

Note

ON THE CORRECT RATE EXPRESSION IN NON-ISOTHERMAL KINETICS

C. POPESCU

Centrul de Cercetări Materii Prime, Auxiliare și Ape Reziduale, Str. Siret 95, Bucharest (Romania)

M. STAN

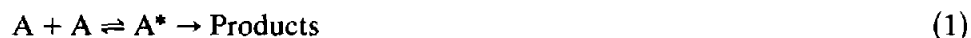
Institutul de Cercetări Textile, Str. L. Pătrășcanu 16, Bucharest (Romania)

E. SEGAL

Polytechnical Institute of Bucharest, Institute of Chemistry, Department of Physical Chemistry and Electrochemical Technology, Bucharest (Romania)

(Received 15 June 1984)

A recent paper by MacCallum [1] proposed a new approach of a two-term equation for the correct rate expression in non-isothermal kinetic processes. He started from the transition state theory (TST) premise, according to which the rate of a chemical process is proportional to the number of activated complexes, A^* , as shown by eqn. (1)



From this equation, with the assumption of constant volume, he derived

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

The reaction rate, $d[A]/dt$, can be obtained from eqn. (2) by differentiation and appropriate arrangement as follows

$$-\frac{d[A]}{dt} = \frac{\partial[A^*]/\partial T|_{[A]}}{\partial[A^*]/\partial[A]|_T} \beta - \frac{d[A^*]/dt}{\partial[A^*]/\partial[A]|_T} \quad (3)$$

β being equal to dT/dt . Using two other simplifying assumptions he obtained

$$-\frac{d[A]}{dt} = [A] \left(k[A] + \frac{E\beta}{2RT^2} \right) \quad (4)$$

But TST states that [2]

$$[A^*] = \text{const. (steady-state premise)}$$

which leads to

$$d[A^*]/dt = 0 \quad (5)$$

and so eqn. (3) becomes

$$-\frac{d[A]}{dt} = \frac{\partial[A^*]}{\partial T} \bigg|_{[A]} \frac{1}{\frac{\partial[A^*]}{\partial[A]} \bigg|_T} \beta \quad (3')$$

The right-hand side of eqn. (3') can be rewritten as follows [3]

$$\frac{\partial[A^*]}{\partial T} \bigg|_{[A]} \frac{1}{\frac{\partial[A^*]}{\partial[A]} \bigg|_T} = \frac{\partial[A]}{\partial T} \bigg|_{[A^*]} \quad (6)$$

and eqn. (3') becomes

$$-\frac{d[A]}{dt} = \frac{\partial[A]}{\partial T} \bigg|_{[A^*]} \beta \quad (7)$$

and since the right-hand side of eqn. (7) has a derivative with respect to one variable, we can renounce the partial derivative and write

$$-\frac{d[A]}{dt} = \frac{d[A]}{dT} \beta \quad (8)$$

or

$$-\frac{d[A]}{dT} = \frac{1}{\beta} \frac{d[A]}{dt} \quad (8')$$

which is the so-called equation of non-isothermal kinetics. Summing up, the approach proposed by MacCallum can scarcely solve the problem of the validity of the two-term rate expression in non-isothermal kinetics.

REFERENCES

- 1 J.R. MacCallum, *Thermochim. Acta*, 53 (1982) 375.
- 2 H. Eyring, J. Walter and G.E. Kimball, *Quantum Chemistry*, Wiley, New York, 14th edn., 1967, p. 308.
- 3 M. Nicolescu, *Mathematical Analysis, Didactică și Pedagogică*, Bucharest, 1977 (in Romanian).