Thermochimica Acta, 210 (1992) 329–330
Elsevier Science Publishers B.V., Amsterdam

Note

More on the correct rate expression in non-isothermal kinetics. Reply to K.O. Strøme [1]

E. Segal

Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bd. Republicii 13, Bucharest 43632 (Romania)

C. Popescu

LACECA Research Centre, Str. Siert 95, Bucharest (Romania)

(Received 6 January 1992)

In some critical comments [1] concerning our note [2], K.O. Strøme reintroduces a two-term rate expression of the form

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = \left(\frac{\partial[A]}{\partial T}\right)_{[A^*]} \beta + \left(\frac{\partial[A]}{\partial[A^*]}\right)_T \frac{\mathrm{d}[A^*]}{\mathrm{d}t} \tag{1}$$

or, taking into account that $\beta = \mathrm{d}T/\mathrm{d}t$

$$\mathrm{d}[A] = \left(\frac{\partial[A]}{\partial T}\right)_{[A^*]} \mathrm{d}T + \left(\frac{\partial[A]}{\partial[A^*]}\right)_T \mathrm{d}[A^*] \tag{2}$$

The author claims that $\mathrm{d}[A]$ as given by eqn. (2) is the exact differential of $[A] = g(T, [A^*])$.

We must emphasize that eqns. (1) and (2) cannot be considered as being correct because (i) as the author has pointed out, $[A^*]$ is constant at a given temperature [1], i.e. $(\partial[A]/\partial[A^*])_T(\mathrm{d}[A^*]/\mathrm{d}t)$ in the righthand term of eqn. (1) should equal zero, since the temperature is kept constant during the derivation; (ii) as correctly pointed out also by the author, $[A^*]$ depends on temperature, i.e. the two variables T and $[A^*]$ are not independent, and thus $\mathrm{d}[A]$ cannot be considered as the exact differential of $[A]$ as stated by eqn. (2).

Correspondence to: E. Segal, University of Bucharest, Bd. Republicii 13, Bucharest, Romania.

[1] This reply has been delayed because Dr. K.O. Strøme's note, for reasons beyond our control, was not available until a few weeks ago.

REFERENCES

1 K.O. Strøme, Thermochim. Acta, 143 (1989) 355.
2 C. Popescu, M. Stan and E. Segal, Thermochim. Acta, 81 (1984) 375.