Corresponding Member of the Academy of Sciences of the USSR S. Z. ROGINSKII, Yu. L. KHAIT

1963

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR S. Z. ROGINSKII, Yu. L. KHAIT

ON THE THEORY OF THE COMPENSATION EFFECT IN DIFFUSION PROCESSES IN SOLIDS

When comparing rate constants that vary with temperature according to equations of the Arrhenius type, for many processes occurring with the participation of condensed phases one observes a strong increase of the pre-exponential factor K_0 with increasing activation energy E ($^{1-5}$). Depending on the temperature T and on the specific form of the relation between K_0 and E, the increase of K_0 leads to more or less complete compensation (and sometimes to overcompensation) of the decrease in K caused by the diminution of the selection factor $\exp(-E/kT)$ (as E increases and $T = \text{const}$). Such an effect is often called the compensation effect (CE). Despite the large number of works devoted to the CE, its causes have still been insufficiently studied and, probably, are not the same in all cases. Recently we (^{5,6}) have shown the fundamental possibility of the appearance of a CE in activation processes owing to the collective nature of the elementary act of random concentration of energy on individual particles (bonds) of a condensed body. In doing so we explicitly took into account that the elementary act of passage over a potential barrier in a condensed body occurs with the participation of many interacting particles of the system, whose collective motion ensures the transfer of energy with average velocity v_0 to the place of its random concentration (^{7}). In this connection the occurrence of a random "surge" of energy on individual particles is accompanied by some decrease of the energy of the surrounding region, of volume Ω, which possesses many degrees of freedom. These circumstances substantially affect the probability of the elementary act of an activation process. In papers (^{5,6}) the pre-exponential factor K_0 is calculated under the assumption of adiabatic isolation of the region Ω during the "lifetime of the surge" of energy on individual particles. As was noted (^{6}), more satisfactory results can be expected if the assumption of adiabatic closure of the volume Ω is abandoned. Study of this question led to a more detailed investigation of the kinetics of formation of a considerable surge of energy on individual particles of condensed bodies, its space-time scales, and the probability of its occurrence (^{8,9}). This investigation, carried out with the aid of methods of the theory of stationary random functions (^{10}), made it possible to take several further steps toward accounting for collective effects in the theory of activation processes and the CE, and led to a pre-exponential factor that is in qualitative agreement with experimental data.

To test the concept set forth in papers ($^{5-9}$), and also to establish the conditions for the appearance of a CE of the type under consideration and the criteria distinguishing it from a CE of other origin, it is of interest to apply this concept to an analysis of the magnitude of the CE for definite types of activation processes. In the present work this is done for self-diffusion in solids.

The experimental values of the pre-exponential factor D_0 in the formula for the diffusion coefficient

$$D = D_0 \exp\left(-\frac{E}{kT}\right) \tag{1}$$

for different solids cover a very broad range (^{1,2,11,12}). In this case an exponential increase of D_0 with increasing E is often observed, which can be described by the relations

$$D_0 = D_{00} \exp(aE^s) \quad \text{or} \quad D = D_{00} \exp(aE^s) \exp\left(-\frac{E}{kT}\right). \tag{2}$$

Here a and D_{00} are practically independent of E and T, and the exponent s is usually taken to be equal to unity. To explain the experimentally observed dependence of D_0 on E, some authors ($^{12-15}$) attempted to apply the theory of absolute reaction rates (^{16}) and the theory of Ya. I. Frenkel (^{17}). In doing so, a linear relation between E and T, proposed by Frenkel (^{17}), was assumed, and the hypothesis of "local melting" was introduced*. However, despite the successes achieved, the causes of the compensation effect observed in the study of diffusion in solids cannot be considered clarified. It is shown below that taking into account the collective nature of the elementary act of diffusion in a solid makes it possible to establish, for the proposed approach, the characteristic dependence of the factor D_0 on E, on the Debye temperature θ, on the velocity v_0, on the coordination number x, on the volume of the elementary cell of the crystal Q, and on the number of degrees of freedom in it γ, and thereby to obtain structurally sensitive formulas for the diffusion coefficient D. Following the scheme developed in works (^{8,9}) for thermal activation processes, we first estimate the space-time scales of the elementary act of diffusion, using for this purpose the statistical theory of vibrations with a continuous spectrum, which is practically cut off at the Debye frequency v_D. We assume that the elementary act of diffusion occurs with probability of order unity when the energy of one (or several) particles accidentally increases to a value $E' \geq E \gg kT$. In this case the momentum in the region of the energy surge takes values $p(E') \gg p(E)$. The mean time $\bar{\tau}^{(1)}$ between the moment t' of the beginning of the surge and the moment $t' + \bar{\tau}^{(1)}$ at which the momentum $p(E')$ reaches its largest value will be called the mean duration of formation of the surge. The mean "lifetime" of the surge $\bar{\tau} = \bar{\tau}^{(1)} + \bar{\tau}^{(2)}$ is called the mean duration of the elementary act of diffusion; here $\bar{\tau}^{(2)}$ is the mean time from the moment $t' + \bar{\tau}^{(1)}$ to the moment

