Translated from *Uspekhi Khimii*, **47**, 212-234 (1978)

Molecular-kinetic Aspects of the Chemical Physics of the Condensed State

A.I.Burshtein

Modern ideas on the elementary chemical step in condensed media are described in relation to reactions involving the transfer of energy, charge, a proton, and valence. It is emphasised that the rates of the above processes in solids and liquids are as a rule limited by the deficiency of free space and not of energy. Local fluctuations in entropy (the packing of the species), enabling the reactants to come into contact with one another in the correct coordination, assume particular importance because of this. The process is controlled either by the equilibrium density of such fluctuations or by the frequency of their generation, which is limited by molecular mobility.
The bibliography includes 81 references.

CONTENTS

I. Introduction 120
II. Theory of encounters 120
III. Reactions controlled by molecular mobility 123
IV. The vacancy mechanism of mobility 129

I. INTRODUCTION

The theory of the elementary chemical transformation in liquid and solid media is in an incomparably less satisfactory state than the theory of the elementary step in the gas phase. This is associated primarily with the fact that the mutual approach of the reacting species in the gas phase is described by the laws of mechanics, while in a dense medium their encounters take place in the course of random migrations in the solvent, i.e. are stochastic. However, the difference is not restricted to a difference in the kinematics of the encounters. Contact with the medium during the elementary step eliminates the energetic limitations which exist in the gas phase, but gives rise to steric hindrance in the reaction pathway associated with a deficiency of the free space required for the organisation of the reaction. Reaction rates in the condensed phase are frequently limited precisely by the amount of space liberated as a result of packing (entropy) fluctuations in the buffer environment surrounding the reacting species, and not in any way by the necessity to overcome energy barriers; the latter are known *a priori* to be not unduly high at a low temperature. Furthermore, when the ideas of gas-phase kinetics are formally applied to the condensed phase, the experimental activation energies are as a rule associated with definite energy barriers, even when they reach 3–4 eV, despite its being quite evident that barriers with this height are quite impossible to overcome. The causes of the very marked temperature dependence of the reaction rate constant should be sought not in the energetics of the elementary step, but in the type of molecular motion in the low-temperature condensed phase (diffusion, rotational mobility, viscous flow).

We shall consider initially the kinematic aspect of the problem and then the entropy-energetic aspect.

II. THEORY OF ENCOUNTERS

The rate constant for a bimolecular reaction occurring when the reacting species moving in a dense viscous medium encounter one another is defined by the expression

$$k = 4\pi R_e D, \qquad (1)$$

where $R_e = R_e(D)$ is the effective radius of the encounter and D the diffusion coefficient. The gas-phase analogue of Eqn. (1) is the formula $k = \sigma v$, where $\sigma = \sigma(v)$ is the effective reaction cross-section and v the relative velocity of the colliding species. In a dense medium the diffusion coefficient is a measure of the rate of mutual approach and separation of the reacting species before the reaction (i.e. is an analogue of v). Accordingly, the $R_e(D)$ relation is the fundamental characteristic of the process mechanism. However, in contrast to $\sigma(v)$, this relation has been scarcely investigated owing to lack of an experimental method for the measurement of the diffusion coefficient.

Furthermore, the expected $R_e(D)$ relation is the same throughout according to the generally accepted point of view and is given by the formula[1]

$$R_e = R\frac{k_p}{k_p + 4\pi RD} = R\frac{k_p}{k_p + k_D}. \qquad (2)$$

Both phenomenological parameters, namely the rate of reaction k_p during contact between the species and the distance R for which contact is established, are assumed to be constant and independent of the diffusion coefficient. The two-parameter Eqn. (2) constitutes the basis of the classification of reactions into kinetically and diffusion controlled. It is derived rigorously within the framework of the phenomenological "grey sphere" model, contact with which results in partial occurrence of the reaction[2]. The constancy of k_p and R is a consequence of the fact that the model rules out interaction at a distance and ignores its anisotropy and the role of motion at the instant of contact.

Furthermore, it became clear in the 1950s that this model is inapplicable to the description of reactions occurring over a considerable distance between the reactants. This happens, in particular, in the resonance transfer of electronic excitation in the long-range (dipole–dipole) interaction between the energy donor and acceptor. The interaction takes place over a distance amounting to several tens of Angstroms with the probability

$$W = a/r^6,$$

even if the distance r between the species remains unchanged during the reaction. However, the diffusion of species towards one another, which promotes their mutual approach, intensifies the energy transfer process, which is faster the smaller the value of r. In order to take into account this factor, Tunitskii and Bagdasar'yan[4] and a number of other workers[5,6] developed the theory of

transfer at a distance accelerated by diffusion, and established that the flux of excited donors, directed towards the acceptor, is usually dissipated long before they come into direct contact (Fig. 1*a*). In this case Eqn. (1) includes the radius of the sphere within which all the donor excitations are quenched before the donors move away from their sites owing to diffusion and where all the excitations arising from outside are therefore destroyed. The more mobile the species, the closer they are able to approach one another before the energy transfer mechanism operates. For this reason, the effective radius of the quenching sphere

$$R_e = \frac{2\pi}{\Gamma^2(1/4)\sin(\pi/4)}\left(\frac{a}{D}\right)^{1/4} \qquad (3)$$

decreases with increase of the rate of diffusion, although the reaction rate constant increases [see Eqn. (1)].

The picture of the process described above remains qualitatively valid also for any other interaction between the reactants, even in a short-range process such as the "exchange" interaction

$$W = W_0 e^{-2\kappa(r-R_0)},$$

where κ^{-1} is the extent of the region of overlapping of the wave functions. In particular, such interaction is involved in the triplet–triplet energy transfer, which is forbidden by dipole factors[7]. However, it ensures electron transfer in glasses and frozen media over distances amounting to several molecular diameters[8-10]. In the absence of diffusion, these reactions are non-exponential, like the dipole–dipole energy transfer[11,12]. Only species present within the quenching zone, i.e. when $r \leq R_e$, react at this (static) stage. At a low concentration of the reactants, the fraction of such species is low, but the remaining reactive species are nevertheless destroyed owing to diffusion at a rate described by Eqn. (1), in which

$$R_e = R_0 + \frac{1}{2\kappa}\left[\ln\frac{W_0}{4\kappa^2 D} + 1.15\right], \qquad (4)$$

as established by Fabrikant and Kotomin[13] and Doktorov and Burshtein[14].

The rates of both transport reactions described are limited by diffusion. However, Eqns. (3) and (4) contrast sharply with the constancy of $R_e = R = \text{const.}$, which follows from Eqn. (2) and corresponds to the usual hypothesis of diffusional control. A special investigation[15] showed that the "grey sphere" model is valid only when an extended interaction between the reactants can be replaced by a step with the equivalent thickness $R - R_0$ (Fig. 1*b*) and the latter must be small compared with the radius of closest approach R_0. Such a thin quenching layer is possible only in exchange quenching[15,16], but in this case too the step approximation $W(r)$ is possible only for a sufficiently high rate of diffusion: when $R_e(D)$ decreases to $R = R_0 + \frac{1}{2}\kappa$, Eqn. (4) is replaced by Eqn. (2), obtained for the "grey sphere" model[14]. On the other hand, if the reaction zone is insufficiently thin, agreement between the results of the distance and contact theories is achieved only at the kinetic stage (for a still higher rate of diffusion), and the phenomenological parameter

$$k_p = 4\pi\int_{R_0}^{\infty} W(r)r^2 dr \qquad (5)$$

acquires the significance of the total rate of reaction in the vicinity of the reaction centre.

Thus the distance theory not only includes the phenomenological contact model, but also imparts to it a microscopic significance. Furthermore, it describes the process also outside the limits of applicability of the contact model, when the rate of diffusion is very low. Despite these undoubted advantages, it is still very much inferior when compared with the theory of transfer reactions in the gas phase. The very fact that one begins with the locally defined probability $W(r)$ and not with the interaction Hamiltonian $\hat{H}(r)$ and a specific process mechanism demonstrates its inadequate microscopic significance. On the other hand, the very idea of transfer probability at any

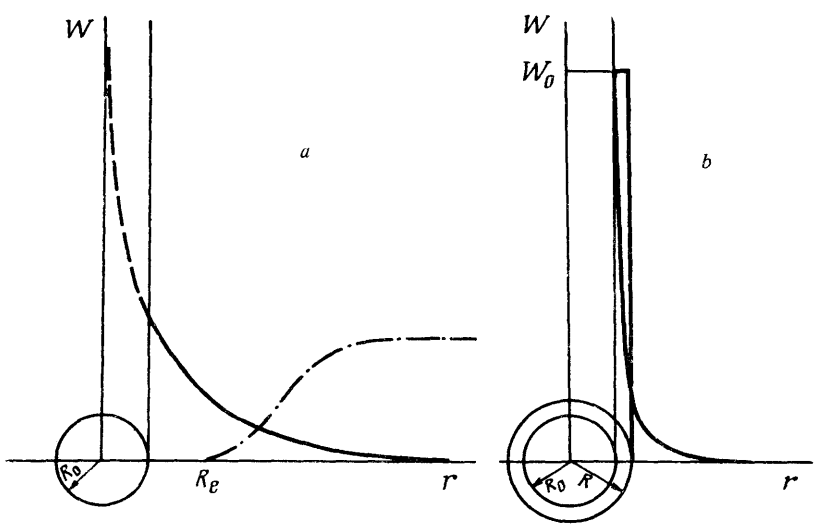


Figure 1. Dependence of the probability of quenching at a distance in dipole–dipole (*a*) and exchange (*b*) interactions on the distance between the reactants. The dash-dot line demonstrates how the stream of excited particles towards the sphere is dissipated in the presence of a strong long-range interaction.

