Thermochimica Acta, 5 (1973) 481–484

Note

Non-isothermal reaction kinetics

G. GYULAI and E. J. GREENHOW
Department of Chemistry, Chelsea College, University of London, Manresa Road, S.W.3 (England)
(Received 10 October 1972)

In the past two years controversy has arisen over a communication by MacCallum and Tanner[1] concerning rate equations used in non-isothermal kinetic systems. The authors claimed that the kinetic equation

$$dC/dt = A\exp(-E/RT)\,f(C) \tag{1}$$

was applicable only to isothermal processes. For non-isothermal reactions they proposed the partial differential equation

$$\frac{dC}{dt} = \left(\frac{\partial C}{\partial t}\right)_T + \left(\frac{\partial C}{\partial T}\right)_t \frac{dT}{dt} \tag{2}$$

which they derived using Kissinger's formulation[2] in which

$$C = f(t, T). \tag{3}$$

This approach has been criticised[3,4] and, in reply, MacCallum has attempted to defend his views and prove the validity of Eqn. (2), using as an argument an analogy in which the related formula

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

is applied to a gas-phase reaction[5]. It is claimed that this latter partial differential equation leads to the correct kinetic expression derived by another method.

We agree neither with the validity of Eqn. (2) nor with the analogy as a proof in this matter. Equation (3), the basis of the derivation of Eqn. (2), is a rather relaxed interpretation of experimental findings. Time and temperature parameters give no direct indication of the apparent value of the conversion C, since any value of C between 0 and 1 could correspond to a given time–temperature data pair depending on the previous "history" of the reaction. If the reaction mechanism and the parameters of the temperature dependence of the rate coefficient remain unchanged during the entire process, this "history" is but the time–temperature relationship from the beginning to the given stage of the reaction. In simpler cases this relationship is a single valued $T = f(t)$ mathematical function, characteristic of the entire reaction range; generally it can be any combination of $T = f(t)$ functions, since the temperature, assuming ideal conditions, can be arbitrarily varied. For this reason, Eqn. (3) must be considered as a path function, and as such it cannot be partially differentiated.

The derivation of Eqn. (2) can be criticised also from the point of view of the chosen variables. Partial differentiation is a very helpful abstraction. It describes the change in a particular physical property with respect to one independent variable while other variables remain constant. The subscript of a partial differential does not refer to momentary values of the parameters specified in it but to the condition of constancy, *i.e.*, that the specified subscript parameters do not change in time.

Time is a unique variable, being the general parameter of any dynamic phenomenon. It is not a state parameter since it changes even if the physical state of a system remains unchanged. It is absurd, therefore, to introduce a condition meaning the constancy of time in time, and there should be no such term as the second one of Eqn. (2).

Temperature cannot be directly related to either concentration or conversion; however, in non-isothermal processes temperature and concentration, or temperature and conversion, may exhibit a parallel change in time. If there is a differential term containing the conversion and the temperature it should be written in a full, not a partial, differential form. $\mathrm{d}C/\mathrm{d}T$ is not equal to zero but:

$$\frac{\mathrm{d}C}{\mathrm{d}T} = \frac{\mathrm{d}C}{\mathrm{d}t}\left(\frac{\mathrm{d}t}{\mathrm{d}T}\right)$$

If a quantity y is determined by $x_1, x_2, \ldots x_n$ independent parameters, then the change in the $y = f(x_1, x_2, \ldots x_n)$ function with respect to time can be given by the following expression:

$$\frac{\mathrm{d}y}{\mathrm{d}t} = \sum_{i=1}^{n}\left(\frac{\partial y}{\partial x_i}\right)_{x_1, x_2, \ldots x_{i-1}, x_{i+1}, \ldots x_n}\left(\frac{\mathrm{d}x_i}{\mathrm{d}t}\right) \tag{5}$$

The concentration, which is the parameter investigated in MacCallum's analogy, is unambiguously determined by two variables: the volume V and the number of moles N_a. Thus:

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \left(\frac{\partial[\mathrm{A}]}{\partial N_a}\right)_V \frac{\mathrm{d}N_a}{\mathrm{d}t} + \left(\frac{\partial[\mathrm{A}]}{\partial V}\right)_{N_a} \frac{\mathrm{d}V}{\mathrm{d}t} \tag{6}$$

This we consider to be the proper expression for $\mathrm{d}[\mathrm{A}]/\mathrm{d}t$. All material interactions which affect the values of N_a and V should be included in the terms $\mathrm{d}N_a/\mathrm{d}t$ and $\mathrm{d}V/\mathrm{d}t$. respectively.