$t' + \bar{\tau}$ of the end of the surge (the particles release the excess energy). During the time $\bar{\tau}^{(1)}$, the energy required for the formation of the surge is delivered, on average, from the surrounding region having volume (^{8,9})

$$\Omega \simeq \frac{4\pi}{3} l^3, \qquad \text{where } l \simeq v_0 \bar{\tau}^{(1)}. \tag{3}$$

In calculating $\bar{\tau}^{(1)}$ we assume (^{8,9}) that the $3N_0$ coordinates $q_i(t)$ form a $3N_0$-dimensional, continuous, stationary, almost everywhere twice differentiable random vector function $\mathbf{R}(t, \xi) = \{q_i(t, \xi)\}$, $i = 1, \dots, 3N_0$, possessing the ergodic property; the random vibrations of the $3N_0$ components of the momentum $p_i(t)$ and the $3N_0$ components of the forces $p_i(t)$, acting on N_0 particles, respectively form $3N_0$-dimensional continuous stationary random vector functions $\mathbf{P}(t, \zeta) = \{p_i(t, \zeta)\}$, $\mathbf{F}(t, \eta) = \{p_i(t, \eta)\}$, possessing the ergodic property; here t is time; ξ, ζ, η are the "numbers" of realizations of the corresponding random functions (^{10}). We shall assume that the spectra of the random functions under consideration are practically cut off at the Debye frequency v_D (^{8,9}). The quantities corresponding to this frequency and having the dimensions of time, length, momentum, and force are

$$t_0 = \frac{h}{k\theta}, \qquad \lambda_D = \frac{hv_0}{k\theta}, \qquad s = \sqrt{mk\theta}, \qquad \sigma = \frac{s}{t_0} = \frac{k\theta}{h}\sqrt{mk\theta}, \tag{4}$$

where m is the mass of the particles. To calculate $\bar{\tau}^{(1)}$, l, we shall use the energetic definition of the duration of a fluctuation, applied in (^{8,9}). Then, taking into account that each atom has $\varkappa$ nearest neighbors, which are channels for supplying to it the necessary energy, we obtain the relations*

$$\bar{\tau}^{(1)} = \beta \frac{h}{\varkappa k\theta} \sqrt{\frac{E}{k\theta}}, \qquad \bar{\tau} \approx 2\bar{\tau}^{(1)}, \tag{5}$$

which characterize the duration of the elementary act of diffusion; here β is a dimensionless coefficient of order unity, reflecting the inaccuracy of the calculation made. From (3) and (5) we obtain the following expressions for l and Ω, and for the number of degrees of freedom n in the volume Ω:

$$l = \beta \frac{\lambda_D}{\varkappa} \sqrt{\frac{E}{k\theta}}, \qquad \Omega = 4\beta^3 \frac{\lambda_D^3}{\varkappa^3} \left(\frac{E}{k\theta}\right)^{3/2}; \tag{6}$$

$$n = \gamma \frac{\Omega}{Q} = 4\gamma\beta^3 \frac{\lambda_D^3}{\varkappa^3 Q} \left(\frac{E}{k\theta}\right)^{3/2}, \tag{7}$$

---

* Explanations based on specifying a definite dependence between E and T were also proposed for other processes (^{18,19}).

where γ is the number of degrees of freedom in a crystal cell of volume Q.

