RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

July 1979

Translated from *Uspekhi Khimii*, 48, 1153-1179 (1979)

U.D.C. 541.15

Excess Electrons in Non-polar Molecular Liquids

B.S.Yakovlev

The results of recent experimental and theoretical studies of the properties of an excess electron in non-polar liquids have been summarised. Various models of electron transfer, and the role of localised and quasi-free states of the excess electron in chemical reactions have been discussed. The bibliography contains 142 references.

CONTENTS

I. Introduction 615
II. The mobility and energy of an excess electron 616
III. Chemical reactions 621

I. INTRODUCTION

The discovery of the solvated electron in water about fifteen years ago laid the foundation for intensive studies of the properties of a "chemically non-combined" or excess electron in molecular liquids. Until recently, these studies were related chiefly to polar media. It was found that an excess electron is one of the most chemically active species and plays an important role in many electrical, photochemical, and radiation-chemical processes[1-4].

Until 1968, experimental studies of the excess electron in non-polar liquids were restricted to the study of the mobility of the electron in liquefied noble gases and diatomic liquids (this work has been reviewed[5-7]). In the last few years, the study of the properties and elementary chemical reactions of the excess electron has been extended to liquids consisting of complex non-polar molecules—liquid hydrocarbons and various organosilicon compounds. This has been made possible by the development of the technique of recording fast reactions, particularly the use of nanosecond techniques, and the improvement of methods of purifying liquids from electron acceptors. Intensive studies in this field began after the possibility of recording an excess electron in liquid hydrocarbons had been demonstrated in the period 1968–1970[8-11].

A large amount of factual material relating to the study of the physical properties and reactivity of an excess electron in non-polar liquids has now accumulated. It has been found that the excess electron is a much more active species in these media than in the polar liquids. The direct experimental data obtained on the mobility and rate constants of the reaction of the electron differed so sharply from the values previously assumed that they led to a change in ideas regarding the time scale of processes involving an excess electron in photochemical and radiation-chemical changes in non-polar liquids. New data are extending the possibility of studying reactions with electron transfer in condensed media. These data can be used in the physics of dielectrics to study the initial stages of electric breakdown, and in experimental nuclear physics to create liquid ionisation chambers. This explains the increasing interest shown by specialists in different fields in the study of the properties of the excess electron in non-polar liquids.

The problems of the behaviour of an electron in molecular liquids, including non-polar liquids, have been reviewed [12-14]. The present review summarises the results of work published up to 1977. Particular attention has been paid to the mobility and reactivity of an excess electron in liquid hydrocarbons. In the last part of the review, new data on the properties of the excess electron are used to discuss the kinetics of the primary electronic processes of the radiolysis of non-polar molecular liquids.

II. THE MOBILITY AND ENERGY OF AN EXCESS ELECTRON

The experimental data at present available on the mobility and reactivity of the excess electron in non-polar liquids relate chiefly to an electron in thermal equilibrium with the medium. In polar liquids, the state of an equilibrium excess electron is localised. The electron in this state is in a potential well, formed as a result of the polarisation interaction of the electron with the dipolar molecules of the medium. For an excess electron in non-polar liquids, generally speaking, it is not clear whether the equilibrium state is localised, since the orientational polarisability of molecules in these media does not play a significant role in the localisation of an electron. According to existing views of the states of an electron in disordered systems [15,16], at thermal equilibrium in a non-polar liquid an excess electron can in principle also exist in a delocalised state. In this state the electron occupies the volume of many molecules, and its interaction with the medium is determined only by their electronic polarisability. It is assumed that the delocalised or quasi-free electron has a much higher mobility than an ion.

As shown below, data on the mobility of the excess electron indicate that in many non-polar liquids an equilibrium electron is neither completely localised nor quasi-free, but is most probably in neither state. It is still possible, however, to regard an excess electron as a species in an "equilibrium" state in processes for which the characteristic time is greater than the relaxation time of various states of the electron. Processes of this kind are usually dealt with in experimental studies of the mobility and rates of chemical reactions of an excess electron in non-polar liquids.

1. Measurements of Drift Mobility

The drift mobility μ or the ratio of the average velocity of the electron v in an electric field to the field strength E

$$\mu = v/E \qquad (1)$$

is one of the most definite characteristics of the motion of an electron in a liquid. Einstein's relationship makes it possible to relate μ to the coefficient of diffusion of the electron $D = k_B T/e\mu$, where k_B is the Boltzmann constant, T the absolute temperature, and e the charge of the electron.

The first reliable measurements of the value of μ for an excess electron in liquid hydrocarbons were made comparatively recently, in 1968–1969 [9-11]. It has now become clear that the failure of the many earlier attempts to carry out these measurements were due to the use of liquids not sufficiently purified from electron acceptors. In most cases, rapid disappearance of the excess electrons and the formation of the negative ions of the acceptor molecules took place. A direct indication of the existence in liquid hydrocarbons of current carriers more mobile than ions was obtained by Tewari and Freeman [8], who detected the formation of short-lived charged species in liquid neopentane under the influence of ionising radiation. The use of thoroughly purified liquids in later work made it possible to determine the average velocity of these species in an electric field from the time of flight over the distance between two electrodes.

The values of μ obtained from these measurements were 10^2–10^5 times greater than the mobility of ions, so that the current carriers recorded were identified as excess electrons. This conclusion was confirmed by studies [10] of the current of electrons photo-injected from a metal into "pure" liquid hydrocarbons. These studies gave the same values of μ.

The purity of the liquids required for the measurement of the time of flight of excess electrons over the distance between electrodes (t_f) can be judged from the lifetime of electrons before their capture by the molecules of acceptors, which in these measurements must be greater than t_f. The acceptable concentration of electron acceptors, estimated from this condition and the known rate constants of reactions involving the capture of an excess electron, often did not exceed 10^{13} cm^{-3}.

The mobilities of excess electrons have now been measured for more than fifty different non-polar molecular liquids, including saturated [9-11,18-38], unsaturated [18,34,39], normal, cyclic [34], and aromatic [40] hydrocarbons, and various organosilicon compounds, such as tetramethylsilane [11,21]. Table 1 gives some published values of μ for liquids at room temperature. More complete data have been published [12-14,38]. The results lead to the following general conclusions.

Table 1. Drift mobility of an excess electron μ, activation energy of the mobility E and the energy of the ground level of a quasi-free electron V_0 in non-polar molecular liquids.

Liquid	T, K	μ, ($cm^2 V^{-1} s^{-1}$)	E, eV	V_0, eV
Tetramethylsilane	296	90[11]	0.018[11]	−0.61[42], −0.62[41] −0.55[43], −0.51[47]
Neopentane	296	70[26,40]	—	−0.43[41,42], −0.35[43]
2,2,4,4-Tetramethylpentane	295	24[21]	0.064[21]	−0.33[50]
2,2,5,5-Tetramethylhexane	293	12[21]	0.05[21]	—
2,2-Dimethylbutane	296	10.9[11]	0.052[11]	−0.24[42], −0.15[46]
2,2,4-Trimethylpentane	296	7[11]	0.06[17], 0.51[33], 0.046[36]	−0.15[42], −0.18[41] −0.14[43], −0.19[52]
Cyclopentane	296	1.1[11]	—	0.17[43], 0.28[42]
Cyclohexane	294	0.35[11], 0.45[21]	0.17[21]	0.01[50]
Butane	296	0.4[11]	—	—
n-Pentane	293	0.15[74]	—	0.01[47]
Benzene	293	0.114[40]	0.32[40]	−0.14[44]
n-Hexane	296	0.09[11], 0.082[29]	0.19[18,28,33] 0.16[36]	−0.09[42], 0.04[41] 0.16[49], 0.2[47]
Toluene	292	0.063[40]	0.15[40]	−0.22[44]
n-Decane	296	0.038[36]	0.21[36]	0.18[49]
n-Pentadecane	296	0.03[35]	0.16[35]	—
Methane	111	400[22,25]	—	0.0[48]
	140	430[20]	−0.007[30]	—
Ethane	130	0.014[30]	0.08[30]	0.22[46]
Propane	175	0.05[30]	—	0.11[50]

1. The mobility of an electron in different liquids, even at a given temperature, cover a wide range of values: from 3×10^{-2} $cm^2 V^{-1} s^{-1}$ in n-decane to 10^2 $cm^2 V^{-1} s^{-1}$ in neopentane and tetramethylsilane. The mobility of the

electron is unusually "sensitive" to the structure of the molecules of the liquid. For example, for n-pentane and neopentane the values of μ differ by a factor of more than 400. The mobilities of the electron in *cis*- and *trans*-butenes differ by a factor of approximately 100. For normal hydrocarbons, the mobility at first decreases rapidly with increase in the number of carbon atoms from two to six. Further increase in the number of carbon atoms leads to only a slight change in μ. The position of the double bond in a molecule determines whether μ increases or decreases. It is difficult to relate the influence of the structure of molecules on the mobility of an excess electron to any single property of the molecules of the liquid. The nature of the movement of an electron in liquid saturated hydrocarbons apparently depends to a considerable extent on the shape of the molecule: more spherically symmetrical molecules correspond to a greater mobility. The greatest mobilities are shown by electrons in methane, neopentane, and tetramethylsilane, which have highly symmetrical molecules.

