RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

December 1975

Translated from *Uspekhi Khimii*, **44**, 2121-2149 (1975)

U.D.C. 541.1,541.124,541.15

The Low-temperature Quantum-mechanical Limit for the Rates of Chemical Reactions

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The influence of quantum-mechanical effects on one of the fundamental laws of chemical kinetics—the Arrhenius law—is considered. Criteria characterising the limits of the low-temperature region where the extent of quantum-mechanical tunnelling transitions exceeds exponentially the transitions over the barrier are quoted. Studies of the low-temperature tunnelling of electrons and hydrogen atoms are briefly mentioned and the history of research on low-temperature radiation-induced solid-phase polymerisation, the development of which led to the discovery of the phenomenon of the low-temperature quantum-mechanical limit for the rates of chemical reactions in relation to the formaldehyde polymerisation reaction, is briefly considered.

The results of experiments using low-inertia calorimeters, whereby it is possible to determine directly the average time (τ_0) required to add one new link to the polymer chain of formaldehyde during its polymerisation by radiation and during postpolymerisation and to establish that below 80 K the increase of τ_0 slows down and that at $T \approx 10$-4 K the time τ_0 reaches a plateau ($\tau_0 \approx 0.01$ s), are described. Possible explanations of the observed low-temperature limit for the rate of a chemical reaction are critically examined and a semiquantitative explanation is given for this phenomenon, which may be particularly common in combined electronic-confirmational transitions in complex biological molecules and may play a definite role in chemical and biological evolution (cold prehistory of life?).

The bibliography includes 56 references.

CONTENTS

I.	Introduction	1019
II.	The tunnel effect in chemical kinetics (general postulates)	1021
III.	Examples of the tunnelling of hydrogen atoms and electrons at low and very low temperatures	1023
IV.	Radiation-induced solid-phase polymerisation at low and very low temperatures	1025
V.	Low-temperature radiation-induced polymerisation of formaldehyde. The observation of the low-temperature limit to the rate of chain propagation	1027
VI.	Interpretation of the low-temperature limit to the rates of chemical reactions	1030

I. INTRODUCTION

Little more than 100 years have elapsed since the discovery (1869) of the first quantitative law of chemical kinetics—Guldberg and Waage's law of mass action. The second fundamental kinetic law is 20 years more recent, having been discovered in 1889. Svante Arrhenius explained the marked temperature dependence of the rates of chemical reactions and derived his famous exponential formula, according to which the reaction rate constant k is proportional to e^{E/k_BT}, where E has since been called the activation energy (k_B is the Boltzmann constant).

It is of interest to recall certain aspects of the discovery of the Arrhenius law. The Swedish scientist investigated the inversion of cane sugar by acids in aqueous solution and suggested that sugar exists in two equilibrium forms, active and inactive, and that the equilibrium between these forms obeys the law of mass action. The rate of inversion is proportional to the concentration of the active form. Furthermore, Arrhenius believed that the rate of inversion is much lower than the rate of interconversion of the active and inactive forms of sugar, i.e. that the chemical reaction does not decrease the concentration of the active form relative to its equilibrium value, which is low in any case, and does not disturb the equilibrium between the active and inactive forms: $C_a/C = K$ (C_a is the concentration of active molecules and C that of inactive molecules). Then the rate of inversion of active sugar molecules is

$$-\frac{dC_a}{dt} \simeq -\frac{dC}{dt} = k_a C_a = k_a K C = kC, \quad (1)$$

where k_a is the actual rate constant and k the observed rate constant.

Arrhenius suggested that the rate constant for the inversion of active sugar molecules k_a is independent of temperature and that the increase of the observed rate of inversion with increasing temperature is wholly determined by the van't Hoff reaction isochore (derived from thermodynamic considerations five years earlier—in 1884):

$$\frac{d\ln k}{dT} = \frac{d\ln K}{dT} = \frac{Q}{k_B T^2}, \quad (2)$$

where Q is the energy required to convert an inactive sugar molecule into an active molecule.

Arrhenius's main idea has remained unchanged until our time. Admittedly Arrhenius assumed that the active form of the initial reactant consists of a chemical modification, whereas now we regard the active form as differing from the inactive form in having a higher energy content. However, the two approaches are by no means completely incompatible. On the contrary, the initial formulation of Arrhenius's idea was actually revived to some extent by the activated complex theory, which treats the rate of reaction on the basis of the equilibrium between the initial reactants and a transition state.

In one way or another we now define the activation energy as the difference between the average energy of the molecules entering into the chemical reaction and the average energy of all the initial molecules. In other words, the activation energy E can be defined as the height of the potential barrier which prevents the mutual approach of the reacting atoms and molecules.

Since the rate constant for a chemical reaction k is proportional to the fraction of reacting molecules with energy exceeding the activation energy E, the distribution of molecules in terms of the kinetic energy W, described by the Boltzmann equation (1868)

$$\frac{1}{N}\cdot\frac{dN}{dW} = \frac{2\pi}{(\pi k_B T)^{3/2}}\sqrt{W}\cdot e^{-\frac{W}{k_B T}}, \quad (3)$$

naturally leads to a temperature variation of the rate of reaction in accordance with the exponential Arrhenius law:

$$k = Ae^{-\frac{E}{k_B T}}. \quad (4)$$

The Arrhenius law has been confirmed by many thousands of examples over a wide range of temperatures and the activation energy has become one of the most important parameters subsequently employed in chemical kinetics.

Clearly, when many chemical reactions occur in a system, the observed temperature variation of the rate of the overall process may be more complex and may not be described by the Arrhenius law. This is illustrated by two examples in Fig. 1. Suppose that two reactions take place in the system: (1) A → B and (2) A → C with activation energies E_1 and E_2 and $E_2 > E_1$. If the formation of C in reaction *2* must be preceded by reaction *1* (for example, reaction *2* proceeds as follows: A + B → C + B), then an apparent increase of the activation energy for the formation of C will be observed as the temperature is reduced with a gradual transition from $E = E_1$ to $E = E_2$. The observed rate of appearance of C is in this case determined by the slower of the two reactions. On the other hand, if the reactions occur simultaneously, then a decrease of temperature entails an apparent decrease of the activation energy for the disappearance of A with a gradual transition from $E = E_2$ to $E = E_1$—the observed rate of decrease of the amount of A is determined by the faster of the two reactions and a decrease of temperature results in an "automatic" selection of the pathway leading to the transformation of A with the smallest activation energy. Looking ahead, we may note that the overall form of the temperature variation of k then resembles the variation obtained for a unique pathway with allowance for quantum-mechanical tunnel effects.

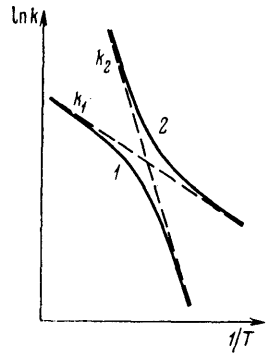


Figure 1. Characteristic temperature variation of the observed rate constant k for the disappearance of the initial reactants or for the appearance of the reaction products in two consecutive (curve *1*) and simultaneous (curve *2*) reactions with different activation energies ($E_2 > E_1$).

The introduction of quantum mechanics led to three most important consequences for chemical kinetics. Firstly, quantum mechanics explained the very presence of a potential barrier in chemical reactions. This barrier arises because electrons obey Fermi-Dirac statistics, i.e. the Pauli principle extends to them—the number of sites in each energy state is limited and for this reason exchange repulsion between electrons takes place. Secondly, when the problem of the excess energy of the reacting atoms and molecules is considered, one must consider in the general case the quantisation of the rotational, vibrational, and electronic forms of this

energy. Thirdly, and this is now the most important factor for our purposes, quantum mechanics led to the discovery of the possibility of various transitions not only over potential barriers but also through these barriers—the so called tunnelling transitions.

II. THE TUNNEL EFFECT IN CHEMICAL KINETICS (GENERAL POSTULATES)

The problem of the possible role of the tunnel effect in chemical kinetics was first formulated by Borgin[1] as early as 1929 and important contributions were made to the theoretical analysis of this problem by Roginskii and Rozenkevich's studies (1930)[2] and by the large series of studies by Bell, starting from 1933–1937.[3]

However, the attempts to observe experimentally the contribution of the tunnel effect at relatively high temperatures did not yield unambiguous results, while the region of low temperatures, where the tunnel effect should be manifested more clearly, remained uninvestigated for a long time. It was not until the 1950's that interest was aroused in the occurrence of all possible chemical reactions at low temperatures and the experimental observation of even very slow reactions of this type became possible (for example by microwave spectroscopy, by tracer atom techniques, etc.). In this connection the present author formulated in 1959 criteria characterising the limits of the low-temperature region where the tunnel effect exceeds Arrhenius transitions over the barriers and the kinetics of tunnelling transitions through symmetrical potential barriers were examined in general terms[4,5].

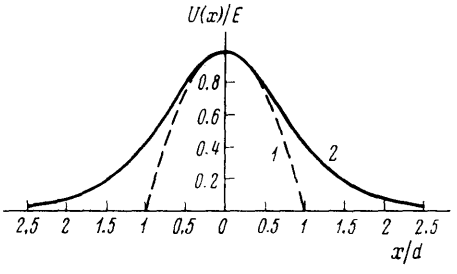


Figure 2. Typical examples of one-dimensional potential barriers: 1) parabolic; 2) Eckart.

Qualitative analysis of the temperature criteria is very simple. For a strong tunnel effect, one requires the "quantisation" of the system, i.e. its "quantum-mechanical size" λ must be greater than its classical size d. On the other hand, a low value of the ratio k_BT/E is needed in order that the transitions over the barrier should be slow. Therefore the following inequality must hold in order that the tunnel effect should predominate: $\lambda/d > k_BT/E$, or, in other words, $\hbar/d\sqrt{2mE} > k_BT/E$ or $T < (\hbar/k_Bd\sqrt{2})\sqrt{E/m}$, where E is the height of the barrier, d its half-width, and m the mass of the tunnelling species. An exact treatment yields an additional multiplier π, so that the temperature T_t below which tunnel effects predominate exponentially over Arrhenius effects is given by the following formula for any barrier described by a parabola at its apex:

$$T_t = \frac{\hbar}{k_B\pi d\sqrt{2}}\sqrt{\frac{E}{m}}. \quad (5)$$

when $E \simeq 1$ eV and $d \simeq 3$ Å, $T_t \simeq 50$ K for protons and $T_t \simeq 1600$ K for electrons.

In the formulae describing the permeability of potential barriers, it is convenient to consider the characteristic energy of the system $\epsilon = \hbar^2/md^2$ and to compare two dimensionless parameters: E/ϵ and E/k_BT.

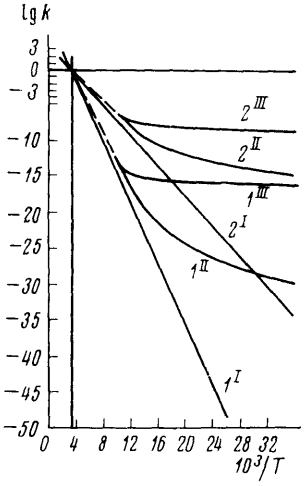


Figure 3. Temperature variation of the rates of reactions involving transitions over barriers (curves *1*II and *2*I) and with allowance for tunnelling through Eckart (curves *1*III and *2*II) or parabolic (curves *1*III and *2*III) barriers; barrier parameters: $a = 50$ (curves *1*) or $a = 25$ (curves *2*).

