On two-term rate equations in non-isothermal kinetics

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Abstract

This paper demonstrates that two-term rate equations cannot be applied in non-isothermal kinetics.

In a recent paper [1], Strøme proposed a new derivation for a two-term rate equation in non-isothermal kinetics by using a thermodynamic approach. In this paper, we aim to prove that this approach does not lead to such a conclusion. Moreover, we demonstrate that one cannot obtain a two-term (or more) rate equation, if the rate refers to the rate of change in the chemical composition of a system.

Strøme [1] starts from the relationship

$$G = RT \ln Q/K \tag{1}$$

where

$$Q = Q(P, p, \alpha) \quad \text{represents the activation ratio} \tag{2}$$

$$K = K(T, p) \quad \text{represents the equilibrium constant} \tag{3}$$

$$\Delta G = \Delta G(T, p, \alpha) \quad \text{represents the Gibbs free energy} \tag{4}$$

and T, p, α are the temperature, pressure and degree of conversion respectively.

Taking the derivative of eqn. (1) with respect to time t one obtains

$$\frac{\mathrm{d}\Delta G}{\mathrm{d}t} = R \ln \frac{Q}{K} \frac{\mathrm{d}T}{\mathrm{d}t} + \frac{RT}{Q} \frac{\mathrm{d}Q}{\mathrm{d}t} - \frac{RT}{K} \frac{\mathrm{d}K}{\mathrm{d}t} \tag{5}$$

For isothermal, isobaric conditions (T and p constant), it follows that K is

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constant and eqn. (5) becomes

$$\frac{d\Delta G}{dt}\bigg|_{T,p} = \frac{RT}{Q}\frac{dQ}{dt}\bigg|_{T,p} \tag{6}$$

Subtraction of eqn. (6) from eqn. (5) leads, after rearrangement, to

$$\frac{1}{Q}\frac{dQ}{dt} = \frac{1}{Q}\frac{dQ}{dt}\bigg|_{T,p} + \frac{1}{K}\frac{dK}{dt} - \frac{\Delta G}{RT^2}\frac{dT}{dt} + \frac{1}{RT}\left(\frac{d\Delta G}{dt} - \frac{d\Delta G}{dt}\bigg|_{T,p}\right) \tag{7}$$

By changing the variable time t with the degree of conversion α

$$\frac{dQ}{dt} = \frac{dQ}{d\alpha}\frac{d\alpha}{dt} \tag{8}$$

Strøme finally obtains

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dt}\bigg|_{T,p} + \frac{\dfrac{1}{K}\dfrac{dK}{dt} - \dfrac{\Delta G}{HT^2}\dfrac{dT}{dt} + \dfrac{\dfrac{d\Delta G}{dt} - \dfrac{d\Delta G}{dt}\bigg|_{T,p}}{RT}}{\dfrac{dQ}{dt}} \tag{9}$$

which is claimed as the true rate equation in non-isothermal, non-isobaric conditions [1].

However, eqn. (2) allows us to write

$$\frac{dQ}{dt} = \frac{\partial Q}{\partial T}\bigg|_{p,\alpha}\frac{dT}{dt} + \frac{\partial Q}{\partial p}\bigg|_{T,\alpha}\frac{dp}{dt} + \frac{\partial Q}{\partial \alpha}\bigg|_{T,p}\frac{d\alpha}{dt} \tag{10}$$

When T and p are constant, eqn. (10) becomes

$$\frac{dQ}{dt}\bigg|_{T,p} = \frac{\partial Q}{\partial \alpha}\bigg|_{T,p}\frac{d\alpha}{dt} \tag{11}$$

By introducing eqns. (10) and (11) into eqn. (7) one obtains

$$\frac{\partial Q}{\partial T}\bigg|_{p,\alpha}\frac{dT}{dt} + \frac{\partial Q}{\partial p}\bigg|_{T,\alpha}\frac{dp}{d\alpha} = \frac{1}{K}\frac{dK}{dt} - \frac{\Delta G}{RT^2}\frac{dT}{dt} + \frac{1}{RT}\left(\frac{d\Delta G}{dt} - \frac{d\Delta G}{dt}\bigg|_{T,p}\right) \tag{12}$$

It is clear that eqn. (12) cannot be used to compute $d\alpha/dt$. The error which led to the wrong result, i.e. eqn. (9), was the use of eqn. (8) for changing the variable instead of the correct relationship given by eqn. (11).