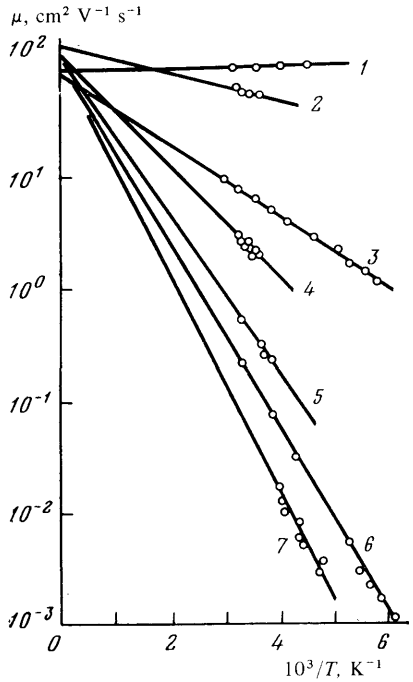


Figure 1. Temperature dependence of the drift potential of an excess electron in various molecular liquids: 1) tetramethylsilane[33], 2) neopentane[20], 3) iso-octane[17], 4) 2-methylbut-2-ene[20], 5) 66% n-hexane in neopentane[20], 6) 3-methylpentane[66], 7) n-hexane[20].

2. For all hydrocarbons studied, except liquid methane[35], the mobility of the electron decreases with decrease in temperature (Fig. 1). The temperature dependence of μ for most saturated hydrocarbons is described by the Arrhenius equation

$$\mu = \mu_0' \exp(-E/k_B T) \qquad (2)$$

with pre-exponential factors μ_0' from 10^2 $cm^2V^{-1}s^{-1}$ to 10^3 $cm^2V^{-1}s^{-1}$. The $\mu(T)$ relationship for liquid ethane and n-pentane is more complex. The activation energy increases with decrease in T in the first case, and decreases in the second. $\mu(T)$ relationships of this kind are also typical of unsaturated hydrocarbons.

3. The mobility of the excess electron is independent of the electric field strength, that is $v \sim E$ up to values of $E \simeq 10^4$ V cm^{-1}. In liquids with a relatively high mobility (liquefied methanol, neopentane, iso-octane), further increase in E leads to a decrease in μ.[23,26,32] In this range of values of E, the velocity of the electron $v \sim E^{0.5}$. This $v(E)$ relationship is characteristic of the movement of an electron in semiconductors, and is usually related to an increase in the average kinetic energy of the electron in the electric field. Another type of relationship was established for liquids with a low mobility: in the range of strong fields, μ increases with increase in E (liquefied ethane, propane, pentane[25-27,38]). A similar relationship was previously found for substances in which the movement of the electron takes place in hops from one localised state to another. It is assumed that in this so-called "hopping" mechanism of electron transfer, the electric field increases the probability of a hop.

4. The mobility of an electron shows a correlation with the energy V_0 of the ground state of the quasi-free electron in the liquid, that is with the energy which must be expended to transfer a stationary electron from a vacuum to a lower delocalised state in the liquid. As a rule, the lower V_0, the higher the mobility of the excess electron. This dependence of μ on V_0 is one of the characteristic features of the movement of an electron in non-polar liquids (for polar liquids, a correlation between μ and V_0 has not been established). It is assumed that the position of the level of a quasi-free electron in some cases also determines the reactivity of the excess electron (see Part III). It is therefore not surprising that the discussion of data on V_0 at present occupies an important place in the examination of the properties of an excess electron in non-polar liquids.

2. Energy of a Quasi-Free Electron

Data on the magnitude of V_0 for non-polar liquids have been obtained chiefly by two methods: from the difference in the work functions for an electron from a metal in a vacuum φ_V and in a liquid φ_l,[41-49] or from the difference in the ionisation potentials of the molecules in the gas I_g and in the liquid I_l.[50,51] The energy of the quasi-free electron is determined in the first method as the difference $V_0 = I_l - \varphi_V$, and in the second case as $V_0 = I_l - I_g - P_+$, where P_+ is the energy of the polarisation of the positive ion in the liquid. The results obtained by the two methods show good agreement.

The values obtained for V_0 for non-polar liquids (see Table 1) lie in a range from −0.6 eV to +0.2 eV, that is they are much higher than the corresponding values for polar liquids (for example, for water $V_0 = -1.3$ eV[4]). Positive values of V_0 mean that it is energetically more favourable for the electron to move into a vacuum from the quasi-free state in the liquid. Experimental confirmation of the existence of this transition is provided by the observation of the effective emission of excess electrons from liquid n-hexane and iso-octane into the gaseous phase[52,53].

A number of attempts have been made to interpret the properties of a quasi-free electron in non-polar molecular liquids using the same approach as in the case of liquefied

gases, since high values of V_0 were previously obtained for the latter. For liquefied gases, from data on the scattering of an electron by atoms in the gaseous phase, it is assumed that an electron cannot approach an atom to a distance less than the so-called radius of a "hard sphere" a. According to the theory[6], in this approach,

$$V_0 = T_k(a, n) + U(\alpha, n), \quad (3)$$

where T_k is the energy, often called "kinetic", although it is the energy of an electron at the foot of the conductivity zone. Physically, this energy is related to the same quantum effect as the increase in the energy of the ground state of an electron in a potential well when the walls of the well approach one another. The role of the walls in the model of the electron being considered is played by the surface of the "hard spheres". As expected from this interpretation, the value of T_k increases with increase in a or the number of molecules in unit volume n. The average polarisation energy U can be calculated[6] from the known polarisability of the atom α and the density of the liquid.

There are at present few data on the reaction of low-energy electrons with complex molecules in a liquid, so that there is much less justification for using this method of calculation for liquid hydrocarbons than in the case of atomic liquids. Nevertheless, the values calculated using Eqn. (3) show good agreement with experimental data in this case also (Fig. 2). The values of a used in this calculation show a qualitative correspondence to data on the scattering of electrons by hydrocarbon molecules in the gaseous phase[54]. Moreover, the calculation of V_0 for a mixture of hydrocarbons from the values of α and a for the components gives good agreement with experiment [14,55].

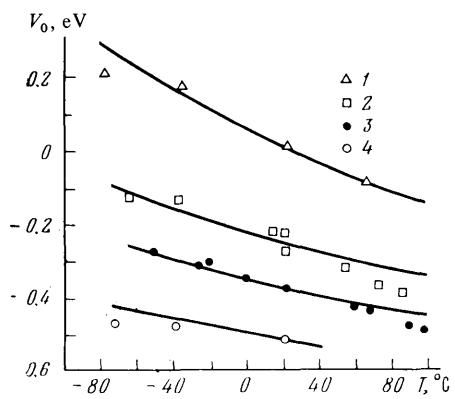


Figure 2. Temperature dependence of the energy of the ground state of a quasi-free electron in liquids. The points give the experimental data[47], and the continuous lines the results of a calculation[47] by the Wigner–Seitz method: 1) n-hexane, 2) iso-octane, 3) 2,2,4,4-tetramethylpentane, 4) tetramethylsilane.

3. Optical Absorption

Because of the high reactivity of an excess electron in non-polar liquids, the measurement of its optical absorption in these media, particularly at room temperature, is more complicated than that for polar liquids. At present, the optical absorption of an excess electron is known for only a few hydrocarbons: for propane at 88 K and 108K,[56] 3-methylhexane at 193 K,[57] and methylcyclohexane at 160K and 293 K.[58] In all cases the form of the absorption spectrum was found to be close to the spectrum of a trapped electron in solid amorphous hydrocarbons. Fig. 3 gives as an example the optical absorption spectra of an excess electron in liquid propane and solid 3-methylpentane.

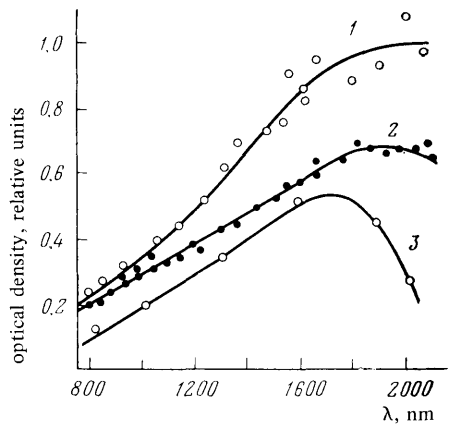


Figure 3. Spectral dependence of the optical absorption: 1) excess electron in liquid propane at 88 K[56] 2×10^{-6} s from the start of a generating pulse of duration 1×10^{-6} s; 2, 3) captured electron in solid amorphous 3-methylpentane at 77 K, 10^{-5} s (2) and 380 s (3) from the start of a generating pulse of duration 10^{-6} s.[59]

The observation of the optical absorption of an excess electron indicates that at least some of the electrons are in a localised state for times greater than the absorption recording time ($> 10^{-8}$ s). At present there is no generally accepted viewpoint on the nature of the localised state of an electron in liquid hydrocarbons. According to a general approach[60], localised states in a liquid may be formed as a result of the capture of an electron by several fluctuations, for example fluctuations in the density or the orientation of the molecules. Studies of the mobility of an electron in a mixture of hydrocarbons[23,29,31] also lead to the conclusion that several molecules take part in the formation of a localised electron.

Of the proposed mechanisms of the localisation of an excess electron in liquid hydrocarbons, the capture of the electron by a cavity between molecules has been examined in most detail[44,61,62]. A similar mechanism was established for liquid helium and neon[6,7], and is assumed for liquid hydrogen and nitrogen[63,64]. Studies of positron annihilation in a number of liquid hydrocarbons[65] confirmed the existence in these liquids of cavities having a radius of ~ 4 Å, suitable for electron capture. Cavities of this size are also postulated in the interpretation of the form of the optical absorption spectrum of a captured electron in solid amorphous hydrocarbons[66]. Numerical calculation[62] of a simple model of a cavity with rectangular walls (see Fig. 4) shows that an electron in a ~ 4 Å cavity may in fact be a stable system in liquid hydrocarbons. For this it must be assumed that the value of the dielectric constant close to the walls of the cavity, determining the energy of

the polarisation of the medium by a localised electron U_{loc}, is greater than the macroscopic value of the dielectric constant. This assumption is justified by the fact that the electron in a cavity "feels" the uncompensated C–H dipole moments of the surrounding molecules. The orientation of these dipoles is apparently responsible for the "blue" shift with time in the absorption spectrum of a captured electron in solid hydrocarbons (see Fig. 3).

