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Technical Information Sheet No 20

Analysis of Accelerating Rate Calorimetry Data: Theory

Results from adiabatic calorimetry experiments may be evaluated

empirically

kinetically

thermodynamically

Analysis may be an interpretation solely of the data (i.e. determining the physico-chemical properties of the reaction) and may be for application (i.e. combining the test information with properties of the equipment used in real-life situations).

Originally the Accelerating Rate Calorimeter was developed by Dow Chemical with as a background thermokinetic theory - and this is the basis for all Accelerating Rate Calorimeter data analysis.

This THT Technical Information Sheet is an attempt to summarise the theoretical base of the Accelerating Rate Calorimeter and show how the theory is behind all calculations carried out with accelerating rate calorimetry data. Publications referenced at the end describe in more detail many theoretical aspects.

At the beginning and as a foundation is the Arrhenius Theory of kinetics and fundamental thermodynamic laws. In addition the description that follows is only valid if the sample or sample-container system is held in a strictly adiabatic environment.

Fundamentals

Arrhenius' empirical observation was that the rate of loss of concentration (i.e. the rate of reaction) was proportional to the concentration of sample raised to a power, n, now called the order of reaction. The constant of proportionality is the rate constant, k. Thus

$$-\frac{dC}{dt} = kC^n$$

The rate constant is dependent on temperature and the universal gas constant, R, thus

$$k = Ae^{-E/RT}$$

Where the (well-known) constant A is the pre-exponential factor and constant E, the activation energy. Later variations of the Arrhenius Theory have suggested that A is temperature dependent (to various powers of T).

For a zero order reaction

$$-\frac{dC}{dt} = k$$

Under closely controlled adiabatic conditions and **only under closely controlled adiabatic conditions**, this basic kinetic rate equation may be re-written

$$\frac{dp}{dt} \equiv \frac{dT}{dt} \equiv -\frac{dC}{dt} = Ae^{-E/RT}C^n$$

Intuitively it can be realised for an exothermic and pressure generating reaction that as concentration is lost, so heat will be produced and so the pressure will rise. In the adiabatic state the temperature will rise.

Thermodynamically, the relationship between the initial concentration, C_0, the concentration, C, at any chosen time, t, may, in an adiabatic state, be related to temperatures. The assumption being that losing all reactant produces all heat and losing a certain amount of reactant produces a pro-rata amount of heat, the amount of concentration of reactant left is proportional to the amount of heat still to be produced

$$C \propto T_f - T$$

$$C_0 \propto \Delta T_{ad}$$

and therefore

$$\frac{C}{C_0} = \frac{T_f - T}{\Delta T_{ad}}$$

or

$$C = \frac{T_f - T}{\Delta T_{ad}} C_0$$

The temperature rise in a fully adiabatic system relates directly to the heat of reaction

$$\Delta T_{ad} \propto \Delta H$$

and the proportionality constant is the specific heat, c_p. This is the fundamental equation for heat of reaction determination in a fully adiabatic system. (Note here that 'C' is used for concentration and 'c', always with a subscript, for specific heat.) Therefore

$$\Delta H = \Delta T_{ad} c_p$$

Differentiating the concentration / temperature relationship with respect to temperature

$$\frac{dC}{dt} = \frac{-C_0}{\Delta T_{ad}}$$

Rules of calculus will allow

$$\frac{dT}{dt} = \frac{dT}{dC}\frac{dC}{dt}$$

and

$$\frac{dT}{dC} = \left(\frac{dC}{dT}\right)^{-1}$$

Therefore

$$\frac{dT}{dt} = \left(\frac{-C_0}{\Delta T_{ad}}\right)^{-1} kC^n$$

Rearranging

$$\frac{dT}{dt} = \frac{\Delta T_{ad} kC^n}{C_0}$$

Substituting k to give the rate at any temperature

$$\left(\frac{dT}{dt}\right)_T = \frac{\Delta T_{ad}}{C_0}\left(\frac{T_f - T}{\Delta T_{ad}}\right)^n C_0{}^n A e^{-E/RT}$$

