thermal hazard technology

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Technical Information Sheet No 5

Temperature of No Return: Application of Accelerating Rate Calorimetry Data Maximum Safe Temperatures and Pack Sizes

THT Technical Information Sheet No. 3 and No. 4 have detailed general interpretation of accelerating rate calorimetry data and specifically the concept of time to maximum rate. Application of accelerating rate calorimetry data to real life scenarios requires a knowledge of the heat loss from the vessel. This is considered qualitatively in THT Technical Information Sheet No. 1.

The basis of stability of a material in a vessel is

$$\text{heat loss capability} > \text{heat production}$$

However the heat produced by a reaction will usually increase exponentially with temperature whereas the heat loss from a vessel will increase linearly. Thus there exists the critical point where

$$\text{heat loss capability} = \text{heat production}$$

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

Therefore there is a need to determine;

Temperature of no return

Maximum pack size

Maximum safe operating temperature

Self- accelerating decomposition temperature, SADT

The heat loss characteristics of the vessel must be known since 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

$$\tau = t_{mr}$$

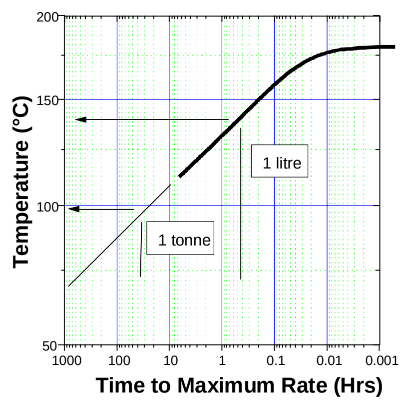
The time constant represents the vessel's adiabaticity and is the time from start of runaway to maximum rate or explosion. Typical values of τ or are shown below

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 ϕ corrected t_{mr} curve is readily available. And from this curves therefore maximum safe temperatures can therefore be read directly.

This is shown in Fig. 1 below.

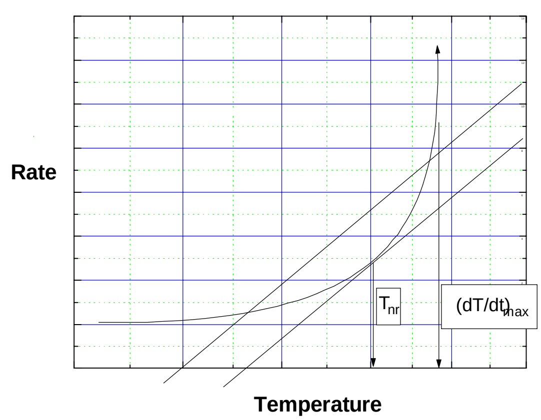
Fig. 1.



Thus the Accelerating Rate Calorimeter can simply evaluate maximum safe sizes or, conversely, maximum safe temperature.

The temperatures determined here are the temperature of no return as shown in the Semenov plot, Fig. 2. The times are the time of the reaction to proceed from the T_{nr} to

Fig. 2.

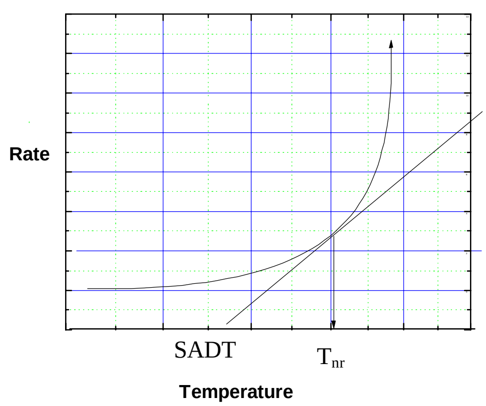


the time the temperature of maximum rate, $(dT/dt)_{max}$. This time is not the same as the time to maximum rate, t_{mr}.

The self-accelerating decomposition temperature, SADT, test is a full scale test prescribed by the United Nations and widely required to estimate safe storage and transportation of chemicals such as organic peroxides which are contained in packs of specific size. Commercial packs are tested in an isolated oven at various isothermal temperatures and over periods of seven days. Typically the temperature is increased in steps of 3°C or 5°C until runaway occurs and the oven is destroyed! This is empirical, time consuming, costly and potentially dangerous. An alternative bench scale test would be desirable. Essentially in the Accelerating Rate Calorimeter the T_{nr} of the material in the vessel will be determined. However the SADT is the ambient temperature at which the system will equilibrate at the (higher) T_{nr}, Fig. 3. (A derivation of this equation is given in Ref. 1).

$$T_{SADT} = T_{nr} - R(T_{nr} + 273)^2 / E$$

Fig. 3.



The temperature of no return is simply read from the time to maximum rate graph and the SADT calculated.

Usually in this application the t_{mr} data must be extrapolated. This can only done with certainty if a single mechanism of decomposition occurs. A comparison of data from the

Accelerating Rate Calorimeter and from full-scale tests has shown that 10 out of 12 organic peroxides have results that compare within 6°C; the two other samples are likely to show complex decomposition, Ref. 2.

Nevertheless as discussed in Ref. 1, the Accelerating Rate Calorimeter is an excellent technique to determine SADT's avoiding lengthy, costly and hazardous full scale testing.

Ref. 1 Fischer H G and Goetz D D, J Loss Prev Process Ind, 4, 305 (1991)

Ref. 2 Whitmore M W and Wilberforce J K, J Loss Prev Process Ind, 6, 95 (1993)