The typical forms of potential barriers are the parabolic barrier $U(x) = (1-x^2/d^2)E$ and the so called Eckart barrier $U(x) = ECh^{-2}x/d$ (Fig. 2). The dependence of lg k on $1/T$ with and without allowance for the tunnel effect is illustrated for both barriers in Fig. 3 with $a = \pi\sqrt{2}\sqrt{E/\epsilon} = 25$ and 50. At low temperatures ($T < T_t$) we have instead of the usual Arrhenius relation a unimolecular reaction rate constant which decreases as $T^{3/2}$ for the Eckart barrier tending towards zero, because the "bottom" of a barrier of this form is infinitely wide. On the other hand, in the case of the parabolic barrier the rate constant for a unimolecular chemical reaction reaches a plateau at low temperatures, tending to a definite limit.

A change from the continuous (Boltzmann) energy distribution to a discrete quantum-mechanical distribution of the tunnelling mass in a typical case of a symmetrical transition between systems, described by Morse potential curves (Fig. 4), does not alter the above criterion for the boundary temperature T_t of the "tunnelling region". For a quantum-mechanical distribution with respect to energy levels, the rate constant reaches a plateau at low temperatures, whatever the form of the barrier, which corresponds to a tunnelling transition from the zero-point vibrational level.

The picture described above is extremely simple but unfortunately has been used very rarely in this form. In the general case the states of the system on either side of the potential barrier are different and this alters the situation radically. Only when the tunnelling species is in a free state on either side of the barrier and is described by a planar wave is its passage through the barrier a non-resonance process and its probability varies monotonically with energy. However, a chemical reaction in no way constitutes a transition of a planar wave through the barrier, but is associated with the transition of a species or a group of species from one potential well to another—above the barrier separating these wells or through it.

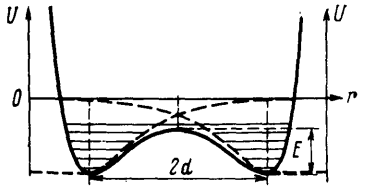


Figure 4. Schematic illustration of the barrier formed by the superposition of two "opposed" Morse potential curves.

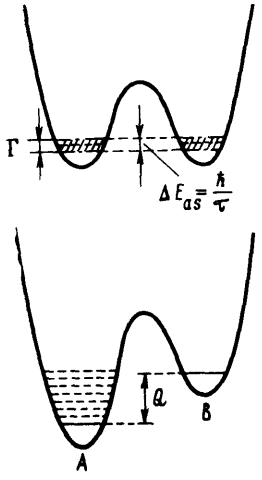


Figure 5. Schematic illustration of the distribution of energy levels in two identical and different potential wells.

The energy states of the system in each potential well are quantised; they are characterised by a set of discrete levels and tunnelling is possible only under resonance conditions, i.e. when the levels are the same in both wells. This can be illustrated by Fig. 5. If two identical "traps" which may contain an electron, for example two protons, are brought closer together, we obtain a system of two equivalent potential wells. In each of these traps taken separately the electron would exist at a certain stationary level (infinitely narrow in the ground state). In the presence of a system of two completely identical wells, the electron is delocalised—it tunnels continuously from one well to the other, and the characteristic time of such subbarrier transition τ_0 is shorter the narrower and lower the barrier separating the wells. Neither the residence of the electron in the left-hand well nor its presence in the right-hand well constitute any longer stationary states of the system and the levels of the electron in each well now have a finite width $\Gamma = \hbar/\tau_0$. In other words, neither the wave function Ψ_l (electron in the left-hand well) nor the function Ψ_r (electron in the right-hand well) are any longer eigenfunctions of the system; such functions are now their combinations—symmetrical: $\Psi_s = (1/\sqrt{2})[\Psi_l + \Psi_r]$, and antisymmetric: $\Psi_a = (1/\sqrt{2})[\Psi_l - \Psi_r]$. This implies that the system can exist in two states differing in energy by $\Delta E_{as} = \hbar/\tau$ (Fig. 5) and the two states Ψ_s and Ψ_a are the same and coincide with Ψ_l and Ψ_r only when $\tau \to \infty$ (when the two wells move apart to an infinite distance).

However, the absolute identity of the two wells is exceptionally rare or altogether impossible†. On the other hand, in the general case when the two wells differ, the levels in them become non-stationary and tunnelling transitions between the wells are possible only when the levels coincide to within $\Delta E = \hbar/\tau$, where $\tau \geqslant \tau_0$; τ_0 is the tunnelling time in the idealised case of identical wells, i.e. for an absolutely symmetrical barrier.

We shall now consider the general case of two different wells for an exothermic transfer of a certain species m between molecules A and B : $A + Bm \to Am + B$. To make the treatment specific, we shall assume that m is an electron, A an oxidant, and Bm a reductant. Since we are interested in the region of low temperatures, we shall further assume that in the initial state all the molecules Bm are in the lowest energy level—the level of zero-point vibrations.

If the level nearest (from below) to the initial level in potential well A is separated from the latter by a distance $\Delta E \gg \Delta E_0$, where $\Delta E_0 = \hbar/\tau_0$, then under adiabatic conditions, i.e. in the absence of interactions between electrons, the nuclei of the molecules A and B, and the surrounding medium, a tunnelling transition is impossible and the state of the electron in well B is stationary (to within a negligibly low rate of the radiation-induced transition: $A + Bm \to Am + B + h\nu$). In fact, under such conditions, there is simply no place to which the energy of the transition ΔE could be transferred.

For the transition to become possible, it is necessary to find a "sink" for this energy or to modify the form of the potential wells (and hence the positions of the levels in them) in such a way that the levels coincide in the two wells, i.e. the condition $\Delta E \leqslant \Delta E_0$ holds. The transfer of the energy ΔE both to an individual molecule and to the crystal lattice can serve as a "sink". In the region of low energies (when $\Delta E \leqslant 0.02$ eV) the dissipation of the energy ΔE is associated with the excitation of the vibrational lattice quanta—phonons. In the present instance we are considering the "softest" region of the vibrational lattice spectrum—its acoustic branches, and there is a

† For example, even the transfer of an electron ($H + H^+ \to H^+ + H$) or an H atom ($H + H_2 \to H_2 + H$) might be regarded as a transition between two absolutely identical wells only in terms of the approximation of a complete absence or a complete equality of the interactions [interaction energies?] of H and H^+ on the one hand and H and H_2 on the other with the surrounding medium, which is not as a rule the case.

possibility not only of single-phonon but also of multiphonon transitions, in particular two-phonon transitions with absorption of the energy ΔE. For large energies (up to 0.2–1 eV), the energy ΔE is consumed in the excitation of normal vibrations in molecules or of high-frequency, optical branches of the vibrational spectra of the molecular crystal lattices.

The interaction of electrons and nuclei, responsible for the dissipation of the electronic excitation energy via vibrational degrees of freedom, permits non-adiabatic electronic transitions in which the Franck–Condon principle does not hold and the internuclear distance changes. At the same time the interaction of electrons and nuclei broadens the levels approximately by the factor $\sqrt{M/m}$, where M is the mass of the nucleus and m the mass of the electron, and this also promotes tunnelling, decreasing ΔE as a result of the possibility of the mutual approach and overlapping of the edges of the broadened levels. The broadening of the levels occurs also due to the interaction of the molecules with their environment (which is characteristic of a condensed phase), when the system comprising two potential wells is no longer adiabatic. Such interaction in fact leads to the appearance of a band in the optical branches of vibrational lattice spectrum instead of the vibrational spectral lines due to individual molecules.

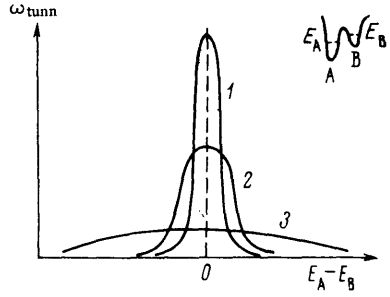


Figure 6. Illustration of the broadening of the levels and of the corresponding decrease of the maximum probability of resonance transitions ω_{tunn}; $(\Gamma A)_1 < (\Gamma A)_2 < (\Gamma A)_3$.

As happens in any type of level broadening, the probability integral for the transition to each given level remains unchanged and consequently the maximum resonance probability of the transition characteristic of narrow levels decreases sharply (Fig. 6). The situation with an extremely high probability of tunnelling transitions within narrow resonances, associated with a complete absence of such transitions between resonances, is replaced by a much weaker (i.e. slow) tunnelling transition over a wide range of energies, which, however, depends little on the excitation energy. The exponential decrease of reaction rate with decreasing temperature should therefore be gradually retarded, reaching a plateau, as in the case of two identical wells; however, even at $T \to 0$ there remains a finite and sometimes measureable probability of a tunnelling transition from the zero-point vibrational level in the initial potential well to the virtually continuous spectrum of vibrations in the final potential well.

Another variant of tunnelling transitions—as a result of the equalisation of the levels in the two wells ($\Delta E \lesssim \Delta E_0$)—is associated with the fluctuations in time of the magnitude of the polarisation interaction of Am and Bm with the surrounding medium, for example the interaction of charged molecules with the dipoles moving around them[6,7]. Such fluctuations correspond to a time dependence of the configurations (depths and shapes) of both potential wells shown in Fig. 5. The levels in the two wells are then displaced (over a period of time) upwards and downwards and in the course of such displacement the positions of the levels in A and B may coincide for a brief period, which implies the occurrence of the resonance condition necessary for tunnelling. However, in this variant the fluctuations are frozen at very low temperatures and, when the levels in the "frozen" wells do not overlap and interaction with the surrounding medium (discussed above) is not included, the rate of reaction tends to zero or more precisely to an extremely low value characteristic of radiation-induced transitions.

Thus, although the quantum-mechanical properties of the substance, namely the presence of the zero-point vibrational level, and the tunnel effect involving transitions through potential barriers lead in principle to the possibility of chemical reactions even at the very lowest temperatures, one can in no way assert *a priori* that chemical reactions can occur at measureable rates in the vicinity of the absolute zero. Only experiments can provide an answer to this question.

III. EXAMPLES OF THE TUNNELLING OF HYDROGEN ATOMS AND ELECTRONS AT LOW AND VERY LOW TEMPERATURES‡

All experimental studies on the problem of tunnelling transitions carried out until recently can be divided into two groups depending on whether processes involving the transfer of hydrogen atoms or electrons were observed.

The available data (quantitative or semiquantitative) for hydrogen-atom transfer reactions, which may indicate an appreciable contribution of tunnelling transitions, are listed in the Table. Among these data, the most complete results were obtained in a study of the displacement of the free-radical state in the radical pairs of γ-irradiated dimethylglyoxime (Yakimchenko and Lebedev[8]). It was shown that the temperature variation of the rate of reaction becomes much less pronounced at low temperatures—the observed activation energy falls from 7.3 kcal mole^{-1} at 190–220 K to 1.4 kcal mole^{-1} at 77–110 K and in addition a marked retardation (by 3–5 orders of magnitude) of the substitution of hydrogen by deuterium is observed. Thus the presence of the tunnel effect was clearly demonstrated. Comparison of the experimental data with the present authors' 1959 calculations[4] (Fig. 7) made it possible to determine the parameters of the activation barrier: $E = 15 \pm 1$ kcal mole^{-1} and $d = 0.6 \pm 0.1$ Å.

‡ The concept of "low temperatures" is fairly arbitrary and in addition is different in physics and chemistry. In physics low temperatures are usually understood as temperatures below 4 K (liquid helium). In chemistry the temperature range from 195 K (dry ice) to 77 K (liquid nitrogen) is referred to as low temperatures, while temperatures below 77 K are regarded as ultralow.

However, all the experimental data on tunnelling by hydrogen atoms so far refer to relatively high temperatures (in excess of 77 K) and the attainment of a plateau by the rate of such reactions has not been observed in any investigation—the observed activation energy has not been less than about 0.05 eV. The attainment of a limiting rate at low temperatures (down to 4.2 K, with a direct determination of the rate) has until very recently been observed only in electron transfer processes. Thus De Vault and Chance[9,10] and Grigorov[11] demonstrated that the rate of electron transfer from cytochrome *c* to chlorophyll is independent of temperature in the range 4.2–77 K (Fig. 8). The present author investigated[12] the trapping of electrons by O^- ions in irradiated alkaline ice and showed that the rate of such trapping $e^-_{tr}+O^- \rightarrow O^{2-}$ does not change between 4.2 and 120 K.

