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AN ANALYSIS OF THE POSSIBLE CAUSES OF APPARENT COMPENSATION EFFECTS WHEN INVESTIGATING A SUBSTANCE UNDER VARYING EXPERIMENTAL CONDITIONS

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The major causes leading to the apparent compensation effect ($\lg A = aE + b$) at the thermal decomposition of one and the same substance in a series of experimental conditions (varying of the mass of the sample, of the heating rate, of disperseness, and at different distances from the equilibrium) were discussed. It was found that the appearance of a compensation effect at the study of the thermal decomposition of one and the same substance demonstrates the incorrect setup of the experiment, resulting in erroneous values calculated for the kinetic parameters.

It has already been stated earlier that the compensation effect ($\lg A = aE + b$) observed at the thermal decomposition of one and the same substance when experimental conditions are changed is only apparent [1].

This apparent compensation effect is encountered more frequently than usually assumed:

(i) Owing to the time and temperature limits in experimental practice, not the complete area of the relationship $\lg A$ *vs.* E_a can be studied, but only a relatively narrow, somewhat diverging band. This gives the illusion of a general compensation effect.

(ii) For a set of processes in which the rate constant is one and the same and the rate increases exponentially with temperature, a linear relationship will exist between $\lg A$ and E_a. Hence any error in the determination of E_a will be compensated by a proportional change in $\lg A$.

(iii) The ignorance of the true mechanism (disregarding of several parallel reaction paths, with a varying share from experiment to experiment) will lead to an apparent compensation effect [2, 3].

(iv) An analogous effect will also be observed if successive stages exist (disregarding of an intermediate complex) [3].

For thermal decomposition most frequently case (ii) will be met. It can readily be shown what the reason for the appearance of a compensation relationship is when the mass of the sample or the heating rate is changed (described in [4] and [5]).

A study of the kinetics of thermal decomposition demonstrates the appearance of a temperature gradient in the sample owing to self-cooling (in endothermic reactions) and self-heating (in exothermic reactions), and hence to an error in the determination of the values of E and A. The type of growth of this error has been analyzed in the literature. It has been shown that for exothermic reactions $E_{\text{observed}} > E_{\text{true}}$, for endothermic reactions $E_{\text{observed}} < E_{\text{true}}$, and an analytical relationship was found between the value of the error $\Delta E/E$ and the Frank-Kamanetsky criterium (Fig. 1 [6]). A similar type of growth in the error of the calculated pre-exponential factor was found, whereas the determined value of the rate constant only slightly changes [6].

Let us consider the Frank-Kamenetsky criterium:

$$\delta = \frac{q\sigma AEr^2e^{-E/RT}}{\lambda RT^2}$$

where q is heat evolution per unit mass, σ the density of the substance, A the pre-exponential factor, E the activation energy of the process, r the radius of the sample, T temperature (K), R the universal gas constant, and λ the thermal conductivity of the sample.

It is obvious that if only the mass of the sample is varied, all other experimental conditions remaining unchanged, the Frank-Kamenetsky criterium δ will change owing to the change of the sample radius r. Since the errors in E and A depend analogously from the criterium δ, an apparent compensation effect $\lg A = aE + b$ will be observed in the experiments (b is constant, due to the only slight dependence of the rate constant of the reaction on δ). In the literature the effect of the value of the heating rate in non-isothermal experiments on the temperature gradient in the sample has been discussed [7]. The error in the determination of the kinetic parameters becomes significant when the dimensionless heating rate parameter $\Omega > 0.1$. Errors in the determination of E and A will here also lead to an apparent

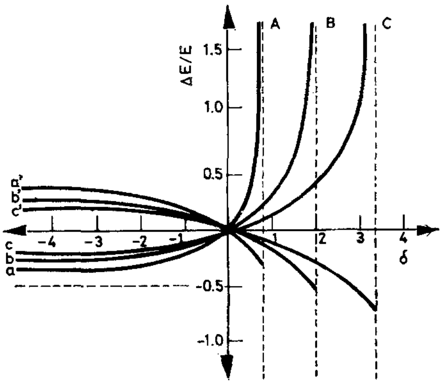

Fig. 1. Dependence of the error in the determination of activation energy on the value of the Frank-Kamenetsky criterium [6]. A — sample in the shape of an infinite plane; B — sample in the shape of a cylinder; C — sample in the shape of a sphere; a', b', c' — the temperature is determined in the centre of the sample; a, b, c — the temperature is determined in the layer adjoining the wall

compensation effect for one and the same substance in a series of experiments where the heating rate is varied.

The empirical formulae cited in the literature for the analytical relationship between the calculated E and A values and sample mass or heating rate (e.g. $E = C_1/u + C_2$; $E = C_3m^2 - C_4m + C_5$ [8]) are obviously mathematical approaches to describe the relationship between E and A, on the one hand, and δ and Ω, on the other hand.

An analogous analysis of the effect of other experimental conditions allows to prepare a list of the major causes leading to the observation of an apparent compensation effect in the thermal decomposition of one and the same substance.

1. *Differences in the intenseness of self-heating or self-cooling* (E and A are true only at values of the Biot criterium $Bi \leq 1$ [7]).

2. *Non-optimum range of heating rate change* (E and A are true only at values of the dimensionless heating rate parameter $\Omega \leq 0.1$ [7]).

3. *Different distances from the equilibrium* (and consequently a different extent of the reverse reaction taking place).

