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Note

On the validity of the steady-state approximation and of two-term rate equations in non-isothermal kinetics. Reply to H.P. Nawada

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Abstract

The validity of the steady-state approximation and two-term rate equations in non-isothermal kinetics are discussed.

Keywords: Kinetics; Non-isothermal

In a short note dedicated to the correctness of the rate expression in non-isothermal kinetics, Nawada [1] reiterates the problems concerning the validity of the steady-state condition and of two-term rate equation for changes undergone by chemical compounds with progressive heating according to a given program. Here we report our views concerning the topic suggested by Nawada.

1. The steady-state condition is actually an approximation. It holds generally for very small (practically vanishing) concentrations of the active intermediate A* [2] (particularly for the discussed case in which the intermediate is the activated complex). Obviously the steady-state concentrations of A* are different for various temperatures but their values are vanishingly small. In such conditions, the steady-state approximation

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$$d[A^*]/dt = 0 \quad (1)$$

still holds. The validity of relationship (1) does not necessarily mean that [A*] is constant, but that [A*] satisfies the steady-state condition [2].

2. In some of our previous papers, like that mentioned by Dr. Nawada as his ref. 5, we have shown that two-term equations for non-isothermal kinetics are physically and mathematically inconsistent, not because [A*] is constant but because under non-isothermal conditions the two variables used in these equations are not independent. In particular, Eq. (3) of Nawada's paper [1] is not correct because [A] and T are dependent variables in non-isothermal kinetics. Thus, all the subsequent quantitative considerations based on Eq. (3) are questionable.

References

[1] H.P. Nawada, Thermochim. Acta, 242 (1994) 239–241.
[2] M. Boudart, Kinetics of Chemical Processing, Prentice Hall, Englewood Cliffs, NJ, 1968, p. 63–67.