REMARK ON THE KINETIC COMPENSATION EFFECT

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In his recent article, Agrawal [1] classified in two basic categories the kinetic compensation effect, exhibited sometimes through a linear relationship of the logarithm of preexponential factor, A, and apparent activation energy, E_{app}, obtained experimentally for a series of related reactions:

(1) For the "true" compensation effect, a common point of concurrence is indicated for the Arrhenius plot of $\ln k_T$ vs $1/T$ at a characteristic temperature at which all rates become apparently equal. Such a concurrence is said to be due to chemical reasons rather than to the propagation of experimental errors.

(2) The "false" compensation effect, however, fails to display clearly such a characteristic point and is said to be due to non-negligible errors, but certainly not to any chemical factors.

The latter standpoint is more agreeable, as such a compensation may simply arise from a misfit of the false kinetic model $F(a)$ instead of the required one, $f(a)$ [2]. Then

$$E_{app} = E - RT \ln [F(a)/f(a)] \tag{1}$$

and

$$\ln A = E - g(a, T, P, \ldots) \tag{2}$$

where the function $g(a, T, P, \ldots)$ is understood to be dependent on a parameter which is misused instead of the appropriate one or one which is missing, e.g. pressure (multiplying $k_p = P^n$), external fields, including their nonconstancy and gradiency, and also other possible extensive parameters of the sample input such as mass, concentration, particle radii or defect distribution. The question arises, however, of whether this approach virtually includes chemical factors or not. On the other hand, the first standpoint, regarding the true kinetic compensation effect to chemical factors, can be explained as a mere mathematical consequence of a natural interdependence between E and $\ln A$ [2].

Pysiak [3] and Militký [4] have already analysed the correlation dependence of the individual terms in question ($\ln k_T$, $\ln A$ and E/RT) and found that the term $\ln A$ appears to be superfluous and hence an unnecessary parameter for the evaluation being accomplished within a narrow temperature interval. To discount such a compensation effect, an enormous extension of this working temperature interval is needed, but this is often inconvenient for experimental reasons. Thus, a reference temperature ϑ (at $k_T = k_\vartheta$) is recommended to be included in the $\ln A - E$ correlation, as a multiplying constant yielding the modified Arrhenius relation in the form

$$k'_T = k_\vartheta \exp[(-E/R)(1/T - 1\vartheta)] \tag{3}$$

(where $A = k_\vartheta$, E, R and T bear the obvious meanings of pre-exponential factor, activation energy, gas constant and temperature, respectively).

The inherent mathematical correlation is worth analysing in more detail [2]:

(i) For the first and the second derivatives of k_T with respect to T we obtain (e.g. Holba [5]):

$$\mathrm{d}k_T/\mathrm{d}T = (E/RT^2)\,k_T \tag{4}$$

$$\mathrm{d}^2k_T/\mathrm{d}T^2 = (E/RT^3)(E/RT - 2)\,k_T \tag{5}$$

the latter being positive if $E > 2RT$ and negative if $E < 2RT$. It follows that the Arrhenius relation can describe any alternative profile concave upwards or convex downwards, or even linear for $E = 2RT$. The entire slope is then established through the selected value of the pre-exponential factor. Moreover, it can be seen that in a narrow temperature interval the Arrhenius relation can be approximated by an arbitrary smooth function [6]. In this respect it should be noted that the mutual dependence of E and A was demonstrated 20 years ago by Šesták [6] when theoretical curves were evaluated and it was not possible to separate the effects of E and A for the given position of the curve.

(ii) The other mathematical proof is based on a functional analysis [2, 4, 7] of the angle θ in which the function in question ($\ln A$ and E/RT or simply 1 and $1/T$) meet each other in the Hilbert space. The resulting formula (Voňka [7])

$$\cos\theta = T_0 T_F[\ln(T_F/T_0)/(T_F - T_0)] \tag{6}$$

shows that the angle does not depend on the functions 1 and $1/T$ only, but also upon the working temperature interval from T_0 to T_F.

If Taylor's expansion is utilized, it simplifies to

$$\theta_{rad} \approx 2(T_F - T_0)/(T_F + T_0) \tag{7}$$

if $(T_F - T_0) \ll (T_F + T_0)$. It follows that an angle below 5° is a clear indication of the mutual dependence of 1 and $1/T$, which means that for $T = 300$ K and 900 K it is not recommended to carry out the kinetic evaluation within $\Delta T (= T_F - T_0)$ lower than 25 K and 80 K, respectively.

More details have already been published in the book [8] and in the review article [9].

This note should not be understood as a criticism of the article by Agrawal [1]; we should appreciate any attempt to collect more experimental evidence to clarify the extent to which the compensation effect is an odd effect of the data teatment based on the flexible exponential form, which is of importance in any evaluation similar to that so far employed in chemical kinetics [1, 2].

References

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