This can be rearranged

$$\left(\frac{dT}{dt}\right)_T = \left(\frac{T_f - T}{\Delta T_{ad}}\right)^n C_0^{\,n-1} \Delta T_{ad} A e^{-E/RT} \qquad \text{Equation 1}$$

But if the self-heat rate is close to or at the onset of the reaction, Equation 1 simplifies to

$$\left(\frac{dT}{dt}\right)_0 = C_0^{\,n-1} \Delta T_{ad} A e^{-E/RT_0} \qquad \text{Equation 2}$$

These are the two fundamental equations of adiabatic kinetics which are the foundation for data analysis of accelerating rate calorimetry results.

Finally, as mentioned earlier, the temperature dependence of the pre-exponential term, A, has been considered in several theories. The rate constant may be rewritten

$$k = \alpha T^{\beta} e^{-E/RT}$$

where

in the Arrhenius theory	$\beta = 0$
in the Collision Theory	$\beta = 0.5$
in the Absolute Rate Theory	$\beta = 1$

However the value of T in the exponential term will dominate over T in the pre-exponential term.

Heat of Reaction Determined by the Accelerating Rate Calorimeter

The fundamental equation for determination of the heat of reaction when a system is fully adiabatic was given in the previous section as

$$\Delta H = \Delta T_{ad} c_p$$

But in any laboratory scale instrument heat must be lost into the sample container. There is a correction required, the well know ϕ correction. However the following mathematics only then apply if no heat is given to or lost from the container, i.e. the system itself is fully adiabatic.

The total heat generated in an adiabatic system is

$$Q_\Sigma = M \Delta H$$

where M is the sample mass, therefore

$$Q_\Sigma = Mc_p \Delta T_{ad}$$

But the heat generated is shared between the sample and the container

$$Q_\Sigma = Q_s + Q_b$$

It causes an equal (system) temperature rise in both the sample and the container

$$Q_\Sigma = M_s c_{ps} \left(\Delta T_{ad}\right)_{sys} + M_b c_{pb} \left(\Delta T_{ad}\right)_{sys}$$

or

$$Mc_p \Delta T_{ad} = \left(M_s c_{ps} + M_b c_{pb}\right)\left(\Delta T_{ad}\right)_{sys}$$

Rearranging

$$\frac{\Delta T_{ad}}{\left(\Delta T_{ad}\right)_{sys}} = \frac{M_s c_{ps} + M\ c_{pb}}{M_s c_{ps}} = \phi$$

The definition of ϕ, or in its more well-known form

$$\phi = 1 + \frac{M_b c_{pb}}{M_s c_{ps}}$$

And therefore

$$\Delta T_{ad} = \phi \left(\Delta T_{ad}\right)_{sys}$$

and finally, thus

$$\Delta H = \phi c_p \left(\Delta T_{ad}\right)_{sys}$$

or more precisely

$$\Delta H = \phi \overline{c_v} \left(\Delta T_{ad}\right)_{sys}$$

where $\overline{c_v}$ is the average specific heat of the sample at constant volume over the course of the reaction, a parameter not normally available. In analysis of Accelerating Rate Calorimeter data, c_p is normally used and is accepted. See THT Technical Information Sheet 100 for the validity of this analysis with a ‘standard’ sample.

Activation Energy Determined by the Accelerating Rate Calorimeter

In an adiabatic system it was derived that

$$\frac{dp}{dt} \equiv \frac{dT}{dt} \equiv -\frac{dC}{dt} = Ae^{-E/RT} C^n$$

i.e.

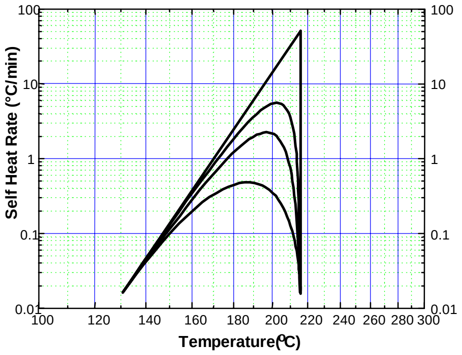
$$\frac{dT}{dt} \propto e^{-E/RT} C^n$$

or for a zero order reaction

$$\frac{dT}{dt} \propto e^{-E/RT}$$

Self-heat rate Accelerating Rate Calorimeter data is therefore plotted on axes of ln(dT/dt) and 1/T (degrees Kelvin) and therefore the slope of the initial part of the self-heat rate curve is -E/R. The activation energy may be readily obtained. However the larger the value of reaction order, n, the greater the ‘concentration effect’, i.e. the rate of reaction is moderated to a much greater extent as reaction proceeds. This is shown in Fig.1 below.