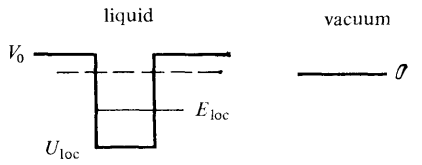


Figure 4. Energy diagram for an electron localised in a cavity. The broken line gives the energy level of the stationary electron in a vacuum, V_0 is the energy of the ground state of the quasi-free electron, and E_{loc} the energy of the localised state.

These proofs of the localisation of the electron in a cavity can only be regarded as indirect, however. It is not excluded that, because of the high dipole moment of individual C–H bonds (~ 0.4 D [67]), the electron is localised, for example, by a "fortuitous coincidence of rotational phases of neighbouring molecules" [11].

4. Some Models of Transfer

The observation of high values of the drift mobilities of an electron in liquid hydrocarbons led immediately to the suggestion that the unusual mobility of the electron in these media is due to the participation, in transfer processes, of an electron in a quasi-free state. Ideas on the high mobility of the quasi-free electron in a liquid had previously been introduced to explain the mobility of the electron in liquefied noble gases. For these media, a theory of the mobility of the quasi-free electron in a liquid was also developed in detail.

The quasi-free electron in monatomic liquids is regarded as a plane wave coherently scattered on atoms. This approach, used by Cohen and Lekner [68,69], was found to be fruitful for the estimation of the mobility of an electron in a weak electric field μ_0, and also in the interpretation of the temperature dependence $\mu_0(T)$ [70] and the dependence of the mobility on the electric field strength in liquid argon. The structure of the liquid was taken into account by means of a radial function of the interatomic distances, and the model potential of the interaction of the electron with an atom was the potential used in the calculation of the energy of the quasi-free electron. According to the theory [68,69]

$$\mu_0 = \frac{2}{3} e (2/\pi m k_B T)^{1/2} / n\sigma S(0), \qquad (4)$$

where $\sigma = 4\pi a^2$ is the cross-section of the elastic scattering of an electron on a sphere having a radius a, $S(0) = nk_BTx$, and x is the coefficient of isothermal compressibility of the liquid.

Fueki and coworkers [54] assumed that Eqn. (4) is also applicable for the mobility of a quasi-free electron in a molecular liquid, if the values obtained from the experimentally determined energies of the quasi-free electron according to Eqn. (3) are used for a. According to their estimates, $\mu_0 = 150 \pm 70$ cm^{2}V^{-1}s^{-1} for various liquids at $T \simeq 300$K. The value $\mu_0 \simeq 150$ cm^{2}V^{-1}s^{-1} for n-hexane, neopentane, and their mixtures is also given by a more rigorous calculation [71] based on a modified Cohen–Lekner theory for monatomic liquids [72].

The data in Table 1 show that the experimental values of the drift mobility of the excess electron in many molecular liquids is much smaller than the assumed values of μ_0 for the quasi-free electron. Moreover, in contrast to the calculated temperature dependence of the mobility of the quasi-free electron, $\mu_0 \sim T^{-3/2}$, for most liquid hydrocarbons the mobility of the excess electron has activational character, which usually indicates that a significant part is played by localised states. Thus the nature of the transfer of an excess electron is different for non-polar molecular liquids, polar liquids, and liquefied noble gases.

The mechanism of electron transfer in non-polar molecular liquids is not clear at present. A common feature of proposed models is the use of ideas on the distribution of the excess electrons between localised and quasi-free states. The following models of the transfer of an excess electron are examined in the literature, depending on the energy distribution of the traps and the mechanism of the liberation of the electron from the trap.

a) "Trap" model

In this model it is assumed that a quasi-free electron in a liquid is captured for a time interval τ_{loc} by structural traps, from which it can be liberated again by thermal excitation. In this case the measured mobility is the sum of the mobilities of the electron in the quasi-free state μ_0 and in the localised state μ_{loc} with allowance for the proportion of the time spent by the electron in these states, that is

$$\mu = \mu_0(1 - P) + \mu_{loc}P, \qquad (5)$$

where P is the probability that the electron is in the localised state.

For the simplest case where all the traps are identical, $P = \tau_{loc}/(\tau_0 + \tau_{loc})$, where τ_0 is the lifetime of the quasi-free electron before capture by the trap. If the mobility of the localised electron is neglected, and it is assumed that $\tau_{loc} = \nu^{-1}\exp(E/k_BT)$, where E is the activation energy of the liberation of the electron from the trap, ν is a frequency factor, and $\tau_0 \ll \tau_{loc}$, then Eqn. (5) gives an Arrhenius type of temperature dependence for the mobility: $\mu = \mu_0\tau_0\nu \exp(-E/k_BT)$. Comparison of the pre-exponential factor of this relationship and the experimental value for $\tau_0 \simeq \nu^{-1}$ leads to the conclusion that μ_0 is approximately the same, ~ 10^2 cm^{2}V^{-1}s^{-1}, for different liquids, in agreement with theoretical estimates.

The pre-exponential factor in the relationship $\mu = \mu_0' \exp(-E/k_BT)$ acquires a different physical significance if a distribution of the traps with respect to energy is assumed. Thus for a linear distribution from 0 to E, we have [29]:

$$\mu = \mu_0(1 + E_1/k_BT)\exp(-E_1/k_BT).$$

Comparison of this form of $\mu(T)$ relationship with the experimental relationship gives values of μ_0 which are smaller, the smaller μ. This change in μ_0 is more realistic, since liquids having a lower value of μ, as a rule,

have less "spherical" molecules, for which stronger scattering of the quasi-free electrons should be expected.

A more complex form of distribution of traps with respect to depth was used by Freeman and coworkers[73,74]. With the assumption that the distribution is Gaussian, and that the position of its maximum is linearly dependent on V_0, they obtained satisfactory agreement with the experimental $\mu(V_0)$ relationship for various hydrocarbons and tetramethylsilane (see Fig. 5).

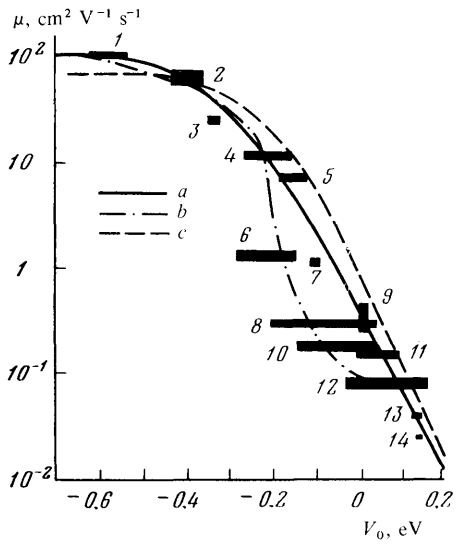


Figure 5. Dependence of the mobility of an excess electron on the energy of the quasi-free electron in a liquid at $T = 294 \pm 2$ K.[74] The lines give the calculated relationships: a) "trap" model with Gaussian distribution, b) "partial localisation" model, c) Kestner–Jortner model. Experimental data: 1) tetramethylsilane, 2) 2,2-dimethylpropane, 3) 2,2,4,4-tetramethylpentane, 4) 2,2-dimethylbutane, 5) iso-octane, 6) cyclopentane, 7) 2,3-dimethylbutane, 8) 2-methylpentane, 9) cyclohexane, 10) 3-methylpentane, 11) n-pentane, 12) n-hexane, 13) n-octane, 14) n-decane.

b) Fluctuation models

Schiller and coworkers[44,61] and Kestner and Jortner[75] tried to describe electron transfer with allowance for fluctuation processes in a liquid. A common feature of these approaches is the assumption that the mobility of the quasi-free electron $\mu_0 \simeq 10^2$ cm^{2}V^{-1}s^{-1} is approximately the same for all liquids.

In the "partial localisation" model[44,61], the probability that an electron is in a localised state P is related to a fluctuation in energy. Here, a central assumption is that there is "unrestrictedly fast exchange of energy between the electron and the molecules of the medium". In accordance with this assumption, the electron is in a quasi-free state if $E_{loc} + E > V_0 + \bar{E}$ (where E and $\bar{E}$ are the energy of the molecules forming the localised state of the electron, and its average value), and becomes localised when $E_{loc} + E < V_0 + \bar{E}$. In this case

$$P = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{V_0} \exp[-(E - E_{loc})^2/2\sigma^2]\, dE,$$

where σ^2 is the dispersion of the distribution with respect to E.

Satisfactory agreement with experimental data for V_0 and μ for $T \simeq 300$ K was obtained for $\sigma = 0.12$ eV (see Fig. 5). The order of magnitude of this value is consistent[44] with the known specific heat capacity of aliphatic hydrocarbons, $C_V = 50$ kcal mole^{-1}K^{-1}.

Kestner and Jortner[75] examined the mobility of a classical electron in a macroscopically non-uniform medium consisting of regions with different potentials of the interaction of the electron with the molecules (V). They assumed that these regions can be divided into two types, depending on the ratio of the values of E and V: "effectively conducting", with electron mobility μ_0, if $E > V$, and "poorly conducting", with electron mobility μ_1 of the order of ionic conductivity, if $E < V$. In this case[75], from the theory of electron transfer in disordered systems[75-78],

$$\mu = \mu_0\left(\frac{3}{2}C - \frac{1}{2}\right), \text{ for } C > 0.4,$$

where C is the volume fraction of the "effectively conducting" regions. Decrease in C from 0.4 to 0 is accompanied by a sharp decrease in μ to the value μ_1 at $C = 0$. To calculated C in various hydrocarbons it was assumed that the difference $\bar{V} - V_0$ (where $\bar{V}$ is the average value of V), and also the average value of E, are constant for all liquids.

