Physical Chemistry

Corresponding Member of the Academy of Sciences of the USSR S. Z. Roginskii and Yu. L. Khait

1960

SovietRxiv

Abstract

Full Text

Physical Chemistry

Corresponding Member of the Academy of Sciences of the USSR S. Z. Roginskii and Yu. L. Khait

On the Question of the Origin of the Compensation Effect in Chemical Kinetics

For the first time, at the end of the twenties, when comparing the activities of catalysts with respect to one and the same reaction, an exponential dependence was found by a number of authors between the kinetic coefficients k_0 and E of the Arrhenius equations $k = k_0 \exp(-E/kT)$, namely $\ln k_0 = \text{const} + \beta E$ ([1–3]). At the same time, independently, one of the authors, together with L. V. Rozenkevich, found, in comparing literature data for monomolecular homogeneous reactions, analogous relationships between kinetic constants ([4]). These conclusions were for some time disputed by Hinshelwood, who later, on the basis of his own investigations, became convinced of the reality and prevalence of the compensation effect (CE) in the kinetics of organic reactions ([5]) and recognized it as one of the fundamental, although still obscure, regularities of chemical kinetics ([6]). In a number of cases the CE was also observed for such purely physical phenomena as diffusion in crystals, electronic (hole) conductivity of semiconductors ([7]), etc. The types of processes and systems in the kinetics of which the CE was observed are very diverse. But the presence of a condensed phase is favorable or necessary for the manifestation of the CE, since for homogeneous reactions in gases reliable examples of the CE are few, and when similar simple reactions are compared, as a rule, independence or only a weak dependence of k on E is observed. The CE is especially important for catalytic reactions, where it is observed when comparing, with respect to one and the same reaction: a) catalysts subjected to different thermal treatment ([8]) and prepared by different methods; b) catalysts with different contents of modifying additives ([9]); and c) different catalysts of one and the same type ([9]). Less systematic data are available concerning the CE of different related reactions on one and the same catalyst ([10]).

In view of the impossibility, in experimental verification, of varying E over several orders of magnitude, the exact form of the dependence $k_0(E)$ cannot be considered firmly established. As G. M. Zhabrova showed ([11]), most experimental data can be satisfactorily described by the equation

$$\ln k_0 = \text{const} + \beta E^n, \tag{1}$$

where n varies from 1 to 3. In a number of cases $n \simeq 1/2$ is also suitable ([4]).

The presence of the CE leads to the fact that, at a certain temperature, activity series near T_{obr} are reversed. In the schematic equation of the theory of absolute rates for simple reactions the CE is absent. The introduction of the kinetic factor $\exp(\beta E^n)$ into the equations of the theory of absolute reaction rates, based on statistical thermodynamics, is equivalent to introducing a kinetic factor into the theory of equilibrium states and cannot be reconciled with statistical thermodynamics. For complex reactions there are more possibilities for the appearance of the CE, but even there the introduction of the factor $\exp(\beta E^n)$ into the theory of absolute reaction rates entails its appearance in the theory of equilibrium states.

To explain the compensation effect, a number of hypotheses have been advanced: for heterogeneous reactions it was assumed that the compensation effect reflects inhomogeneity with an exponential distribution of active centers over activation energies ([2]); this explanation is not applicable to homogeneous reactions. Additional equilibria were postulated, with a Brønsted dependence of E on their thermal effect. The involvement of quantum-mechanical effects (tunnel transitions) ([4], [10]) can be justified only for certain electronic mechanisms and for hydrogen reactions at low temperatures ([12], [13]). It falls away as any general explanation of the compensation effect. In the old statistical theory of monomolecular reactions, Kassel, Rice, and others ([14], [16]) obtained a factor $k_0 \sim E^n$, which for large n is difficult to distinguish from $\exp(\beta E)$. After the work of L. D. Landau ([15]), this theory did not gain acceptance. To summarize, it must be acknowledged that in more than 30 years it has not been possible to find any satisfactory explanation of the compensation effect. The fact that the compensation effect is observed in processes and systems of very different nature gives grounds to suppose that its appearance follows from certain general laws of statistical kinetics.

The specific features of particular systems and processes may lead to an enhancement or weakening of that part of the compensation effect which is common to a broad class of systems and processes. Below an attempt is made to give an explanation of the compensation effect on the basis of a statistical method, developed by one of the authors, for calculating the rates of activation processes in condensed bodies ([17]), without resorting to detailed mechanical models. This method is based on the idea that an activation process consists of a finite (countable) set of elementary acts. Each elementary act is due to the fact that an energy E', equal to or exceeding a certain critical value $E \gg kT$, is randomly collected on individual bonds in a volume d^3, of the order of the volume of one particle, at the expense of a certain lowering of the energy of other degrees of freedom of the surrounding volume l^3. The volume l^3 proves to be macroscopically small, since the rate of energy transfer in the system is finite and not very large (electromagnetic energy transfer in the system is not considered), while the duration of an elementary act is small. More precisely, the dimensions of the volume l^3, from which on average the energy $E' \geq E \gg kT$ is drawn, are bounded by the conditions

$$l^2 < \frac{Ed^3}{a\hbar l_0}\tau_0; \qquad \frac{l^3}{ad^3} > \frac{E_i}{kTa}, \tag{2}$$

where l_0 and τ_0 are the mean length and mean time of the free path of the quasiparticles (particles) that carry energy (for example, phonons), under the condition that $E \gg kT$. In inequalities (2) the parameter a is limited to a few units. In ([17]) it was taken into account that an elementary act of an activation process is accompanied by an abrupt, appreciable temporal change in the state of the region l^3 (an event of a discontinuous random process ([18])).