Fig. 1.



The activation energy must be obtained from the slope of the initial part of the slope only and this is a zero order activation energy. For reactions which are not zero order the activation energy obtained in this way will not be correct, but errors will be on the side of safety and the conclusion will be a ‘worst case’ result. This analysis must be done if all of the reaction data is not available, i.e. the portion before and after the maximum self-heat rate. In this way an activation energy might be determined from a portion of data - though clearly care should be taken in this or in cases where there may be multiple reactions. For a full kinetic analysis all of the data describing the reaction must be available and obtained under strict adiabatic conditions.

However from a starting point of the two equations derived for adiabatic kinetics the activation energy may also be obtained either as a plot over the range of interest or as a model which can statistically fitted to the data with minimum error. The latter approach will also determine the reaction order and thus here a complete reaction data set must be available.

In the Accelerating Rate Calorimeter the activation energy plot is determined according to the equation

$$E = \frac{R\ln\left[\frac{\left(\frac{dT}{dt}\right)_T}{\left(\frac{dT}{dt}\right)_0}\right]}{\left[\left(\frac{1}{T_0}-\frac{1}{T}\right)+\left(\frac{T_f - T_{mr}}{T_{mr}{}^2}\right)\right]\ln\left(\frac{T_f - T}{\Delta T_{ad}}\right)}$$

This plotting equation is derived thus from the Equation 1

$$\left(\frac{dT}{dt}\right)_T = \left(\frac{T_f - T}{\Delta T_{ad}}\right)^n C_0{}^{n-1}\Delta T_{ad} A e^{-E/RT}$$

At the onset this simplifies as in the Equation 2

$$\left(\frac{dT}{dt}\right)_0 = C_0{}^{n-1}\Delta T_{ad} A e^{-E/RT_0}$$

Rearranging

$$\left(\frac{dT}{dt}\right)_0 e^{E/RT_0} = C_0{}^{n-1}\Delta T_{ad} A$$

Substituting into Equation 1

$$\left(\frac{dT}{dt}\right)_T = \left(\frac{T_f - T}{\Delta T_{ad}}\right)^n \left(\frac{dT}{dt}\right)_0 e^{-E/RT} e^{-E/RT_0}$$

and at the maximum rate as derived in the next section, the reaction order is

$$n = \frac{E}{RT_{mr}{}^2}\left(T_f - T_{mr}\right)$$

Substituting, taking logs and rearranging

$$\frac{R\ln\left[\frac{\left(\frac{dT}{dt}\right)_T}{\left(\frac{dT}{dt}\right)_0}\right]}{\frac{1}{T_0}-\frac{1}{T}}\frac{1}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right) = \frac{E}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)+\left(\frac{E}{RT_{mr}}\right)\left(T_f - T_{mr}\right)\ln\left(\frac{T_f - T}{\Delta T_{ad}}\right)$$

Simplifying

$$\ln\left[\frac{\left(\frac{dT}{dt}\right)_T}{\left(\frac{dT}{dt}\right)_0}\right]=\frac{E}{R}\left[\left(\frac{1}{T_0}-\frac{1}{T}\right)+\frac{1}{T_{mr}{}^2}\left(T_f-T_{mr}{}^2\right)\ln\left(\frac{T_f-T}{\Delta T_{ad}}\right)\right]$$

Rearranging to give the plotting equation

$$E=\frac{R\ln\left[\frac{\left(\frac{dT}{dt}\right)_T}{\left(\frac{dT}{dt}\right)_0}\right]}{\left[\left(\frac{1}{T_0}-\frac{1}{T}\right)+\left(\frac{T_f-T_{mr}}{T_{mr}{}^2}\right)\right]\ln\left(\frac{T_f-T}{\Delta T_{ad}}\right)}$$

The alternative approach available with the Accelerating Rate Calorimeter is to kinetically model the heat rate. A predicted heat rate is obtained and this is improved statistically to give a best fit. This is the method to determine both E and n and to perform this the data must completely describe the reaction.

