

Note

THE CORRECT RATE EXPRESSION FOR NON-ISOTHERMAL KINETIC PROCESSES

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It is some 10 years or so since I first became involved in the question of the validity of non-isothermal rate equations [1] and still papers appear devoted to this subject [2]. The specific objection to my proposals has been that conversion and time are not state functions, and therefore the use of partial derivatives in my original paper was incorrect. While the controversy was not totally resolved, it seemed, following a number of papers by Šesták and co-workers [3,4], that the bulk of opinion was against my approach, although clear proof one way or the other was lacking.

One piece of evidence of detail rather than of principle which is frequently quoted as demonstration of the validity of the single term rate expression is that shown in Fig. 9 of ref. 3, in which Holba and Šesták plot rate of reaction (as fractional conversion) vs. T according to the one term [eqn. (15), ref. 3] and the two term [eqn. (22), ref. 3] rate expressions. The authors claim that the fair agreement between the one term theory and experimental plots, compared with their evaluation of the two term expression, constitutes good evidence for the validity of the one term rate expression. Using their two term expression they calculate that the maximum rate is almost an order of magnitude higher than that observed experimentally. Their method of calculation is not clear but it is obvious that some serious error has been incorporated since α for all three curves goes to unity then the area under the curves for the plots of the two theoretical rates vs. temperature should be equal to each other and should be the same as that for the experimental plots. Indeed if the two term plot is scaled down to achieve this requirement then it appears that this function gives a closer fit to experimental observations than the single term analogue.

I have now developed an alternative derivation based on accepted physico-chemical principles which I believe resolves the problem of whether a one or two term rate expression is applicable to non-isothermal kinetics.

The basic premise is that of the transition state theory which proposes that the rate of a chemical reaction is proportional to the number of activated complexes, A^* , which are themselves in equilibrium with reactant molecules A as shown by eqn. (1).



This population of activated complexes is governed by two independently variable state functions, namely the population of A species and the temperature (T) of the system. It is assumed that the pressure and volume are constant. Thus we may write

$$A^* = f(A, T) \quad (2)$$

Since, by assumption, the volume remains constant the population can be replaced by the concentration resulting in eqn. (3)

$$[A^*] = f'([A], T) \quad (3)$$

Thus

$$\frac{d[A^*]}{dt} = \left(\frac{\delta[A^*]}{\delta[A]} \right)_T \frac{d[A]}{dt} + \left(\frac{\delta[A^*]}{\delta T} \right)_{[A]} \frac{dT}{dt} \quad (4)$$

Let $dT/dt = \beta$ and eqn. (4) can be written as

$$-\frac{d[A]}{dt} = \frac{(\delta[A^*]/\delta T)_{[A]}\beta}{(\delta[A^*]/\delta[A])_T} - \frac{d[A^*]/dt}{(\delta[A^*]/\delta[A])_T} \quad (5)$$

Equation (5) represents the change in $[A]$ when both $[A]$ and T vary with time. The second term on the right-hand side of eqn. (5) can be simplified by solving the equation for the particular condition $\beta = 0$, resulting in the isothermal rate expression

$$-\frac{d[A]}{dt} = k[A]^2 \quad (6)$$

Thus

$$k[A]^2 = -\frac{d[A^*]/dt}{(\delta[A^*]/\delta[A])_T} \quad (7)$$

Equation (6) is based on the assumption of a simple second-order decomposition reaction with isothermal rate coefficient k . This assumption is convenient and in no way invalidates the derivation. Thus eqn. (5) can be written

$$-\frac{d[A]}{dt} = \frac{(\delta[A^*]/\delta T)_{[A]}\beta}{(\delta[A^*]/\delta[A])_T} + k[A]^2 \quad (8)$$

By use of eqn. (9) this equation can be further simplified

$$K = \frac{[A^*]}{[A]^2} \quad (9)$$

in which K is the equilibrium constant for eqn. (1). Appropriate differentiation of eqn. (9) results in

$$(\delta[A^*]/\delta[A])_T = 2KA \quad (10)$$

and

$$(\delta[A^*]/\delta T)_{[A]} = (E/RT^2) K[A]^2 \quad (11)$$

in which E is the activation energy for the reaction $A \rightarrow \text{Products}$.

Substituting eqns. (10) and (11) in eqn. (8) gives

$$-\frac{d[A]}{dt} = [A] \left(k[A] + \frac{E\beta}{2RT^2} \right) \quad (12)$$

Equation (12) represents the correct expression for the rate of a reaction occurring under conditions of varying temperature. This derivation is based on partial differentials involving independent state functions, concentration and temperature, and therefore cannot be criticised on the grounds used against my previous equations.

It is not the purpose of this note to re-examine or to criticise the proposals of other authors. My objective is simply to propose a clear proof of the statement made in an earlier paper [1] that the appropriate rate expression for non-isothermal reactions involves two terms, as shown in eqn. (12).

REFERENCES

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