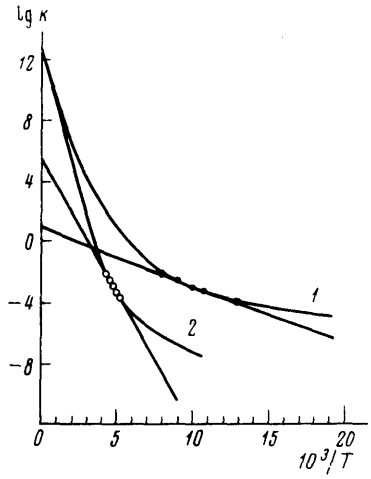


Figure 7. Calculated and experimental temperature variation (in terms of the Arrhenius coordinates) of the rates of reactions involving the transfer of hydrogen atoms (curve *1*) or deuterium atoms (curve *2*) in γ-irradiated dimethylglyoxime crystals.

In all similar cases one is dealing with the tunnelling transfer of electrons over large distances, amounting to several tens of angstroms (for $d \simeq 30$ Å and $E \simeq 1$ eV, we have $T_t \simeq 160$ K). The occurrence of such transfer explains the large radii corresponding to the trapping of electrons by acceptors[13] and the low concentrations of the ionic species stabilised on radiolysis[14] and holds out great promise that a whole series of new kinetic phenomena may be discovered. For example, in the low-temperature radiolysis of solid organic substances a decrease of the probability of electron stabilisation should be observed with increase in the concentration of traps in excess of limiting concentrations of ions, $[T] > [I]_{lim}$, since, under conditions where the distance between traps is less than the distance of effective tunnelling transfer, an electron tunnelling from one trap to another will roll down towards the cation B^+. Another, more "chemical" effect is associated with the fact that the displacement of the reactants in solid-phase reactions usually takes place at very low frequencies ($\nu_m \simeq 1\ s^{-1}$) and therefore species with charges of different signs (A^- and B^+) will neutralise one another in consequence of electron transfer by tunnelling before they meet in the reaction cage, i.e. while there are still several layers of neutral matrix molecules M between them.

$$A^- + M + B^+ \rightarrow A + M + B\ .$$

The subsequent reaction, if it occurs at all, would now involve a homolytic mechanism.

Thus, by ensuring the occurrence of reactions between spatially separated species in the solid phase, the tunnel effect can alter the reaction mechanism and even the final radiolysis products formed. Estimates have demonstrated the possibility of this type of electron trapping and of the separation in time of charge recombination processes and the subsequent chemical reaction even in viscous liquids. In general, in the liquid phase the tunnel effect weakens significantly the influence of the electrostatic interaction between reactants bearing charges of the same sign.

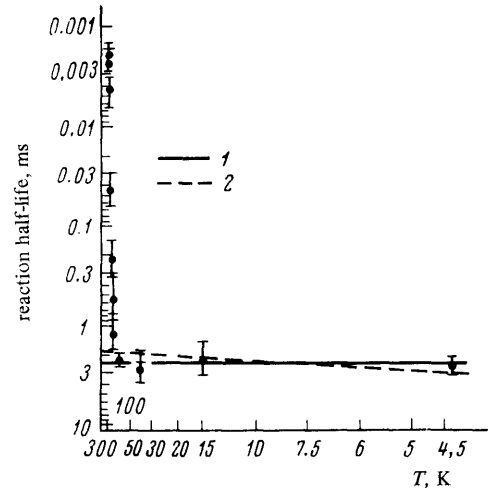


Figure 8. Experimental data of De Vault and Chance[9,10] for the rate of oxidation of cytochrome *c* by chlorophyll at different temperatures: 1) $E = 0$; 2) $E = 4$ cal mole^{-1}.

In polymer chemistry and in biochemistry the tunnel effect can ensure electron transfer between macromolecular fragments which cannot collide, for example because of steric hindrance. A theoretical interpretation of electron transfer by tunnelling over large distances between complex biological molecules with allowance for the possibility of simultaneous conformational changes in these molecules has been recently developed by Chernavskii, Blyumenfel'd, and other Soviet workers (see, for example, Refs. 15 and 16) and we shall return to this topic.

However, it must be emphasised that so far electron transfer from one species to another can hardly be called a genuine chemical reaction. Such a reaction necessarily involves a rearrangement of atoms or at least a change in valence bond lengths and in the corresponding angles, i.e. a displacement of atoms in space.

Reactions with transfer of hydrogen atoms by tunnelling.

Reaction	T, K	Pre-exponential factor Z, s^{-1}	E, cal $mole^{-1}$	System	Remarks
$HON[C(CH_3)_2]NO^{\cdot} \rightarrow ON[C(CH_3)_2]NOH$, i.e. $R:NO^{\cdot} + R:NOH \rightarrow R:NOH + R:NO^{\cdot}$	77—110	H:1.5	1400±70	γ-Irradiated dimethylglyoxime single crystals	O.E.Yakimchenko and Ya.S.Lebedev, Int. J. Rad. Phys. Chem., 3, 17 (1971)
	190—220	D:6·10⁴	7300±700		
	270—310	H:3·10⁴	17700±700		
	310—340	D:1.7·10¹³	24200±400		
$\dot{C}H_3 + CH_3CN \rightarrow CH_4 + \dot{C}H_2CN$	77—87	$(k^H/k^D > 140$ at 87 K)	1400±100	γ-Irradiated acetonitrile	R.J.Le Roy et al., J.Phys. Chem., 76, 546 (1972)
$\dot{C}H_3 + \sim Si(CH_3)_2-O \sim \rightarrow CH_4 + \sim Si(\dot{C}H_2)(CH_3)-O \sim$	77—105	H:$10^{0.6}$	1500	Polyphenylmethylsiloxane (amorphous phase)	E.L.Zhuzhgov, Thesis, Novosibirsk, 1973
		H:$10^{0.9}$	1500		
		H:$10^{1.5}$	2200	Polydimethylsiloxane (amorphous phase)	
		H:$10^{2.1}$	2200	Polyphenylmethylsiloxane (crystalline phase)	
				Polydimethylsiloxane (crystalline phase)	
$\dot{H} + \sim C(CH_3)_2CH_2C(CH_3)_2 \sim \rightarrow H_2 + \sim C(CH_3)_2\dot{C}H \cdot C(CH_3)_2 \sim$	100—150	H:$10^{8.2}$	2000±400	Reaction on the surface of polyisobutylene	A.M.Dubinskaya and P.Yu.Butyagin, Dokl. Akad. Nauk, SSSR, 211, 141 (1973)
$\dot{H} + \sim CH_2CH_2O \sim \rightarrow H_2 + \sim CH_2\dot{C}HO \sim$	100—150	H:$10^{4.9}$	1200±300	Reaction on the surface of polyepoxyethane	

IV. RADIATION-INDUCED SOLID-PHASE POLYMERISATION AT LOW AND VERY LOW TEMPERATURES

Typical examples of chemical reactions in the full sense of this word include polymerisation reactions. These are chain reactions: after the appearance under the influence of light, radiation, or other factors of the primary active centre, i.e. after the endothermic chain initiation step, the subsequent exothermic chain propagation process, ending in chain termination, takes place spontaneously.

It is not surprising that low-temperature solid-phase polymerisation (particularly radiation-induced polymerisation, i.e. initiated by penetrating radiation) has long attracted the attention of investigators. The first example of such polymerisation was the observation of the radiation-induced polymerisation of solid acrylamide by Mesrobian et al. in 1954[17]. Subsequently a number of fundamental studies on solid-phase radiation-induced polymerisation at low temperatures were carried out by Magat, Shapiro, and others in France, by Okamura, Tabata, and others in Japan, and by Bamford and others in England.

The history of the early studies on this problem has been discussed in a number of monographs and reviews (see, for example, Refs. 18–25) and there is therefore no point in considering it in detail here. A common feature of these early investigations was that the yield of the polymer from a particular radiation dose on the frozen monomer at a specific low temperature was not determined at the experimental temperature but only after heating and fusion of the irradiated monomer. As a result, it remained uncertain, even in those cases where the slope of the curves relating the yield of the polymer to the irradiation dose [characterising the radiation yield of the polymerisation (i.e. the number of polymerising molecules G per 100 eV of the radiation energy)] was independent of temperature, whether this was not caused, for example, simply by the fact that during the low-temperature irradiation only the initial active polymerisation centres are generated, while the polymeric chains grow after irradiation or even during the warming process, for example, always at the same temperature (at the melting point).

The next stage was the investigation of the solid-phase polymerisation of a number of monomers at the Institute of Chemical Physics of the USSR Academy of Sciences, where the usual gravimetric determination of the yield of polymers after warming the irradiated monomers was supplemented by monitoring the warming process calorimetrically[25–28]. Since it was impossible to observe under these conditions the additional heat evolution due to polymerisation, it was concluded that the solid monomers were polymerised directly in the course of irradiation. The results of such experiments are presented in Fig. 9. Seemingly they lead to the conclusion that there is no activation energy for the polymerisation of many solid monomers even at relatively high temperatures—from the melting point down to liquid nitrogen temperature. Subsequently it was, however, shown that at that time such a conclusion would have been premature and unjustified.

In many cases the temperature variation of the yield of the radiation-induced solid-phase polymerisation was found to differ significantly from a simple plateau and depended markedly on the phase state of the irradiated monomers (the example of acrylonitrile proved to be particularly complex[29,30]). It became clear that the sensitivity of the calorimeters used in the investigations[25–28] was far too low to ensure the observation of postpolymerisation during the warming process.

Finally, it must be specially emphasised that the temperature independence of the polymerisation radiation yield (it was in fact this quantity and not the true rate of propagation of polymer chains that was determined in all the investigations where the polymer yield–radiation dose curves were measured) does not by itself demonstrate that the low-temperatures solid-phase polymerisation is a non-activated process, because the radiation yield G depends (this will be discussed further below) on two kinetic constants—the rate constants for the propagation and termination of polymer chains—and the temperature variation of G is accordingly determined by at least two fundamental activation energies. Even the most accurate measurements of the slopes of the polymer yield–dose curves (i.e. the determination of the radiation yields of polymerisation) cannot alone provide information about the rate of polymerisation, but they do give information about the rate constants for the fundamental polymer chain propagation and termination processes and about the presence or absence of activation energy in these fundamental processes as long as the time resolution of the measuring method does not become shorter than the characteristic time of the polymer chain propagation process. It became clear that it is necessary not only to improve sharply the accuracy of the calorimetric method

but also to decrease at the same time its inertia, so that one must learn to observe the magnitude and rate of heat evolution during irradiation itself rather than during the postpolymerisation and heating of the irradiated monomers. Since the retardation of any activated processes must be manifested more clearly the lower the temperature of the medium, the extension of research on radiation-induced solid-phase polymerisation to lower temperatures—to liquid helium temperature (4.2 K)—became extremely urgent.

In 1965 Abkin and coworkers at the Karpov Physicochemical Institute observed the formation of polymers in tetrafluoroethylene and acrylonitrile irradiated at liquid helium temperature[31]. Almost simultaneously a group of investigators at the Institute of Chemical Physics submitted for publication reports of the formation of polymers in acrylonitrile and hexamethylcyclotrisiloxane irradiated at 4 K.[32] Both publications appeared at the beginning of 1966. However, in the light of what has been said about the apparent absence of an activation energy in radiation-induced solid-phase polymerisation above 77 K (Fig. 9), it is clear that these data[31,32] could not provide an answer to the question whether the polymers were really formed during irradiation at liquid helium temperature (they were even less likely to yield the rate of propagation of the polymer chain under these conditions) or in the subsequent process during heating. Thus the problem of the possible direct polymerisation in the vicinity of 4 K continued to remain controversial.