Earlier in this section the following equation was derived from the fundamental equations of adiabatic kinetics

$$\left(\frac{dT}{dt}\right)_T=\left(\frac{T_f-T}{\Delta T_{ad}}\right)^n\left(\frac{dT}{dt}\right)_0 e^{-E/RT}e^{-E/RT_0}$$

In the modeling approach, $\ln\left(\frac{dT}{dt}\right)_T$ is plotted against -1/T and compared to the experimental data. Initially E and n are varied to get the best fit, but it is also possible to vary T_0, T_f and ΔT_{ad} and also $(dT/dt)_0$.

After this has been carried out it is possible to use the ϕ corrected values of ΔT_{ad} and $(dT/dt)_0$ in a remodeling attempt and a ϕ corrected self heat rate plot is generated.

Reaction Order Determined by the Accelerating Rate Calorimeter

In the previous section, the method of obtaining the reaction order by modeling the self-heat rate data was discussed. But in many experiments this is either not possible since the reaction is not fully described, three may be complex mechanism, overlapping reactions or autocatalysis. In such cases it is often chosen to determine simply the zero order activation energy, which would be a worst case result. However in their development of the Accelerating Rate Calorimeter, Townsend and Tou devised the concept of k*, a pseudo zero-order rate constant in attempts to find the order of reaction where not all data was available,

$$\left(\frac{dT}{dt}\right)_T = \left(\frac{T_f - T}{\Delta T_{ad}}\right)^n C_0^{\,n-1} \Delta T_{ad} A e^{-E/RT}$$

Which may be rewritten as

$$\left(\frac{dT}{dt}\right)_T = \left(\frac{T_f - T}{\Delta T_{ad}}\right)^n C_0^{\,n-1} \Delta T_{ad} k$$

Now if k* is defined thus

$$k^* = kC^{n-1}$$

then

$$\left(\frac{dT}{dt}\right)_T = \left(\frac{T_f - T}{\Delta T_{ad}}\right)^n \Delta T_{ad} k^*$$

Rearranging

$$k^* = \frac{\left(\frac{dT}{dt}\right)_T}{\left(\frac{T_f - T}{\Delta T_{ad}}\right)^n \Delta T_{ad}}$$

and

$$k^* = kC^{n-1} = C_0^{\,n-1} A e^{-E/RT}$$

Taking logs

$$\ln k^* = \left(AC_0^{\,n-1}\right) - \frac{E}{R}\frac{1}{T}$$

This is the plotting equation that has been used in accelerating rate calorimetry. Since $k^*=kC_0^{n-1}$, plots of k* against 1/T for different values of n will produce a straight line is the correct value of n is chosen, but curves if the n value is incorrect. And from the slope of the line the activation energy may be obtained.

However it is also possible, if all the data is available, to simply calculate the reaction order. At the maximum of the self-heat rate the change in self-heat rate with time is zero, therefore

$$\frac{d\left(\frac{dT}{dt}\right)_{mr}}{d\frac{1}{T_{mr}}} = 0$$

and

$$\frac{d\left(\frac{dT}{dt}\right)_{mr}}{dT} = 0$$

therefore

$$-T^{2}\,\frac{d\left(\frac{dT}{dt}\right)_{mr}}{dT} = 0$$

Using equation 1 as before

$$\left(\frac{dT}{dt}\right)_{T} = \left(\frac{T_f - T}{\Delta T_{ad}}\right)^{n} C_0^{\,n-1}\Delta T_{ad}\, A e^{-E/RT}$$

