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Note

COMMENTS ON THE NOTE "ON THE CORRECT RATE EXPRESSION IN NONISOTHERMAL KINETICS" BY C. POPESCU, M. STAN AND E. SEGAL

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The argument in the note cited above, [1], against the two-term rate expression proposed for non-isothermal reaction kinetics [2], is not tenable for the following reason. The basic assumption made that [A*] = constant, (steady state premise) [1], is only (generally approximately (?)) true at constant temperature for a closed system. At different temperatures steady state will occur at altered [A*] values. This is expected because A* and A are assumed to be in a state of equilibrium, which is a function of temperature, and so therefore, is, also [A*]. Thus, in general the conditions of steady state change in non-isothermal reactions, eqn. (7), ref. 1, is accordingly not valid in non-isothermal cases (disregarding the missing negative sign on the right-hand side, which originates in eqn. (6)), nor is the transition from eqn. (7) to eqn. (8). One obtains in place of eqn. (7)

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

and, since $\beta \equiv \mathrm{d}T/\mathrm{d}t$

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

where d[A] is the (exact) differential of $[\mathrm{A}] = g(T, [\mathrm{A}^*])$, which is simply another form of eqn. (2), ref. 1, and is a general expression for the 'equilibrium' between these species.

REFERENCES

1 C. Popescu, M. Stan and E. Segal, Thermochim. Acta, 81 (1984) 375.
2 J.R. MacCallum, Thermochim. Acta, 53 (1982) 375.

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