Strøme's paper, and also many others, attempts to propose a relationship of the type

$$\frac{d\alpha}{dt}\bigg|_{NI} = \frac{d\alpha}{dt}\bigg|_{I} + \lambda(\alpha, T)\frac{dT}{dt} \tag{13}$$

It is obvious that in this way two functions, which are not defined, are introduced, the "non-isothermal reaction rate" $d\alpha/dt|_{NI}$, and the "isothermal reaction rate" $d\alpha/dt|_{I}$, which are assumed to depend on each other. For

the definition of the reaction rate, the following relationships still apply

$$\frac{d\alpha}{dt} = f(\alpha)k(T)$$

$$\alpha = \alpha(t)$$

$$T = T(t) \tag{14}$$

Attempts to obtain eqn. (13) from eqn. (14) are logically inconsistent because from the conclusion (eqn. (13)) the hypothesis itself, i.e. eqn. (14), is denied. Indeed, various errors affecting the demonstrations have been detected throughout papers proposing two-term expressions for the reaction rate [2–4].

In fact, using relationship (14) one obtains by integration

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = F(\alpha) = \int_0^t k(T(t)) \, dt \tag{15}$$

Equation (15) allows the degree of conversion at any time t to be calculated

$$\alpha = F^{-1}\left[\int_0^t k(T(t)) \, dt \right] \tag{16}$$

The evaluation of the degree of conversion requires the calculation of the integral

$$I = \int_0^t k(T(t)) \, dt \tag{17}$$

for the given experimental conditions (isothermal or non-isothermal).

In the following we shall consider two experiments for the same reaction: an isothermal experiment at temperature T_I, and a non-isothermal experiment, taking place from the initial temperature T_i to the final one T_f. For the same time t_0 from the beginning of the experiment, the integral from eqn. (17) becomes

$$I_I = \int_0^{t_0} k(T_I) \, dt = k(T_I)t_0 \tag{18}$$

so respectively

$$I_{NI} = \int_0^{t_0} k(T(t)) \, dt = k(T_{NI})t_0 \tag{19}$$

where I_{NI} is the integral calculated from non-isothermal conditions and I_I is that calculated under isothermal conditions. The integral I_{NI} was computed using the mean value theorem [5], T_{NI} being a temperature between T_i and T_f, $T_{NI} \in [T_i, T_f]$.

Using eqn. (18) or eqn. (19) in eqn. (16), one obtains

$$\alpha_I = F^{-1}(k(T_I)t_0)$$ (20)

and

$$\alpha_{NI} = F^{-1}(k(T_{NI})t_0)$$ (21)

Obviously for

$$T_I = T_{NI}$$ (22)

one obtains

$$\alpha_I = \alpha_{NI}$$ (23)

Equation (14), taking into account eqns. (22) and (23), becomes

$$\left.\frac{d\alpha}{dt}\right|_I = f(\alpha_I)k(T_I) = f(\alpha_{NI})k(T_{NI}) = \left.\frac{d\alpha}{dt}\right|_{NI}$$ (24)

It follows that during a non-isothermal experiment, for any time interval from the beginning of the experiment, the reaction rate has the same value as that computed for an isothermal experiment occurring at the temperature $T_I = T_{NI}$, after the same time interval from the beginning of the experiment. In other words, at any moment the value of a non-isothermal reaction rate equals the value of the isothermal reaction which occurs at a suitable chosen temperature. Consequently if eqn. (14) holds, one cannot obtain a relationship of the form of eqn. (13). Equation (13) may be considered as a constitutive equation, by which the two new functions, the "non-isothermal reaction rate" and the "isothermal reaction rate", are introduced.

As already discussed by Kratochvil and Šesták [6], "a constitutive equation of a chemical system implies that the value α at time t depends on the time t and the instantaneous value of the temperature T at t, regardless of its previous temperature history. In other words eqn. (13) represents an equation of state."