A number of interesting studies designed to solve this problem were carried out in subsequent years by Abkin and coworkers. They investigated the polymerisation of four monomers: tetrafluoroethylene (TFE), acrolein, vinyl acetate, and acrylonitrile; the study of the first two substances was particularly detailed. Experiments involving the addition of inhibitors to TFE irradiated at low temperatures or its "bleaching" (irradiation with visible or ultraviolet light leading to the destruction of active polymerisation centres) made it possible to separate the polymerisation effects during irradiation and postpolymerisation. After the application of corrections for postpolymerisation, the polymerisation yield at 77 K was found to be close to 2% (for an irradiation dose of about 50 Mrad).[33] As regards irradiation in liquid helium, "additional data indicating the formation of small amounts of polymer in the TFE crystal irradiated at 4.2 K were obtained with the aid of the radiothermoluminescence method".[33] This conclusion was supported also by the formation of fluoroalkyl macroradicals of the type $\sim CF_2-\dot{C}F-CF_2\sim$ detected by ESR in the irradiation of TFE near 4 K.[34]

Acrolein was a second object of detailed study by Abkin and coworkers[35,36]. Using the variation of the relative contributions of the isotactic and syndiotactic addition of new units to the growing polymer chain with the irradiation temperature of the solid monomer, which they observed by infrared spectroscopy, the authors[35-38] showed that part of the polymer is formed directly during irradiation even at the temperature of liquid helium. The initial macroscopic rate of polymerisation, defined as $dP/dt = (k_i k_p/k_t) I[M_0]$ {where k_i, k_p, and k_t are the rate constants for polymer chain initiation, propagation, and termination respectively, I is the intensity of ionising radiation (dose rate), and $[M_0]$ is the initial monomer concentration} was about 0.1% h^{-1} at I = 1800 rad s^{-1}.[37]

In their interpretation of the results of these experiments, the authors[37] concluded that the formation of polyacrolein at very low temperatures indicates an appreciable

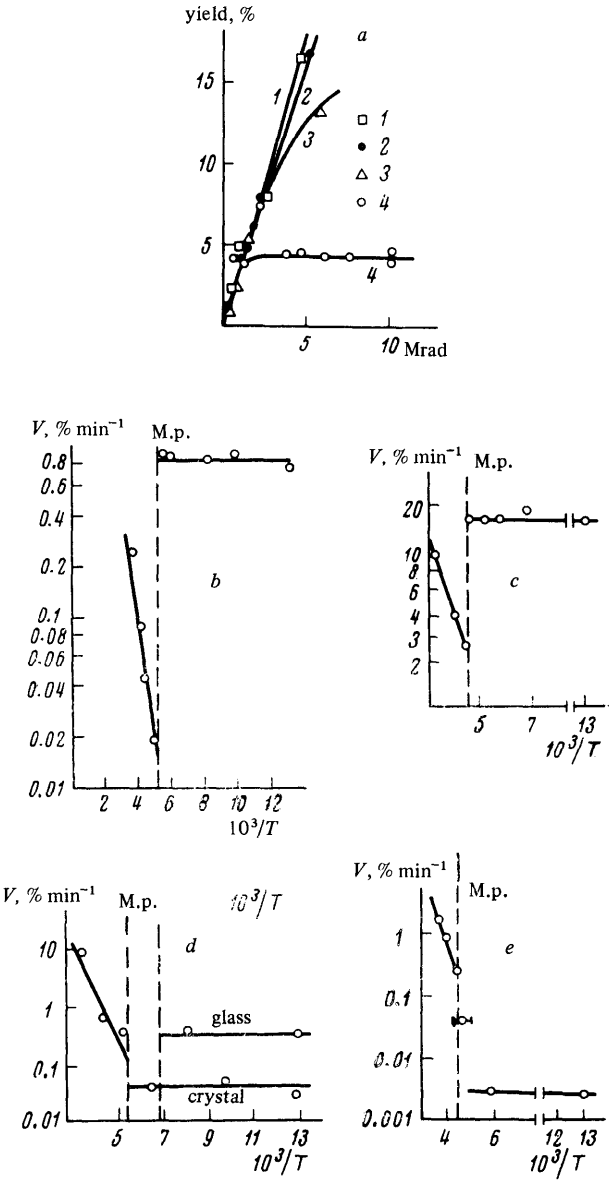


Figure 9. *a*) Variation of the polymer yield with radiation dose for acrylonitrile (AN) in the solid state at different temperatures [temperature (K): 1) 166; 2) 153; 3) 133; 4) 77]; *b*)–*e*) variation of the initial slope (V) of the polymer yield–radiation dose curves with the reciprocal of temperature for four monomers according to data obtained in studies[26-28] in which the gravimetric determination of the yield of polymer in warmed irradiated monomers was supplemented by the calorimetric monitoring of the warming process [*b*) AN, $I \simeq 0.3$ Mrad min^{-1}; *c*) formaldehyde (FA), $I \simeq 10$ Mrad min^{-1}; *d*) vinyl acetate (VA), $I \simeq 10$ Mrad min^{-1}; *e*) methyl methacrylate (MMA), $I \simeq 0.75$ Mrad min^{-1}]. The plateau at low temperatures (apparent absence of activation energy) corresponds to the following radiation yields of the polymerisation reaction: $G \simeq 400$ (AN), $G \simeq 10$ (VA—glass) and $G \simeq 1$ (VA—crystal), $G \simeq 5 \times 10^8$ (FA), and $G \simeq 3$ (MMA). The data in this figure were taken from studies carried out at the Institute of Chemical Physics of the USSR Academy of Sciences at the beginning of the 1960's.[25-28]

mobility of the monomer molecules in the irradiated crystal, and the attainment of a "limiting" yield of the polymer (i.e. the appearance of a plateau on the yield–dose curves) at very low percentage conversions suggests that only a small fraction of monomer molecules exhibit this type of high mobility. Abkin and his coworkers expressed the view that mobile molecules of this kind are distributed in the regions of dislocations and extended defects at the monomer grain boundaries and that in such regions diffusion is considerably facilitated and may proceed virtually without activation energy.

Analysing the role of ionising radiation in low-temperature polymerisation processes, Abkin and coworkers concluded that, "in solid-phase polymerisation the effect of radiation is manifested not only in initiation steps but also in chain propagation reactions as a result of the transformation of the radiation energy into the kinetic energy of the molecules localised near dislocations"[30]. They believe that, together with radiation, the energy of polymerisation itself is a factor which may ensure chain propagation: "radiation-induced polymerisation in the crystal is possible only as a result of the conversion of the radiation energy into the energy of intermolecular motion. This conversion is probably only the initial step in the growth of the polymer chain; subsequently chain propagation takes place owing to the energy evolved on polymerisation".[40]

Calculation (from the numerical characteristics of the relations between the yield and dose indicated above) of the so called radiation yields of polymerisation G, i.e. the number of molecules polymerising per 100 eV of the radiation energy, gives the following values: $G \simeq 4$ for TFE at 77 K and $G \simeq 2.5$ for acrolein at 4 K. Much higher radiation yields are usually characteristic of chain reactions. However, on the hypothesis that polymer chains cannot grow throughout the crystal but only at dislocations and extended defects, the yield of the polymer must be attributed only to the part of the energy absorbed in regions capable of polymerisation and not to the entire radiation energy absorbed by the solid monomer, which may significantly increase the values of G compared with those quoted above.

The development of the present author's research, in which the observation of the formation of a polymer in monomers irradiated at liquid helium temperature was continued[32], followed different paths. The author assumed the necessity for a direct determination of the rate constants for the propagation (k_p) and termination (k_t) of polymer chains.

The length of kinetic chains ν is determined by the ratio of the probabilities of the propagation and termination of these chains: $\nu = k_p/k_t$. The macroscopic rate constant for the accumulation of the polymer in the irradiated monomer, determined from the yield–dose curves, is a complex quantity, which, as stated above, is defined by the expression $k = k_i k_p/k_t = k_i\nu$. Therefore the absence of a temperature variation of this effective constant (or in other words the independence of the radiation yield of the polymer G of temperature) by itself implies merely a small difference between the activation energies for chain propagation and termination, but not that each of these quantities is itself small.

Another variant of solid-state polymerisation involving an apparent absence of activation energy is possible. It was pointed out by the present author as early as 1963–1965[26-28] to explain the apparent absence of activation energy in the solid-phase polymerisation of a number of monomers illustrated in Fig. 9—from the melting point down to 77 K: "We are dealing with a polymerisation mechanism in which the chain length is not determined by the competition between chain termination and propagation at each unit but by some kind of steric conditions, i.e. when the chain length is predetermined by the properties of the material. All temperature dependence then disappears from the expression for the rate of radiation-induced polymerisation $\{k_i I[M_0]\nu\}$, where the only temperature-dependent term is usually the chain length. However, in this case the chain propagation time is determined by the presence of activation energy in each unit of the chain ..."[26,28].

In the light of these considerations, the present author's aim was to determine directly the propagation time of the polymer chain $\tau = 1/k_t = \nu/k_p$ and its temperature variation in order to establish how temperature influences the duration of the fundamental polymer chain propagation steps $\tau_0 = \tau/\nu = 1/k_p$, whether or not the rates of these fundamental steps tend to a limit or become vanishingly small as the temperature is reduced.

V. LOW-TEMPERATURE RADIATION-INDUCED POLYMERISATION OF FORMALDEHYDE. THE OBSERVATION OF THE LOW-TEMPERATURE LIMIT TO THE RATE OF CHAIN PROPAGATION

In a series of studies in 1971–1972 by a group of workers at the Institute of Chemical Physics and the Branch of the Institute at Chernogolovka, including Barkolov, Kaplan, Kiryukhin, and the author of the review, it was possible to observe for the first time the phenomenon of the low-temperature limit to the rate of the chemical reaction in the radiation-initiated polymerisation of formaldehyde (FA). Here the fundamental chemical polymer chain propagation step may be, as shown in Fig. 10, the tunnelling transfer of either an electron or a hydrogen atom. However, in both cases the polymerisation should be accompanied by the approach of the formaldehyde molecule as a whole to the polymer chain, since the density of polyformaldehyde is higher than that of the initial monomer. Consequently the fundamental polymer chain propagation step involves a decrease in the effective distance between neighbouring CH_2O groups by an amount $\Delta\bar{a} = \bar{d}_0 - \bar{a}_f$, where $\bar{d}_0$ is the corresponding distance in the monomer crystal and $\bar{a}_f$ in the polymer chain. At the same time the valence angles of the CH and CO bonds are also altered. Thus in this case the fundamental chemical reaction step takes place in the full sense of the word.

In a series of the present author's experiments on the low-temperature radiation-induced polymerisation of formaldehyde in the solid phase[41-44] by a calorimetric method, the polymer chain propagation time was determined directly. At temperatures exceeding 80 K this time was found with the aid of an adiabatic low-inertia film calorimeter[42]. The design of the calorimeter is illustrated in Fig. 11. It consisted of an aluminium disc *1* 20 mm in diameter and 0.05 mm thick. A resistance thermometer *2* and a calibration heater *3* were glued to the lower side of the disc. The disc was suspended on thin conducting leads within a copper heat shield *4*. The entire assembly was placed in a glass vacuum jacket provided with a carbon adsorption pump *5*. The complete calorimeter was placed in a Dewar vessel containing liquid nitrogen.

Gaseous formaldehyde was frozen onto the calorimeter disc via a heated Kovar capillary *6*. The weight of the test substance in the experiments using this calorimeter

was varied from 15 to 75 mg, which corresponded to a layer thickness on the calorimeter disc of 0.1–0.5 mm. In order to record the calorimeter signal, a multichannel moving coil oscillograph was used. In the determination of the inertia of the calorimeter the calibration current pulse and the calorimeter response were recorded simultaneously on the same apparatus. The calibration was achieved in two ways—with the aid of the calibration heater and by heating the calorimeter by γ-radiation (this leads to uniform heating of the calorimeter disc with the monomer). Fig. 12 shows that the inertia of the calorimeter was 0.3–0.5 s.

