Short Communications

COMPARISON OF METHODS OF DETERMINATION OF ADIABATIC TIMES TO MAXIMUM RATE OF EXOTHERMIC REACTIONS

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The prediction of time to maximum rate from kinetic parameters is very difficult. This is because the t_{mr} values are extremely sensitive to small errors in the measured activation energy. It is felt that the determination of kinetic parameters needs to be supplemented by further thermal tests. Alternatively t_{mr} can be measured directly.

Thermally unstable materials play an important role in the modern chemical and allied industries. By their nature, such reactive chemicals apart from being useful, are also potentially hazardous, if their associated exotherms are not kept under control.

Safety in processing, storage and transport is normally achieved by means of a thermal hazard evaluation whose results are used to specify normal operating conditions and the action to be taken in the event of a runaway thermochemical reaction. It must be remembered that with such runaway reactions the rate of reaction is accelerated by self-heating. There are normally two main aspects to such an evaluation, as follows.

1) The acquisition of heat generation rate as a function of temperature. Typically, the engineer would use such information to determine if active cooling is required and to specify the main design parameters of the cooling system such as coolant temperature and cooling area.

2) The acquisition of "adiabatic time to maximum rate" (t_{mr}) as a function of temperature. Such data would enable the designer to know how much time would be available in the event of a loss of control and hence to specify what courses of action could be taken.

Both of the above aspects are important, but for the purpose of the present discussion only the second aspect is considered in more detail.

Determination of t_{mr}

Basically there are two approaches to the determination of t_{mr} for a particular chemical system. Firstly, by the use of an adiabatic technique such as the ARC (*tm*), it can be measured directly. Secondly it can be estimated from a knowledge of the kinetic parameters, which may be typically obtained by the use of techniques such as DTA, DSC or isothermal measurements [1].

Whichever approach is adopted, the resulting data must be used with caution. The amount of caution must of course reflect the inaccuracies incurred in the data acquisition. For instance, both techniques could be in serious error if the exothermic change under consideration included a significant autocatalytic component which had not been taken into account.

Such cases apart, the direct measurement of t_{mr} by means of the ARC (*tm*) has significant advantages over the indirect technique. The dynamic adiabatic course of the reaction is studied under the most unfavourable conditions with regard to explosion safety. Implicitly contained in the recorded time-temperature curve are all the thermal, kinetic and physical property data of the reaction mass. This time-temperature curve can then be modified to plot time backwards from the maximum rate of reaction and thus describes the event in terms of t_{mr}, or "response time". t_{mr} can then be estimated from temperature, the importance of which is obvious when dealing with runaway reactions. ARC values are usually accurate with a few percent at worst.

In the past it has been customary to quantify the runaway reaction using procedures developed from chemical kinetics. If one starts with a kinetic formula that describes reaction rate as a function of temperature, a formula can be derived that approximates the adiabatic time temperature runaway curve.

The normal starting point would be a rate equation, written in thermal terms, such as:

Rate of self heating $= m$ °C/min

$$= \frac{A\Delta H}{Cp} \exp\left(-Ea/RT\right)\frac{(T_{AB} - T)^N}{(T_{AB} - To)} . \tag{1}$$

Where A = frequency factor
ΔH = heat of reaction
Cp = specific heat
Ea = activation energy
R = universal gas constant
T_{AB} = adiabatic temperature
To = initial temperature
N = reaction order