point in space is specific to a condensed medium alone. In the gas phase one can only consider the results of the collision as a whole, but it is impossible to divide it into stages in an additive manner. The use of probabilities which are intrinsically additive becomes possible in condensed media, because any energy level E_i acquires a certain width Γ_i owing to the interaction with the solvent (Fig. 2). This restricts the free dynamic development of the transfer process to very short periods of the order of $(\Gamma_1 + \Gamma_2)^{-1} = \Gamma^{-1}$, after which the process begins to resemble to some extent α-decomposition occurring with the probability

$$W = \frac{2}{\hbar^2}\frac{b^2}{\Gamma_1+\Gamma_2}, \quad b = \langle 1|\hat{H}|2\rangle = b_0 e^{-\varkappa(r-R_0)},$$

where $\langle 1|$ is the donor state, $|2\rangle$ is the acceptor state, and $E_1 \simeq E_2$. It is clear from this that the description of the transfer process throughout its extent in terms of probability is legitimate only when the encounters between the species during which the process takes place have a duration much longer than Γ^{-1}. Otherwise it is absolutely essential to generalise the theory in such a way that it permits a free dynamic development of the transfer process during the encounter.

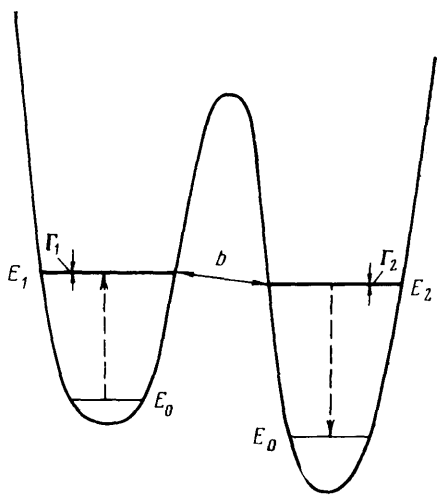


Figure 2. An energy scheme for the resonance transfer reaction. The dashed arrows indicate the excitation and deactivation of quasi-resonance levels.

Evidently the "encounter theory", which must satisfy this requirement, is not only kinematically more complex than the collision theory, but involves a greater number of parameters taking into account the interaction with the medium. The difficulties in devising this theory were overcome quite recently[14,16,17]. Formally, the apparatus of the theory describes resonance reactions in the liquid just as logically as in the gas. All the results of the distance theory were reproduced, and the limits of its applicability were established[14]. It was found that deviations from the "contact" formula (2) occur not only for slow diffusion, when it is overtaken by transfer at a distance, but also for extremely fast diffusion, which is able to switch the interaction on and off at a rate faster than the rate of relaxation[14]. In the latter case the interacting species can be regarded as just as free from interaction with the medium during the encounter as during the collision in the gas phase. The only difference is that the initiation and arrest of the interaction during the collision are predetermined in the course of free migration, while during the encounters between reactants in the liquid phase the occurrence of interaction is just as random as diffusion itself.

A general consequence of quantum mechanics is quadratic propagation in time of the resonance transfer process. At the dynamic stage, for very rapid diffusion, the probability of the reaction therefore depends quadratically on its duration τ_e, namely as $4b_0^2\tau_e^2/\hbar^2$, where $\tau_e = R_0/2\varkappa D$. After multiplying by the frequency of encounters $(4\pi R_0 D)$, we obtain

$$k = \frac{4\pi R_0^3 b_0^2}{\hbar^2 \varkappa^2 D}. \qquad (6)$$

This expression is the liquid-phase analogue of the Born approximation in the scattering theory. It follows from this that R_e diminishes quadratically as diffusion is accelerated:

$$R_e = \frac{R_0^3 b_0^2}{\hbar^2 \varkappa^2 D^2}. \qquad (7)$$

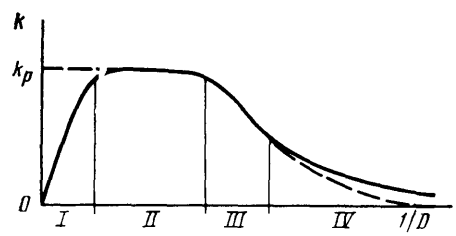


Figure 3. Dependence of the rate constant for a bimolecular reaction on the mutual diffusion coefficient: I) dynamic stage; II) kinetic stage; III) diffusion-controlled stage; IV) transfer over a long distance. The dashed curve illustrates the analogous relation obtained within the framework of the "grey sphere" model.

The qualitative deviations of the $R_e(D)$ or $k(D)$ relations (Fig. 3) from the generally accepted relations might become the subject of a special investigation if, together with the reaction rates, it was possible to measure molecular mobility. It is clear from the above formulae that this would make it possible to infer not only the type of interaction, but also its parameters, mechanism, and the "narrow" reaction stage. Unfortunately, the general kinetic standard procedure involves the measurement of the rate constant and at best its temperature dependence but never its dependence on D. This places liquid-phase kinetics in the same situation as that of its gas-phase analogue before the appearance of the molecular beam technique. No definite conclusions can be drawn about the intimate mechanism of the chemical reaction solely from the rate constant, while the choice of interaction parameters remains appreciably arbitrary.

Because of this, the theory continues to be extremely general. No other factors, apart from the charged state of the species[13,18,19], which hinders or promotes their mutual approach, are taken into account. Nevertheless, the interaction is almost always anisotropic. As a rule, the reaction centres occupy only a small section of the sphere associated with the molecule and rotational motion is an important factor, promoting contact between the reactants[20,21]. For example, this is the situation in spin exchange[22,23] and certain slow radical substitution reactions[24]. Furthermore, the reaction centre may be shielded by the solvation or hydration shell, the penetration of which (or residence in the latter) should limit the rate of the process in many instances. Finally, the presence of ligands in the reaction complex can both promote and hinder contact depending on the conformation, which should result in a direct dependence of the kinetically controlled reaction on the frequency of conformational transitions. It may be that, apart from the deviations from the contact model described above, caused by the unduly slow or unduly fast diffusion, there should be others associated with the fact that the molecule is not a sphere with a radius R and that contact with it is not simply of any type but must involve "adhesion" at the required site and in a convenient configuration. Although these claims are qualitatively evident, they have not been formulated in a strictly quantitative form, mainly because there is no possibility of comparing such a detailed theory with adequate experimental data.

III. REACTIONS CONTROLLED BY MOLECULAR MOBILITY

The transfer of an electron, proton, and valence in nonpolar matrices does not as a rule require the overcoming of high potential barriers, and yet frequently shows an anomalously marked temperature dependence. We believe that this is evidence that the rate of diffusion of charge and valence is not limited by the height and extent of energy barriers but by the mobility of the matrix. Because of this, the observed rates of physicochemical processes are simply none other than the frequencies of molecular motions—vibrations, librations, and rotations, which have been the subject of acoustic and dielectric studies. Many specific examples discussed below support this claim.

Electron Transfer

In 1960 Tal'roze and Blyumenfel'd[25] observed a dark electrical conductivity $\sigma(T)$ in a large class of polymers with conjugated bonds. The anomaly was that activation energy for conduction in these substances varied from 0.2 to 4 eV, but the associated change in the pre-exponential factor (over the range of 60 orders of magnitude) fully compensated the changes in energy. In other words,

$$\sigma = \sigma_0 \exp(-E/k_B T),$$

but

$$\ln \sigma_0 = \alpha + \beta E, \qquad (8)$$

where α and β are invariant in the given series of compounds (Fig. 4).

This phenomenon, called the compensation effect (CE), has been known in the physics of semiconductors since 1937 as the Meyer–Neidel effect[26,27], but it had been observed even earlier in chemical studies: in 1926 Constable[28] established that CE is characteristic of catalytic oxidation reactions and Roginskii and Rozenkevich found it in homogeneous unimolecular reactions[29]. After some controversy, Hinshelwood[30] recognised CE in 1947 as "one of the fundamental although incomprehensible relations of chemical kinetics", and subsequently Kobeko, who observed the effect in the most direct manner in styrene polymerisation reactions[31], concluded that "CE is a general law of chemical kinetics". In the 1960s CE was observed in the decomposition reactions of aliphatic azocompounds and many hydroperoxides[32]. Furthermore, it was established that, in the reactions associated with alkaline hydrolysis[33], the compensation effect is to a large extent limited to an analogous compensation expressed by the temperature dependence of the solvent viscosity[34].

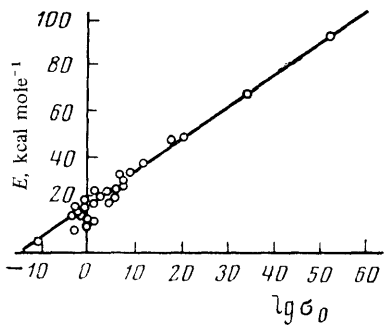


Figure 4. The compensation effect in the conductivities of a number of polymers according to Tal'roze and Blyumenfel'd[25].