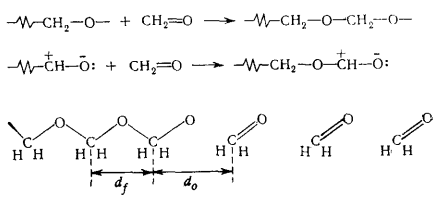


Figure 10. Fundamental processes and a simplified schematic geometrical illustration of the polymerisation of formaldehyde.

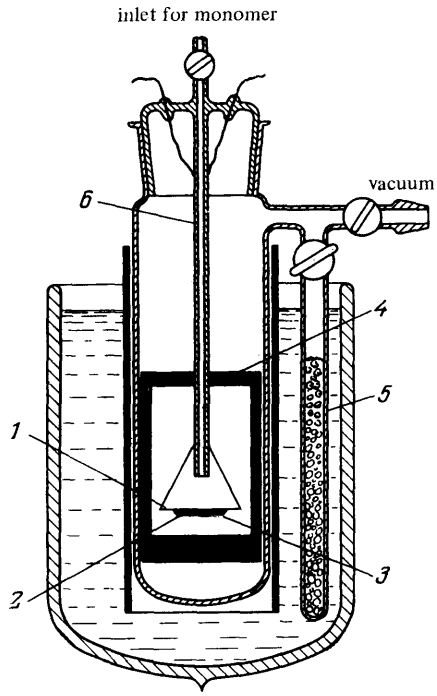


Figure 11. Schematic illustration of the low-inertia adiabatic film calorimeter.

Most of the present author's experiments on radiation-induced polymerisation were carried out using the γ-radiation from ^{60}Co apparatus. However, since the radiation sources in this apparatus were raised mechanically to the working position so that the dose rate reached a maximum in 60–70 s, the kinetics of the initial polymerisation stage might have been distorted by the change in the intensity of the initiating radiation with time. To avoid this, the bremsstrahlung from an electron accelerator with an energy of 5 MeV was used to initiate the polymerisation in the above experiments. This radiation source could be switched on and off in only a few microseconds.

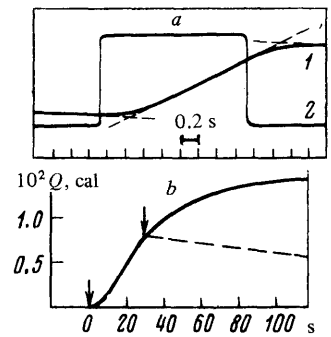


Figure 12. *a*) Calibration oscillogram for the film calorimeter [1) time variation of the calorimeter signal; 2) current flowing through the calibration heater of the calorimeter]; *b*) kinetics of heat evolution in the polymerisation of formaldehyde in the field of γ-bremsstrahlung [temperature 80 K; weight of formaldehyde 0.03 g (thickness of layer approximately 0.2 mm); dose rate 7 rad s^{-1}]. The arrows indicate the instants when the electron beam was switched on and off. Dashed line—calorimeter signal in the calibration experiment.

Initially the dose rates of the bremsstrahlung were measured with the aid of a film calorimeter—they varied linearly in the range from 3 to 40 rad s^{-1} with increase of the electron current on the stopping target from 1 to 12 μA. Fig. 12 presents the results of experiments on the polymerisation of solid formaldehyde in the bremsstrahlung field. The rate of polymerisation reached a constant value (the attainment of a linear increase of heat evolution with time) in 2–3 s; this is also the polymer chain propagation time, after which the rate of chain termination is equal to the rate of the radiation-induced initiation, i.e. the number of chains growing simultaneously in the system becomes constant.

In the temperature range 4–80 K a diathermal calorimeter, the design of which is illustrated in Fig. 13, was used to measure the polymer chain propagation time in solid formaldehyde. The calorimeter shell consisted of a thin-walled Kovar capillary *1* (2 mm in diameter), which was evacuated after the introduction of the monomer, filled with the helium heat exchanger, and sealed off. A calibration heater *2* was wound on the outer surface of the Kovar capillary and a copper–gold–iron thermocouple *3* was attached. The thermocouple recorded to within 0.5 K the temperature drop across the diathermal shell, i.e. between the calorimeter shell *1* and the copper shield *6*, which was in thermal contact with liquid helium, i.e. was at a temperature of 4.2 K. Thus the absolute measurement of experimental temperature was achieved with the aid of this capillary at the All-Union Institute of

Physicotechnical and Radiotechnical Measurements (VNIIFTRI) in accordance with a USSR State Standard. The calorimeter was suspended in a glass vacuum jacket *4* surrounded by the copper shield. The entire assembly was placed in a helium bath within a glass cryostat *5*, so that the temperature could be varied by raising the capillary with the formaldehyde to a particular height above the level of liquid helium in the bath and also by balancing the evaporator heater and the calorimeter heater. The calorimeter was calibrated both with the aid of the calibration heater and by heating the calorimeter by the γ-radiation itself, a special low-inertia device with a dropping lead diaphragm for rapid (about 0.05 s) application of the radiation field being used in these experiments.

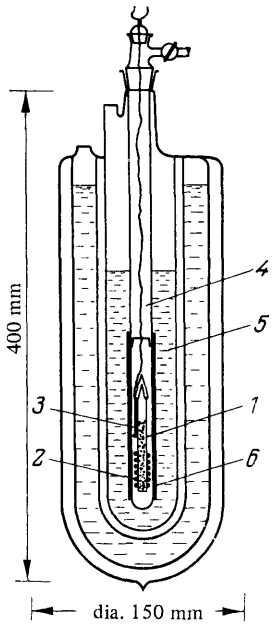


Figure 13. Schematic illustration of the diathermal calorimeter used in low-temperature experiments.

By fitting the $W = W_0(1 - e^{-t/\tau})$ curve to the plot in Fig. 14 (curve *1*) of the increasing rate of polymerisation after switching on the initiating radiation, it was possible to determine the characteristic process time τ, i.e. the average polymer chain propagation time in formaldehyde. Below 10 K, this time approached 10 s. Analogous experiments with polyformaldehyde, which was heated entirely by the absorption of γ-radiation, made it possible to measure the characteristic calorimeter time τ_c at different temperatures ($\tau_c \simeq 1$–4 s at 4–20 K)—see curve *2* in Fig. 14.

For a correct interpretation of the experiments carried out near the helium temperature (5–20 K), the problem of the possible increase of temperature within the irradiated monomer block as a result of the radiation energy and heat of polymerisation is extremely significant. The heat capacity of a substance near the absolute zero decreases sharply as the temperature is reduced. An idea about the maximum possible temperature rise within the monomer block can be obtained by estimating the adiabatic temperature rise in the system during 2–3 s, i.e. the period during which thermal equilibrium was established in the system. There are no literature data for the heat capacities of solid formaldehyde. Using the same calorimeter, the present author estimated the specific heat of formaldehyde at 6–7 K, approximately 2×10^{-3} cal $g^{-1} K^{-1}$ being obtained (the accuracy of these determinations did not exceed 50%). We may note that the result was of the same order of magnitude as the low-temperature specific heats of other organic substances, for example acrylonitrile (6×10^{-3} cal $g^{-1} K^{-1}$ at 10 K) and benzene (0.8×10^{-3} cal $g^{-1} K^{-1}$ at 6 K). It also proved to be close to the estimates based on the Debye approximation, if one assumes that the Debye temperature $\theta \simeq 100$ K, the value determined for a number of molecular crystals.

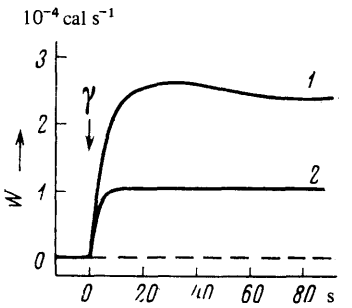


Figure 14. Variation of the rate of heat evolution in the initial period of the irradiation of specimens in the diathermal calorimeter: 1) irradiated tubes with the monomer (0.25 g); 2) irradiated tubes with polyformaldehyde (polymer sample 0.25 g, about 1 g together with tube); dose rate $I = 45$ rad s^{-1}.

Curve *2* in Fig. 14 shows that the heat evolution due to the absorbed radiation (45 rad s^{-1}) in the 0.25 g specimen (about 1 g together with the support) did not exceed 10^{-4} cal s^{-1}. In view of the specific heat of formaldehyde stated above, this corresponds to an adiabatic heating rate of about 0.1 K in 2–3 s. The heat evolution due to the polymerisation of formaldehyde at the above dose rate amounted to about 1.5×10^{-4} cal s^{-1} in a 0.25 g specimen (Fig. 14, curve *1*). This heat evolution was capable of giving rise to a heating rate somewhat higher than that due to irradiation but not exceeding 0.5 K in 2–3 s.

In separate experiments with an adiabatic calorimeter at 80–140 K, the present author determined the heat of polymerisation of formaldehyde, which proved to be 8.5 ± 1 kcal $mole^{-1}$. Having adopted the same value also at lower temperatures and having determined experimentally the rate of heat evolution due to polymerisation at different specified dose rates, the author was able to determine directly the radiation yield G of the low-temperature solid-phase polymerisation. This yield is of the order of 10^7 at 140 K, 10^5 at 80 K, and 10^3 at 4 K. Such high radiation yields, which had never been observed previously at low temperatures, are themselves of considerable interest, demonstrating the possibility of the spontaneous propagation of long chains even in the vicinity of the absolute zero.

However, the values of G combined with experimental chain propagation times are of even greater interest.

In fact, having determined experimentally on low-inertia calorimeters the polymer chain propagation time τ at different temperatures (the variation of $\lg\tau$ with $1/T$ is represented by curve *1* in Fig. 15), the author was able to reach fairly definite conclusions about the average time τ_0 required for the fundamental step involving the addition of a single new link to the growing polymer chain. If the radiation yield of chain initiation, i.e. the yield of the reaction involving the creation of the initial active centres, is g, then in the absence of chain transfer the length of the polymeric molecule is $\nu = G/g$ monomer units and the average time required for the addition of a new link to the chain is $\tau_0 \simeq \tau/\nu$. The efficiency of chain initiation by ionising radiation may be regarded as independent of temperature: $g \simeq$ const. Having put $g \simeq 1$ (the value characteristic of the formation ions or radicals) to make the treatment concrete, we adopted $\tau_0 \simeq \tau/G$ as a fairly accurate estimate. Curve *2* in Fig. 15 represents the variation[45] of $\lg\tau_0$ with $1/T$.

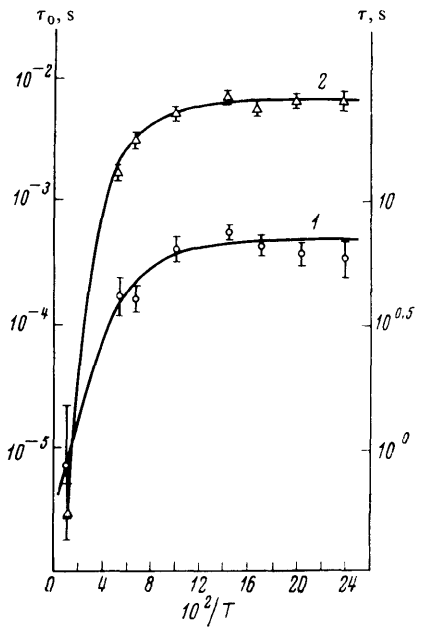


Figure 15. Temperature variation (in terms of the Arrhenius coordinates) of the total polymer chain propagation time τ (curve *1*) and of the average time required for the increment by one new unit of the polyformaldehyde chain $\tau_0 = \tau/G$ (curve *2*).