Fig. 5 shows that this model is also consistent with experimental data for various liquids. As in other treatments, an exception is provided by the data on μ and V_0 for liquid methane.

c) "Hopping" model

For liquids having a relatively low electron mobility $\mu < 1$ cm^{2}V^{-1}s^{-1}, a transfer mechanism without conversion of the electron to a quasi-free state has also been proposed[79-81]: the electron remains in a localised state until a fluctuation produces in its proximity the same kind of trap, into which the electron "hops". In this case the activation energy of the mobility will be related to the processes of new trap formation and the "hopping" of the electron between traps. This so-called "hopping" mechanism of transfer is used to interpret the mobility of an electron in a large number of solids in which the electron has a low mobility[82], and also in polar[3] and weakly polar molecular liquids.

For liquid normal hydrocarbons at $T \simeq 300$ K, an indication of the hopping mechanism may be provided by data[36], according to which, with increase in the number of carbon atoms in the molecule $n_C > 7$, the mobility of the electron remains approximately constant (~ 0.04 cm^{2}V^{-1}s^{-1}), whereas V_0 continues to increase. In the transfer models examined above, this means that for $n_C > 7$, the quasi-free state does not make a contribution to the mobility, although its value still remains much greater than the mobility of ions.

---o0o---

Thus the comparison of various models of the transfer of an excess electron in non-polar liquids with experiment involves the introduction of many simplifying assumptions. There are insufficient experimental data on $\mu(T)$ and $V_0(T)$ relationships to establish the transfer mechanism, since different models on the whole give satisfactory agreement with experiment. It is therefore necessary to introduce other experimental data. Information on the mobility of a quasi-free electron μ_0 and the density of the energy levels of an excess electron in a liquid $n(E)$ are particularly important. The use of one of the direct methods for determining μ_0—measurement of the Hall effect—is difficult for non-polar liquids, because of the low concentration of excess electrons, and has not yet given any results. The experimental determination of the $n(E)$ relationship can in principle be based on a study of the spectrum of the photo-detachment of an electron from a negative ion in a liquid, by analogy with the method of impurity photoconductivity for semiconductors. The possibility of recording photoconductivity due to the photo-detachment of an electron from negative ions in a non-polar liquid was recently demonstrated[83-85].

A fundamental difference between the mechanisms examined for the transfer of an excess electron in non-polar and polar liquids is the postulate that there is an appreciable probability that the electron is in a delocalised quasi-free state. This characteristic feature of non-polar liquids makes it possible to use direct experimental methods to study the reactivity of a delocalised electron—a short-lived species in condensed matter which is comparatively new in chemical kinetics.

III. CHEMICAL REACTIONS

The view that an excess electron has high reactivity arose in a study of the radiolysis of solutions of electron acceptors[86] long before the drift mobilities of the electron in "pure" liquids were measured. The estimation of the rate constants of the elementary reactions of an electron from the results of these studies was difficult, however, because of the complex kinetics of radiolysis processes. The use of thoroughly purified liquids in experiments made it possible to employ more direct methods to study the reactivity of an excess electron. One of the first direct methods was based on the determination of the lifetime of an excess electron in solution by recording the kinetics of the decrease in its optical absorption[56-58].

The method most widely used at present is pulse electrical conductivity, first used to determine the rate constants of the reactions of an electron by Fuochi and Freeman[19] and Yakovlev and coworkers[87].

Pulse Electrical Conductivity Method

In this method, the electrical conductivity of solutions is measured in a direct current circuit with the pulse generation of excess electrons in it (Fig. 6). The electrons are generated by the ionisation of solvent molecules by hard radiation (high-energy electrons, bremsstrahlung) or by two-quantum photo-ionisation of impurity molecules[24,88]. The ionisation of molecules in an amorphous substance leads to the formation of two types of electron–ion pair: pairs in which the electrons recombine with "their own" positive ion or an ion of "their own" tracks (so-called "primary" recombination), and pairs which avoid primary recombination or "free charges". The electrical conductivity method is convenient in that it is "sensitive" only to "free" electrons and ions, since the pairs taking part in the "primary" recombination do not make an overall contribution to the transfer of charge in a constant electric field. Processes involving "free" species can be described by the equations of ordinary homogeneous kinetics, and this simplifies considerably the analysis of the data obtained.

Since the mobility of an excess electron is much greater than the mobility of ions, excess electrons make the greatest contribution to the electrical conductivity with the condition that their concentration is comparable with the concentration of ions. These conditions are produced, for example, after the action of a short pulse of ionising radiation for times comparable with the lifetime of the excess electrons in solution. The rate of disappearance of the electrons in a solution is determined by several processes: recombination with positive ions in solution or at an electrode, and reactions with impurity molecules. Since electrical conductivity can be measured at very low concentrations of electrons ($\sim 10^8$ electron cm^{-3}) and large distances (~ 1 cm) between the electrodes, the experimental conditions can be selected so that one of these processes is the chief process.

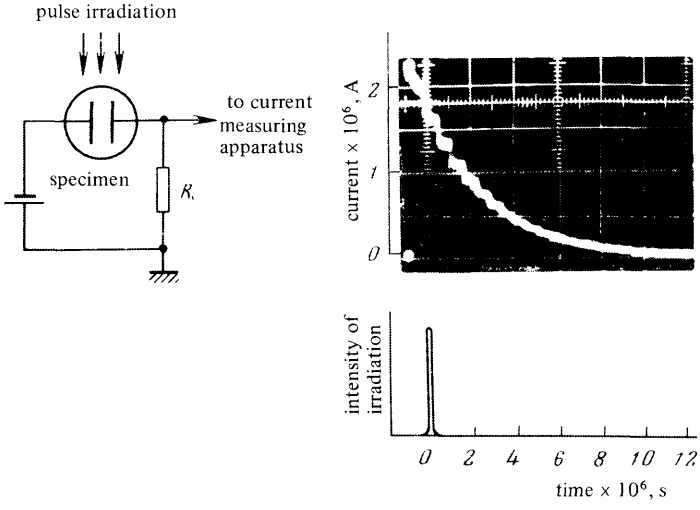


Figure 6. Measurement of the current of excess electrons in the pulse electrical conductivity method. The oscillogram of the current for a solution of pyrene in n-hexane at a concentration 1×10^{14} cm^{-3}.[28]

If the disappearance of the electrons takes place chiefly at the electrodes, it follows that for generation which is uniform throughout the volume, at $t = 0$, the decrease in the current will be described by a linear time dependence:

$$I \sim (1 - t/t_{\lim}) \text{ for } t < t_{\lim}.$$

Most of the data on the mobility of an excess electron have been obtained by recording relationships of this kind.

Under conditions in which the electrons disappear chiefly as a result of their capture by a molecule of an acceptor A

$$e^- + A \rightarrow A^-, \qquad (6)$$

when $[A] \gg [e^-]$, the decrease in the current will be described by an exponential relationship

$$I(t) \sim [e^-] \sim \exp(-t/\tau_3) \qquad (7)$$

where $\tau_3^{-1} = \Sigma k_i[A_i]$, $[e^-]$ is the concentration of excess electrons, k_i the rate constant of reaction (6), and $[A_i]$ the concentration of the acceptor i.

To illustrate this form of time dependence of the current, Fig. 6 gives the oscillogram of the current induced by a pulse of ionising radiation in a solution of pyrene in liquid hexane at a concentration of 1×10^{14} cm^{-3}. As follows from Eqn. (7), an increase in the concentration of the acceptor is accompanied by a decrease in the lifetime of the excess electron in solution (see for example Fig. 7). The rate constant of the capture reaction can be determined from the time of the exponential decrease in current if the duration of the generating pulse is sufficiently short, or from an analysis [29,87] of the more complex character of the change in current if $\tau_{pulse}^{-1} < k[A]$.

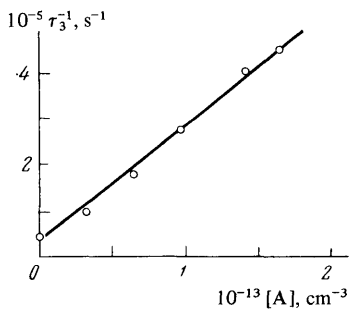


Figure 7. Plot of the reciprocal of the lifetime of an excess electron in liquid iso-octane solutions at 296 K against the pyrene concentration [17].

The electrical conductivity method has now been used to measure a large number of rate constants for the reactions of an excess electron in various liquid hydrocarbons. These reactions involve chiefly the capture of the excess electron by a neutral molecule of an acceptor (5) and the recombination of the electron with a positive ion

$$e^- + M^+ \rightarrow \text{(disappearance of } e^-\text{)}. \qquad (8)$$

2. Recombination Reaction

In the experimental study of reaction (8) in liquid hydrocarbons, it is usual to select conditions in which recombination is the chief process responsible for the disappearance of the excess electrons in the volume between the electrodes. In this case, data on the kinetics of the electrical conductivity, induced in the liquid by the pulse of ionising radiation, during [29,87,89] or after [89-91] the pulse make it possible to determine the ratio k_r/μ, where k_r is the recombination rate constant, and, when μ is known, to obtain k_r.

Fig. 8 gives the dependence of k_r on the mobility of the excess electron in various hydrocarbons and tetramethylsilane. For liquid hydrocarbons with an electron mobility $\mu < 10$ cm^{2}V^{-1}s^{-1}, the values of k_r, within the limits of accuracy of the measurements (~ 10%), satisfy the Langevin relationship

$$k_r = 4\pi e\mu/\varepsilon \qquad (9)$$

where ϵ is the dielectric constant. Eqn. (9) is based on the assumption that the reaction rate is limited by the diffusion of the recombining species, and that their path length before the loss of momentum l is shorter than the distance r_c at which the energy of the Coulombic interaction between the positive current and the electron is equal to k_BT (for non-polar liquids at $T \simeq 300$K, $r_c \simeq 300$ Å). For the excess electron, the last condition agrees with the assumed relatively low value of the mobility of the quasi-free electron ($\mu_0 \simeq 10^2$ cm^{2}V^{-1}s^{-1}), which corresponds to $l \simeq 60$ Å.