The last observation might serve as the starting point for the interpretation of the effect in all its manifestations. However, there always remains the possibility that CE is associated with the very formulation of the experiment, the scope of which is frequently limited by the narrowness of the available temperature range. By a tendentious selection of specimens[35] or by postulating competition between two simultaneous reactions[36], it is easy to account for the compensation of the energy factor by the entropy factor if both are within reasonable limits. However, the CE observed in the electrical conductivity of organic structures[25] cannot for this reason be accounted for in a trivial manner, which gives rise to the problem of the origin of the exceptionally high activation energies appearing in the compensation series. Their occurrence in conduction in high-molecular-weight compounds was later confirmed for a large class of highly unsaturated polymers[37-39]. It is striking that the activation energy varies from specimen to specimen in a random manner, reaching 5 eV in certain cases. This phenomenon has been included as an experimental fact in monographs on organic semiconductors[40] and biopolymers[41], but a likely explanation for it has not so far been found.

The existence of activation energies exceeding all reasonable limits has been observed not only in electrical conduction, and not necessarily in the solid state. The activation energies for many catalytic processes[42] and a

large class of liquid-phase enzymatic reactions, where CE is a universal phenomenon[43,44], are just as large. However, even if one admits that the phenomenon is non-trivial in a compensation series where the energies vary from several kcal mole^{-1} to 120 kcal mole^{-1} and more, one must treat with much caution many "simple" explanations of CE in series where the energy varies within reasonable limits. The widespread nature of the phenomenon makes it necessary to assume that its cause is extremely general and only its manifestations are not always anomalous (involving unduly large activation energies).

The appearance of activation energies of 4–5 eV is most paradoxical in electrical conduction, where the elementary step is particularly simple. The conductivity of the substance $\sigma = e\mu n$, where n is the concentration of current carriers and μ their mobility, is known to be linked to the diffusion coefficient by the Einstein relation:

$$\mu = \frac{eD}{k_B T}, \qquad (9)$$

where e is the charge and T the temperature. In inorganic semiconductors the temperature relation $\sigma(T)$ is determined by the excitation of charges in the conductivity band, i.e. by the equilibrium current carrier density $n(T)$. However, a simple estimate shows that, when $E = 2$ eV, the forbidden gap is so wide ($2E$), that at room temperature there is not even one free carrier per specimen. In other words, in organic semiconductors with large values of E precisely the opposite situation should obtain: $n \simeq$ const., as in metals, and the temperature relation $\sigma(T)$ should originate mainly from the temperature dependence of the mobility of current carriers. The constancy of n can be explained by the fact that high-molecular-weight semiconductors contain a multiplicity of impurities, which need not necessarily be extraneous inclusions, consisting of low-molecular-weight oligomers with enhanced electron-donating or electron-accepting capacity, which ionise the main molecules. The current carriers thus generated move freely via the system of conjugated bonds within the molecule, experiencing difficulties only in the transfer from one molecule to another. If such transitions take place W times per second, their sum amounts to diffusion with the coefficient

$$D = \frac{a^2}{6} W, \qquad (10)$$

where a is the scale of the spatial displacement of the current carrier in each elementary step of the intermolecular transfer (an analogue of the lattice period).

Taking into account Eqns. (9) and (10), it is reasonable to expect that the anomalous temperature relation $\sigma(T)$ is caused by the fact that the transition probability $W(T)$ is based on an activated process. However, until recently, it has been assumed that the electron independently traverses very large intermolecular distances, but not always "successfully" ($q \ll 1$†), repeating its attempts ν times per second from each end of the molecule. If this were so, it would be difficult to postulate any marked temperature dependence of the transition probability

$$W = \nu q. \qquad (11)$$

In fact ν, the frequency of the intramolecular vibrations of the electron is constant, while the intermolecular transition is activated only when it takes place over a barrier. However, it is impossible to relate the observed activation energy to the height of this barrier. Even, for an attack frequency $\nu \simeq 10^{15}$ Hz, the transition through a 2 eV barrier would take place at a frequency of 10^{-7} Hz, i.e. only a few times per year.

The solution, pointed out by Gutmann as late as 1969,[45] is to abandon the usual treatment of charge migration as if the latter occurred in a frozen medium with a fixed geometry and positions of the molecules. In this approach, which is generally accepted in the theory of the solid state, the current carrier indeed has no choice but to overcome the barriers encountered in its path. In fact, there is always an alternative: either to pass through the barrier despite its considerable extent or to wait until it is lowered as a result of the mutual migration of molecules to such an extent that it becomes virtually "transparent". On the other hand, if the intermolecular distances are such that the barriers are on average insurmountable, only the latter possibility remains.

This is apparently the situation in organic semiconductors. The frequency of attempts ν in Eqn. (11) has the significance of the frequency of intermolecular contacts arising during thermal motion and not of the frequency of attacks (which is known to be high).

Table 1. Comparison of the activation energies for combustion and dielectric losses (measured in electron-volts).

Substance	$E_{cond.}$, eV	E_{loss}, eV
Chlorpromazine	1.5	1.4
Promethazine	1.5	1.37
Trifluoropyrazine	1.4	1.4
Poly(ethylene terephthalate)	1.65	0.66—0.87
Albumin	1.1	0.8
Polyacrylonitrile	0.85	0.61
Gelatin	1.5	1.14—1.3
Collagen	1.36	1.1

The probability of tunnelling at these instants $q \leq \frac{1}{2}$ can be very close to its limit ($\frac{1}{2}$) and the temperature dependence of conductivity, mobility, and the diffusion coefficient is then determined mainly by the temperature dependence of the frequency $\nu(T)$, which limits the rate of the process. Using these considerations, Gutmann decided to compare the measured activation energies for conduction and the dielectric losses, which constitute a direct means of measuring $\nu(T)$. The author notes that the "data compared proved to be very scanty because the objects investigated as dielectrics were as a rule not studied from the standpoint of their conductivity, and conversely".[45] Nevertheless he was able to make such a comparison (Table 1), partly on the basis of his own observations and partly on the basis of literature data, demonstrating the striking agreement of the results. The author explains the observed slightly higher activation energy for conduction (by 0.2 eV) by the necessary preliminary separation of the paired spins, which ensures the resonance mechanism of electron transfer. However, the main part of the activation energy and sometimes the entire activation energy is required solely for the creation of a "sterically convenient orientation of two molecules relative to one another, in which the energy barrier separating them is temporarily lowered".[45] In order to achieve this

†Here q is the fraction of successful attempts.

favourable configuration, the molecules must bend, twist, or execute librations within narrow confines, and this stage actually limits the rate of the process. Electron transfer is merely an example of the reactions which may be controlled by molecular mobility, ensuring that the reactants come into contact in the required coordination.

Unfortunately, we have no data permitting a comparison of the activation energies for conduction and dielectric relaxation in the series of polymers where CE is observed. However, there is no doubt that such comparison would reveal their identity. The enormous activation energies and their consequent compensation by anomalously large pre-exponential factors in the expression for the rate of relaxation of dielectric losses in polymeric media are encountered extremely frequently[46].

Naturally, by reducing CE in electrical conduction to CE in molecular mobility, we do not as yet explain this phenomenon. However, the demonstration of the very fact that the reaction is controlled by molecular motion is important for chemical kinetics. Whether or not CE constitutes an unambiguous indication of such control can be elucidated only by a wide-scale comparison of the results of acoustic, dielectric, and molecular-kinetic investigations of condensed media with the rates of the elementary chemical reactions which occur in the latter. To what extent such a comparison can succeed is seen most clearly in relation to a simpler system, which we shall now analyse.

Proton Transfer

The anomalously high intrinsic conductivity of ammonium salt crystals, which is higher by 5–6 orders of magnitude than that of the corresponding alkali metal salts, constitutes an important reason for giving preference to the proton mechanism of charge transfer rather than to the usual vacancy mechanism associated with the motion of heavy masses. However, this hypothesis became concrete only recently as a result of a multistage experimental study of the formation and migration of a free proton in a crystal lattice[47,48]. In order to identify the mechanism, the proton-donating NH_4HSO_4 admixture was introduced by cocrystallisation from aqueous solution into $(NH_4)_2SO_4$ (AS), and $NH_4H_2PO_4$ (ADP) crystals; the concentration of the admixture was followed by titrating the solution after dissolving the given single crystal in water. As expected, the conductivity increased linearly with increasing concentration of the electron-donating molecules.

By following the concentrations in specimens with admixtures (n_0), it is possible to determine in the simplest way the proton mobility $\mu(T) = \sigma(T)/en_0$ and to compare its temperature variation

$$\mu(T) = \mu_0 \exp(-E_m/k_B T) \qquad (12)$$

with the temperature variation of the intrinsic conductivity

$$\sigma(T) = e\mu(T) \cdot n(T) = \sigma_0 \exp(-E/k_B T),$$

where

$$n(T) = \sqrt{\frac{k_d}{k_r}[NH_4^+]} \propto \exp\left(-\frac{E_0}{2k_B T}\right) \qquad (13)$$

is the equilibrium density of the protons generated as a result of thermal dissocation

$$NH_4^+ + SO_4^{2-} \underset{k_r}{\overset{k_d}{\rightleftarrows}} NH_3 + HSO_4^-$$

(k_d and k_r are the dissociation and recombination rate constants respectively). This comparison makes it possible to separate the contributions to the activation energy E by the dissociation energy E_0 and by the activation energy for motion E_m: $E = E_0/2 + E_m$. The values of E_0 and E_m proved to be virtually identical for protons in AS crystals: $E_m = 0.49$ eV and $E_0 = 0.5$ eV ($E = 0.76$ eV). However, although the origin of E_0 is evident, the nature of E_m still needs to be analysed.

