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Note

COMMENTS ON "VARIATION OF THE MAXIMUM RATE OF CONVERSION AND TEMPERATURE WITH HEATING RATE IN NON-ISOTHERMAL KINETICS"

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A recent paper [1] discusses the variation of the maximum rate *value* of conversion with heating rate in non-isothermal kinetics. A dependence of the value of conversion at maximum reaction rate, α_m, on the heating rate $\beta \equiv dT/dt$ is derived

$$\frac{d\alpha_m}{d\beta} = \frac{f(1-\alpha_m)}{\beta} \cdot \frac{\left(\frac{d\alpha}{dt}\right)_m}{f(1-\alpha_m)\frac{E}{RT_m^2} - \frac{1}{\beta}\frac{df(1-\alpha_m)}{dT}\left(\frac{d\alpha}{dt}\right)_m}$$

where E is the activation energy, R is the universal gas constant, T_m is the temperature corresponding to $\alpha = \alpha_m$ and $f(1-\alpha)$ is the kinetic function. In the original paper $(d\alpha/dt)_m$ has been written as $(d\alpha_m/dt)$, a notation which we think is misleading and have corrected accordingly.

We have to point out further that the derived relation is wrong. The physical dimension of the denominator in the second factor on the right-hand side of the equation

$$f(1-\alpha_m)\frac{E}{RT_m^2} - \frac{1}{\beta}\frac{df(1-\alpha_m)}{dT}\left(\frac{d\alpha}{dt}\right)_m$$

is $[T]^{-1} - [T]^{-2}$, and therefore not only self-inconsistent but also erroneous, as it should be $[t]^{-1}$ in order that the two sides of the equation balance dimensionally. Moreover, eqn. (7a) given in the paper [1] does not follow algebraically from the derived relation.

More importantly, we suggest that the conceptual assumption with which the derivation has started is invalid. The basic relation used by the authors of [1]

$$\frac{d\alpha}{d\beta} = \frac{1}{\beta}\frac{d\alpha/dt}{d\beta/dT}$$

implies that α can be treated as a function of β or T. In fact, α is not a

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function of any variable or sets of variables. This point has been argued before in different contexts: see refs. 2–4. Under non-isothermal conditions only $d\alpha/dt$ may be assumed to be describable by a functional relation, as re-stated in for example, ref. 5.

Finally, we note that in a previous paper [6] the dependence of α_m on β has already been calculated without the invalid assumption. The result given there is

$$\frac{d\alpha_m}{d\beta} = -\frac{f(1-\alpha_m)}{\beta} \cdot \frac{(\beta/AT_m)^2(2+U)\int_0^{\alpha_m} d\alpha/f(1-\alpha) - f(1-\alpha_m)}{(\beta/AT_m)^2(2+U) - f(1-\alpha_m)f''(1-\alpha_m)/U}$$

where A is the pre-exponential factor in the rate constant, and $U \equiv E/RT_m$. As stated there, $dT_m/d\beta$ can be derived in a similar way.

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