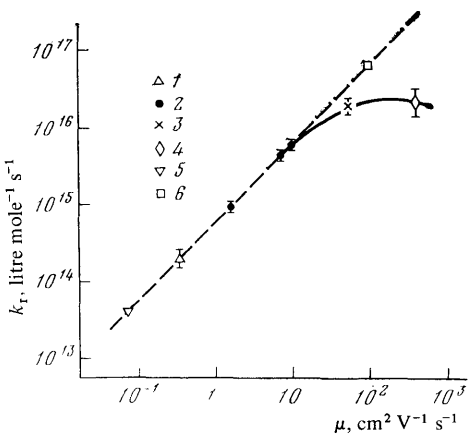


Figure 8. Dependence of the rate constant for electron-ion recombination on the mobility of an excess electron in non-polar liquids: 1) cyclohexane, 296 K [87]; 2) iso-octane, 200, 296, and 340 K [90]; 3) neopentane, 296 K [89]; 4) methane, 110 K [87]; 5,6) n-hexane, tetramethylsilane, 296 K. [29]

For liquids with a high excess electron mobility (neopentane, tetramethylsilane), the recombination rate constant has the highest values for bimolecular reactions in a liquid, ~ 10^{15} litre mole^{-1}s^{-1}. It is at present not clear whether the value of k_r for these liquids obeys the Langevin relationship: some data [19,29] give a ratio k_r/μ equal to the theoretical value, whereas other data [89] give values for this ratio which are smaller by factors of 1.5 for neopentane and 15 for liquid methane.

3. Capture Reactions

The reaction rate constants k for the capture of an electron in many non-polar liquids are now known for various acceptors. The following list of acceptors for which constants have been determined gives some idea of the range of studies carried out: O_2, [24,25,29,57,91-97] I_2, [92] CO_2, [91,93,95,98] N_2O, [33,84] SF_6, [33,99] CCl_4, [24,33,62,91-93,95,96] CH_3I, [29] C_2H_5Cl, [33] C_2H_5Br, [29,33] C_2HCl_3, [33] C_2H_3Cl, [33] biphenyl [24,96,91-93], pyrene [28,62,87,96,99], perylene [96], naphthalene [91], diphenylanthracene [93], and alcohols [91,100]. For "good"

electron acceptors, such as CCl_4, SF_6, N_2O, etc, in liquid hydrocarbons at $T \simeq 300$ K, the rate constants lie in the range 10^{12}–10^{14} litre mole^{-1}s^{-1}, that is they are 10–10^3 times greater than the rate constants of the analogous reactions of the hydrated electron.

Since in polar liquids the rate of the fast reactions of an electron are limited by the diffusion of the electron to the molecule of the acceptor, it is natural to relate the unusually high value of k primarily to the high mobility of the excess electron in non-polar liquids. The increase in k on going to liquids exhibiting a high mobility is also observed for non-polar liquids with a relatively low electron mobility (< 10 cm^{2}V^{-1}s^{-1}). For these liquids, the increase in reaction rate with increase in temperature characteristic of chemical reactions is also observed (Fig. 9). The dependence of k on T and μ for the capture of an electron by various acceptors in liquids with a high electron mobility is more unusual: k increases with decrease in T and decreases on going to liquids exhibiting a higher mobility.

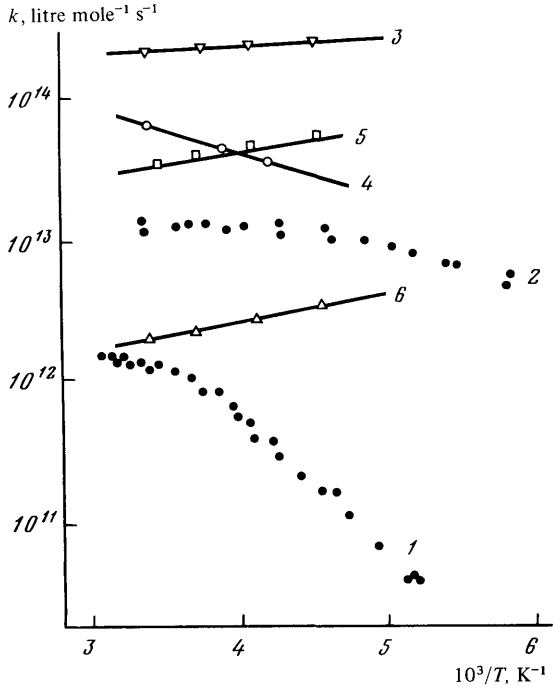


Figure 9. Temperature dependence of the rate constants for the capture of an excess electron by acceptor molecules: 1) and 2) pyrene in n-hexane[28] and iso-octane[17]; 3,4,5), and 6) SF_6, CCl_4, C_2HCl_3 and N_2O in tetramethylsilane[33].

The study of the mechanism of the capture of an electron in non-polar liquids has only begun. One of the tasks in this field is to determine the state, localised or quasi-free, in which the electron is captured by the acceptor molecule.

4. Role of the Localised and Quasi-Free Electron

With allowance for the two states of an excess electron in non-polar liquids—localised e^-_{loc} and quasi-free e^-_0—the kinetic scheme for the capture reaction can be represented in the form

$$\begin{array}{ccc} e^-_0 + A & \xrightarrow{k_0} & A^- \\ \downarrow\uparrow & & \nearrow \\ e^-_{loc} + A & \xrightarrow{k_{loc}} & \end{array}$$

From various estimates[101,102], the time required to establish the equilibrium $e^-_0 \rightleftharpoons e^-_{loc}$ is much shorter ($< 10^{-11}$ s) than the characteristic reaction times in the experimental determination of rate constants ($> 10^{-8}$ s), so that the values of the constants can be broken down into two components

$$k = k_{loc} P + k_0 (1 - P) \qquad (10)$$

where P is the probability of localisation, and k_{loc} and k_0 the reaction rate constants for the capture of an electron in localised and quasi-free states.

Which of these states makes the main contribution to the reaction rate? In the examination of this question for a qualitative estimate of the magnitude of P it is convenient to use the relationship

$$P = 1 - \mu/\mu_0, \qquad (11)$$

applicable for the trap model of the mobility of an excess electron, with the assumption that the mobility of the quasi-free electron is approximately the same for different liquids.

a) Reactions of a localised electron

It may be expected that for liquids for which the degree of localisation of an excess electron is high, so that its mobility is low, the localised state plays an important role in the chemical reactions of the excess electron.

For the capture of an electron by an O_2 molecule, which is a "poor" electron acceptor in non-polar liquids, this assumption is confirmed by the determination of the reaction rate constant $k(O_2)$ in various liquid hydrocarbons. The experimental data[94,97,103] show that the values of $k(O_2)$ are approximately constant for all liquids with low electron mobility studied (n-hexane, methylcyclohexane, cyclohexane, iso-octane), although for these liquids, the coefficient of diffusion of the electron and hence μ change by a factor of more than 70 (see Fig. 10). Eqns. (10) and (11) and the dependence of $k(O_2)$ on μ indicate that the main contribution to the reaction rate is made by the localised electron.

It may be assumed that the molecules of "good" acceptors in hydrocarbons having a low electron mobility also capture chiefly excess electrons in a localised state. In fact, the rate constants for the reactions of an electron with these acceptors are extremely high. For example, in n-hexane at $T \simeq 300$ K for SF_6, CO_2, pyrene, C_2H_5Br, etc., $k > 10^{12}$ litre mole^{-1}s^{-1}. If the contribution of localised electrons to the reaction rate were not the main contribution, then from Eqns. (10) and (11) it would be necessary, for these values of k, to assume values of $k_0 \simeq k/(1-P)$ which are too high. Thus in the "trap" model of transfer for $k = 10^{12}$ litre mole^{-1}s^{-1}, $\mu = 0.1$ cm^{2}V^{-1}s^{-1}, and $\mu_0 = 10^2$ cm^{2}V^{-1}s^{-1}, it would be necessary to assume that $k_0 = 1.2 \times 10^{15}$ litre mole^{-1}s^{-1}, which is greater than the limiting value for the reaction of a thermal electron in the gaseous phase $k_{lim} = \pi\lambda^2 v$, where $2\pi\lambda$ is the de Broglie wavelength, and v the velocity of the electron.