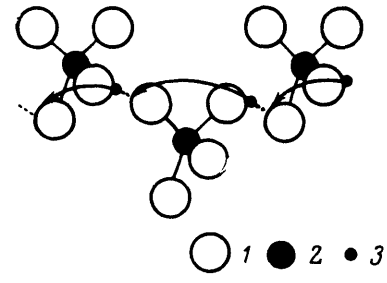


Figure 5. Schematic illustration of the multistage migration of a proton within and between the cells of the anionic sublattice: 1) oxygen atom; 2) sulphur atom; 3) proton. The arrows indicate the intraionic migrations of the proton and the circles illustrate the interionic migrations.

The migration of an intrinsic or impurity proton in the crystal lattice consists of elementary steps each of which is none other than a resonance transfer reaction of the type

$$HSO_4^- + SO_4^{2-} \underset{W}{\overset{W}{\rightleftarrows}} SO_4^{2-} + HSO_4^-. \qquad (14)$$

The experimental mobility $\mu = (ea^2\gamma/k_B T)W$, where γ is the geometrical factor (instead of 1/6) taking into account the possibility of proton transfer to any of the anions forming part of the first coordination sphere, can be expressed in terms of the probability of this process W in accordance with Eqns. (9) and (10). Having measured μ, it is easy to calculate

$$W = \frac{\mu k_B T}{e a^2 \gamma} = \nu q. \qquad (15)$$

Evidently we encounter in Eqn. (15) the same alternative as in Eqn. (11). Although the probability W can be found readily, it is in no way clear to what the temperature dependence should be attributed: the probability of overcoming the barrier $q(T)$ separating the two anions or to the frequency of the approaches to the barrier $\nu(T)$. The latter is determined either by the rotation of the HSO_4^- ion or by proton transfer within the latter from one side to the other (Fig. 5). Rotation (a change in coordination) is a necessary condition for the translational motion of the charge carrier and it can be no less difficult than proton transfer along the line of the hydrogen bond between neighbouring lattice sites. In fact the distance between the sites in the tetragonal structure of the ADP crystal is 4.2 Å, while the distance traversed by the proton on moving from an oxygen atom of its "own" anion to a "foreign" anion does not exceed 0.35 Å. In this situation it is

natural to suppose that the intramolecular transition may be the rate-limiting stage for the process as a whole.

Experimental proof of this was obtained by studying the temperature and frequency dependence of the complex dielectric constants of AS and ADP crystals. Direct measurements demonstrated the identity not only of the activation energies for conduction and dielectric relaxation, but also of the absolute values of the relaxation time τ_d and the rotation time $\tau_c = \nu^{-1}$ (Table 2) subject to the condition that $q = \frac{1}{2}$. The latter implies that whenever a favourable coordination is established the proton has sufficient time, while the coordination persists, to be equally distributed between neighbouring anions. The only difficulty is the creation of such a favourable situation and not the transfer step itself, which, judging from certain data[49], takes place at a frequency $\nu = 10^{13}$ s^{-1}, while the reorientation takes place, according to Table 2, at a frequency not greater than 10^6 times a second.

Table 2. Comparison of the activation energies and relaxation times for conduction and dielectric losses.

Ammonium salt	E_m, eV	E_d, eV	$10^5\tau_c$, s	$10^5\tau_d$, s
$(NH_4)_2SO_4$	0.49±0.03	0.51±0.04	3.3	5.5
$NH_4H_2PO_4$	0.54±0.03	0.50±0.04	8.3	4.6

Thus the seemingly elementary reaction (14) can be arbitrarily subdivided into two stages: the reorientation of the carrier anion

$$HSO_4^- \underset{\nu}{\overset{\nu}{\rightleftarrows}} SO_4H^-$$

and the intrinsic transfer (tunnelling) of a proton from one carrier to another:

$$SO_4H^- + SO_4^{2-} \underset{q}{\overset{q}{\rightleftarrows}} SO_4^{2-} + HSO_4^-,$$

the former being rate-limiting. This constitutes an example of a reaction controlled by molecular mobility in a pure form.

The ideas described apparently make it possible to consider the problem of the specific regulation of the rates of certain solid-phase protolytic reactions in a different way. Thus, on thermal decomposition, ammonium perchlorate (AP) initially dissociates:

$$NH_4ClO_4 \rightarrow NH_3 + HClO_4,$$

while the proton, having moved in the manner described above in the anionic AP sublattice, enters an unstable anion (ClO_4^- in the defective section of the lattice or as an impurity ClO_3^- anion) and destabilises it further, which leads to the initiation of the autocatalytic decomposition process. Consequently, by introducing additional protons into the AP lattice (from proton-donating additives) or by reducing the concentration of the conductivity protons present in the lattice (by introducing proton acceptors such as ammonia, HPO_4^{2-}, CO_3^{2-}, etc.), it is possible to decrease or increase correspondingly the thermal stability of this widely used solid-phase oxidant, which was recently demonstrated by direct experiments[50].

Recombination of Radicals

The thermal annealing of the radicals arising in a solid matrix under the influence of penetrating radiation has been the subject of chemical research in the course of two decades. After the discovery of the electron spin resonance method, these studies became particularly vigorous. However, despite the possibility of identifying radicals and of following their transformations, unambiguous and generally accepted explanations of the known anomalies in the kinetics of their recombination (pronounced departure from steady-state conditions, "shelves", etc.) have not so far been proposed. Virtually nothing is known about the mechanism of the spatial migration of radicals via molecular crystals, let alone glasses and polymers, and even diffusion coefficients have been measured only in exceptional instances. Nevertheless the mutual approach of radicals (or valences) in space constitutes a necessary preliminary stage before their recombination, which itself requires almost no activation energy. It is therefore natural to suppose that the rate of the process as a whole is as a rule limited by diffusion and that its temperature dependence and the CE frequently encountered in the process simply exhibit features characteristic of the temperature variation of the diffusion coefficient $D(T)$.

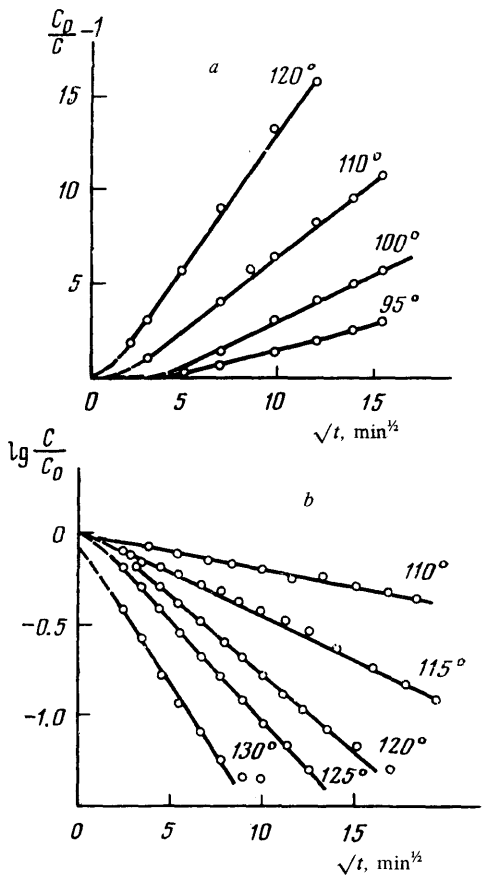


Figure 6. "Square root" plots designed to express in a linear form the kinetic curves for the unimolecular and bimolecular recombination of radicals in crystals of succinic (*a*) and 3,3-pentamethyleneglutaric (*b*) acids.

The present author and Tsvetkov[51] recently found direct evidence for this by observing that the kinetic curve for the unimolecular and bimolecular recombination reactions can be expressed in a linear form by plotting $\ln C$ and C^{-1} respectively against $\sqrt{t}$, whereas usually the variable plotted along the abscissa axis is t and not $\sqrt{t}$ (C is the concentration of radicals). The recombination in irradiated crystals of succinic and 3,3-pentamethyleneglutaric acids proceeds in this way at temperatures close to the melting point or the polymorphic transition temperature[51] (Fig. 6). Analogous "square root" kinetics had also been observed previously in vitreous matrices[52-55] and had been interpreted in the same spirit.