Let us calculate the diffusion coefficient. For this purpose, consider the energy balance of the processes taking place in the volume Ω and accompanying the formation of a random energy fluctuation. The energy of the particles surrounding the fluctuation undergoes twofold changes (^{8,9}): (a) it decreases by an amount $E' \gtrless E$ owing to the transfer of energy into the region of the fluctuation; (b) it increases by an amount $\Delta U(\bar{\tau}^{(1)})$ owing to the influx into the volume Ω of energy from other parts of the system, which to a certain extent (if not completely) compensates the loss. These circumstances were taken into account in (^{8,9}) by describing the energy fluctuations with the aid of a four-dimensional (space-time) random normal field, stationary in t and homogeneous in the coordinates, of volume energy density. Using the method developed there and the relations found thereby, and also taking into account expressions (6) and (7) and the formula $D = f\rho^2/6\tau_d$, we obtain the final expression

$$D = D_0 \exp\left(-\frac{E}{kT}\right), \tag{8}$$

where the pre-exponential factor D_0 is calculated from the formulas

$$D_0 = D_{00} \exp\left[g\left(\frac{\theta}{T}\right)^2 \sqrt{\frac{E}{k\theta}}\right] \exp\left[-\frac{\theta}{\delta T}\left(\frac{E}{k\theta}\right)^{1/4}\right] \exp\left[\delta\left(\frac{E}{k\theta}\right)^{3/4}\right]; \tag{9}$$

$$D_{00} = \frac{f\varkappa^4 Q\rho^2 k\theta}{16\beta^4\lambda_D^3\gamma h}\left(\frac{k\theta}{E}\right)^2, \qquad g = \frac{\varkappa^3 Q}{8\beta^3\gamma\lambda_D^3}; \qquad \delta = 2\beta^{1/2}\left(\frac{\lambda_D^3\gamma}{\varkappa^3 Q}\right)^{1/2}; \tag{10}$$

ρ^2 is the mean square displacement in the elementary act of diffusion, f is a quantity depending on the type of crystal lattice; τ_d is the mean time between two successive energy fluctuations on the same particles. In view of the fact that $\sqrt{n} \gg 1$, among the three exponential multiplier functions in (9) the principal role is played by the factor

$$\exp\left[\delta\left(\frac{E}{k\theta}\right)^{3/4}\right] = e^{\sqrt{n}}. \tag{11}$$

This permits, in some cases, the expression for D_0 to be represented in the following simplified form:

$$D_0 \approx D_{00} \exp\left[\delta\left(\frac{E}{k\theta}\right)^{3/4}\right] = D_{00} \exp\left(a' E^{3/4}\right), \tag{12}$$

where $a' = \delta/(k\theta)^{3/4}$. Formulas (8)–(12) relate D and D_0 to the experimentally measured quantities: E, θ, $\varkappa$, v_0, Q, and γ, which characterize the structure of the solid, the interaction between its particles, and the spectrum of their collective vibrations. The only quantity that we have not determined exactly is the dimensionless parameter $\beta \approx 1$. The value of β for different

we shall choose so that the calculated values D_{0v} of the factor D_0 coincide with its values D_{0e} found experimentally. Calculation by formulas (8), (9) of the self-diffusion coefficients of metals with cubic crystal lattices (bcc and fcc) leads to agreement of D_{0v} and D_{0e} for $\beta \approx 1.1 \div 1.3$. Consequently, β changes little in passing from one substance to another and therefore practically does not hinder the use of formulas (8)–(12) for the analysis of experimental data.

