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Note

Discussion on the correctness of the rate expression for non-isothermal kinetics

H.P. Nawada

Thermodynamics Section, Metallurgy Division, IGCAR, Kalpakkam, Tamil Nadu, PIN-603 102, India

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Abstract

The complexity of the rate expression for nonisothermal kinetics is illustrated considering the time derivative of the population of activated complexes. Extension of the problem to conventional solid-state kinetics may require inclusion of additional temperature sensitive terms in the rate expression.

Keywords: Excitated state; Kinetics; Non-isothermal; Rate expression

More than two decades ago, MacCalluam and Tanner questioned the validity of the non-isothermal rate expression [1] which was commonly used in the literature. MacCalluam also proposed a two-term rate expression [2] to replace the conventional single-term rate equation. Popescu et al. [3] disagreed with MacCalluam's two-term rate equation, arguing that the concentration of activated complex molecules A* is constant under steady state conditions. These authors cited this argument from quantum chemistry considerations after Eyring et al. [4]. Recently, Segal and Popescu [5] reaffirmed the views of Popescu et al. in a reply to comments made by Strømme [6]. The use of the constancy of A* by Segal and Popescu and Popescu et al. is inappropriate because this is only an assumption employed in one of the methods of solving the 'unimolecular gas phase reaction' taking place under steady state conditions. Thus the constancy of A* tacitly assumes isothermal–isobaric conditions. Translating these conditions into mathematical form, it should have been written as

$$(\partial A^*/\partial t)_{T,P} = 0 \tag{1}$$

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instead of

$$\mathrm{dA}^*/\mathrm{d}t = 0 \tag{2}$$

as represented by Popescu, Segal and co-workers [3, 5]. It should be noted that Eq. (1) is a partial derivative whereas Eq. (2) is not.

Because Eq. (1) describes only isothermal processes, it cannot be readily extended to non-isothermal processes with the same zero value for the derivative. Hence, Eq. (2) is not of the correct form to describe $\mathrm{dA}^*/\mathrm{d}t$ under such conditions and it can take any value, as in Eq. (4) of ref. 2, namely

$$\mathrm{dA}^*/\mathrm{d}t = [(\partial \mathrm{A}^*/\partial[\mathrm{A}])_T]\ \mathrm{d}[\mathrm{A}]/\mathrm{d}t + (\partial \mathrm{A}^*/\partial t)_{[\mathrm{A}]}\beta \tag{3}$$

where β represents $\mathrm{d}T/\mathrm{d}t$. However, MacCalluam had equated the rate constant k with the equilibrium constant K (hereafter designated $K^{\#}$, corresponding to the equilibrium process $\mathrm{A} + \mathrm{A} = \mathrm{A}^*$) in deriving the equations

$$(\partial[\mathrm{A}^*]/\partial[\mathrm{A}])_T = 2k[\mathrm{A}] \tag{4}$$

$$(\partial[\mathrm{A}^*]/\partial[T])_{[\mathrm{A}]} = (E/RT^2)K^{\#}[\mathrm{A}]^2 \tag{5}$$

The familiar relationship between k and $K^{\#}$ was given by Laidler [7]

$$k = \Gamma K^{\#} k_{\mathrm{B}}(T/h) \tag{6}$$

where Γ is the transmission coefficient, k is the rate constant for the overall reaction $\mathrm{A} + \mathrm{A} \rightarrow$ products, and k_{B} is the Boltzmann constant. Becauce Γ is generally considered to be unity, Eq. (6) is reduced to

$$k = K^{\#} k_{\mathrm{B}}(T/h) \tag{7}$$

Rearranging, one obtains

$$k[h/(k_{\mathrm{B}}T)] = [\mathrm{A}^*]/[\mathrm{A}]^2 \tag{8}$$

From the above, Eqs. (4) and (5) can be derived and are given as

$$(\partial[\mathrm{A}^*]/\partial[\mathrm{A}])_T = 2k(h/k_{\mathrm{B}}T)[\mathrm{A}] \tag{9}$$

$$(\partial[\mathrm{A}^*]/\partial T)_{[\mathrm{A}]} = k(h/k_{\mathrm{B}}T)[\mathrm{A}]^2(E/RT^2 - 1/T) \tag{10}$$

where E is the activation energy for the above unimolecular reaction. Substituting Eq. (9) and Eq. (10) in the expression

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k[\mathrm{A}]^2 + [(\partial[\mathrm{A}^*]/\partial T)_{[\mathrm{A}]}\beta]/(\partial[\mathrm{A}^*]/\partial[\mathrm{A}])_T \tag{11}$$

which was derived by MacCalluam, the following rate equation can be obtained

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k[\mathrm{A}]^2 + ([\mathrm{A}]\beta/2)[E/RT^2 - 1/T\} \tag{12}$$

The same equation, Eq. (12), can be derived using the relation $E = \Delta E^{\#} + RT$ which was given by Laidler [8]. It should be noted that $\Delta E^{\#}$ is the increase in energy in passing from the initial to the activated state.

The salient difference between the present approach and MacCalluam's is the inclusion of RT along with $\Delta E^{\#}$, which might either become insignificant or reduce the effect of the first term under certain limiting conditions. Equation (12), even in its present form as a three-term expression, could at best give the rate for an ideal homogeneous gas phase reaction only. The term 'ideal' actually refers to those conditions under which the partition functions combined in K^* simplify into an Arrhenius type of exponential term. In a rigorous treatment of the rate equation, factors such as the temperature dependence of the various partition functions, as well as that of the transmission coefficient, and the reshuffling of energy between energized molecules and activated molecules should also be taken into account. On extrapolation of the above treatment to either a condensed phase or heterogeneous reaction kinetics, there would be many additional temperature-sensitive terms, e.g. activity coefficients of reactants and products, and the electrostatic effect, which would need to be incorporated into the rate equation.

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