The decrease of concentration with increasing $\sqrt{t}$ always precedes the steady-state stage of the reaction, where it is controlled by diffusion ($k_p \gg k_D$) [see Eqn. (2)]. If after irradiation radicals are scattered throughout the bulk of the specimen randomly and uniformly and their motion in any direction takes place identically, then, according to the generally accepted theory[2], the rate constant for the diffusion-controlled reaction is

$$k_D(t) = 4\pi RD\left[1+\frac{R}{\sqrt{\pi Dt}}\right]. \qquad (16)$$

As in Eqn. (2), here R is the radius of the sphere which in this instance is "black". At the beginning of the annealing process the second term on the right-hand side of Eqn. (16) always predominates over the first and at this stage the recombination kinetics are therefore defined by the following equations:

$$(a)\ \frac{C_0}{C}-1=\tilde{k}\sqrt{t}\quad\text{or}\quad(b)\ \ln\frac{C}{C_0}=-\tilde{k}\sqrt{t}, \qquad (17)$$

Indeed the $C(t)$ relation can be expressed in a linear form by means of the above "square root" plots and the effective reaction rate constant $\tilde{k}$ is

$$(a)\ \tilde{k}=8R^2C_0\sqrt{\pi D}\quad\text{or}\quad(b)\ \tilde{k}=8R^2M\sqrt{\pi D}, \qquad (18)$$

where M is the concentration of the reactants involved in the first-order reaction. However, the non-steady stage, associated with the "square root" destruction of the species in direct proximity to the "black sphere", lasts only for an instant $t \ll R^2/\pi D$, i.e. for a very short time if R has molecular dimensions. During this period, only those few radicals which were generated along side one another or at a distance of one–two "steps" from one another can be destroyed. In fact a considerable proportion if not all the radical centres detected by ESR are destroyed in the non-steady stage of the reaction. Because of this, interpretation of the experimental data in terms of the above formulae yields for R a value many times greater than the size of the molecule or of the monomeric unit of the polymer: 40–80 Å. Such enormous capture radii can be accounted for solely by heterophase fluctuations in the prefusion region[56]: the appearance of unstable microscopic nuclei of the liquid phase within which the mobility of the species is very high. Two radicals which have entered such a "cauldron" have a greater chance of meeting and recombining, while a single radical simply moves in space, but over a considerable distance, of the order of magnitude of the fluctuation radius[51].

Unfortunately the situation remains paradoxical even if a hypothesis of this kind is adopted. When the radius of the black sphere, whose penetration leads to the inevitable destruction of radicals, is compared with the average distance between them at the beginning of annealing, the binary approximation within the framework of which Eqn. (16) was obtained ceases to be legitimate. Furthermore, certain kinetic curves indicate directly the internal inconsistency of their description in terms of this formula. This is clearly seen if the experimental results are expressed by a plot of $(C^{-1} - C_0^{-1})/t$ against $1/\sqrt{t}$; in this case Eqn. (16), describing the kinetics of bimolecular recombination, leads to a straight line[55], because

$$(C^{-1}-C_0^{-1})/t = 4\pi RD + 8R^2\sqrt{\frac{\pi D}{t}}. \qquad (19)$$

The intercept which the line makes on the ordinate axis is none other than the steady-state rate of reaction (1). However, among the results quoted by Butyagin[55], there are also instances where the intercept is zero (Fig. 7, right-hand column); this involves the destruction of radicals in thermovulcanised rubber, where one can either assume that $R = \infty$ and $D = 0$, or that there is no steady-state stage in the reaction at all.

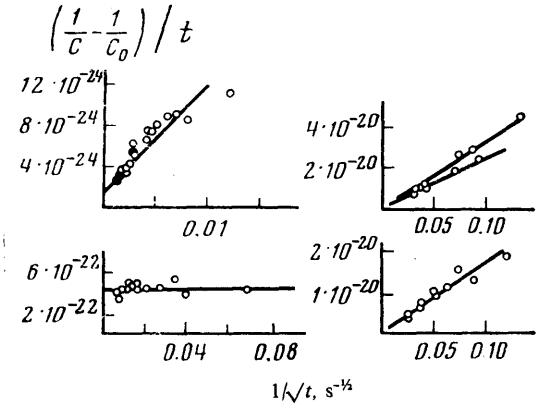


Figure 7. Kinetics of the destruction of radicals in the presence of a steady-state stage in the reaction (*a*) and in its absence (*b*) according to Butyagin[55].

The possibility of a non-steady-state course of the reaction from beginning to end merits special investigation. Such a possibility exists if diffusion takes place as a one-dimensional or two-dimensional process, but "square root" kinetics are obtained only in the one-dimensional case. The latter naturally arises if one of the radicals is always stabilised on the surface and the other in the bulk phase, or if both are formed at an edge dislocation consisting of a narrow (with a thickness of the order of magnitude of several atomic dimensions) tunnel in the crystal lattice. In order to ensure a markedly non-steady-state process, it is necessary to assume in addition that the initial distribution of radicals is very non-uniform. They must be generated close to one another compared with the distance by which they can be separated during diffusion. When the initial distribution is Gaussian with a width l, the destruction takes place in accordance with the law[57]

$$p=\frac{C}{C_0}=\frac{2}{\pi}\arctan\left(\frac{2}{l}\sqrt{\frac{Dt}{\pi}}\right), \qquad (20)$$

if the radicals are assumed to be "black" and to recombine already in the first encounter.

The fundamental difference between Eqns. (20) and (19) is due to rejection of both fundamental assumptions of Waite's theory leading to Eqn. (16): the homogeneity of three-dimensional diffusion and the uniformity of the initial distribution of species. The process described by Eqn. (20) also consists of two stages; approximately half of the initial number of radicals are destroyed at each stage. However, the last stage is non-steady-state to the end and the recombination kinetics are close to the "square root" type whatever variables are used (Fig. 8). For any initial distribution $\varphi(x)$ (provided that it is narrow!), they can be represented in the following form:

$$\frac{C}{C_0} = \frac{l}{\sqrt{\pi Dt}}, \quad t \gg \frac{l^2}{D}, \quad C \ll C_0, \tag{21}$$

where $l = \int_0^\infty x\varphi(x)dx$ is the first moment of the distribution. Comparison of this destruction law with Eqn. (17a) readily shows that

$$\tilde{k} = \frac{\sqrt{\pi D}}{l}, \tag{22}$$

and $\tilde{k}$ therefore depends on the diffusion coefficient in exactly the same way as in Eqn. (18), although the values and significance of the spatial characteristics in the two formulae are different.

The above explanation of the profoundly non-steady-state nature of the process shows that at least the functional relation between the effective rate constants defined by Eqn. (18) and the diffusion coefficient can be accepted with confidence‡. This makes their comparison legitimate and their temperature dependence can be regarded as corresponding exclusively to the $D(T)$ relation. Although the constants for the two reactions investigated fit on the Arrhenius temperature relation $\tilde{k} = k_0 \exp(-E/k_B T)$ and have similar values of $\tilde{k}$, the activation energies and the pre-exponential factors ($k_0 = 3 \times 10^{18}$ s$^{-1/2}$ and $E = 36.4$ kcal mole^{-1} for 3,3-pentamethyleneglutaric acid, and $k_0 = 3 \times 10^9$ s$^{-1/2}$ and $E = 18.4$ kcal mole^{-1} for succinic acid) differ from one another very markedly. Furthermore, a typical compensation effect due to diffusion is present. According to Eqn. (18), the activation energy for diffusion E_q is twice as large as the activation energy corresponding to the effective rate constant and reaches 3 eV for 3,3-pentamethyleneglutaric acid.

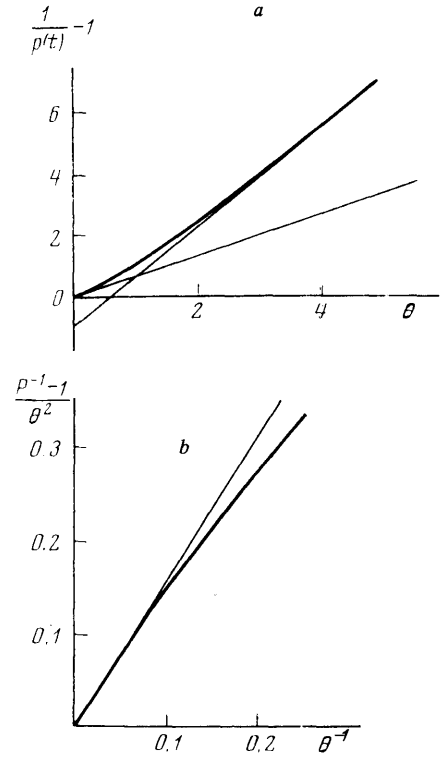


Figure 8. Kinetics of the non-steady-state recombination under the conditions of one-dimensional diffusion represented by plots in terms of the coordinates of Burshtein and Tsvetkov[51] (*a*) and Butyagin[55] (*b*); $p(t) = C/C_0$, $\theta = (2/l)\sqrt{Dt/\pi}$.

The compensation effect in the recombination of radicals had also been observed previously. It was interpreted phenomenologically as a result of the S-shaped pronounced $E(T)$ dependence, close to linearity[58]:

$$E(T) = E_0(1 - \beta k_B T).$$

The steep decrease of the activation energy, which can explain the compensation effect in a narrow temperature range, was attributed to the unfreezing of the rotational mobility of the polymeric chain, i.e. not in any way "to the structure and properties of the radicals but to the structure of the polymer as a whole"[58]. Direct measurements performed on pure amorphous glycerol showed that the activation energies for the rotation (dielectric losses) and recombination of radicals are identical[59]. On the other hand, the non-Arrhenius S-shape of the relation between $\ln k$ and $1/T$ was later confirmed by a special study of recombination in irradiated frozen benzene[60] and was regarded by the authors as evidence in support of the hypothesis that the activation barrier to self diffusion (or the migration of valence) decreases with increase of temperature. Finally, direct experimental confirmation has

‡ Experimental evidence has become available quite recently, showing that the non-steady-state ("square root") kinetics are also characteristic of disproportionation reactions in the cage which do not require diffusion[80,81]. In particular[80], the reaction of the methyl radical with the matrix, $CH_3^\cdot + RH = CH_4 + R^\cdot$, is markedly non-steady-state and proceeds in accordance with the law $C = C_0 \exp(-\sqrt{kt})$. The difference between the rates of transformation of different radicals, which is the reason why the reaction is non-steady-state, may be attributed in this instance solely to the local inhomogeneity of the matrix, energetic or structural. The phenomenon has been interpreted[80] on the assumption that the transfer of H· has a tunnel and quasi-resonance mechanism and that the distribution of the resonance deficiency is Gaussian. The feasibility of this explanation of the "square root" decomposition shows that diffusion may not be the only cause of such behaviour and special proof is therefore required that it controls the process.

been obtained quite recently that the activation energies for recombination and diffusion in crystals are very close[61,62], i.e. that the nature of both phenomena is indeed the same.