4. *Change in disperseness* (within the limits $d_{max}/d_{min} = 6$). Delmon already observed that if the scattering of the size of particles in the sample does not exceed $d_{max}/d_{min} = 6$, then, for the homotetic shrinkage of the particles, the kinetic equation $d\alpha/dt = k(1 - \alpha)^{2/3}$ will practically not be distorted up to conversions of $\alpha = 50\%$. In the case of wider limits for particle size, the formal order of reaction will increase from $n = 2/3$ to $n = 1$ and $n = 2$ [9]. However, the increased formal order of reaction will always result in a parallel growth of E and A, corresponding to the equation of the compensation relationship [10].

5. *Changes in the share of intergranular diffusion* (owing to the presence of a very fine fraction). In the thermal decomposition of very fine fractions, intergranular diffusion exchange becomes significant [11], and the limit of disperseness where this takes place varies from substance to substance. In Fig. 2, dehydratation data for various narrow fractions of the EDTA chelate MgMnL · 9 H_2O are presented. The kinetic curves were constructed from gas evolution measured in a continuous reactor [10] ($m = 10.0$ mg, $w_{He} = 60$ cm^3/min, $u = 3$°/min). To analyze the kinetic mechanism, we utilized the integral program TA I B [12, 13].

For the fraction 400 μm to 50 μm, the kinetics of the process, in the conversion interval $0.5\% < \alpha < 50\%$, were best approached by the equation of the shrinking spheres [$d\alpha/dt = k(1 - \alpha)^{2/3}$]; for the fraction <50 μm the dehydratation kinetics are described by the diffusion equation. As may be seen from the figure, the reproducibility of the value E is $\pm 2.5\%$ for the fraction 400 μm to 80 μm, and $\pm 5.8\%$ for the fraction 400 μm to 70 μm. Further reduction of particle size sharply increases retardation of the process by diffusion, while calculation with the unchanged equation of shrinking spheres results in lower and lower values of E and A. For the fraction 4 to 50 μm, the dehydratation process is described best of all by the equation of three-dimensional diffusion ($E = 187$ kJ/mol, $\lg A = 23.9$). The calculation using the equation of shrinking spheres supplies another point to the straight line of the compensation effect.

6. *Change in the share of diffusion across the layer of the substance* (large test specimen in a standard crucible). Our data indicate that in thermolysis of sample masses ≥ 100 mg in the standard crucible of the Derivatograph, the kinetics are controlled by the diffusion of the gas to the surface across the layer of the substance. In the intermediate diffusion kinetic mode of operation, the compensation relationship will also be observed at changes of the mass of sample.

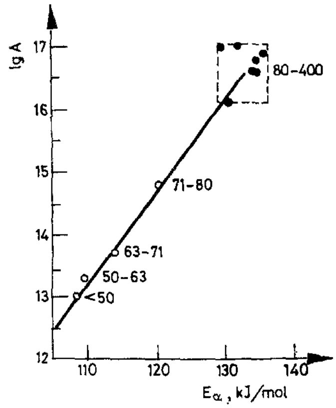

Fig. 2. Dehydratation of the EDTA chelate MgMnL · 9 $H_2O \rightarrow$ MgMnL + 9 H_2O. Apparent compensation effect observed at the change of the disperseness of the substance (kinetic parameters calculated by means of the equation of shrinking spheres): Group of points 80—400 μm. Separately studied fractions 315—400 μm, 200—315 μm, 160—200 μm, 125—160 μm, 100—125 μm, 90—100 μm, 80—90 μm

The true kinetic parameters of the thermal decomposition process can only be obtained under very strict experimental conditions. Any change in these conditions beyond certain limits will result in the erroneous calculation of E_a and A values, owing to the share of diffusion, reverse reaction, or the presence of temperature gradients or conversion gradients in the sample.

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Résumé — On a étudié les causes principales de l'effet de compensation apparent ($\lg A = aE + b$) lors de la décomposition thermique de la même substance dans differentes conditions expérimentales, en faisant varier notamment la masse du prélèvement, la vitesse du chauffage, la dispersion et l'écart à l'équilibre. On a trouvé que l'apparition d'un effet de compensation lors de l'étude de la décomposition thermique de la même substance résultait de l'exécution incorrecte de l'expérience qui mène à des valeurs fausses lors du calcul des paramètres cinétiques.

Zusammenfassung — Die Hauptursachen, welche zum scheinbaren Kompensationseffekt ($\lg A = aE + b$) der thermischen Zersetzung ein und derselben Substanz führen, wurden unter verschiedenen Versuchsbedingungen untersucht: unter Änderung der Probenmasse, der Aufheizgeschwindigkeit, der Dispersität und der Entfernung vom Gleichgewicht. Es wurde festgestellt, daß das Auftreten eines Kompensationseffekts bei der Untersuchung der thermischen Zersetzung ein und derselben Substanz auf die unrichtige Durchführung des Experiments hinweist, die zur Berechnung falscher Werte der kinetischen Parameter führt.

Резюме — Проанализированы важнейшие причины, приводящие к появлению кажущегося компенсационного эффекта ($lg A = aE + b$) при термолизе одного и того же вещества в серии экспериментов: при изменении массы вещества, скорости подъема температуры, дисперсности, при разной степени удаления от равновесия. Отмечено, что появление компенсационных зависимостей при изучении термолиза одного вещества свидетельствует о некорректной постановке эксперимента, приводящей к расчету ошибочных значений кинетических параметров.