Differentiating this equation with respect to temperature at the temperature of maximum rate

$$\frac{d\left(\frac{dT}{dt}\right)_{T}}{dT} = C_0^{\,n-1}\Delta T_{ad} A\left[\left(\frac{T_f - T}{\Delta T_{ad}}\right)^{n} e^{-E/RT}\,\frac{E}{RT_{mr}{}^{2}} + n\left(\frac{T_f - T}{\Delta T_{ad}}\right)^{n-1} e^{-E/RT_{mr}}\,\frac{-1}{\Delta T_{ad}}\right] = 0$$

This simplifies to

$$\left[\left(\frac{T_f - T}{\Delta T_{ad}}\right)^{n} e^{-E/RT}\,\frac{E}{RT_{mr}{}^{2}} - \frac{n}{\Delta T_{ad}}\left(\frac{T_f - T}{\Delta T_{ad}}\right)^{n-1} e^{-E/RT_{mr}}\right] = 0$$

$$\left[\left(\frac{T_f - T}{\Delta T_{ad}}\right)^{n} \frac{E}{RT_{mr}{}^{2}} - \frac{n}{\Delta T_{ad}}\left(\frac{T_f - T}{\Delta T_{ad}}\right)^{n-1}\right] = 0$$

$$n = \frac{E\left(T_f - T_{mr}\right)}{T_{mr}^{\;2}}$$

This latter equation being well-known for determination of reaction order.

Time to Maximum Rate by the Accelerating Rate Calorimeter

A key aspect of accelerating rate calorimetry is the ability to plot the Time to Maximum Rate after ϕ correction.

This is very valuable though often extrapolation of the data back to lower temperatures must be done. As detailed in THT Technical Information Sheet No 4 this must be done with caution since it is only easy to do this if the data shows a single reaction with simple reaction mechanism i.e. the data obeys Arrhenius kinetics. If possible it is better to model the data using the method available with the Accelerating Rate Calorimeter and as described mathematically earlier, then extrapolate the modeled reaction. Care should be taken that there are not low energy, low temperature reactions or a change in reaction mechanism.

The advantage in getting t_{mr} information direct from raw data is clear, the data is obtained from a reliable simulation and after ϕ correction would match real life data. The disadvantage of calculating the t_{mr} from data such as DSC data is that errors in the activation energy have an exponential effect on the results! Errors in A, ΔT and c_p will have a linear effect and errors in n will have little effect, since at the start of the reaction where the bulk of the time occurs, the concentration effect is minimal.

However an approximate solution to determine t_{mr} was given by Townsend and Tou.

Since the time to maximum rate is usually required at temperatures near the start of reaction, Equation 2 of adiabatic kinetics can be the starting point

$$\left(\frac{dT}{dt}\right)_0 = C_0^{\,n-1}\Delta T_{ad}\,Ae^{-E/RT_0}$$

or at any temperature near T_0

$$dt = \frac{dT}{C_0^{\,n-1}\Delta T_{ad} A e^{-E/RT}}$$

Integrating between time, $t_{T,}$, to get to the maximum rate from the chosen temperature, T, and the time of maximum rate, t*, it is possible to get the time to maximum rate, t_{mr}

$$t_{mr} = t^* - t_T$$

then

$$\int_{t_T}^{t^*} dt = \int_{T}^{T_{nr}} \frac{e^{E/RT} dT}{C_0^{\,n-1}\Delta T_{ad} A}$$

And to make the integration easier the assumption was made that $A = \alpha T^2$, therefore

$$t^* - t_T = t_{mr} = \int_{T}^{T_{nr}} \frac{e^{E/RT} dT}{C_0^{\,n-1}\Delta T_{ad}\alpha T^2}$$

rearranging

$$t_{mr} = \int_{T}^{T_{nr}} \frac{\left(-\frac{R}{E}\right)}{C_0^{\,n-1}\Delta T_{ad}\alpha}\left(-\frac{E}{R}\right)\frac{e^{E/RT}}{T^2} dT$$

thus

$$t_{mr} = \frac{-R}{C_0^{\,n-1}\Delta T_{ad}\alpha E} e^{E/RT}\Bigg]_{T}^{T_{mr}}$$

$$t_{mr} = \frac{-R}{C_0^{\,n-1}\Delta T_{ad}\alpha E} e^{E/RT}\Bigg]_{T}^{T_{mr}}$$