IV. THE VACANCY MECHANISM OF MOBILITY

In view of the foregoing, it is natural to seek an explanation of the compensation effect outside the limits of chemical kinetics: in the mechanisms of the organisation of diffusion. However, the existence of a compensation effect is known reliably only for the diffusion of a number of metals into fused copper and for the self-diffusion of iron in its melts[63] (Fig. 9). Unfortunately the activation energies and pre-exponential factors in such cases vary outside the normal limits. On the other hand, in those instances where anomalies were encountered and were interpreted very successfully, the compensation effect had not been the subject of the investigation. We are dealing with extremely high (compared with potential barriers) activation energies and the correspondingly unduly high (by several orders of magnitude) pre-exponential factors in the expressions for the self-diffusion coefficients for atomic[64] and ionic crystals[65,66]. Despite the small scale of the effect, its explanation, which has withstood an experimental test, is the only reliable basis for considering the causes of the anomalously high activation energies and their compensation.

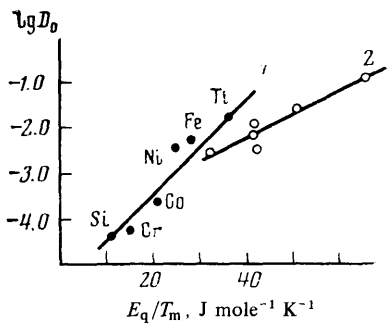


Figure 9. The compensation effect in the diffusion of metals in liquid copper (line *1*) and the self-diffusion of iron in Fe–C according to Shurygin and Shantarin[63] (curve *2*).

The migration of an atom (or ion) from its lattice site to a neighbouring site takes place most readily when the latter is vacant. Such a situation arises each time when the vacancy (Schottky defect) migrating in the crystal appears in the first coordination sphere. By treating such events as "encounters" between the vacancy and the ion, it is possible to determine their frequency by Eqn. (1), putting $R = a$ (a is the lattice constant), i.e. $W = 4\pi a D_V n_V$, where n_V is the equilibrium density of the vacancies and D_V is their diffusion coefficient. By migrating into a vacancy, the given species migrates over a distance $\sim a$, and the sequence of such migrations constitutes diffusion with the coefficient described by Eqn. (10), which in the given instance assumes the following form:

$$D = \gamma a^2 W = D_v P_v, \tag{23}$$

where $P_V \simeq a^3 n_V$ is the fraction of vacant sites in the crystal lattice. In this very familiar expression[65] D_V is a kinetic parameter and P_V a strictly equilibrium parameter. In principle, both depend on temperature, since the compensation effect in diffusion can originate both from kinetic and equilibrium causes.

Initially it was believed that the observed anomaly in the $D(T)$ relation is associated exclusively with the temperature relation $E_V(T)$ due to the barrier which the ion must overcome on being displaced into the nearest vacant site. The barrier between the sites is generated by the repulsion potential between neighbouring molecules and the ion must cross this barrier in order to enter the vacant site. The height of the barrier naturally depends on the distances between the sites. When the neighbouring molecules move apart as the crystal expands, liberating a pathway, the height of the barrier should decrease with temperature and the decrease should be linear:

$$E_v = E_0 + \frac{\mathrm{d}E_v}{\mathrm{d}v}\left(\frac{\partial v}{\partial T}\right)_p T = E_0[1 - \lambda\gamma T], \tag{24}$$

where E_0 is the height of the barrier at $T = p = 0$, $\lambda = (1/v)(\partial v/\partial T)_p$ the isobaric coefficient of thermal expansion, $\gamma = -\mathrm{d}\ln E_V/\mathrm{d}\ln v$ a numerical parameter, which can be readily estimated provided that the repulsion potential is known (the specific volume $v \simeq a^3$). For example, we have $\gamma = 4$ for $E_V \simeq 1/a^{12} \simeq 1/v^4$. The linear decrease of $E(T)$, pointed out for the first time by Frenkel'[64], constitutes an excellent imitation of the Arrhenius relation and, by causing an unduly high activation energy, necessitates the compensation of such increase by the pre-exponential factor:

$$D_v = D_a e^{-E_v/k_B T} = D_a e^{\lambda\gamma E_0/k_B} \cdot e^{-E_0/k_B T} = D_0 e^{-E_0/k_B T}. \tag{25}$$

However, when the compensation effect originates in this way, the activation energies can only be a little higher than the usual values [$(E - E_0)/E_0 \simeq \lambda\gamma T \simeq 1$] and the pre-exponential factor should not differ unduly from the true value. Even for ionic crystals, where the pre-exponential factor is too high by only four orders of magnitude, the kinetic compensation effect can account for only two orders of magnitude, i.e. for half of the observed effect. In this connection, Mott and Gurney[65] pointed out that the remaining half of the effect is evidently associated with the analogous effect as a function of $P_V(T)$. The increase of the density of vacancies with temperature is determined by the thermodynamics of the crystals and can be very marked near the melting point or the polymorphic transition temperature. A completely analogous situation occurs in pure metals and solid substitutional solutions where atoms diffuse via the vacancy mechanism[64]. The latter is regarded as involving local fusion due to a random aggregation of vacancies[67,68].

The kinetic and equilibrium compensation effects make equal contributions to the observed undue increase of the pre-exponential factor for ionic crystals, but whereas the former is interpreted at a microscopic level, the latter is introduced exclusively to make the theory consistent with experiment. The formula for the effect found empirically by Bugakov[69]

$$D = D_m e^{E/k_B T_m} e^{-E/k_B T}$$

is identical with Eqn. (8) and identifies $(\beta k_B)^{-1}$ with the melting point T_m. As the melting point is approached,

the density of vacancies increases sharply and the probability of their binary, ternary, and higher-order collisions, leading to aggregation and microfusion, increases still more steeply, providing the driving force for diffusion and the reactions which it controls.

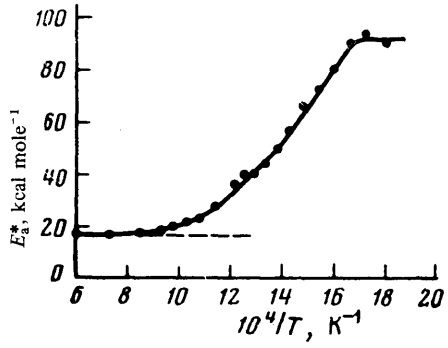


Figure 10. Dependence of the effective activation energy E_a^* for the viscous flow of the B_2O_3 glass over a wide temperature range.

In comparing the kinetic and equilibrium compensation effects as the possible causes of the appearance of anomalies of still greater magnitude, characteristic of molecular crystals and glasses, it is natural to give preference to the equilibrium effect. The fact that the temperature dependence of viscous flow and self-diffusion in such media has been attributed for a long time to the probability of the appearance of vacancies of molecular size v^* can be regarded as independent evidence in support of this choice. According to the free-volume theory [70,71], this probability is

$$P_v = \exp\left(-\frac{v^*}{v - v_0}\right), \qquad (26)$$

where v is the specific volume and v_0 is assumed equal to the intrinsic molecular volume (or the specific volume when $T = p = 0$). In the free volume theory the appearance of vacancies is attributed exclusively to entropy fluctuations; solely owing to the ordering of the structure and without an energy expenditure, such fluctuations lead to the accumulation of the free volume due to many molecules in one place, in the form of a cavity of specified size. Naturally, the greater the volume of this cavity v^*, the smaller the probability of its formation. On the other hand, the greater the average free volume per molecule $v - v_0$, the greater the frequency of cavities whose size is sufficient for spatial migration of the diffusing species in the latter. Consequently the isobaric temperature relation $P_V(T)$ is associated exclusively with thermal expansion. In vitreous matrices over a range of approximately 50°C near the glass point T_g the change in free volume is such that it converts Eqn. (26) into the so-called WLF formula [71,72] or Falcher's law:

$$P_v = \exp\left[-\frac{\text{const}}{T - T_0}\right], \quad T_0 < T_g. \qquad (27)$$

Despite its approximate nature, this law shows that the effective activation energy $(\partial \ln p_V/\partial T^{-1})_p$ increases rapidly with decrease of temperature and may be much greater than any potential barriers, as happens in the presence of the compensation effect.

Direct and precise measurements of the activation energy for low-temperature viscous flow and rotational relaxation in a reference glass such B_2O_3 showed [73] that the activation energy reaches 96 kcal mole^{-1} at low temperatures (Fig. 10). In the light of this finding, the appearance of an anomalous compensation effect in diffusion-controlled reactions such as recombination is quite natural.