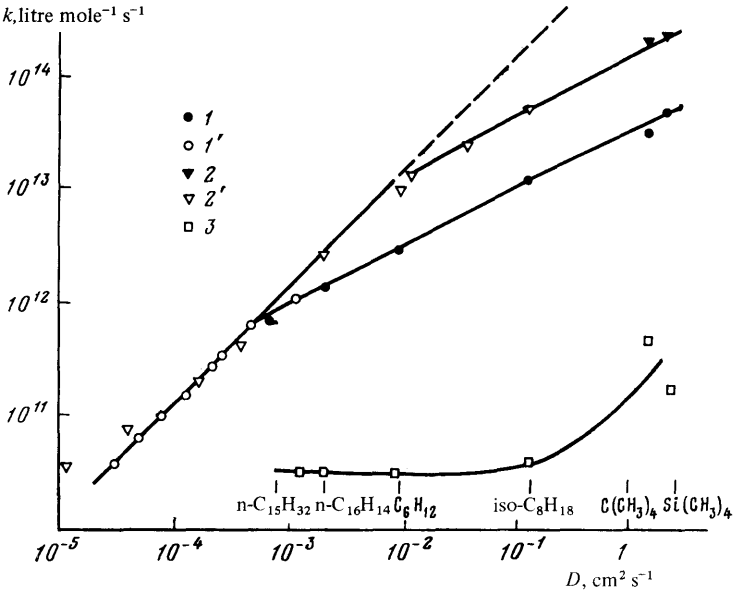


Figure 10. Relationship between the coefficient of diffusion of an excess electron and the reaction rate constants for the capture of the electron by the molecules of: 1,1′) pyrene in n-hexane, cyclohexane[28], iso-octane[17], pentadecane, and neopentane[135]; 2,2′) SF_6 in propane, ethane, n-hexane[99], and iso-octane[43]; 3) O_2 in methylcyclohexane, n-hexane, cyclohexane, iso-octane, neopentane, and tetramethylsilane[94,103]. The points *1*, *2*, and *3* relate to room temperature. The broken line corresponds to the relationship $k = 4\pi DR$ for $R = 16$ Å.

b) Reactions limited by diffusion

Fig. 10 gives data on the dependence of the rate constants for the capture of an electron by "good" acceptors on the diffusion coefficient of the excess electron D. The values of D were determined from the mobility of the electron using Einstein's relationship $D = kT\mu/e$. It can be seen that at values of $D < 10^{-3}$ cm^2s^{-1} (or $\mu < 0.1$ $cm^2V^{-1}s^{-1}$), the values of k are approximately proportional to D. This $k(D)$ relationship indicates that the reaction rate is limited by the diffusion of the excess electron to the acceptor molecule. For reactions of this type in non-polar liquids, the values of the radius of the reaction, characterising the distance between the species at the moment of electron transfer, are unusually high. Table 2 shows that the Debye–Smoluchowski equation for the radius of the reaction $R = k/4\pi\ (D + D_A)$, where $D_A \ll D$ is the diffusion coefficient of the molecule of the acceptor, gives values of 10–30 Å for the reactions of electron capture in liquid hydrocarbons, whereas for the diffusion-limited reactions of the solvated electron in water, R amounts to 2–3 Å.

The reason for the high values of the radii of reactions in liquid hydrocarbons is not clear. Estimates[28,104] show that it is difficult to attribute these values to the polarisation interaction of the excess electron and the acceptor molecule. If it is assumed that the electron is captured by the acceptor chiefly from the localised state, the high values of R can in principle be attributed to the large radius of the localised electron[28]. Radii of 20–30 Å for the localised electron are also postulated in the discussion of data on the mobility of an excess electron in liquid propane and pentane in strong electric fields[37].

It is possible, however, that the values obtained for R are effective values and are associated with a tunnel reaction mechanism.

Table 2. Radii of the reaction for the capture of an excess electron, calculated from the equation $R = ek/4\pi k_B T\mu$.

Acceptor	Liquid	T, K	μ, $cm^2\ V^{-1}\ s^{-1}$	k, litre $mole^{-1}\ s^{-1}$	R, Å
Pyrene	pentadecane	296	$3\cdot10^{-2}$ [135]	$6.6\cdot10^{10}$ [135]	11.6
SF_6	n-hexane	246	$1.8\cdot10^{-2}$ [99]	$3.8\cdot10^{11}$ [99]	13.5
C_2H_5Br	n-hexane	250	$2.3\cdot10^{-2}$ [28]	$5.0\cdot10^{11}$ [28]	13.8
Pyrene	n-hexane	250	$2.3\cdot10^{-2}$ [28]	$5.9\cdot10^{11}$ [28]	16.3
C_2HCl_3	n-hexane	253	$2.24\cdot10^{-2}$ [33]	$6.4\cdot10^{11}$ [33]	18
SF_6	propane	139	$3\cdot10^{-3}$ [99]	$7.2\cdot10^{10}$ [99]	26.5
SF_6	ethane	142	$4\cdot10^{-2}$ [99]	$1.0\cdot10^{12}$ [99]	27.5
SF_6	ethane	110	$1.3\cdot10^{-3}$ [99]	$5.0\cdot10^{11}$ [99]	55

c) Tunnel mechanism of capture

This mechanism has recently been frequently introduced in the discussion of the capture of an excess electron in polar liquids and solids[105–108]. With allowance for the diffusion of the electron and the acceptor molecule[108], the reaction rate constant for capture by a tunnel mechanism can be represented in the form $k = 4\pi DR_{eff}$, where the effective radius of the reaction is given by

$$R_{eff} = R_c + [1.15 + \ln(\alpha'/\beta^2 D)]/\beta, \qquad (12)$$

R_a is the sum of the radii of the acceptor molecule and the localised electron, α' a frequency factor, and $\beta = 2\hbar^{-1}[2m(V_0 - E_{loc})]^{1/2}$ is the attenuation factor of the wave function of the localised electron.

Eqn. (12) makes it possible to explain the high values of the radius of the reaction for the capture of an electron in liquid hydrocarbons. In fact, for these media the magnitude of the electron tunneling barrier $V_0 - E_{loc}$, equal in the simple trap transfer model to the activation energy of the mobility of the electron, is apparently less than 0.2 eV. If it is assumed that $\alpha' \simeq 10^{13}\ s^{-1}$, as is usually done for tunnel reactions in solid solutions [108], then for $V_0 - E_{loc} = 0.2$ eV and $D \simeq 10^{-4}\ cm^2 s^{-1}$, Eqn. (12) gives $R_{eff} \simeq 3R_a$. This estimate, for $R_a \simeq 5$ Å, shows qualitative agreement with the experimental data for the capture of an electron by "good" acceptors in liquid hydrocarbons characterised by low excess electron diffusion coefficients. It should be noted that the tunnel reactions of an electron in non-polar liquids differ from those in polar liquids in that the barrier to tunneling is appreciably smaller (for water, $V_0 - E_{loc} \simeq 1.5$ eV [108]). This means that, other conditions being equal, the rate of tunnel transfer from a distance of ~ 20 Å is $\geq 10^8$ times higher in liquid hydrocarbons than in water.

The assumption that the magnitude of the electron tunneling barrier in liquid hydrocarbons is approximately equal to the activation energy of the mobility of the electron also makes it possible to understand the order of magnitude of k for liquids with a high electron diffusion coefficient $D > 10^{-3}\ cm^2 s^{-1}$. In this range of values of D, the ratio k/D for many "good" acceptors decreases with increase in D (see for example Fig. 10), indicating that diffusion restrictions on the rate of reaction are removed. A qualitative estimate of the rate constant k' for the reaction not restricted by diffusion can be obtained by assuming that the concentration of localised electrons is independent of the distance r to the acceptor molecule. In this case

$$k' = \int_{R_a}^{\infty} 4\pi r^2 \omega(r)\, dr, \qquad (13)$$

where $\omega(r) \simeq 10\alpha' R^2 e^{-\beta(r-Ra)}/4r^2$ [108] is the probability of tunnel transfer, if the distance between the localised electron and the acceptor molecule is equal to r.

Eqn. (13) for $\alpha' \simeq 10^{13}\ s^{-1}$, $B_a = 5$ Å, and $V_0 - E_{loc} \simeq 0.1$ eV gives $k' \simeq 10^{13}$ litre $mole^{-1} s^{-1}$, which is of the same order of magnitude as the experimental values of k for acceptors such as N_2O, CCl_4, pyrene, biphenyl, and CO_2 in liquids with a high excess electron mobility (iso-octane, neopentane). At present, however, the tunnel mechanism of capture is not unambiguous for non-polar liquids with a high excess electron mobility. It is possible that as a consequence of the low degree of localisation of the electron in these liquids, the acceptor captures the electron in a quasi-free state.

d) Reactions of the quasi-free electron

The chemical reactions of a delocalised electron in condensed media have recently been introduced to interpret fast reactions involving electrons formed in the tracks of charged particles. It is assumed that in polar liquids, the delocalised state of the track electron, often called "dry", precedes the formation of the solvated electron. Attempts to determine the reactivity of "dry" electrons have been based on the study of the influence of an acceptor on the yield of solvated electrons [109-114] or the probability of positronium formation in a positron track [115-117]. Because of the short lifetime of the "dry" electron in polar liquids and the complex nature of the kinetics of track processes, the use of these methods to study the elementary reactions of a delocalised electron presents considerable difficulties. In the case of non-polar liquids, it is possible to use for this purpose a more direct method based on the study of the reactions of excess electrons which have avoided track recombination. The use of this method for electrons in liquefied noble gases, for which the quasi-free state of an electron is stable, has shown [118,119] that the reaction rate constants for the capture of a quasi-free electron may reach extremely high values (for example, 3×10^{14} litre × $mole^{-1} s^{-1}$ for SF_6 in liquid xenon).

In non-polar molecular liquids, the study of the reactions of the quasi-free electron is complicated by the fact that the reactions of the excess electron in the localised state are also possible. In the case of the reactions of an excess electron not restricted by diffusion, the reaction rate constant for the capture of a quasi-free electron k_0 can be estimated from Eqns. (10) and (11) and the experimental $k(\mu)$ relationship for different liquids. This approach has been used [94,103] to study the reaction

$$e_0^- + O_2 \rightarrow O_2^-. \qquad (14)$$

As already noted, the reaction rate constant for the capture of an excess electron by an O_2 molecule is approximately the same for different liquid hydrocarbons having an electron mobility $\mu < 10\ cm^2 V^{-1} s^{-1}$. On going to liquids with high values of μ (neopentane, tetramethylsilane), the value of the constant increases considerably (see Fig. 10). This increase can be attributed to an increase in the contribution of the quasi-free electron e_0^- to the reaction rate. The values obtained with this assumption for the rate constant of reaction (14), $k \simeq 3 \times 10^{11}$ litre × $mole^{-1} s^{-1}$ at 300 K, and the activation energy, < 0.01 eV [94,103], agree with the results of the study of the capture of a quasi-free electron in liquid krypton and argon [119].

