thermal hazard technology

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Technical Information Sheet No 10

Thermodynamic Analysis of Accelerating Rate Calorimetry Data

A full mathematical description of thermodynamic analysis of Accelerating Rate Calorimeter data is given in THT Technical Information Sheet No. 20. This is relatively simple though materials that show complex overlapping reactions will cause difficulties. To obtain reliable heat of reaction information the exotherm must be tracked adiabatically. Reactions which have mechanism change to yield spontaneous explosive-type reaction with rates of self- heating 100°C/min to 1000°C/min can not be followed adiabatically. Heats of reaction obtained for these types of reaction will be low, the error maybe 10% to 50%. But it is easy to get the heat of reaction of Di-tertiary butyl peroxide, DTBP, for example.

Therefore often it is better to do tests at higher ϕ value to obtain a reliable heat of reaction. In the Accelerating Rate Calorimeter the ϕ correction has been proven reliable to values of ϕ =5 and above and in allowing heat loss into the bomb to moderate reaction, the reaction can be followed accurately. This, indeed, is the proven principle of the bomb or combustion calorimeter.

In DSC and many other characters the heat of reaction is the area under the peak. This is not the case in adiabatic calorimetry.

In any adiabatic test, as heat is generated so the temperature must rise

$$\Delta H \ \alpha \ \Delta T$$

In a fully adiabatic test (no sample container or infinite sample mass or ϕ =1) the constant of proportionality is the specific heat and therefore

$$\Delta H = c_p \ \Delta T$$

In an accelerating rate calorimetry test the heat of reaction (as derived in THT Technical Information Sheet No. 20) is given by

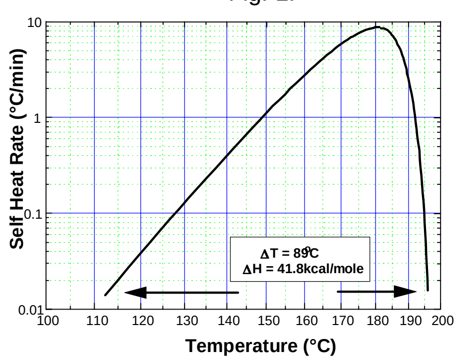
$$\Delta H = c_p \ \phi \ \Delta T$$

Note that if ΔH is calculated thus, the purity of the sample must be considered and the specific heat ought to be $\overline{c_v}$, the average specific heat over the course of the reaction at constant volume not constant pressure.

However as shown in THT Technical Information Sheet No 100 the ability of the Accelerating Rate Calorimeter to determine ΔH is proven with DTBP.

Fig. 1 below shows the result with DTBP. Literature values for the heat of reaction are

Fig. 1.



close to 42 Kcal/mole and thus this data shows very good agreement and hence the adiabaticity of the Accelerating Rate Calorimeter. Indeed this is a test which could be done to verify performance of the Accelerating Rate Calorimeter or to compare it with other calorimetry devices.