Furthermore, since high activation energies and their compensation are characteristic of the rotational mobility of glasses, there is reason to expect that the compensation effect may be characteristic also of certain kinetically controlled reactions in glasses and liquids, which require contact between the reactants in the correct coordination. The stereospecificity of the reaction is expressed by the fact that its rate on contact between the reactants depends on the position of the point of contact on the reaction sphere of radius R:

$$k_p = k_p(\theta, \varphi),$$

where θ and φ are the angular coordinates of the point. In terms of the terminology of the model, this implies that the sphere is non-uniformly grey and, although there is a possibility of contact at any point with equal probabilities, owing to its different effectiveness, there is a multiplicity of different values of k_p, occurring with the probability

$$dW = f(k_p')\,dk_p'. \qquad (28)$$

Generally speaking, this distribution is diffuse compared with the model of a uniformly grey sphere, to which corresponds the distribution $f(k_p') = \delta(k_p' - k_p)$ or the model of a white sphere with grey spots, for which $f = (1 - q)(k_p') + q\delta(k_p' - k_p)$, where q is the steric factor equal to the relative area of the reactive surface. The relative rotation of the reactant simulates the rate of reaction during contact, and by virtue of this is capable of accelerating the process to some extent as a function of the form of $f(k_p')$. This implies that at the kinetic stage the process is controlled by rotational migration, the frequency ν of which may exhibit the same temperature dependence as the coefficient of translational diffusion. Griva and Denisov justly noted [21] that the proportionality $k = k_p \propto \nu$ (Fig. 11) "is a new phenomenon and is not predicted either by the theory of collisions in a liquid or by the activated complex theory". The authors explained this correlation on the hypothesis that, when it rotates, the molecule must overcome potential barriers generated by the environment. Orientation favourable for the reaction obtains in the vicinity of the maximum of one of the barriers. It is therefore reached only by molecules with sufficient rotational energy, the number of which is greater the faster the rotation. This view constitutes a modification of the activated complex theory in which an angular variable is the reaction coordinate [79].

However, the position favourable for reaction is not necessarily energetically unfavourable. If all the orientations are energetically equivalent, the rate of reaction is determined solely by its stereospecificity and by the mechanism of the reorientations and not in any way by the activation energy. This situation has been the subject of a special study for different models of chemical asymmetry under the conditions of jump reorientations by large and small angles in the cage. The rate of reaction over long periods, where it follows an exponential law, may depend on the frequency of the reorientations both linearly and in terms of the "square root" law ($\propto \sqrt{\nu}$). [74]

The dependence of the rate constant for the rotational or translational mobility of the reactant is a general feature of reactions controlled by molecular mobility, including those with kinetic limitations.

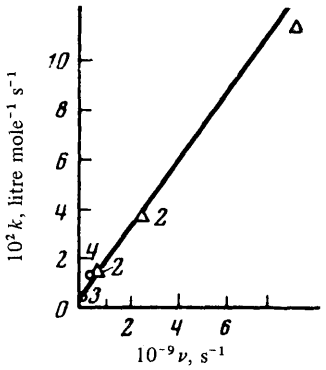


Figure 11. Direct proportionality between the rate constant for a liquid-phase reaction and the frequency of rotation of the reactant (a nitroxy-radical) at 22°C according to Griva and Denisov[24]: 1)–4) various solvents.

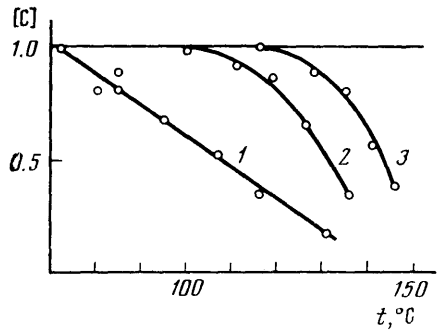


Figure 12. Curves for the annealing of radicals in crystalline adipic acid at different pressures: 1) 1 bar; 2) 2.8 kbar; 3) 4.15 kbar.

There exists a simple possibility of testing whether the process is activated and suffers from insufficient energy for its occurrence or from a deficiency of free space necessary for the organisation of the elementary migration step. The point is that v = const. during isochoric heating and the probability defined by Eqn. (26) does not change as the temperature rises. This fact, namely the independence of the isochoric viscosity of simple liquids of temperature, has been used by Bachinskii as the basis of the free volume theory of viscosity[75]. Like Jost, having carried out isochoric measurements of diffusion coefficients in ionic crystals, he demonstrated very elegantly that the marked isobaric temperature relation $D(T)$, which is a consequence of thermal expansion, is abolished when the volume is fixed[66]. Assuming that the main factor in the recombination of radicals is the appearance of vacancies, which loosen the structure and facilitate the diffusion of species toward one another, the present author carried out an experiment involving the annealing of radicals in a high-pressure bomb, which makes it possible to prevent or hinder the expansion of the crystalline specimen during heating[76]. As expected, the recombination at the usual annealing temperatures did not occur at all, and the greater was the applied pressure, the higher was the rise in the heat treatment temperature necessary to achieve an appreciable transformation for a specified duration of heat treatment (Fig. 12).

Thus the only definite claim that can be made is that the compensation effect is associated with the steric difficulties in the organisation of the elementary step in a continuous medium. The liberation of space as a result of the aggregation of vacancies is more important than the accumulation of energy, which in any case cannot be used to achieve migration through a dense screen of molecules. Having been uniformly distributed in the first coordination sphere, the nearest neighbours create an impenetrable potential barrier and only fluctuations in their packing can create a breach in this wall. It is therefore not surprising that all investigators, whatever their concern (diffusion into metals[63], recombination of radicals[58-60], or solvation phenomena[77]), inevitably concluded that the compensation effect has a cooperative mechanism. The difficulties associated with the differentiation of the assembly of molecules involved in the elementary step, out of the total number present, constitute a problem which has not been solved theoretically and which is relatively unsusceptible to experimental investigation. However, progress in this field is necessary, since it is potentially capable not only of explaining the elementary step but also of leading to the discovery of means of controlling it.

---o0o---

Even a simple change of emphasis, involving a change of attention from the energy to the entropy (packing) factor, is methodologically important for the chemical physics of the condensed state. The present author recently re-examined from this point of view the entire set of facts associated with the destruction of radicals generated by penetrating radiation in solid matrices[78]. It was found that the heterophase fluctuations associated with the transient local softening of the structure should lead in the first place (long before the unfreezing of diffusion) to the destruction of radical pairs and, increasing in scale with increasing temperature, should successfully "anneal" radicals increasingly remote from one other, which has been indicated by experimental data. When the fluctuations reach an extent sufficient not only for the establishment of contact but also for the spatial migration of the molecules, the static annealing of radical pairs gives way to diffusion-controlled destruction of randomly scattered radicals. Concepts of this kind might change from qualitative or semiquantitative ideas to rigorous constructions if the nature of molecular mobility did not have to be guessed at from indirect chemical data and could be inferred fairly definitely from direct physical measurements.

Unfortunately the chemical physics of condensed media has greatly outstripped molecular physics, and the lagging behind of the latter makes it virtually pointless to accumulate further uninterpreted data on the rate constants for elementary reactions in solid and liquid molecular media.

Nevertheless information about the structure of catalytically active centres, the complex, solvation, and hydration shells, the defective structures of crystals, and the short-range order in liquids, and especially the extension of the extremely scanty available information about molecular mobility in all such systems might sharply reduce the arbitrary features in the interpretation of chemical processes and permit a critical choice between the physical models of the elementary step.