The assumption that the capture of an electron in a quasi-free state predominates in liquids characterised by a high electron mobility makes it possible to explain the negative activation energy for various reactions, and also the existence of a maximum on the curve giving the dependence of k on the energy of the quasi-free electron (see Fig. 11). For the interpretation of these results, existing views on the reaction of low-energy electrons with molecules in the gaseous phase have proved useful.

e) Comparison with gas-phase data

At present, only the first attempts [33,103,120,121] have been made to examine theoretically the capture of a quasi-free electron by an acceptor molecule in a liquid. These attempts are based on the assumption that the mechanism of these reactions is analogous to that of the reactions of ar electron with molecules in the gaseous phase. In the last case it is usually assumed [123,124] that for an electron with a low energy (< 3 eV) the reaction takes place in two stages:

$$\text{I.}\quad e_0^- + A \underset{\tau_1^{-1}}{\overset{k'}{\rightleftarrows}} (A^-)^*$$

$$\text{II.}\quad (A^-)^* \rightarrow A^-$$

$$(A^-)^* \rightarrow B^- + D \quad .$$

Stage I is the formation of an intermediate vibrationally excited ion $(A^-)^*$ (τ_1 is the lifetime of the ion with respect to self-ionisation), and stage II is the stabilisation of the

ion as a result of collision with a third particle or dissociation. For the first stage of the reaction, the difference from the gaseous phase is that in the liquid, the term of the initial state (acceptor molecule + delocalised electron) is displaced along the energy scale by an amount V_0, and the term of the final state (the negative ion of the acceptor) is displaced by an amount equal to the energy P_- of the electronic polarisation of the molecules of the medium by the negative ion, situated in the same environment as the acceptor molecule before electron capture. Thus in the gaseous phase the formation of various states of the negative ion takes place at an electron energy ϵ_m, whereas in the liquid this requires the kinetic energy of the quasi-free electron

$$\tilde{\epsilon}_m = -V_0 + P_- + \epsilon_m \ . \qquad (15)$$

For many negative ions in non-polar liquids, $-P_- = 1.5 \pm 0.8$ eV.[85,121] Thus a thermalised quasi-free electron in a liquid with $-0.6 < V_0 < +0.2$ eV may lead to the formation of the same states of the negative ion as an electron in the gas with an energy 0.3–2.5 eV.

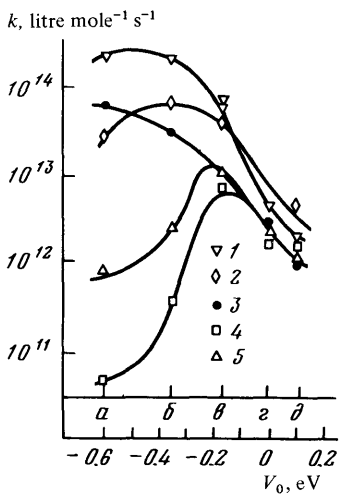


Figure 11. Relationship between the energy of a quasi-free electron V_0 and the reaction rate constants for the capture of an excess electron by molecules of SF_6 (1), C_2HCl_3 (2), CCl_4 (3), C_2H_5Br (4), N_2O (5).[33] The values of k and V_0 were measured for the following liquids at room temperature: tetramethylsilane (a), neopentane (b), isooctane (c), cyclohexane (d), and n-hexane (e).

In this approach it is possible to attribute the maxima on the curve giving the dependence of k on V_0 (see Fig. 11) to the fact that the thermal energy of the quasi-free electron corresponds to a maximum cross-section for the formation of the intermediate ion, that is $3/2k_BT = \epsilon_m - V_0 + P_-$. For the C_2HCl_3 molecule, for example, $\epsilon_m = 0.4$ eV,[125] so that for $P_- \simeq -0.7$ eV,[33] a maximum capture cross-section should be expected at $V_0 \simeq -0.3$ eV, in agreement with the data in Fig. 11. Since for $3/2k_BT > \epsilon_m - V_0 + P_-$ a decrease in V_0 leads to deterioration in the resonance conditions, it is also possible to understand the decrease, unusual for classical diffusion theory, in the reaction rate constant on going to liquids with a higher electron mobility and hence a lower value of V_0. A decrease in k with decrease in V_0 is characteristic of not only C_2HCl_3 but also other acceptors: N_2O, CO_2, and C_2H_5Br, the molecules of which have a negative electron affinity in the gaseous phase[33,120].

The assumption that the mechanism of the capture of a quasi-free electron is analogous to that of the reaction in the gas also makes it possible to explain the negative activation energies for various reactions involving the capture of an excess electron in a non-polar liquid (see Fig. 9). In fact, for $3/2k_BT > \epsilon_m - V_0 + P_-$, decrease in temperature leads to an improvement in the conditions for resonance, since V_0 increases (see Fig. 2). Moreover, an estimate[103] of the absolute magnitude of the rate constant of the reaction $e_0^- + O_2 \rightarrow O_2^-$, based on gas-phase data on the cross-section for the formation of the intermediate ion O_2^-, gives satisfactory agreement between experiment and the activation energy and the order of magnitude of k.

5. Excess Electrons in the Primary Processes of Photolysis and Radiolysis

Recent quantitative data on the mobility and reactivity of an excess electron are extending considerably the possibilities provided by the analysis of the kinetics of various electronic processes in molecular liquids. Of greatest interest among these, judging from the number of published papers, are the primary photochemical and radiation-chemical processes in liquid solutions.

As already noted, the ionisation of molecules in a liquid leads to the formation of two types of electron–ion pair: pairs involved in "primary recombination", and pairs which avoid this recombination, or "free" charges. In the formation of electron–ion pairs under the influence of ionising radiation[126,127] or as a result of two-quantum ionisation[128], only a small fraction of the electrons become "free" (from 2% in liquid n-hexane to 20% in neopentane). For many-component systems, the direction of the chemical processes taking place after ionisation is determined to a great extent by the proportion of electrons captured by acceptor molecules before recombination.

The theoretical approaches used to describe the kinetics of "primary" recombination in the presence of electron acceptors are based on the theories of diffusion and drift in the Coulombic field of the electrons, which are regarded as classical charged particles, in thermal equilibrium with the medium[129–132]. The most widely accepted theory at present is that proposed by Hummel[130] and subsequently developed for radiation problems[132–134].

This theory examines the distribution with respect to lifetimes $n(t)$ of the number of electrons undergoing "primary" recombination in the pure solvent. It is assumed that among these electrons, the proportion of electrons recombining with a positive ion in the presence of an acceptor is given by

$$N = \int_0^\infty n(t)\, e^{-k[A]t}\, dt, \qquad (16)$$

where k is the rate constant of the capture reaction. In this approach, the moment of time corresponding to the recombination of the negative ion A^- formed by the capture of an electron by the acceptor can be expressed simply in terms of the lifetime of the electron in the pure solvent $t(e^-)$ and the ratio of the drift mobilities of the electron and the ion r_d. In fact, for classical particles, the rate of

recombination is inversely proportional to the sum of their mobilities, so that $t(A^-) = t_c + [t(e^-) - t_c]r_d$, where t_c is the time of electron capture, and $t(A^-)$ the time of ion recombination. A knowledge of the distribution of the mobilities and the rate constants of the charged species makes it possible to obtain a complete description of the kinetics of "primary" recombination.

Eqn. (16), which is the Laplace transform for the function $n(t)$, makes it possible to establish the distribution of electrons with respect to lifetime up to the moment of recombination from the experimental dependence of N on [A]. In the case of the radiolysis of non-polar solutions, for the determination of $N([A])$ in the Hummel–Schuler theory, the empirical dependence of the yield of the ions A^- on the concentration of the acceptor[86] is used:

$$G(A^-) = G_{fi} + G_{prim}\frac{(\alpha[A])^{1/2}}{1+(\alpha[A])^{1/2}}, \qquad (17)$$

where G_{fi} is the yield of "free" ions, $G_{prim} \simeq 4$ is a parameter interpreted as the yield of electrons taking part in "primary" recombination, and α a coefficient which depends on the properties of the acceptor and the solvent. From Eqn. (17) it follows that

$$1 - N = \frac{(\alpha[A])^{1/2}}{1+(\alpha[A])^{1/2}}. \qquad (18)$$

According to a calculation[132] based on Eqns. (16) and (18), $\alpha = k/\lambda$, where λ is a coefficient characterising the rate of the "primary" recombination, and the distribution function has the form:

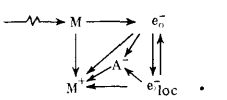
$$n(t) = -\frac{d}{dt}\left[e^{\lambda t}\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{\sqrt{\lambda t}} e^{-x^2}dx\right)\right]. \qquad (19)$$

The value of λ can be estimated from experimental data for k and α. For example, for liquid cyclohexane at $T \simeq 300$ K, this estimate gives $\lambda \simeq 2 \times 10^{11}$ s^{-1},[33] which for $n(t)$ of form (19) corresponds to a time of recombination of 50% of the electrons $t_{1/2} = 0.6\,\lambda^{-1} = 3 \times 10^{-12}$ s.

Values recently obtained for k and the mobility of an excess electron show satisfactory agreement[135-139] within the framework of the diffusion models with data for the yield of negative ions in liquids with a relatively low electron mobility ($\mu < 10$ cm^{2}V^{-1}s^{-1}). Moreover, the results of the study of the $n(t)$ relationship, obtained by measuring the optical density of electrons[56,58], lead to $\int_t n(t)dt \sim t^{-1/2}$, which corresponds to Eqn. (19) for $t \gg \lambda^{-1}$. It has also been established that diffusion theory effectively described the kinetics of the decrease in the quantity of biphenyl ions formed in the nanosecond radiolysis of a solution of biphenyl in cyclohexane[140].