Let us present some consequences following from the relations obtained. First, formulas (8)–(12) are in qualitative agreement with formula (2), since with the existing accuracy of experiment it is impossible to distinguish the values $s' = 3/4$ in (8)–(12) from the value $s' = 1$, and the quantities δ and a' in (9)–(12) do not depend on T and E. Second, from (9)–(12) it follows that D_0 depends exponentially on θ and is determined mainly by the dimensionless activation energy $\varepsilon = E/k\theta$. In view of the fact that for different substances θ varies over a wide range (for example, for Fe $\theta_{\mathrm{Fe}} = 420^\circ$, and for Pb $\theta_{\mathrm{Pb}} = 88^\circ$), it follows from (9)–(12) that D_0 may change in a very complicated manner. Other conditions being equal, a decrease in θ is associated with an increase in D_0. In accordance with this, for example, D_{0v} for self-diffusion of γ-Fe and Pb differ only slightly (for $\beta \approx 1.2$), although $E_{\mathrm{Fe}} \approx 74$ kcal/g · mole, while $E_{\mathrm{Pb}} \approx 28$ kcal/g · mole. Third, since, according to (10), $\delta \sim 1/\varkappa^{3/2}$, for bcc metals ($\varkappa_1 = 8$), other conditions being equal, one may expect larger values of D_0 than for fcc metals ($\varkappa_2 = 12$). This circumstance makes it possible, for example, to explain the large difference in the experimental values $D_{0\alpha}$ and $D_{0\gamma}$ for self-diffusion in α-Fe and γ-Fe ($D_{0\alpha} = 3.4 \cdot 10^4 \div 2.3 \cdot 10^3$ cm^2/sec, $D_{0\gamma} = 5.8$ cm^2/sec), which is observed at activation energies $E_\alpha \approx E_\gamma \approx 77 \div 73$ kcal/g · mole ([1,12]). In this case $\beta \approx 1.2$.

The explanation proposed by us cannot, of course, apply to all observed cases of the compensation effect, since it does not take into account a number of factors that may prove essential in some concrete systems (restrictions leading to the fact that not every surge of energy causes an act of diffusion; simultaneous diffusion by two or more mechanisms, etc.). However, in a number of cases the relations found make it possible to approach from a new point of view the understanding of certain causes of the compensation effect in solids, and to connect it more closely with the structure and spectrum of vibrations of their particles.

Institute of Chemical Physics

---

* In ([8,9]), for simplicity, in estimating $\bar{\tau}^{(1)}$ and Ω, not $\varkappa$ channels for the supply of energy were taken into account, but one; therefore $\varkappa$ does not appear in the formulas.

Academy of Sciences of the USSR

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

Received
12 VI 1963

REFERENCES CITED

1. V. Zait, *Diffusion in Metals*, IL, 1958.
2. V. I. Boltaks, *Diffusion in Semiconductors*, 1961.
3. E. Cremer, Adv. Catal., **7**, 7 (1955).
4. P. M. Zhabrov, *Uspekhi khimii*, **24**, 598 (1955).
5. S. Z. Roginskii, Yu. L. Khait, DAN, **130**, 366 (1960).
6. S. Z. Roginskii, Yu. L. Khait, *Izv. AN SSSR, ser. khim.*, No. 5, 771 (1961); No. 7, 1198 (1961).
7. Yu. L. Khait, *Izv. AN SSSR, ser. fiz.*, **24**, 202 (1960); DAN, **134**, 883 (1960).
8. Yu. L. Khait, in the monograph: *Radiolysis of Hydrocarbons*, Section B, Vol. VI, Izd. AN SSSR, 1962, p. 158.
9. Yu. L. Khait, *Proceedings of the Second All-Union Conference on Radiation Chemistry*, Izd. AN SSSR, 1962, p. 28.
10. A. M. Yaglom, *UMN*, **7**, No. 5 (1952).
11. R. Barrer, *Diffusion in Solids*, IL, 1948.
12. S. D. Gerpriken, D. Ya. Dekhtyar, *Diffusion in Metals and Alloys*, 1960.
13. Ya. I. Dekhtyar, *Voprosy fiz. met. i metalloved.*, No. 3, 122 (1952).
14. G. J. Dines, Phys. Rev., **79**, 123 (1950); J. Appl. Phys., **21**, 1189 (1950).
15. K. A. Osipov, *Certain Activated Processes in Metals and Alloys*, Izd. AN SSSR, 1962.
16. S. Glasstone, K. Laidler, G. Eyring, *The Theory of Rate Processes*, 1949.

17. Ya. Frenkel, *Kinetic Theory of Liquids*, Izd. AN SSSR, 1945.

18. Ya. S. Lebedev, Yu. D. Tsvetkov, V. V. Voevodskii, *Kinetics and Catalysis*, No. 1, 496 (1960).

19. G. Likhtenshtein, *Kinetics and Catalysis*, No. 2 (1963).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.