If, during the reaction ($\mathrm{A} \rightarrow 2\mathrm{B}$), we feed material A of concentration c (mole/l) into the reaction vessel at a constant rate z (l/min), and both the temperature and pressure remain constant, we can write:

$$\frac{dN_a}{dt} = (zc - kN_a) \tag{7}$$

$$\frac{dV}{dt} = (z + kN_a RT/P_a^0) \tag{8}$$

Hence:

$$\frac{d[A]}{dt} = \frac{1}{V}(zc - kN_a) - \frac{N_a}{V^2}(z + kN_a RT/P_a^0) \tag{9}$$

If there is no feed the equation becomes

$$\frac{-d[A]}{dt} = k[A](1 + [A]RT/P_a^0) \tag{10}$$

or in terms of pressure

$$\frac{-dP_a}{dt} = kP_a\left(1 + \frac{P_a}{P_a^0}\right) \tag{11}$$

and the desired kinetic equation has been obtained.

If we feed only inert material into the reaction vessel, then

$$\frac{-d[A]}{dt} = [A][k(1 + [A]RT/P_a^0) + z/V] \tag{12}$$

that is

$$\frac{-dP_a}{dt} = P_a[k(1 + P_a/P_a^0) + z/V]. \tag{13}$$

If one considers Eqn. (4) and the procedure by which Eqn. (11) was derived by MacCallum the following comments can be made:

In the present case, with only two state variables, the first terms of Eqns. (4) and (6) are equivalent since, if the volume is kept constant, the only source of concentration change is the change of N_a with time. Had there been more than two variables the position would have been more complicated. The second term of Eqn. (4) has been expressed by the author as $-N_a/V^2\,(dV/dt)$. This derivation is valid only when N_a is considered constant; in this case it is much more correct to write this term in the following form

$$\left(\frac{\partial[A]}{\partial V}\right)_{N_a} \cdot \frac{dV}{dt}$$

which is the second term of Eqn. (6), derived above.

The fact that Eqn. (4) gives the correct kinetic expression can be explained as follows:

1. There are only two determining variables (N_a and V).
2. The condition of constancy of time has been replaced by that of constancy of N_a, since the former must have been inoperable.
3. The volume and concentration are directly related, but it should be noted that this cannot be assumed about conversion and temperature in Eqn. (2). This weakens the analogy and, if in addition we consider that the heating rate in Eqn. (2) can be arbitrarily chosen while, in the analogy dV/dt depends on the reaction rate and has no external source, it becomes clear that the demonstration is short of elements of proof.

Finally, we do not find relevant the comment in the reply on the physical significance of the debated second term of Eqn. (2) *i.e.* "Kissinger suggests that the velocity of thermal motion of the particles increases, and this would seem reasonable. According to even the simplest of theories on reaction kinetics, however, this would imply some influence on the rate of reaction".

This is true as far as the reaction rate is concerned, but there is neither indication nor experimental proof that the increased velocity of thermal motion would affect the apparent number of the reacting particles. The influence of the temperature on the reaction rate is described by the Arrhenius equation and taken into consideration in all non-isothermal evaluating procedures. The application of this equation to non-isothermal processes may well need further modifications but, we think, not on the basis of the MacCallum suggestions.

REFERENCES

1 J. R. MacCallum and J. Tanner, *Nature*, 225 (1970) 1127.
2 H. E. Kissinger, *J. Res. Nat. Bur. Stand.*, 57 (1956) 217.
3 J. Gilles and H. Tompa, *Nature*, 229 (1971) 57.
4 R. A. W. Hill, *Nature*, 227 (1970) 703.
5 J. R. MacCallum, *Nature*, 232 (1971) 41.