By combining the methods of statistical thermodynamics with the principle of detailed balance, it was shown that the probability W (per unit time) of an elementary act of an activation process of a definite type in the region l^3 can be obtained by integrating the expression

$$\frac{kT\,(U_c - E)}{\hbar}\exp\left(-\frac{F_c - F_0}{kT}\right)\exp\left(\frac{S(U_c - E) - S(U_c)}{k}\right) \tag{3}$$

over all admissible values of the energy U_c of the region l^3 ([17]). Here F_c, $S(U_c)$, $S(U_c - E)$, $T(U_c - E)$ represent the free energy, entropy, and temperature of the volume l^3, corresponding to the energies U_c and $U_c - E$.

In ([17]) the fact was used that expression (3) has a maximum, and integration over U_c was not carried out. In this way the approximate formula was obtained

$$W \simeq W_0 q \exp\left(-\frac{E}{kT}\right), \tag{4}$$

in which the dependence of W_0 on E was not considered (q is the relative concentration of the substances responsible for the process ρ under consideration). In this case, the number of elementary acts of an activation process of a definite type in a volume V, referred to unit time, was calculated by the formula $N_1 = \frac{V}{l^3}W$, where V is the volume of the system. Here, using the relation

$$W \approx q\,\frac{k}{\hbar\sqrt{2\pi}}\int T(U_c - E)\exp\left(-\frac{(\Delta U)^2}{2a^2}\right)\exp\left(\frac{S(U_c - E) - S(U_c)}{k}\right)\frac{dU_c}{a}, \tag{5}$$

let us consider the question of the dependence of W_0 on E, where $\Delta U = U_c - \overline{U}$, $\overline{U}$ is the mean energy of the volume l^3; $a^2 \approx kcT^2$ is the mean square of the energy fluctuation in it, and c is its heat capacity. Formula (5) is obtained by integrating (3) with replacement of the factor $\exp\left(-\frac{F_c - F_0}{kT}\right)$ by a normalized Gaussian distribution, for which only the Boltzmann principle is valid ([19]). We shall restrict ourselves to the case where the relation $\partial^n c/\partial T^n \approx 0$ ($n = 1, 2, \ldots$), valid under ordinary conditions, is satisfied. Expanding $S(U_c - E)$ in $E <$

U_c and using the fact that $\partial^n c/\partial T^n = 0$, we obtain $S(U_c - E) - S(U_c) \approx k \ln \left[1 - \frac{E}{cT(U_c)}\right]^{c/k}$. Taking into account that $c/k \gg 1$ and $\lim_{n\to\infty}(1 - x/n)^n = e^{-x}$, we find $S(U_c - E) - S(U_c) = -\frac{E}{T(U_c)}$, which together with (5) gives

$$W \approx \frac{kq}{\hbar\sqrt{2\pi}} \int T(U_c - E) \exp\left(-\frac{(\Delta U)^2}{2a^2}\right) \exp\left(-\frac{E}{kT(U_c)}\right) \frac{dU_c}{a}. \tag{6}$$

To compute the integral in (6), we shall use the possibility of representing $T(U_c)$ and $T(U_c - E)$ in the form $T(U_c) = T + \frac{\Delta U}{c}$, $T(U_c - E) = T + \frac{\Delta U - E}{c}$. Making in (6) the change of variables $y = (\Delta U - E)/a$, taking into account that usually $\left(\frac{\Delta U}{cT}\right)^2 \ll 1$, and integrating over the interval $(-\infty, \infty)$, we finally obtain

$$W \approx q \frac{kT}{\hbar} \left(1 + \frac{kT}{a}\right) \exp\left(\frac{E^2}{2a^2}\right) \exp\left(-\frac{E}{kT}\right) \tag{7}$$

or

$$W_0 \approx q \frac{kT}{\hbar} \left(1 + \frac{kT}{a}\right) \exp\left(\frac{E^2}{2a^2}\right). \tag{8}$$

In order that the factor $\exp(E^2/2a^2)$ play an appreciable role, it is necessary that the condition

$$E^2/2a^2 > 1, \tag{9}$$

be fulfilled, where inequality (9) assumes that $E^2/2a^2$ is of the order of several units or more. But since it follows from (2) that $l^2 < \frac{Ed^3}{a\hbar l_0}\tau_0$, and $a^2 \approx kT^2 c_0 \rho l^3$ (c_0 is the specific heat, ρ is the density), (9) is fulfilled under the condition

$$\frac{E^2}{a^2} > \sqrt{\frac{E}{kT}} \left(\frac{k}{c_0 \rho d^3}\right) \left(\frac{\hbar v a}{dkT}\right)^{3/2}. \tag{10}$$

