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Note

ON THE CORRECT RATE EXPRESSION IN NON-ISOTHERMAL KINETICS

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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)

$$A + A \rightleftharpoons A^* \rightarrow \text{Products} \tag{1}$$

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

$$[A^*] = f([A], T) \tag{2}$$

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

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

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

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

But TST states that [2]

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

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which leads to

$$d[A^*]/dt = 0 \tag{5}$$

and so eqn. (3) becomes

$$-\frac{d[A]}{dt} = \left.\frac{\partial[A^*]}{\partial T}\right|_{[A]} \frac{1}{\left.\dfrac{\partial[A^*]}{\partial[A]}\right|_T} \beta \tag{3'}$$

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

$$\left.\frac{\partial[A^*]}{\partial T}\right|_{[A]} \frac{1}{\left.\dfrac{\partial[A^*]}{\partial[A]}\right|_T} = \left.\frac{\partial[A]}{\partial T}\right|_{[A^*]} \tag{6}$$

and eqn. (3') becomes

$$-\frac{d[A]}{dt} = \left.\frac{\partial[A]}{\partial T}\right|_{[A^*]} \beta \tag{7}$$

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

$$-\frac{d[A]}{dt} = \frac{d[A]}{dT} \beta \tag{8}$$

or

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

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.
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3 M. Nicolescu, Mathematical Analysis, Didactică şi Pedagogică, Bucharest, 1977 (in Romanian).