In the range 80–150 K, τ_0 increases with decrease of temperature in accordance with the Arrhenius law with an activation energy $E \simeq 2000$–2500 cal mole^{-1} and reaches $\tau_0 \simeq 10^{-5}$ s at 80 K. At lower temperatures there is a marked deviation from the Arrhenius law—the average time required for the addition of a single chain unit tends to the constant value $\tau_0 \simeq 10^{-2}$ s, while extrapolation in accordance with the Arrhenius equation would yield unreasonably large values (about 10^{30} years at 10 K and 10^{100} years at 4.2 K).

The question naturally arises whether or not macroscopic heating of the formaldehyde specimens occurred in the present author's experiments owing to the ^{60}Co radiation energy and the heat of polymerisation. However, the above estimates make it possible to give a quite definite negative answer to this question. In principle, one can imagine the possibility of more marked local heating in regions adjoining the new polymer chain unit just formed, owing to the heat of the fundamental chain propagation step. However, during a period of the order of 10^{-2} s, such heating under the conditions of isotropic heat conduction would have to include a region with a linear dimension of the order of tens of micrometers and is therefore quite negligible.

VI. INTERPRETATION OF THE LOW-TEMPERATURE LIMIT TO THE RATES OF CHEMICAL REACTIONS

Thus a kind of limit has been observed experimentally for the rate of chain propagation in radiation-initiated solid-phase polymerisation of formaldehyde at low temperatures. After this the general problem of the interpretation of the low-temperature limit of the rates of chemical reactions became crucial, because it can be treated in different specific ways.

According to the ideas of Abkin and his coworkers[35–40] quoted above, the growth of polymer chains at low temperatures is not a spontaneous process but is due to the influence of external radiations, which, as it were, "prod" the growing chains. The necessity for such "prodding" leads to a decrease of the radiation yield of the chain reactions from $G = g\nu$ to g. The ambient temperature should then naturally play a markedly secondary role in determining the rate of polymer formation. In the case of the formaldehyde polymerisation reaction investigated by the author, the enormous radiation yields of polymerisation mentioned above constitute evidence against this explanation. However, the decisive objection to the idea that the low-temperature growth of formaldehyde polymer chains occurs as a result of the additional energy supplied by radiation is provided by an experiment carried out very recently at the Institute of Chemical Physics[46] in which postpolymerisation of formaldehyde was observed directly at liquid helium temperature at which the monomer was also irradiated. The diathermal calorimetric technique described above (Figs. 13 and 14) was used in this experiment, but with the difference that, owing to the special magnetic seal employed, it was possible not only to switch on but also to switch off the ^{60}Co radiation field very rapidly, in several hundredths of a second. The positions of the plateaux in the initial parts of curves *1* and *2* in Fig. 16 (curve *1*—for a 0.25 g formaldehyde sample; curve *2*—for the analogous polyformaldehyde sample; the total weight of the irradiated calorimeter cell was about 1.5 g and the dose rate $I \simeq$ 60 rad s^{-1}) show that, in the radiation field at $T \simeq 4$–5 K, the calorimeter records the polymerisation of formaldehyde with a radiation yield $G \simeq 2 \times 10^3$. After the rapid switching off of γ-irradiation, polymerisation does not cease instantaneously (like heat evolution due to the irradiation of polyformaldehyde, where the characteristic time for the decay of heat evolution is determined by the relaxation of the calorimeter and amounts to approximately 2–3 s for curve *2*), but its rate decreases with a characteristic time (curve *1*) $\tau \simeq 10$–20 s, i.e. virtually the same as the time needed for the growth in the rate of

polymerisation at liquid helium temperature in the radiation field. Thus the propagation of formaldehyde polymer chains at 4–5 K was demonstrated experimentally also in the absence of irradiation and its rate was determined and found to be virtually the same as in the radiation zone.

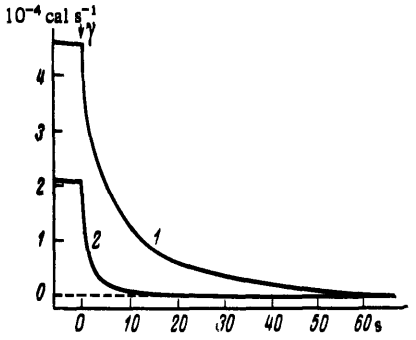


Figure 16. Variation of the rate of heat evolution during the irradiation of specimens in the diathermal calorimeter and after the cessation of irradiation (this instant is indicated by an arrow). Overall weight of the cells with the substance about 1.5 g; weight of formaldehyde (curve *1*) and polyformaldehyde (curve *2*) specimens about 0.25 g; ^{60}Co irradiation dose rate $I \simeq 60$ rad s^{-1}; experimental temperature $T \simeq 4$–5 K.

Semenov suggested that non-activated solid-phase polymerisation processes may develop via the energy chain mechanism involving the migration of an exciton (an excitation quantum) along the growing chain[25,47]. However, under these conditions the linear rate of chain propagation would be expected to be of the same order of magnitude as the velocity of sound in the solid (about 10^5 cm s^{-1}), the time required to add a new link to the growing polymer chain would be $\tau_0 \simeq 10^{-13}$ s, and the total chain propagation time for the above values of G would be in the range $\tau \simeq 10^{-10}$–10^{-6} s. The experimental values of τ are higher by many orders of magnitude.

According to the results of Benderskii et al.,[48] optical phonons traversing relatively large distances arise in molecular crystals under illumination; the time of their conversion into acoustic phonons, i.e. into heat, is fairly long (about 10^{-6} s). Since the end of the growing polymer chain may be regarded as a trap for optical phonons, there is a possibility of an additional supply of energy to the polymer chain from another chain growing at the same time. In this case $\tau_0 \simeq 10^{-2}$ s would no longer represent the time required for the spontaneous increase of chain length by a single unit, but would represent the time required for the addition at the end of the chain of a phonon from some other, "foreign" chain. However, τ_0 would then be inversely proportional to the total number of chains growing simultaneously in the system or, in other words, to the dose rate of the radiation (I) initiating the polymerisation. However, the present authors experiments demonstrated the independence of τ_0 of I.

Ovchinnikov's calculations[48,50] indicate the possibility of the existence in molecular crystals of localised long-lived vibrational states with lifetimes up to several seconds (the results of the calculation for nitrogen N_2 at $T = 30$ K). The slowness of the "de-excitation" of such state is in fact due to the factor already discussed above, namely the non-resonance mechanism of the single-quantum energy transfer from the excited to the non-excited oscillator: owing to the anharmonicity of the intramolecular vibrations, the energy difference between two high levels $\Delta E_n = E_n - E_{n-1}$ is smaller than $\Delta E_1 = E_1 - E_0$ and the transfer of the energy E_n to a non-excited neighbouring molecule is possible only with simultaneous absorption of phonons, i.e. when the lattice energy is employed. In the complete absence of coupling between the two oscillators, the rate of this process would become vanishingly low near the absolute zero, and the lifetime of the molecule at the E_n level would be determined by very slow radiation-induced transitions $E_n \rightarrow E_0$ or by the multiquantum resonance transfer of the entire energy E_n.

The involvement of long-lived vibrational states in low-temperature polymerisation as active terminal groups would require a constant additional energy supply to the growing chain due to its intrinsic heat of polymerisation and its probability would be almost unity [more precisely $(\nu - 1)/\nu$ or $(G-1)/G$]. Furthermore, the available experimental data support the view that the active centres for the growing polymer chain of solid formaldehyde at low temperatures are stabilised long-lived ions rather than any excited states.

When irradiated formaldehyde is warmed outside the radiation zone, the calorimeter detects a fairly rapid postpolymerisation—at lower temperatures the lower the irradiation temperature, the higher the dose, and the more sensitive the calorimeter (as mentioned above, after irradiation at 4 K the present author was able to observe recently postpolymerisation even at the irradiation temperature[46]). However, on optical bleaching of the irradiated specimen, its solid-phase postpolymerisation (before fusion) is completely suppressed. The bleaching effect is in fact characteristic of ions and can be accounted for by their ejection from traps and neutralisation. Hence one may conclude that the active centres in low-temperature formaldehyde polymerisation are ionic.

A characteristic feature of ionic active centres is known to be their involvement in ion–molecule reactions which do not require activation energy and frequently proceed with geometrical or larger cross-sections. The study of such gas-phase reactions was begun by Tal'roze[51,52] and their possible role in the condensed phase has been frequently mentioned in the literature. However, the time required for the addition of a new link to the growing chain of solid polyformaldehyde at low temperatures ($\tau_0 \simeq 10^{-2}$ s at $T \rightarrow 0$), which is too short for a transition over the barrier, is at the same time found to be too long for a barrier-free non-activated transition and makes it necessary to return to the idea of quantum-mechanical transitions through activation barriers with which this review was begun.

Having compared all the experimental data, we shall now consider the explanation of the quantum-mechanical low-temperature limit to the rate of polymerisation of formaldehyde on the basis of tunnelling transitions from the zero-point vibrational level, which are naturally impossible for any endothermic reaction[45]. An attempt will be made below to describe quantitatively this explanation without going into its mathematical details and almost without formulae.

As stated above, polymerisation may involve electron or hydrogen atom transfer, but it is in any case associated with a displacement of the monomer molecule as a whole. The tunnelling displacement of the formaldehyde

molecule over a distance $\Delta d = d_0 - d_f$, is undoubtedly a slower process than the tunnelling by an electron, since $M/m = 5.5 \times 10^4$ (M is the mass of formaldehyde and m that of the electron). As regards the tunnelling by a proton over a distance close to d_0, one cannot claim *a priori* that this process is faster than the tunnelling by formaldehyde over a distance $\Delta d \ll d_0$. However, the present author's direct experiments demonstrated the absence of a significant difference between the rates of polymerisation of normal and deuteriated formaldehyde at low temperatures (about 4 K).[53] On this basis, one may assume that, regardless of the polymerisation mechanism, tunnelling by the formaldehyde molecule as a whole in fact constitutes the rate limiting step for the process at low temperatures.

We shall consider the addition of formaldehyde molecules to a growing polymer chain on the basis of the quantum-mechanical theory of relaxation processes[54-56]. This theory arose mainly in connection with the problem of the radiationless relaxation of excited electronic states in molecules. It is based on the adiabatic Born–Oppenheimer theory and is applicable over an extremely wide range of conditions.

The different states of formaldehyde molecules are represented in terms of the adiabatic approximation by the potential curves in Fig. 17. The adiabatic potential curve a describes the state of the formaldehyde molecule joined to the growing polymer chain, curve b_1 represents the state of the initial monomer molecule, and curve b_2 represents the state of the next, neighbouring molecule (the zero on the abscissa axis is displaced to the right for this curve by an amount $\Delta d = d_0 - d_f$). Curves a and b_1 and b_1 and b_2 do not intersect. According to the rules of quantum mechanics, such intersection is prevented owing to the occurrence of particular interactions in the system described by the curves and instead of their intersection a gap arises between them.

At the initial instant the two monomer molecules are in states b_1 and b_2 and well a is vacant. Within the framework of the adiabatic approximation, this situation corresponds to a stable stationary state§, since none of the levels in well b_1 (at ultralow temperatures only the zero-point vibrational level is populated in this well) overlaps with any of the levels in the deeper well a.

In other words, not only are the monomer molecule and the growing polymeric active centre themselves stable in isolation, but also, in the absence of both a "free" transition over the barrier (i.e. at fairly low temperatures) between the two wells and under the conditions of the overlapping of their levels, even the monomer molecule adjoining the terminal group would be fully stable. However, owing to the interaction of the reacting molecules with the surrounding medium, i.e. owing to energy exchange with the lattice, the situation changes and there arises the possibility of an exothermic chemical reaction, in our example the polymerisation of formaldehyde, even at the absolute zero.

