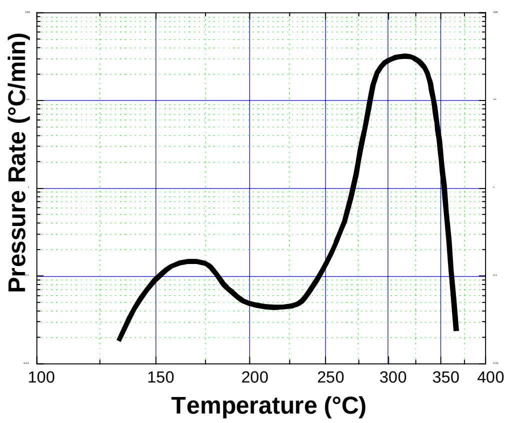
There are two pressure against temperature plots, linear pressure against linear temperature and log pressure against reciprocal temperature. Should the pressure be data a straight line on the first plot pressure generation is generally considered to be by formation of non- condensable gas, should the pressure data be a straight line on the second plot, pressure generation by formation of

Fig. 17.



condensible gas (vapour pressure) is indicated. The pressure data is important because it is pressure which causes damage in an incident, however the pressure data must be normalised because the void volume in the test is usually different from that in the real situation, Fig. 17. If the pressure data is important, it may be possible to vary the sample size to give a similar sample to void volume ratio as in the real situation. The pressure rate plot is also important it indicates the pressure rate at every temperature but the pressure rate data should be considered along with the temperature rate data, Fig. 18. Very fast pressure rates may possibly be only an effect of very fast self-heating rates.

Fig. 18.



The pressure rate against self-heating rate plot would be a straight line if just one process was occurring, as the heat was produced so pressure was produced. If the process is more complex then there may be a break or change in gradient of this plot.

If the results of the test show a single reaction mechanism, it would be possible to do a full kinetic analysis. If the results are more complex the kinetic analysis may be restricted to a determination of the activation energy for a zero order (worst case) reaction as discussed in THT Technical Information Sheet No 9 and 10.