

Kinetics of Non-isothermal Processes

OUR recent communication¹ on the rate equations used in non-isothermal kinetic systems has aroused some controversy and two groups^{2,3} have objected to the use of the partial differential equation

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

The rate can also be expressed in terms of the concentration of reactant A which decomposes by a first order mechanism to product B in the manner $A \rightarrow 2B$. Thus

$$\frac{d[A]}{dt} = \left(\frac{\partial[A]}{\partial t}\right)_T + \left(\frac{\partial[A]}{\partial T}\right)_t \frac{dT}{dt} \quad (2)$$

Felder and Stahel² use an argument involving instantaneous changes in temperature without a corresponding change in concentration, and show that concentration is a path, rather than a state, function. Their key assumption, however, amounts to setting $(\partial C/\partial T)_t$ equal to zero and their conclusions seem to support our thesis that this factor is significant and, if it were accounted for, C would then be, in their terms, a state function.

Gilles and Tompa³ suggest that T and t are not independent variables, and base their conclusions on the fact that $[A]$ is the solution of a differential equation of the type

$$\frac{d[A]}{dt} = -k(T)[A] \quad (3)$$

Equation (3), however, is the differential equation which summarizes experimental observations (Felder and Stahel's comments on this fact are relevant) made under conditions of constant temperature (that is, $dT/dt=0$), and in that sense it is a functional relationship. I would assert that the correct form of equation (3) is

$$\left(\frac{\partial[A]}{\partial t}\right)_T = -k(T)[A]$$

Whether or not the use of partial differentials is valid can be decided by the following considerations. Temperature is only one of the physical parameters which may be varied during a kinetic reaction; the volume of solution, or reaction vessel in a gas phase reaction, could also be changed systematically during an isothermal decomposition, just as in non-isothermal experiments the temperature is linearly raised for a system of constant volume. It is perfectly feasible, for example, to add an inert diluent at a constant rate during the decomposition of A in solution. By analogy with equation (2) we have

$$\frac{d[A]}{dt} = \left(\frac{\partial[A]}{\partial t}\right)_V + \left(\frac{\partial[A]}{\partial V}\right)_E \frac{dV}{dt} \quad (4)$$

where dV/dt is chosen as a constant, b . At any instant of time, $[A]=N_a/V$, where N_a is the number of moles of A in the volume of solution V , and thus

$$\left(\frac{\partial[A]}{\partial V}\right)_E = -N_a/V^2 \quad (5)$$

Equation (4) now becomes

$$\frac{-d[A]}{dt} = -\left(\frac{\partial[A]}{\partial t}\right)_V + \frac{bN_a}{V^2} \quad (6)$$

$$= [A]\left(k + \frac{b}{V}\right) \quad (7)$$

This equation can be tested by considering the decomposition of A to be carried out in the gas phase with only reactant A initially present at pressure P_a^0 , and the pressure of the system to remain constant at this value. The volume therefore increases and as $[A]$ equals P_a/RT equation (6) becomes

$$\frac{-dP_a}{dt} = kP_a + \frac{bP_a}{V} \quad (8)$$

At any time the total number of moles present is $(2-N_a)$ and it can be deduced that

$$\begin{aligned} b &= -\frac{RT}{P_a^0} \frac{dN_a}{dt} \\ &= k \frac{P_a V}{P_a^0} \end{aligned} \quad (9)$$

Substituting equation (9) into equation (8) yields

$$\frac{-dP_a}{dt} = kP_a(1 + P_a/P_a^0) \quad (10)$$

Equation (10) is the correct expression, as derived by another method in standard texts⁴, for this reaction in the conditions stated. The approach through a partial differential equation is therefore valid.

I shall finally consider what were initially Kissinger's⁵, and then Hill's⁶, conclusions about the physical interpretation of the term $(\partial[A]/\partial T)_t$. They both propose that, if the time is fixed, the number and position of the particles are also fixed, and consequently the term is zero. By analogy they would argue that in equation (4) $(\partial[A]/\partial V)_t$ is also zero. Physically $(\partial[A]/\partial V)_t$ can be varied at will simply by altering the rate of addition of inert diluent gas. The necessity for retaining this term in equation (4) is shown by the derivation of the correct rate expression for this situation in chemical kinetics.

We are left therefore with the problem of interpreting the physical significance of $(\partial[A]/\partial T)_t$. Kissinger suggests that the velocity of thermal motion of the particles increases, and this would seem to be reasonable. According to even the simplest of theories on reaction kinetics, however, this would imply some influence on the rate of reaction.

Hill's reference⁶ to an arrow in flight is fascinating. Certainly the arrow in flight can be considered stationary at any instant of time. If the arrow were, however, undergoing change during its flight, for example, if it were burning, it would appear to be at rest but the extent to which it had been consumed would depend on the instant of time chosen relative to the beginning of the flight. In these circumstances the state of the arrow must be defined with reference to the starting condition. The same reasoning must apply to a system undergoing chemical change.

Felder and Stahel make a sound point when they emphasize the importance of attaining thermal equilibrium, but this would seem to be more of a practical than a theoretical problem. Certainly the thermodynamic concept of temperature does not seem to have been violated in the arguments presented here.

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³ Gilles, J. M., and Tompa, H., *Nature Physical Science*, **229**, 57 (1971).

⁴ Frost, A. A., and Pearson, R. G., *Kinetics and Mechanism* (Wiley, New York, 1961).

⁵ Kissinger, H. E., *J. Res. Nat. Bur. Stand.*, **57**, 217 (1956).

⁶ Hill, R. A. W., *Nature*, **227**, 703 (1970).