REFERENCES

1. S.G. Entelis and R.P. Tiger, "Kinetika Reaktsii v Zhidkoi Faze" (Kinetics of Liquid-Phase Reactions), Izd. Khimiya, Moscow, 1973, p. 20.
2. T.R. Waite, J. Chem. Phys., 28, 103 (1958).
3. T. Förster, Ann. Phys., 2, 55 (1948).
4. N.N. Tunitskii and Kh.S. Bagdasar'yan, Optika i Spektrosk., 15, 100 (1963).
5. S.F. Kilin, M.S. Mikhelashvili, and I.M. Rozman, Optika i Spektrosk., 16, 1063 (1964).
6. I.N. Vasil'ev, V.P. Krongauz, and V.A. Krongauz, Kinetika i Kataliz, 5, 792 (1964); 48, 2404 (1967).
7. L.V. Mikava and I.M. Rozman, Optika i Spektrosk., 36, 347 (1974).
8. K.I. Zamaraev, R.F. Khairutdinov, A.I. Mikhailov, and V.I. Gol'dzhanskii, Dokl. Akad. Nauk SSSR, 199, 640 (1971).
9. R.F. Khairutdinov, A.I. Mikhailov, and K.I. Zamaraev, Dokl. Akad. Nauk SSSR, 200, 905 (1971).
10. K.I. Zamaraev and R.F. Khairutdinov, Chem. Phys., 4, 181 (1974).
11. T. Förster, Z. Naturforsch., 4A, 321 (1949).
12. A.D. Galanin, Zhur. Eksper. Teor. Fiz., 28, 485 (1955).
13. N. Ya. Fabrikant and E.A. Kotomin, Uch. Zap. Latv. Univ., 208, 78–92, 108–122 (1974).
14. A.B. Doktorov and A.I. Burshtein, Zhur. Eksper. Teor. Fiz., 68, 1349 (1975).
15. A.I. Burshtein and A.G. Kofman, Optika i Spektrosk., 40, 304 (1976).
16. A.I. Burshtein and Yu.I. Naberukhin, Preprint ITF-74-160R, Kiev, 1974.
17. K.M. Salikhov, Teor. Eksper. Khim., 10, 310 (1974).
18. E.I. Bodunov, Optika i Spektrosk., 34, 490 (1973).
19. T.A. Shakhverdov and E.I. Bodunov, Optika i Spektrosk., 34, 1112 (1973).
20. K.S. Schmitz and J.M. Schurr, J. Phys. Chem., 76, 534 (1972).
21. K. Solc and W.H. Stockmayer, Intern. J. Chem. Kinetics, 5, 733 (1973).
22. N.E. Edelstein, A. Kwok, and A.H. Maki, J. Chem. Phys., 41, 3473 (1964).
23. M.L. Berkovich and K.M. Salikhov, Teor. Eksper. Khim., 9, 586 (1973).
24. A.P. Griva and E.T. Denisov, Dokl. Akad. Nauk SSSR, 219, 640 (1974).
25. V.L. Tal'roze and L.A. Blyumenfel'd, Dokl. Akad. Nauk SSSR, 135, 1450 (1960).
26. W. Meyer and H. Neidel, Phys. Z., 38, 1014 (1937).
27. F.F. Vol'kenshtein, "Elektronnaya Teoriya Kataliza na Poluprovodnikakh" (Electronic Theory of Catalysis in the Presence of Semiconductors), GIFML, Moscow, 1960, p. 134.
28. H. Constable, Proc. Roy. Soc., A108, 355 (1926).
29. S.Z. Roginskii and L.V. Rozenkevich, Zhur. Fiz. Khim., 1, 293 (1930).
30. C. Hinshelwood, J. Chem. Soc., 694 (1947).
31. P.P. Kobeko, "Amorfnye Veshchestva" (Amorphous Substances), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1952, p. 88.
32. E.T. Denisov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1298 (1960).
33. O.A. Kiseleva and I.V. Sapozhnikov, Izv. Vys. Shkoly, Khim. i Khim. Tekhnol., 3, 848 (1960).
34. I.V. Sapozhnikov, Z.G. Lipetskaya, and I.I. Darienko, Zhur. Fiz. Khim., 36, 916 (1962) [Russ. J. Phys. Chem., No. 4 (1962)].
35. L.A. Blyumenfel'd, "Problemy Biologicheskoi Fiziki" (Problems of Biological Physics), Izd. Nauka, Moscow, 1974, p. 11.
36. A.I. Burshtein, B.I. Pishchevitskii, and S.P. Sham, Dokl. Akad. Nauk SSSR, 153, 852 (1963).
37. I.L. Kotlyarovskii, M.P. Terpugova, N.M. Bazhin, and M.F. Bashkirov, Izv. Akad. Nauk SSSR, Ser. Khim., 1620 (1966).
38. M.P. Terpugova, I.L. Kotlyarevskii, A.A. Mityushova, and M.F. Bashkirov, Izv. Akad. Nauk SSSR, Ser. Khim., 662 (1967).
39. V.G. Kostrovskii, E.D. Litman, A.I. Shpon'ko, V.G. Mazur, M.P. Terpugova, and I.L. Kotlyarovskii, Vysokomol. Soed., 13, 1721 (1971).
40. F. Gutmann and L. Lyons, "Organic Semiconductors" (Translated into Russian), Izd. Mir, Moscow, 1970, Chapter 7, p. 3.
41. L.I. Boguslavskii and A.V. Vannikov, "Organicheskie Poluprovodniki i Biopolimery" (Organic Semiconductors and Biopolymers), Izd. Nauka, Moscow, 1968, Chapter 1.
42. D.V. Glebov, Yu.A. Kolbanovskii, and A.S. Chernyshova, Khim. Vys. Energii, 8, 444 (1974).
43. G.I. Likhtenshtein, Biofizika, 11, 24 (1966).
44. G.I. Likhtenshtein, Doctoral Thesis, Institute of Chemical Physics, Moscow, 1971.
45. F. Gutmann, Japan. J. Appl. Phys., 8, 1417 (1969).
46. K. Higasi, "Dielectric Relaxation and Molecular Structure", Sapporo, Japan, 1961.
47. E.F. Khairetdinov, A.I. Burshtein, and V.V. Boldyrev, Fiz. Tverd. Tela, 15, 3029 (1973).
48. E.F. Khairetdinov, V.V. Boldyrev, and A.I. Burshtein, J. Solid State Chem., 10, 288 (1974).
49. R. Blini, J. Sterisnick, M. Jamsek-Vilfan, and S. Zumer, J. Chem. Phys., 54, 187 (1971).
50. E.F. Khairetdinov and V.V. Boldyrev, J. Solid State Chem., 11, 67 (1974).
51. A.I. Burshtein and Yu.D. Tsvetkov, Dokl. Akad. Nauk SSSR, 214, 369 (1974).
52. P. Yu. Butyagin, Pure Appl. Chem., 15, 641 (1972).
53. L.D. Campbell and F.D. Foley, Austral. J. Chem., 30, 57 (1972).
54. T.I. Gorbovitskaya, V.N. Belevskii, L.T. Bugaenko, and V.M. Byakov, Article Deposited at the All-Union Institute of Scientific Information (VINITI) (No. 5668-3, Dep. from 20th March, 1973); Ref. Zhur. Khim., 1661118 (1973).
55. P. Yu. Butyagin, Vysokomol. Soed., 16, 63 (1974).
56. Ya.I. Frenkel', Zhur. Eksper. Teor. Fiz., 2, 952 (1939).
57. A.G. Kofman and A.I. Burshtein, Chem. Phys., (in the Press).
58. Ya.A. Lebedev, Yu.D. Tsvetkov, and V.V. Voevodskii, Kinetika i Kataliz., 1, 496 (1960).
59. V.K. Ermolaev, A.D. Milov, and V.A. Tolkachev, Khim. Vys. Energii, 3, 224 (1969).
60. A.I. Mikhailov and Ya.S. Lebedev, Zhur. Fiz. Khim., 42, 1005 (1968) [Russ. J. Phys. Chem., No. 4 (1968)].

61. A.R.McGhie, H.Blum, and M.Labes, J.Chem.Phys., **52**, 6141 (1970).
62. A.R.McGhie, H.Blum, and M.Labes, Mol.Crystals, **5**, 245 (1969).
63. P.M.Shurygin and V.D.Shantarin, Zhur.Fiz.Khim., **42**, 463 (1968) [Russ.J.Phys.Chem., No. 2 (1968)].
64. S.D.Gertsriken and I.Ya.Dekhtyar, "Diffuziya v Metallakh i Splavakh v Tverdoi Faze" (Diffusion in Solid Metals and Alloys), Fizmatgiz, Moscow, 1960.
65. N.F.Mott and R.W.Gurney, "Electric Processes in Ionic Crystals" (Translated into Russian), Inostr. Lit., Moscow, 1950, Chapter 11.
66. W.Jost, "Diffusion in Solids, Liquids, Gases", Acad.Press, New York, 1960, p.111.
67. H.N.Nachtriev and G.S.Handler, Acta Metall., **2**, 797 (1954).
68. K.A.Osipov, Izv.Akad.Nauk SSSR, Otd.Tekh.Nauk, 35 (1957).
69. V.Z.Bugakov, "Diffuziya v Metallakh i Splavakh" (Diffusion in Metals and Alloys), Gostekhizdat, Moscow, 1949, p.35.
70. M.H.Cohen and D.Turnbull, J.Chem.Phys., **31**, 1164 (1959).
71. A.I.Burshtein, "Molekulyarnaya Fizika" (Molecular Physics), Izd.Novosibirsk.Gos.Univ., Novosibirsk, 1975, Vol.2, p.171.
72. M.W.Williams, R.F.Landell, and J.D.Ferry, J.Amer.Chem.Soc., **77**, 3701 (1955).
73. P.B.Macedo and A.Napolitano, J.Chem.Phys., **49**, 1887 (1968).
74. A.I.Burshtein and B.I.Yakobson, Chem.Phys. (in the Press).
75. A.I.Bachinskii, "Izbrannye Trudy" (Selected Works), Izd.Akad.Nauk SSSR, 1960, Vol.I, p.49.
76. S.A.Dzyuba, V.A.Tolkachev, and A.I.Burshtein, Dokl.Akad.Nauk SSSR, **223**, 633 (1975).
77. G.P.Likhtenshtein, Zhur.Fiz.Khim., **44**, 1908, 1913 (1970) [Russ.J.Phys.Chem., No.8 (1970)].
78. Ya.S.Lebedev and A.I.Burshtein, Chem.Phys., **12**, 259 (1976).
79. E.T.Denisov, Izv.Akad.Nauk SSSR, Ser.Khim., 51 (1976).
80. B.V.Bol'shakov, M.P.Fuks, V.A.Tolkatchev, and A.I.Burshtein, "Proceedings of the IV Symposium on Radiation Chemistry, Keszthely, Hungary, 1976".
81. B.V.Bol'shakov and V.A.Tolkachev, Chem.Phys. Letters, **40**, 468 (1976).

Institute of Chemical Kinetics
and Combustion, Siberian Division
of the USSR Academy of Sciences,
Novosibirsk