thermal hazard technology

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Technical Information Sheet No 6

Onset Temperature: Application of Accelerating Rate Calorimetry Data Safety Margins of Chemical Processes and Storage

The Arrhenius equation, the foundation of chemical kinetics tells us that only at a temperature of absolute zero, will no chemical reaction occur. At ever increasing temperatures the rate will get faster and faster. The Arrhenius equation defines the rate as proportional to the exponential of the absolute temperature:

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

From this has come the idea that the rate of reaction doubles with approximately every 10°C of temperature rise. In an Accelerating Rate Calorimeter test an exothermic reaction will be detected at a specific temperature. However there are several test criteria which may influence this:

- Heat step size
- Onset sensitivity
- Samples mass
- Bomb mass
- Other test conditions

With heat steps of 3°C or 5°C, the onset temperature can only be an increment of the selected heat step. Repeated tests with a particular sample may show onset at either of

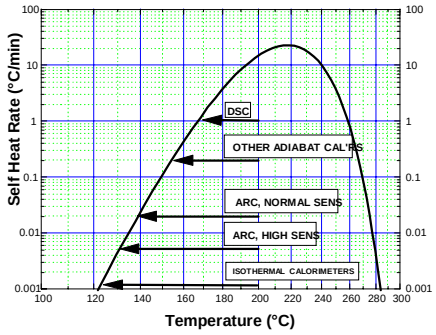
two consecutive steps. In one test the onset may just be missed and in the next just caught, but the observed on set will vary by 3°C or 5°C.

Reducing the sensitivity from 0.02°C/min to 0.005°C/min may reduce the onset temperature by 5-10°C, or maybe by a much greater temperature if minor, low energy, reactions occur, perhaps due to impurities.

The amount of sample and mass of bomb will contribute to the thermal inertia, ϕ, and, as described in THT Technical Information Sheet No 22, the greater the heat loss into the container the higher the onset temperature. Finally other experimental conditions can affect the onset temperature, an example is isothermal ageing.

Therefore whilst the onset temperature is important, it is very important onset temperature is understood not to be a simple number and thus 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 (e.g. isothermal micro-calorimeters) and instruments of lower sensitivity (e.g. vent size devices and DSC) will give onset at higher temperatures. This is illustrated in Fig. 1.

Fig. 1 .



An early Accelerating Rate Calorimeter publication, Ref. 1, detailed differences in accelerating rate calorimetry and differential scanning calorimetry data.

However 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

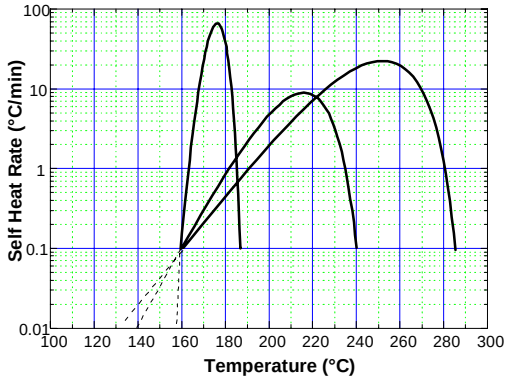
The real life considerations may be:

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

This list could be extended considerably.

Accelerating rate calorimetry data of samples with differing activation energy indicates part of the problem. The activation energy relates directly to the slope of the self-heat rate curve, Fig. 2. Extrapolation as shown clearly indicates that with a similar onset, a sample with a higher the activation energy (steeper slope of self-heat rate curve) can be safely processed with a lower safety margin.

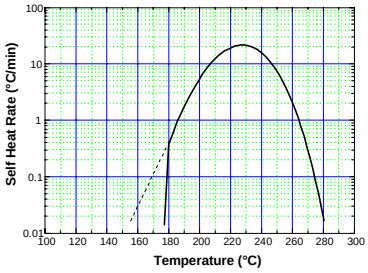
Fig. 2.



Further discussion on this is given in Ref. 2.

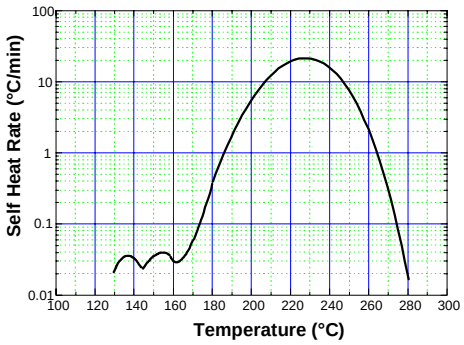
For an autocatalytic decomposition, Fig. 3, the true onset may be batch-to-batch variable and will differ with samples of different thermal history. Here the actual onset temperature is very misleading, the Arrhenius portion extrapolated back in temperature would give a worst case onset, but extrapolating the initial data would be very dangerous.

Fig. 3.



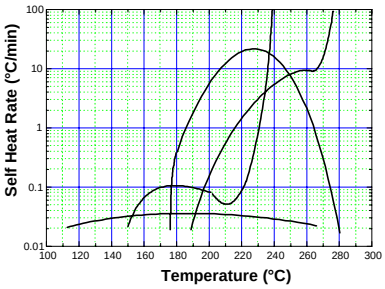
It is also very difficult to define a true onset for samples with initial minor exotherms. This is shown in Fig. 4 overleaf.

Fig. 4.



There is no simple answer to what safety margin ought to be allowed from any set of data. However the final figure, Fig. 5, simply poses the question - which is the most dangerous sample A, B, C or D? Of course the answer will depend upon what real life scenario is being stimulated!

Fig. 5.



Ref 1. Fenlon W J, Plant & Operations Progress 3, 197 (1984)

Ref 2. Hofelich T C & Thomas R C, Int Symp Runaway Reactions, Boston 1989.