States a and b_1 can be regarded as two different electronic states of the polyformaldehyde active centre (poly-FA*)–formaldehyde system. State a, in which formaldehyde is displaced to the growing chain and there is a rightward "jump" of the terminal free valance, corresponds to the ground electronic state of the system in Fig. 18. State b_1, in which the formaldehyde molecule is separated from the growing polymer chain, corresponds to the electronically excited state. Owing to the interaction of the electrons and nuclei in the poly-FA*–formaldehyde system, the adiabatic approximation breaks down and the $b_1 \rightarrow a$ transition becomes possible, i.e. the system may relax via the chemical chain propagation step. Mathematically such relaxation is related to the presence in the Hamiltonian of a higher-order term involving the small Born–Oppenheimer parameter $\kappa = (m/M)^{1/4}$, called the non-adiabatic operator.

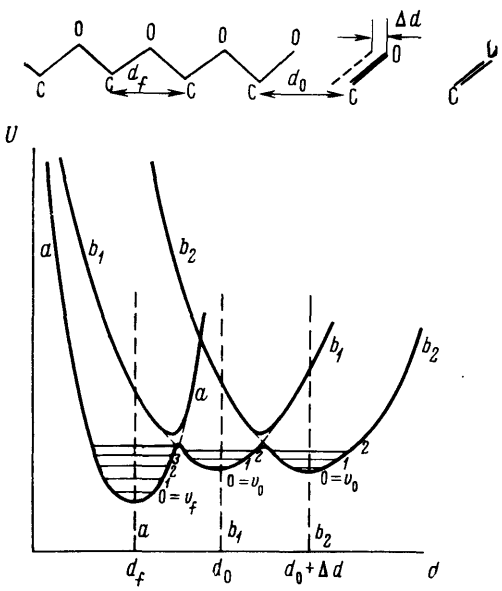


Figure 17. Upper part—simplified schematic illustration of the disposition of the solid FA monomer molecules and of the polymer chain. Lower part—schematic illustration of the tunnelling transitions of the CH_2O groups in polymerisation ($b_1 \rightarrow a$) and in filling the "cavities" arising during polymerisation in the vicinity of the terminal group of the polymer chain ($b_2 \rightarrow b_1$): a) diabatic potential curve for the formaldehyde molecule attached to the growing polymer chain; b_1) analogous curve for the initial monomer molecule; b_2) analogous curve for the next monomer molecule (the zero on the abscissa axis for this curve has been displaced to the right by an amount Δd).

The next formaldehyde molecule can undergo resonance migration from state b_2 to the vacated well b_1 with subsequent addition to the polymer chain ($b_1 \rightarrow a$), etc.

In the initial state (subscript 0) the system is at the level of zero-point vibrations: $\upsilon_0 = 0$, and the vibrational frequency of the monomeric formaldehyde molecule is ω_0, which is much less than the vibrational frequency of the monomeric CH_2–O unit in the final state (subscript f), i.e. in the polymer chain, which is ω_f. Owing to the interaction between the electronic states 0 and f, due to the non-adiabatic operator $\hat{L}$, there is a possibility of the radiationless transition $0 \rightarrow f$ to the level of the final state which is nearest as regards vibrational energy. The

§ To within extremely slow transitions $\upsilon_1 \rightarrow a$ with emission of a photon.

probability of such a transition is defined by the expression (see, for example, Henry and Kasha[54])

$$W_{0f} = \frac{2\pi}{\hbar} L_e^2 F_{0,v_f} \rho_f, \qquad (6)$$

where $L_e = \int \Psi_0 \hat{L} \Psi_f d\tau_e$, Ψ_0 and Ψ_f are adiabatic (without taking into account the interaction with the medium) electronic wave functions of the initial and final states, and F_{0,v_f} is the so called Franck–Condon factor (the square of the overlap integral of the vibrational wave functions of the initial and final states¶).

The multiplier ρ_f is defined as the density of the vibrational levels in the final state. In the absence of the inhomogeneous broadening of the levels, ρ_f differs from zero only within the limits of the level Γ (the Breit-Wigner formula) and the transition $0 \rightarrow f$ can occur only when the levels in wells b_1 and a coincide, i.e. in the presence of resonance. In the case of pronounced broadening it is possible to estimate ρ_f simply as $\rho_f \simeq 1/\hbar\omega_f$. The multiplier ρ_f is then $\hbar\omega_f/\Gamma$ times smaller than at the maximum of the non-broadened resonance line (with a width Γ).

It follows from the properties of the non-adiabatic operator that $\left|\frac{L_e}{\hbar\omega_e}\right| \propto \kappa^3$ where ω_e is the characteristic frequency of the electronic transitions. The Franck–Condon factor depends very markedly (exponentially) on the tunnelling distance $\Delta\vec{d}$ and the mass of the tunnelling group M:

$$F_{0,v_f} \propto f(v_f, \beta) \cdot \exp\left[-\frac{1}{1+\beta^2} \cdot \frac{M\omega_f}{\hbar} \cdot (\Delta d)^2\right], \qquad (7)$$

where $v_f = Q/\hbar\omega_f$, Q is the heat of polymerisation, $\beta = \sqrt{\omega_f/\omega_0}$, and the function f contains Hermitian polynomials.

For estimates, it was assumed that $\omega_e/2\pi \simeq 10^{15}$ s^{-1}, $\omega_f/2\pi c \simeq 1000$ cm^{-1}, and $\omega_0/2\pi c \simeq 100$ cm^{-1}, and $Q \simeq 0.37$ eV (so that $v_f = 3$) was determined experimentally. However, the quantity Δd, which is extremely important for the calculations, remained unknown, because it was impossible to find in the literature data on the geometry of the formaldehyde monomer crystals and even the density of solid formaldehyde at low temperatures is unavailable. However, it is clear that the density of the monomer must be lower than the density of the polymer, because the distance between the neighbouring formaldehyde monomer molecules (planar triangles) $\begin{matrix} H \\ \diagdown \\ C{=}O \\ \diagup \\ H \end{matrix}$ is determined by the relatively large van der Waals radii of the carbon and oxygen atoms and the distance between neighbouring CH_2O groups in the polymer chain is determined by the smaller lengths of the valence bonds; (for example, in polyoxymethylene the C–O bond length is 1.43 Å, which corresponds, for nearly tetrahedral valence angles, to a distance between two neighbouring carbon or oxygen atoms in the polymer chain $d_f \simeq 2.4$ Å).

Extrapolation of the densities of liquid formaldehyde at higher temperatures to the melting point yields $\rho_0 \simeq 1$ g cm^{-3} and the density of polyoxymethylene is $\rho_f \simeq 1.43$ g cm^{-3}. Assuming that $\Delta d \simeq d_f[(\rho_f/\rho_0)^n - 1]$, where $n = 1/3-1$, we obtain a very wide range of values of $\Delta d \simeq 0.3-1$ Å.

The author therefore decided to proceed as follows: the experimental value $W_{0f} \simeq 1/\tau_0 \simeq 10^2$ s^{-1} was adopted and a test was made to discover whether this corresponds to a reasonable value of Δd on the assumption of the tunnelling of the CH_2O group as a whole. Such "reverse" calculation gave $\Delta d \simeq 0.4-0.5$ Å, which is consistent with the above estimates.

The filling of the "vacancy" formed on polymerisation by neighbouring formaldehyde molecules proceeds via a tunnelling resonance transition between zero-point vibrational levels of two neighbouring equivalent wells, $b_{n+1} \rightarrow b_n$ (Fig. 17), i.e. as if by diffusion in the monomer lattice of the cavity formed on polymerisation.

The observed rate of polymerisation is limited either by the fundamental step involving the addition of a new unit to the polymer chain ($0 \rightarrow f$) or by the transport of monomer molecules to the terminal unit ($0 \rightarrow 0$)†. However, it is significant that at very low temperatures both processes have quantum-mechanical mechanisms and are due to tunnelling transitions from the zero-point vibrational level. With increase of temperature, as higher vibrational levels in the initial and final states are filled, the transitions over the barrier begin to play an increasing role and the rate of reaction begins to obey the Arrhenius law (for $M = 30$, $E \simeq 0.1$ eV, and $\Delta d \simeq 0.5$ Å, the boundary between the tunnel and Arrhenius regions is at $T_t \simeq 25$ K).

Thus, although the necessary data are not as yet available for an accurate calculation of the probability of the occurrence at the absolute zero of the chemical reaction involved in the polymerisation of formaldehyde studied by the present author, the estimates obtained are in reasonable agreement with experimental results. Nevertheless, it would also of course be desirable to analyse at least semiquantitatively other possible models and examples of the occurrence of the low-temperature limit to the rates of this and other chemical reactions. At the same time one should bear in mind that, other conditions being equal, the parameter which determines the contribution of the tunnel effect to the observed rate of the process is the product md^2 [or $\sqrt{m}d$—see Eqn. (5) for the characteristic "tunnel temperature"], where m is the mass of the tunnelling species and d the tunnelling distance.

Whereas tunnelling over a distance of tens of angstroms may be typical for an electron at low temperatures, while for a proton the distance is 1–2 Å, for groups with a molecular weight M tunnelling through a barrier with a width $d \simeq 1/\sqrt{M}$ (Å) becomes immeasurably slow and the barrier cannot be overcome in this way. It is therefore possible that the author was lucky to "encounter" formaldehyde, which proved to be one of the extremely rare successful systems for which it is possible to observe and investigate quantitatively the tunnelling of whole molecules or molecular groups.

¶ Eqn. (6) takes into account only one of the complications (mentioned above), which hinder exothermic tunnelling transitions between non-identical potential wells–the necessity for the breakdown of the Franck–Condon principle, i.e. the occurrence of an electron–nucleus interaction. The rate of transfer of the transition energy to the surroundings is not taken into account here, it being assumed that it is much higher than the rate of the transition itself.

† The transport of monomer molecules to the terminal unit (the transition of formaldehyde from well b_{n+1} to well b_n, diffusion of the cavity) can occur, in contrast to chain propagation ($b_1 \rightarrow a$), as a resonance tunnelling transition. Nevertheless, the rate of this transition need not necessarily exceed the rate of intrinsic chain propagation, because, as can be seen from Fig. 17, owing to the exothermic heat of the chemical reaction, the width of the barrier in the $b_1 \rightarrow a$ transition is much smaller than in the $b_{n+1} \rightarrow b_n$ transitions.

It is significant that the present author's findings for the low-temperature polymerisation of formaldehyde constitute to a certain extent models for tunnelling electron transfer between complex biological molecules, already mentioned above, when such transfer requires a conformational change in the biological molecules as an obligatory concomitant process. Although the occurrence of such complex electron transfer has not so far been observed experimentally, it has been postulated[15,16] as an intermediate stage in a process where only the location of the electron is altered but not the geometry of the valence bonds of the oxidant and reductant. Interaction under conditions where the possibility of a non-resonance tunnelling transition of an electron is ensured because it is accompanied by conformational changes in biological macromolecules is illustrated in Fig. 18.[15,16]

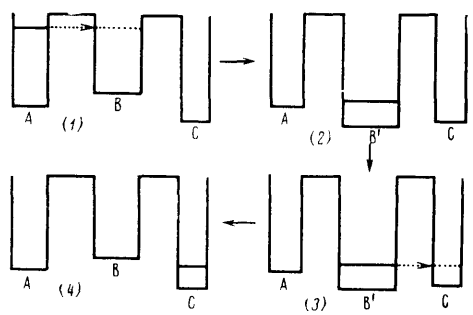


Figure 18. Schematic illustration of electron transfer from the reductant (A) to the oxidant (C) accompanied by conformational transitions of the transferring agent ($B \rightleftharpoons B'$).