The time to maximum rate can then be estimated by numerically integrating the equation. Alternatively the approximate solution developed by Townsend [2] could be used

$$t_{mr} = \frac{RT^2}{m\,Ea} . \tag{2}$$

Discussion

In general, the accuracy of t_{mr} values depends on the accuracy of the values of A, Ea, ΔH, m, Cp which are used as inputs. Errors in N have only a small effect on t_{mr}.
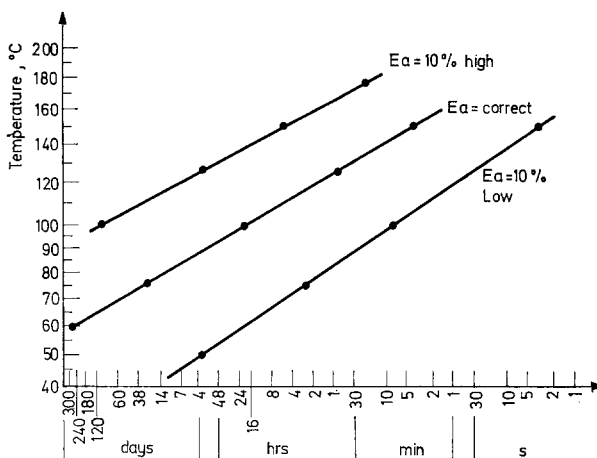
Fig. 1.

This is because most of the time that makes up t_{mr}, occurs at the beginning of the reaction when concentration changes are small.

Errors in A, ΔH and Cp will obviously have a linear effect.

However, Ea appears in an exponential term in Eq. 1 and much larger effects can be anticipated. This point is considered further by means of the following illustration. Consider an exothermic reaction which is described by the following parameters.

$$A = 10^{15}(s^{-1}), \quad N = 1, \quad \Delta H/Cp = 500° \quad \bar{E}_a = 153.8 \text{ kJ/mole} .$$

Considering adiabatic self heating between 0° and 500°, the rate at any temperature can be written as follows.

$$m = 500 \times 60 \times 10^{15} \exp \left(\frac{-153.8}{RT} \right) \left(\frac{500 - T}{500} \right)^1 .$$

Values of m so obtained are then substituted into Eq. 2 to yield t_{mr}.

The results of this calculation are shown in Table 1 and graphically in Fig. 1 for five separate cases. "A" is the correct case where a value of 153.8 kJ/mole has been used for Ea. Cases, B, C, D and E show the effect of 5% and 10% errors in Ea on both high and low sides.

The results show clearly that errors of even 5% in the value of E_a, have an enormous effect on the resulting t_{mr} values. The following example is presented to illustrate the point.

Example

Consider during a process development that the design philosophy is to operate 2 hours from maximum rate, to give a first alarm at 1 hour (leaving time to attempt remedial action) and an evacuation alarm at 10 minutes.

Table 1

Effects of errors in activation energy on adiabatic time to maximum rate

	Case C	Case B	Case A	Case D	Case E
	10% high	5% high	Correct $Ea = 153.8$	5% low	10% low
T, °C	t_{mr}	t_{mr}	t_{mr}	t_{rr}	t_{mr}
50				64.8 day	93.76 h
60			210.04 day	13.8 day	21.69 h
75		294 day	21.67 day	38.41 h	2.84 h
100	97.22 day	8.53 day	18.0 h	1.59 h	8.42 m
125	3.84 day	9.44 h	58.22 min	6.00 min	37.0 s
150	5.43 h	33.4 min	4.52 min	32.04 s	3.80 s
175	26.87 min	3.58 min	28.54 s	3.81 s	0.51 s

If the designers data included a high error in E_a, he would select the 10% following temperatures

> operating temperature   158°
> first alarm   166°
> evacuation alarm   185°

In fact (from case A) we can see this would result in

> operation   =   2 minutes from maximum rate
> first alarm   =   1 minutes from maximum rate
> evacuation alarm = 0.1 minute from maximum rate

Of course, in practice it is much more likely that the designer will build in a safety margin. Doing so will have the penalty of imposing a lower processing temperature than is needed. In our example, it may be decided to add 10% to the activation energy. This will have the effect of moving to case E and operating at a temperature of 78° which is fully 40° below what is required from a safety point of view (case A).

References

1. T. OZAWA, J. Thermal Anal., 2 (1970) 301.
2. D. I. TOWNSEND and J. C. TOU, Thermochim. Acta, 37 (1980) 1.