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Note

Non-isothermal rate equations*

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Recently it has been suggested that the currently accepted procedures for developing non-isothermal kinetic equations are fundamentally in error and must be modified[1-3]. In particular, it is contended[1] that if the temperature (T) changes with time (t), then the time derivative of the reactant concentration, C, is given by

$$\frac{dC}{dt} = \left(\frac{\partial C}{\partial t}\right)_T + \left(\frac{\partial C}{\partial T}\right)_t \frac{dT}{dt} \tag{1}$$

Kissinger[4] and, more recently, Hill[5], however, have shown that the term, $(\partial C/\partial T)_t$, is always zero. Fixing the time fixes the positions of all the particles in the system[4]; hence, if time is held constant, C must also be constant.

More confusing is the introduction of two time scales (thermal and isothermal time)[2,3]. The introduction of a new variable (thermal time) which is simply dependent on the temperature variable not only appears unnecessary, but raises fundamental problems. It is difficult to visualize the particles of a system simultaneously following two different time scales in their motions. The justification of introducing two time scales for a single experiment also appears faulty—it is based on a comparison between two different isothermal experiments. Furthermore, as shown below, the final result obtained using two time scales appears to be correct only as an approximation.

The large number of non-isothermal kinetic theories which have been published is not evidence that the fundamental procedures are incorrect. Instead, it simply reflects the fact that for a conventional linear temperature rise, an equation which is difficult to integrate in an easily applied form is obtained. The large number of non-isothermal kinetic theories simply represent attempts to obtain applicable equations despite the unwieldy exact integrated equation.

It can be shown by very simple mathematical operations that there is no fundamental error in extending isothermal kinetic equations to non-isothermal reactions. Although the treatment given below is no more than an exercise in funda-

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mental calculus, it does illustrate that the currently accepted procedures are correct when no assumptions are made other than that the rate equation[†]

$$\frac{dC}{dt} = -C^n k \tag{2}$$

and the Arrhenius equation

$$k = A \exp(-E^*/RT) \tag{3}$$

are valid *only* for *isothermal* reactions.

A hypothetical experiment using a reaction which obeys Eqns. 2 and 3, when carried out isothermally, may be conducted in the following manner. First, the temperature is maintained at T_0 from time 0 to Δt, at which time it is instantaneously changed to T_1. The sample is then held at temperature T_1 until time $2\Delta t$, at which time the temperature is intantaneously changed to T_2; the process may be continued indefinitely. Over each isothermal time interval, Eqns. 2 and 3 are valid, as is the integrand of Eqn. 2; for example, for the first isothermal time interval

$$f(C_1, C_0) = -A \exp(-E^*/RT_0)\Delta t \tag{4}$$

where $f(C_1, C_0) = \ln(C_1/C_0)$ when $n = 1$ and $f(C_1, C_0) = (C_1^{-n+1} - C_0^{-n+1})(-n+1)^{-1}$ when $n \neq 1$. Eqn. 4 may be generalized:

$$f(C_{i+1}, C_i) = -A \exp(-E^*/RT_i)\Delta t \tag{5}$$

where i is the number of times that the temperature is instantaneously changed. It can readily be seen from Eqn. 5 that

$$f(C_{i+1}, C_0) = -A \sum_{j=0}^{j=i} \exp(-E^*/RT_j)\,\Delta t \tag{6}$$

Any values for the temperature changes may be chosen. If, for example, they are chosen so that $T_{i+1} - T_i = \Delta T =$ a constant for all i, then the following equation may be written:

$$\Delta T/\Delta t = \beta \tag{7}$$

where β is a constant. Eqn. 6 then becomes

$$f(C_{i+1}, C_0) = -(A/\beta) \sum_{j=0}^{j=i} \exp(-E^*/RT_j)\,\Delta T \tag{8}$$

Temperature intervals, ΔT, of any size may be chosen. There is no mathematical or physical reason why they may not be infinitesimally small or

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[†] It has long been recognized that many heterogeneous reactions (to which non-isothermal methods are usually applied) do not obey the usual homogeneous kinetic equations. However, that does not affect the arguments given here. Non-isothermal kinetic methods may be applied to homogeneous reactions. Also, to include heterogeneous reactions, Eqn. 2 could be generalized as $dC/dt = f(C)g(T)$, or some other similar expression.

$$f(C, C_0) = -(A/\beta) \lim_{\Delta T \to 0} \left(\sum_{j=0}^{j=i} \exp(-E^*/RT_j)\,\Delta T\right)$$

$$= -(A/\beta) \int_{T_0}^{T} \exp(-E^*/RT)\,\mathrm{d}T \qquad (9)$$

which is, of course, the same result obtained by a straightforward combination of Eqns. 2 and 3 with the linear temperature rise equation, $\beta = \mathrm{d}T/\mathrm{d}t$. As previously mentioned, the integrand of Eqn. 9 is somewhat unwieldy for practical application.

It should be pointed out that any type of heating program may be chosen—there is no restriction for a linear temperature increase. If, for example, the temperature jumps are carried out so that $(1/T_{i+1})-(1/T_i) = \Delta(1/T) =$ a constant for all i, then

$$\Delta(1/T)/\Delta t = \theta \qquad (10)$$

where θ is a constant. In this case, on carrying out the same procedures as for the linear case above, an easily integrated equation is obtained with the result:

$$f(C, C_0) = (AR/\theta E^*)\,[\exp(-E^*/RT) - \exp(-E^*/RT_0)] \qquad (11)$$

which explains the special nature of using a hyperbolic heating rate as has previously been suggested[2,3]. As can be seen, for temperatures such that $T \gg T_0$, Eqn. 11 reduces to the equation previously obtained by the introduction of two time scales[2,3].

It may be concluded that the currently accepted procedures for obtaining non-isothermal kinetic equations are not fundamentally in error.

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