Electron transfer from a reductant (potential well A) to an oxidant (well C), occurring with the evolution of energy Q, proceeds only with participation of an intermediate transferring agent. The state of equilibrium of the oxidised form of the transferring molecule is described by the potential well B, while the state of equilibrium of its reduced form is different, owing to the polarisation of the medium, and is described by the potential well B′. When the electron enters well B at the level in resonance with the initial well A, the medium is polarised and the conformational transition $B \rightarrow B'$ takes place, and, when the new electronic level in well B′ is in resonance with a level in well C as a result of this transition, there is a possibility of electron transfer to C and of the reverse conformational transition $B' \rightarrow B$.

Thus the non-resonance electron transition (1) → (4) (Fig. 18) is regarded as the sum of two resonance tunnelling electron transitions: (1) A → B and (3) B → C and two conformational transformations $B_1 \rightarrow B_2'$ and $B_3' \rightarrow B_4$. The main evolution of energy in a set of transitions of this kind occurs in the stage (3) → (4) owing to the conformational transformation of the transferring molecule, which has given up the electron, to the equilibrium configuration for the oxidised form: $B_3' \rightarrow B_4$.

In accordance with the foregoing, the evolved energy Q may be dissipated by the excitation of either phonons or the normal vibrations in the transferring molecules which are fairly strongly linked to the electronic state of the system.

The rate of the combined electronic-conformational transitions should probably tend to a limit on reducing the temperature, as described above for the polymerisation of formaldehyde. Since the processes of the type described should depend on the energy difference between the occupied electronic level of the reductant and the vacant level of the oxidant, it is believed[15,16] that they may be regulated by membrane potentials.

However, the fundamental importance of the above results, the role of the low-temperature tunnelling of not only electrons and protons but also of whole segments of biological molecules or molecular groups, is by no means restricted to this important problem of molecular biology, which is concerned with electronic and conformational transitions.

The detailed study of the low-temperature limit to the rates of chemical reactions and the extension of the reactions investigated towards temperatures still lower than 4 K may be of even wider fundamental significance. For example, the occurrence of chemical reactions at ultralow temperatures makes it necessary to consider seriously whether it would be possible to revive an organism subjected to prolonged freezing under conditions where the influence of external chemical reaction initiators (for example, various types of radiation) is not excluded.

However, another consideration is even more important—near the absolute zero the entropy factors, which are very important in the thermodynamics of chemical reactions, cease to play a role and therefore the equilibria of all reactions are displaced towards exothermic processes, including even those which lead to the formation of highly ordered systems. Furthermore, one should bear in mind the possibility of a kind of autoregulation of the direction of such spontaneous reactions—processes with a relatively small heat evolution (closer to resonance processes) should proceed with greater probability and, as the complexity of the molecules formed increases, the probability of the dissipation of the evolved energy via intramolecular degrees of freedom becomes more pronounced. Admittedly, the rates of reactions near the absolute zero are greatly reduced but, in relation to natural evolutionary processes, one can boldly recall Mayakovskii's words: "eternity awaits both you and me and it would cost us little to waste an hour or two".

It is quite possible that, at the low temperatures in space under the conditions of initiation by cosmic rays, even the most complex molecules, up to proteins, can be reliably formed, although the rate of their formation is extremely slow, and that slow chemical reactions at low and ultralow temperatures, which are, however, clearly directed towards the maximum heat evolution, may play a definite role in the processes involved in chemical and biological evolution. There is a possibility of what one might call a "cold prehistory of life".

REFERENCES

1. D. G. Bourgin, Proc. Nat. Acad. Sci. U.S.A., No. 15, 357 (1929).
2. S. Z. Roginskii and L. Rozenkevich, Z. Phys. Chem., 10, B 47 (1930).
3. R. P. Bell, Proc. Roy. Soc. A, 139, 466 (1933); 148, 241 (1935); 158, 128 (1937).
4. V. I. Gol'danskii, Dokl. Akad. Nauk SSSR, 124, 1261 (1959).
5. V. I. Gol'danskii, Dokl. Akad. Nauk SSSR, 127, 1037 (1959).

6. V. G. Levich, "Kinetics of Reactions with Charge Transport [from "Physical Chemistry" (Edited by H. Eyring, D. Henderson, and W. Jost), Vol. 9-b], Acad. Press, New York, 1970, p. 985.
7. R. R. Dogonadze and A. M. Kuznetsov, "Kinetika Khimicheskikh Reaktsii v Polyarnykh Rastvoritelyakh" (Kinetics of Chemical Reactions in Polar Solvents), Symposium "Fizicheskaya Khimiya. Kinetika, II (Ser. Itogi Nauki i Tekhniki)" [Physical Chemistry. Kinetics, II (Advances in Science and Engineering Series)], VINITI, Moscow, 1973.
8. O. S. Yakimchenko and Ya. S. Lebedev, Int. J. Radiat. Phys. Chem., 3, 17 (1971).
9. R. De Vault and B. Chance, Biophys. J., 6, 825 (1966).
10. B. Chance, R. De Vault, V. Legallais, L. Mela, and T. Yonetani, "Fast Reactions and Primary Processes in Chemical Kinetics", Nobel Symposium 5, Stockholm, 1967, p. 437.
11. L. N. Grigorov, Candidate's Thesis, Moscow, 1970.
12. K. I. Zamaraev, R. F. Khairutdinov, A. I. Mikhailov, and V. I. Gol'danskii, Dokl. Akad. Nauk SSSR, 199, 650 (1971).
13. R. F. Khairutdinov, A. I. Mikhailov, and K. I. Zamaraev, Dokl. Akad. Nauk SSSR, 200, 905 (1971).
14. A. I. Mikhailov, Dokl. Akad. Nauk SSSR, 197, 136 (1971).
15. L. N. Grigorov and D. S. Chernavskii, Biofizika, 17, 195 (1972).
16. L. A. Blumenfeld and D. S. Chernavskii, J. Theor. Biol., 39, 1 (1973).
17. R. B. Mesrobian, P. Ander, D. S. Ballantine, and G. J. Dienes, J. Chem. Phys., 22, 565 (1954).
18. M. Magat, Khim i Tekhnol. Polimerov, No. 7–8 (1960).
19. P. G. Garrat, Polymer, 3, 323 (1962).
20. M. Magat, Khim i Tekhnol. Polimerov, No. 3 (1963).
21. S. Okamura, Chimia (Switz.), 1, 9 (1963).
22. A. Shapiro, Khim i Tekhnol. Polimerov, No. 4 (1964).
23. M. A. Bruk, Symposium, "Uspekhi Khimii Polimerov" (Advances in Polymer Chemistry), Moscow, 1966, p. 42.
24. H. Morawetz, Symposium, "Fizika i Khimiya Tverdogo Sostoyaniya Organicheskikh Soedinenii" (The Physics and Chemistry of the Solid State of Organic Compounds) (Translated into Russian), Izd. Mir, Moscow, 1967, p. 242.
25. N. N. Semenov, N. S. Enikolopyan, and V. I. Gol'danskii, Rev. Chim., 7, 501 (1962).
26. I. M. Barkalov, V. I. Gol'danskii, N. S. Enikolopyan, S. F. Terekhova, and G. M. Trofimova, "Industrial Uses of Large Radiation Sources", IAEA, Vienna, 1963, Vol. 1, p. 193.
27. I. M. Barkalov, V. I. Gol'danskii, N. S. Enikolopyan, S. F. Terekhova, and G. M. Trofimova, J. Polymer. Sci., C, 897, 909 (1963).
28. I. M. Barkalov, V. I. Gol'danskii, N. S. Enikolopyan, S. F. Terekhova, and G. M. Trofimova, Vysokomol. Soed., 6, 92, 98 (1964).
29. I. G. Gusakovskaya and V. I. Gol'danskii, Khim. Vys. Energii, 2, 46 (1968).
30. D. A. Kritskaya, A. N. Ponomarev, and V. L. Tal'roze, Khim. Vys. Energii, 2, 54 (1968).
31. M. A. Bruk, V. F. Gromov, I. V. Chernykh, P. M. Khomikovskii, and A. D. Abkin, Vysokomol. Soed., 8, 961 (1966).
32. I. M. Barkalov, D. A. Gareeva, V. I. Gol'danskii, N. S. Enikolopyan, and Al. Al. Berlin, Vysokomol. Soed., 8, 1140 (1966).
33. M. A. Bruk, K. K. Chuiko, L. V. Eroshina, V. A. Aulov, and A. D. Abkin, Vysokomol. Soed., 14, A, 794 (1972).
34. V. I. Muromtsev, R. A. Asaturyan, M. A. Bruk, A. D. Abkin, and I. G. Akhvlediani, Khim. Vys. Energii, 3, 252 (1969).
35. E. I. Finkel'shtein, A. D. Abkin, and E. Ya. Gorbatov, Khim. Vys. Energii, 3, 466 (1969).
36. E. I. Finkel'shtein and A. D. Abkin, Khim. Vys. Energii, 3, 447 (1969).
37. E. I. Finkel'shtein and A. D. Abkin, Khim. Vys. Energii, 3, 449 (1969).
38. E. I. Finkel'shtein and A. D. Abkin, Vysokomol. Soed., 11A, 855 (1969).
39. A. D. Abkin, P. M. Khomikovskii, E. V. Volkova, and V. I. Lukhovitskii, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 18, 246 (1973).
40. A. D. Abkin, A. P. Sheinker, and G. N. Gerasimov, in "Radiatsionnaya Khimiya Polimerov" (Radiation Chemistry of Polymers) (Edited by V. A. Kargin), Izd. Nauka, Moscow, 1973.
41. D. P. Kiryukhin, A. M. Kaplan, I. M. Barkalov, and V. I. Gol'danskii, Vysokomol. Soed., 12B, 491 (1970).
42. D. P. Kiryukhin, A. M. Kaplan, I. M. Barkalov, and V. I. Gol'danskii, Dokl. Akad. Nauk SSSR, 199, 857 (1971).
43. D. P. Kiryukhin, A. M. Kaplan, I. M. Barkalov, and V. I. Gol'danskii, Vysokomol. Soed., 14A, 2115 (1972).
44. D. P. Kiryukhin, A. M. Kaplan, I. M. Barkalov, and V. I. Gol'danskii, Dokl. Akad. Nauk SSSR, 206, 147 (1972).
45. V. I. Gol'danskii, M. D. Frank-Kamenetskii, and I. M. Barkalov, Dokl. Akad. Nauk SSSR, 211, 133 (1973).
46. D. P. Kiryukhin, I. M. Barkalov, and V. I. Gol'danskii, Vysokomol. Soed., 16B, 565 (1974).
47. N. N. Semenov, Khim. i Tekhnol. Polimerov, No. 7–8 (1960).
48. V. A. Benderskii, V. Kh. Brikenstein, V. L. Broude, and A. G. Lavrushko, Solid State Comm., 15, 1235 (1974).
49. A. A. Ovchinnikov, Zhur. Eksper. Teor. Fiz., 57, 263 (1969).
50. A. A. Ovchinnikov and N. S. Erikhman, Zhur. Eksper. Teor. Fiz., 61, 2391 (1971).
51. V. L. Tal'roze and A. K. Lyubimova, Dokl. Akad. Nauk SSSR, 86, 909 (1952).
52. V. N. Kondrat'ev and E. E. Nikitin, "Kinetika i Mekhanizm Gazofaznykh Reaktsii" (Kinetics and Mechanism of Gas-Phase Reactions), Izd. Nauka, Moscow, 1974, Chapter X (Author of Chapter V. L. Tal'roze).
53. V. I. Gol'danskii, D. P. Kiryukhin, and I. M. Barkalov, Khim. Vys. Energii, 8, 279 (1974).
54. B. R. Henry and M. Kasha, Ann. Rev. Phys. Chem., 19, 161 (1968).
55. W. Siebrand, J. Chem. Phys., 46, 440 (1967).
56. S. H. Lin and H. Eyring, Proc. Nat. Acad. Sci. U.S.A., 69, 3192 (1972).

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