THE COMPENSATION EFFECT AND THE TRUE ACTIVATION ENERGIES OF CERTAIN CHEMICAL PROCESSES

1963

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

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THE COMPENSATION EFFECT AND THE TRUE ACTIVATION ENERGIES OF CERTAIN CHEMICAL PROCESSES

(Presented by Academician S. S. Medvedev, 3 VII 1963)

For the first time the idea of a varying activation energy as the cause leading to the compensation effect (CE) was used by Ya. S. Lebedev, Yu. D. Tsvetkov, and V. V. Voevodskii ([1]). Quite recently, a paper by G. I. Likhtenshtein ([2]) on the same subject was published. We approached this question somewhat differently from the authors indicated (see also ([3])).

If some chemical process can proceed by two (or more) independent paths, for example spontaneously and homogeneously catalytically, then, as is well known, the experimental value of the rate constant $-k$ —will be expressed as

$$k = A_s e^{-E_s/RT} + A_k x e^{-E_k/RT}, \tag{I}$$

where A_s and A_k are the pre-exponential factors of the spontaneous and catalytic processes, E_s and E_k are their activation energies; x is the concentration of the catalyst.

In this case the experimental data obtained in a narrow temperature interval may be well approximated by the simple Arrhenius equation:

$$\ln A = \ln k + E/RT, \tag{II}$$

where A and E are certain effective pre-exponential factor and activation energy, obtained directly from experiment. In this case

$$-E = \frac{\partial \ln k}{\partial \left(\frac{1}{RT}\right)} = -\frac{A_s E_s e^{-E_s/RT} + A_k E_k x e^{-E_k/RT}}{A_s e^{-E_s/RT} + A_k x e^{-E_k/RT}}, \tag{III}$$

as is easy to see, proves to be a function of the catalyst concentration and therefore changes from sample to sample. Similarly, A—the experimental pre-exponential factor, determined through k and E—is also a function of the same variable x. Starting from (III), (II), and (I), we obtain

Fig. 1

Figure 1: Fig. 1

$$\ln A = \ln A_s - \frac{E_s}{RT} + \ln\left(1 + \frac{E_s - E}{E - E_k}\right) + \frac{E}{RT}. \qquad \text{(IV)}$$

For

$$E \gg \frac{E_s + E_k}{2},$$

i.e., in the region where the contribution of the catalytic process is small, the logarithm of the right-hand side can be expanded in a series, and in the first approximation one obtains:

$$\ln A = \left[\ln A_s - \frac{E_s}{RT} + \frac{E_s}{(E_s - E_k)}\right] + \left[\frac{1}{RT} - \frac{1}{(E_s - E_k)}\right] E = a + \frac{1}{RT_0} E, \quad \text{(IVa)}$$

which exactly corresponds to the course of the compensation straight line, and the "conversion temperature" ([3])

$$T_0 = T \Big/ \left(1 - \frac{RT}{E_s - E_k}\right)$$

differs insignificantly from the mean temperature of the measurement interval $-T$.

In the region where $E \ll \frac{E_s + E_k}{2}$, when the rate of the process is determined mainly by the catalytic component, deviations from the straight line (IVa) should be observed, and at $E = E_k$ an increase in the pre-exponential factor is obtained (without further change in E) exclusively at the expense of an increase in the catalyst concentration.

We tested these relationships on the well-studied reaction of the interaction of peroxide with iodide ion, using W(VI) as the catalyst ([4]).

The reaction rate was determined photometrically on an FEK-N-57 from the rate of liberation of J_2. The change in photocurrent (coloration) was recorded with a self-recording potentiometer with a high-resistance input. The measurements were carried out in a thermostated cuvette at temperatures of 20, 30, and 40°C and were processed according to equation (II) (Fig. 1).

Fig. 1. Dependence of the rate constant on temperature; tungsten concentration $7.7 \cdot 10^{-7}$ mol/l

Fig. 2

Figure 2: Fig. 2

The experimental values of E and $\lg A$ found in this way are compared in Fig. 2 with the characteristic ν-shaped curve described by the exact formula (IV), and deviate from it by no more than the experimental error. At the same time it turned out that within the limits of the left branch of the ν-curve (the compensation part) the rate of the overall reaction changes by ( )10 times, while the catalyst concentration changes by almost three orders of magnitude; E_s = 12.5 kcal, $\lg A_s = 9.25$; $E_k = 5.1 \pm 0.5$ kcal, $\lg A_k = 10.2 \pm 0.3$; $T_0 = 438°$K (65°C). It follows from this that, at least for the given system, the approach developed in the present article is not only fully confirmed by experiment, but also makes it possible to find the true values of the activation energy and the pre-exponential factor of the pure catalytic process, for which it is sufficient to know the course of the curve as $E \to E_k$.

Fig. 2. Experimental values of A and E for catalyst concentrations 0; $4.4 \cdot 10^{-8}$; $9.6 \cdot 10^{-8}$; $7.7 \cdot 10^{-7}$; $2.9 \cdot 10^{-6}$; $8.3 \cdot 10^{-6}$; $5.2 \cdot 10^{-5}$; $2.1 \cdot 10^{-4}$ mol/l (from right to left along the ν-curve below); 1, 2 —ν-functions for the case with E_k equal to 8 and 2 kcal, respectively

Formally, these same data can be obtained from T_0, which specifies the difference $(E_s - E_k)$, and E_s, i.e., from the right-hand part of the curve. However, since in most cases $(E_s - E_k) \gg RT$, the value of T_0 is not critical, differs little from T, and therefore the slope of the compensation straight line turns out to be practically the same for different catalysts with different E_k (see Fig. 2). This creates the illusion of a single compensation series for different catalysts.

It is possible that the same approach can be extended to the case of noncatalytic chemical processes ([5],[6]), for example, to the simultaneous course of a reaction of first and second order. When $E_I < E_{II}$, T_0 will be lower than the mean experimental temperature, which, apparently, is true for hydrolysis reactions of complex cobalt compounds ([7]). This raises doubts as to the validity of the values of E, the activation energies found in the cited and other works.

The authors consider it necessary to note that an analogous effect, observed—

···in semiconductors during the transition from the intrinsic conduction mechanism to the impurity mechanism was interpreted from analogous positions by V. S. Kuznetsov (private communication). Discussion of this work also provided the impetus for formulating the present problem.

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Received
24 VI 1963

CITED LITERATURE

[1] Ya. S. Lebedev, Yu. D. Tsvetkov, V. V. Voevodskii, *Kinetics and Catalysis*, **1**, 498 (1960). [2] G. I. Likhtenshtein, *Kinetics and Catalysis*, **4**, 35 (1963). [3] S. Z. Roginskii, Yu. L. Khait, *DAN*, **130**, 366 (1960). [4] K. B. Yatsimirskii, V. I. Rigin, *ZhAKh*, **13**, 112 (1958). [5] U. Iugai, *Bull. Chem. Soc. Japan*, **30**, 873 (1957). [6] A. I. Shatenshtein, *Isotopic Exchange and the Substitution of Hydrogen in Organic Compounds*, Publishing House of the Academy of Sciences of the USSR, 1960, p. 92. [7] V. I. Vasil' eva, K. B. Yatsimirskii, *ZhNKh*, **7**, No. 11, 2520 (1962). [8] Collection: *Catalysis. Electronic Phenomena*, IL, 1958, p. 86.

Note: Figure translations are in progress. See original paper for figures.