Thus, for not too small E, inequality (10), and together with it condition (9), turn out to be fulfilled. It follows from (10) that,

a large value of the rate v of energy transfer, as well as an increase in the density $\rho \sim 1/d^3$, favor the manifestation of the compensation effect. Therefore, condensed media, and especially solids, are favorable for the manifestation of the compensation effect. The formulas obtained indicate that $\exp(E^2/2\alpha^2)$, generally speaking, depends on T. But, as will be seen below, this dependence, against the background of the factor $\exp(-E/kT)$, turns out to be barely noticeable. Usually, to describe experimental data one plots the dependence of $Z = \ln W$ on $x = 1/kT$. Taking the logarithm of (7) and substituting $\alpha^2 = kT^2 c$, we find

$$Z = A - xE\left(1 - \frac{Exk}{2c}\right), \tag{11}$$

where

$$A = \ln\frac{kT}{\hbar}\left(1 + \frac{kT}{a}\right).$$

Usually $cT = \frac{c}{kx} > E$ (since $cT \approx 10 \div 50$ eV, $E \approx 1 \div 4$ eV). Therefore the second term in parentheses in (11) (even though it depends strongly on T) will, over the relatively small temperature intervals in which measurements are usually carried out, give small deviations from a straight line with slope $-E$. This conclusion agrees with experiment. On the other hand, however, $E^2/2\alpha^2$ represents the product of two factors, $E/2cT < 1$ and $E/kT \gg 1$. Therefore, for certain values of E, condition (9) is satisfied, and the factor $\exp(E^2/2\alpha^2)$ may change the reaction rates by several orders of magnitude.

Thus, it is possible that the compensation effect can be explained by the fact that the conditional probability of concentration of excess energy $E' \geq E \gg kT$, proportional to $\exp[-E/T(U_c)k]$, depends on the local (time-dependent) temperature $T(U_c)$ of the region l^3 in which the elementary act occurs. But $T(U_c)$, corresponding to the maximum (3) (or to the maximum of the integrands in (5) and (6), equal to $T_m \approx T + E/c$, depends on E. This leads to a more complex dependence of the rate of the process on E and to the occurrence of the compensation effect. Let us note that the condition $\partial^n c/\partial T^n \approx 0$, the neglect of correlations between regions l^3, and the use of the Gaussian distribution establish certain limits to the explanation of the compensation effect considered above.

Further work should: a) carry out a quantitative estimate of the proportionality coefficients entering the basic formulas, which will make it possible to obtain more accurate estimates of $\exp(E^2/2\alpha^2)$ for individual special cases; b) verify the validity of the various values of n in (1); c) examine in greater detail and verify the dependence of $\exp(E^2/2\alpha^2)$ on T, and also clarify several other questions connected with the application of the results obtained and the prospects for their development.

Received6 VIII 1959

REFERENCES

1. H. Constable, Proc. Roy. Soc., A, **108**, 355 (1926).

2. G. M. Schwab, E. Cremer, Zs. phys. Chem., A., **144**, 243 (1929).

3. A. Balandin, Zs. phys. Chem., B, **19**, 451 (1932); ZhFKh, **4**, 257 (1933).

4. S. Z. Roginskii, L. V. Rozenkevich, ZhFKh, **1**, 293 (1930); S. Roginsky, L. Rosenkewitsch, Zs. phys. Chem., B, **10**, 293 (1930).

5. C. Hinshelwood et al., J. Chem. Soc., **1937**, 538, 858, 862, 1575.

6. C. Hinshelwood, J. Chem. Soc., **1947**, 694.

7. F. F. Vol' kenshtein, *Electrical Conductivity of Semiconductors*, 1947.

8. A. B. Shefter, DAN, **89**, 619 (1953).

9. S. Z. Roginskii, *Adsorption and Catalysis on Inhomogeneous Surfaces*, Izd. AN SSSR, 1947.

10. E. Cremer, Adv. in Catal., **7**, 75 (1955).

11. G. M. Zhabrova, Uspekhi Khimii, **24**, 598 (1955).

12. R. P. Bell et al., Trans. Farad. Soc., **54** (1958). Reports at the 8th Mendeleev Congress on General and Applied Chemistry, Collection of Abstracts of Reports and Communications of Foreign Scientists, 1959, p. 40.

13. V. I. Gol' danskii, DAN, **124**, No. 6 (1959).

14. L. S. Kassel' , *Kinetics of Homogeneous Gas Reactions*, L., 1937.

15. L. D. Landau, Sov. Phys., **10**, 67 (1936).

16. V. N. Kondrat' ev, *Kinetics of Chemical Reactions*, 1958.

17. Yu. L. Khait, Abstracts of Reports at the 2nd All-Union Conference on the Physics of Dielectrics, Izd. AN SSSR, 1958.

18. B. V. Gnedenko, *Course in Probability Theory*, 1954.

19. M. A. Leontovich, *Statistical Physics*, 1944.

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