Figure 1 shows the plot of a non-isothermal experiment in the (T, α) plane. For any point of the curve, for an element of it ds, one may write [5]

$$\frac{ds}{dt} = \sqrt{\left(\frac{d\alpha}{dt}\right)^2 + \left(\frac{dT}{dt}\right)^2} = \delta_1 \frac{d\alpha}{dt} + \delta_2 \frac{dT}{dt}$$ (25)

δ_1 and δ_2 being the two parameters which fulfil the condition

$$\delta_1^2 + \delta_2^2 = 1$$ (26)

Equation (25) becomes an eqn. (13)-type relationship if one defines ds/dt as the non-isothermal reaction rate and dα/dt as the isothermal reaction rate.

The formal identities of eqns. (13) and (25) become apparent. It must be stressed that the function ds/dt, considered as the non-isothermal reaction
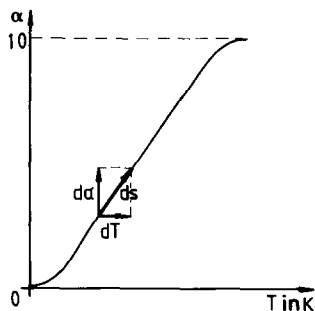
Fig. 1. The plot of a non-isothermal experiment.

rate, will change even if the chemical composition of the system does not change but only its temperature changes.

These results may be extended for "non-isothermal, non-isobaric reaction rates" by writing for the element of curve, in the space (T, p, α), the relationship

$$\frac{ds}{dt} = \sqrt{\left(\frac{d\alpha}{dt}\right)^2 + \left(\frac{dT}{dt}\right)^2 + \left(\frac{dp}{dt}\right)^2} = \delta_1 \frac{d\alpha}{dt} + \delta_2 \frac{dT}{dt} + \delta_3 \frac{dp}{dt} \tag{27}$$

where

$$\delta_1^2 + \delta_2^2 + \delta_3^2 = 1$$

If ds/dt is considered to be the "non-isothermal, non-isobaric reaction rate", from eqn. (27) it follows that one may have a reaction rate even if without changing the chemical composition of the system: the temperature and/or pressure of the system is changed.

We consider that application of the term "chemical reaction rate" to processes that occur without a change in the chemical composition, i.e. vaporisation, melting, heating, changing the pressure, etc., is not justified. Consequently, we consider ds/dt as being the rate of the system evolution in a non-isothermal, non-isobaric regime, along the path given in Fig. 1, and $d\alpha/dt$ as being the rate of the chemical reaction, defined as given by eqn. (14).

Taking into account these considerations, eqn. (27) may be interpreted more easily. It states that the rate of the system evolution during an experiment which occurs with a change in temperature, pressure and chemical composition, depends on the rate of temperature change, rate of pressure change and rate of chemical reaction.

The state of a system is described by the Gibbs free enthalpy G [7]

$$G = G(T, p, \alpha) \tag{28}$$

whose derivative with respect to time leads to

$$\frac{dG}{dt} = \frac{\partial G}{\partial \alpha}\bigg|_{T,p} \frac{d\alpha}{dt} + \frac{\partial G}{\partial T}\bigg|_{\alpha,p} \frac{dT}{dt} + \frac{\partial G}{\partial p}\bigg|_{\alpha,T} \frac{dp}{dt} \qquad (29)$$

The mathematical identity of eqns. (27) and (29) suggests that

$$\frac{ds}{dt} = \frac{dG}{dt} \qquad (30)$$

and

$$\delta_1 = \frac{\partial G}{\partial \alpha}\bigg|_{p,T} = \mu$$

$$\delta_2 = \frac{\partial G}{\partial T}\bigg|_{\alpha,p} = -S \qquad (31)$$

$$\delta_3 = \frac{\partial G}{\partial p}\bigg|_{\alpha,T} = -V$$

Equations (30) and (31) suggest also physical meanings for the variables of eqn. (30), i.e. ds/dt is the rate of system state change, δ_1 is the chemical potential μ, δ_2 is the entropy of the system S, and δ_3 is the volume of the system V.

In summary, it follows that relationships of the type of eqn. (13) are, in fact, various forms of eqn. (29) and the consideration of the rate of change of the state of the system as being the chemical reaction rate under non-isothermal, non-isobaric conditions is an incorrect extension of this definition.

Consequently, the chemical reaction rate, understood as the rate change of the chemical composition of the system is defined completely by eqn. (14). This definition does not depend on the kind of experiment performed for the study of the reaction, i.e. isothermal or non-isothermal, non-isobaric.

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