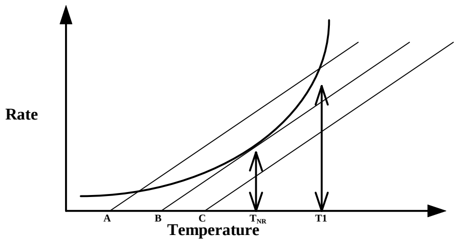
simplifying

$$t_{mr} = \frac{1}{C_0^{\,n-1}\Delta T_{ad}\alpha T^2 e^{-E/RT}}\Bigg]_{T}^{T_{mr}}$$

Temperature of No Return by the Accelerating Rate Calorimeter

Further interpretation of Accelerating Rate Calorimeter data may be carried out by applying the data to a real life situation. Here information on the vessel is required.

The temperature of no return T_{nr} is the maximum safe temperature of a material in a vessel in a specific environment. This may be the illustrated in the well-known Semenov Plot, Fig 2 below. Temperature of No Return is discussed in detail in THT Technical Information Sheet No 5.



Self-heating of a reaction and heat loss from a vessel, at 3 ambient temps, A, B and C. A can control the sample to temp T1, B is at the critical temperature T_{NR} and C cannot control the thermal runaway.

Fig. 2.

Heat generation may be described

$$\frac{dQ_g}{dt} = Mc_p \frac{dT}{dt}$$

At the onset of reaction, where as described by Semenov, a zero order reaction mechanism can be assumed without significant error (since the concentration effect is insignificant) the rate can be replaced by Equation 2 derived earlier.

$$\frac{dQ_g}{dt} = Mc_p C_0^{\,n-1} \Delta T_{ad} A e^{-E/RT}$$

The heat removal is described

$$\frac{dQ_r}{dt} = US(T - T_0)$$

At the critical temperature, the Temperature of No Return

$$\frac{dQ_r}{dt} = \frac{dQ_g}{dt}$$

thus

$$US(T - T_0) = Mc_p C_0^{n-1} \Delta T_{ad} A e^{-E/RT}$$

and also at the Temperature of No Return

$$\frac{d\left(\frac{dQ_r}{dt}\right)}{dT} = \frac{d\left(\frac{dQ_g}{dt}\right)}{dT}$$

Simplifying

$$US = Mc_p C_0^{n-1} \Delta T_{ad} A e^{-E/RT} \frac{E}{RT_{nr}^{\ 2}}$$

Substituting

$$US = Mc_p \left(\frac{dT}{dt}\right)_{T_{nr}} \frac{E}{RT_{nr}^{\ 2}}$$

Rearranging

$$\frac{RT_{nr}^{\ 2}}{\left(\frac{dT}{dt}\right)_{T_{nr}} E} = \frac{Mc_p}{US}$$

Alternatively

$$\left(Q_g\right)_{T_{nr}} = \frac{Mc_p}{US}$$

This is the formula used for determination of heat production from vessels.

Appendix: Terms Used

t = time
T = temperature
p = pressure
M = mass
C = concentration
E = activation energy
A = pre-exponential factor
n = reaction order
k = rate constant
R = universal gas constant
Q = heat, power
c_p = specific heat
U = overall heat transfer coefficient
S = surface area
ΔH = heat of reaction
dT/dt = self-heat rate
ϕ = thermal inertia
α = const in temp dependent pre-exponential factor
β = power of T in temp dependent in pre-exp factor

ΔT = temperature rise
ΔT_{ad} = adiabatic temperature rise

C_0, T_0 etc = initial concentration, temperature etc
T_f , t_f etc = final temperature, time etc
t_{mr} = time to maximum rate
t^* = time of maximum rate
T_{mr} = temperature of maximum rate
T_{nr} = temperature of no return
k^* = pseudo-zero order rate constant
other subscripts used
s = sample
b = bomb
Σ = total
sys = system
g = generated
r = removed