In the interpretation of the results in all these cases, the electron was regarded as a classical particle with a mobility equal to the drift mobility of the excess electron. In relation to recently discussed models of the movement of an electron in a non-polar liquid, which assume the participation of quasi-free and localised states of the electron, these ideas can be justified if two conditions are satisfied. Firstly, the free path l of the quasi-free electron must be less than the characteristic dimension of the problem being considered[141]. In the study of the kinetics of "primary" recombination, this dimension is the distance from the positive ion on which the electron is thermalised. For most excess electrons generated by ionising radiation in a non-polar liquid, this distance is 60–100 Å.[40] In photo-ionisation it may be even smaller (~ 30 Å[50]). Since the assumed value of the mobility of a quasi-free electron, $\sim 10^2$ cm^{2}V^{-1}s^{-1}, corresponds to $l \simeq 60$ Å, this condition is apparently fulfilled only for a small proportion of the excess electrons, thermalised at distances greater than the average thermalisation length. Secondly, the processes being considered must be sufficiently slow, compared with the time taken for equilibrium to be established between the quasi-free and localised states, since otherwise it is not possible to use the drift mobility to determine the rate of recombination of the electron, and the constant k to calculate the probability of the capture of an electron by an acceptor molecule.

In the more general case it is necessary to consider a scheme of "primary" recombination including processes involving the capture and recombination of a quasi-free electron before localisation:



In contrast to diffusion models, the description of the kinetics of the processes in this scheme requires data on the spatial and time distribution separately for both the quasi-free e_0 and localised e^-_{loc} electrons and the probabilities of their reactions with an acceptor molecule.

The satisfactory agreement, described above, between diffusion theories and experiment is apparently related to the fact that in all cases the processes considered were comparatively slow, with characteristic times greater than the lifetime of the localised electron. For cyclohexane, for example, the lifetime of an electron in a localised state is $\tau_{loc} \simeq 10^{-10}$ s at $T = 300$ K, if it is assumed that the energy of liberation of an electron from a structural trap in the liquid is equal to the activation energy of the mobility of the electron (0.17 eV[21]), and the frequency factor is $\nu \simeq 10^{13}$ s^{-1}. Thus by using nanosecond technique for kinetic studies of "primary" recombination in this liquid, it is possible to "feel" only those electrons which are captured many times by the traps. This conclusion also applies to the method of studying kinetics based on an analysis of the concentration dependence of the yield of the negative ions of the electron acceptors, at concentrations of the acceptor $[A] \leq 10^{-2}$ M, for which $k[A] < \tau^{-1}_{loc}$.

At acceptor concentrations $[A] \simeq \tau^{-1}_{loc} k^{-1}$, the acceptor will efficiently capture electrons which have undergone a small number of transitions between localised states. The value of the drift mobility of the electron cannot be used to describe the motion of these electrons and hence the kinetics of the recombination of the negative ions for which they are the precursors.

At even higher acceptor concentrations, the quasi-free electron may be captured by an acceptor immediately after ionisation, before it is thermalised or localised in a structural trap. This possibility at $[A] > 10^{-1}$ M is assumed, for example, in the discussion of the influence of electron acceptors on the yield of "free" ions[142] or on the probability of positronium formation in a positron track[116,117]. In this case the equilibrium distribution of the excess electron with respect to states is broken down, so that Eqn. (16) becomes inapplicable.

Thus the determination of the distribution function of the electrons $n(t)$ from the experimental dependence of $G(A^-)$ on [A] at $t < \tau_{loc}$ can hardly be reliable. This possibly explains why the time of the "primary" recombination of 50% of the electrons in liquid cyclohexane, estimated by this method (3×10^{-12} s), was found to be shorter than the

lifetime of the electron in a localised state (10^{-10} s), assumed from data on the mobility of the excess electron.

Thus the use of the diffusion approach in the analysis of electron processes following ionisation is justified only for processes with a characteristic time $\gg \tau_{loc}$. In the examination of processes involving an excess electron for times $< \tau_{loc}$, the data at present available on the reactivity and mobility of the excess electron are inadequate. It is necessary to have data on the dynamics of the thermalisation and localisation of the electron, on the proportion of electrons recombining with a "free" ion without the stage involving localisation in the liquid, and on the distribution of these electrons with respect to their lifetime before recombination. Direct quantitative data of this kind will apparently be obtained in the near future by the use of nanosecond techniques.

REFERENCES

1. A.K.Pikaev and A.M.Brodskii, Khim.Vys.Energ., 6, 224 (1972).
2. E.J.Hart and M.Anbar, "The Hydrated Electron" (Translated into Russian), Atomizdat, Moscow (1973).
3. A.V.Vannikov, Uspekhi Khim., 44, 1971 (1975) [Russ.Chem.Rev., No.11 (1975)].
4. V.A.Benderskii and A.M.Brodskii, "Fotoemissiya iz Metalla v Rastvor Elektrolita" (Photo-emission from a Metal into an Electrolyte Solution), Izd. Nauka, Moscow (1977).
5. S.A.Rice, Acc.Chem.Res., 1, 81 (1968).
6. B.E.Springett, J.Jortner, and M.H.Cohen, J.Chem. Phys., 48, 2720 (1968).
7. J.Jortner, Actions Chimiques et Biologiques des Radiations, 14 (1970).
8. P.H.Tewari and G.R.Freeman, J.Chem.Phys., 49, 4394 (1968).
9. E.E.Conrad and J.Silverman, J.Chem.Phys., 51, 450 (1969).
10. R.M.Minday, L.D.Schmidt, and H.T.Davis, J.Chem.Phys., 50, 1473 (1969).
11. W.F.Schmidt and A.O.Allen, J.Chem.Phys., 52, 4788 (1970).
12. W.F.Schmidt, HMI-Report B 156, Berlin-Wansee, 1974.
13. H.T.Davis, L.D.Schmidt, and R.G.Brown, Electron in Fluids, ed.J.Jortner and N.R.Kestner, New York, 1973, p.393.
14. H.T.Davis and R.G.Brown, Adv.Chem.Phys., 31, 329 (1975).
15. I.M.Lifshits, Uspekhi Fiz.Nauk, 73, 617 (1964).
16. N.F.Mott and E.A.Davis, "Electronic Processes in Non-crystalline Materials" (Translated into Russian), Izd.Mir, Moscow, 1974, p.6.
17. I.A.Bortsev and B.S.Yakovlev, Int.J.Radiat.Phys. Chem., 7, 15 (1975).
18. R.M.Minday, L.D.Schmidt, and H.T.Davis, J.Chem.Phys., 54, 3112 (1971).
19. P.G.Fuochi and G.R.Freeman, J.Chem.Phys., 56, 2333 (1972).
20. R.M.Minday, L.D.Schmidt, and H.T.Davis, J.Phys.Chem., 76, 442 (1972).
21. J.P.Dodelet and G.R.Freeman, Canad.J.Chem., 50, 2667 (1972).
22. W.F.Schmidt and G.Bakale, Chem.Phys.Letters, 17, 617 (1972).
23. G.O.Beck and J.K.Thomas, Chem.Phys.Letters, 13, 259 (1972).
24. G.O.Beck and J.K.Thomas, J.Chem.Phys., 57, 3649 (1972).
25. G.Bakale and W.F.Schmidt, Z.Naturforsch., 28a, 511 (1973).
26. G.Bakale and W.F.Schmidt, Chem.Phys.Letters, 22, 164 (1973).
27. W.F.Schmidt, G.Bakale, and U.Sowada, J.Chem. Phys., 61, 5275 (1974).
28. B.S.Yakovlev, I.A.Boriev, and A.A.Balakin, Int.J.Radiat.Phys.Chem., 6, 23 (1974).
29. A.O.Allen and R.A.Holroyd, J.Phys.Chem., 78, 796 (1974).
30. M.G.Robinson and G.R.Freeman, Canad.J.Chem., 52, 440 (1974).
31. G.Bakale, W.Tauchert, and W.F.Schmidt, J.Chem.Phys., 63, 4470 (1975).
32. A.A.Balakin and B.S.Yakovlev, Khim.Vys.Energ., 9, 82 (1975).
33. A.O.Allen, T.E.Gangwer, and R.A.Holroyd, J.Phys.Chem., 79, 25 (1975).
34. K.Shinsaka, J.-P.Dodelet, and G.R.Freeman, Canad.J.Chem., 53, 2714 (1975).
35. J.M.L.Engelis and A.J.M.Kimmenade, Chem. Phys.Letters, 42, 250 (1976).
36. L.Nyikos, E.Zador, and R.Schiller, Proc.IV Int. Symp. of Radiation Chemistry, Keszthely, Hungary, 1976.
37. U.Sowada, G.Bakale, and W.F.Schmidt, Khim.Vys. Energ., 10, 323 (1976).
38. W.F.Schmidt, Canad.J.Chem., 55, 2197 (1977).
39. J.-P.Dodelet, K.Shinsaka, and G.R.Freeman, J.Chem.Phys., 59, 1293 (1973).
40. K.Shinsaka and G.R.Freeman, Canad.J.Chem., 52, 3495 (1974).
41. R.A.Holroyd and M.Allen, J.Chem.Phys., 54, 5014 (1971).
42. R.A.Holroyd, J.Chem.Phys., 57, 3007 (1972).
43. R.A.Holroyd, B.K.Dietrich, and H.A.Schwarz, J.Phys.Chem., 76, 3794 (1972).
44. R.Schiller, Sz.Vass, and J.Mandics, Int.J.Radiat. Phys.Chem., 5, 491 (1973).
45. R.A.Holroyd and W.Tauchert, J.Chem.Phys., 60, 3715 (1974).
46. S.Noda and L.Kevan, J.Chem.Phys., 61, 2467 (1974).
47. R.A.Holroyd, S.Tames, and A.Kennedy, J.Phys. Chem., 79, 2857 (1975).
48. S.Noda, L.Kevan, and K.Fueki, J.Phys.Chem., 79, 2866 (1975).
49. J.-P.Dodelet, K.Shinsaka, and G.R.Freeman, Canad.J.Chem., 54, 743 (1976).
50. R.A.Holroyd and R.L.Russell, J.Phys.Chem., 78, 2128 (1974).
51. J.Bullot and M.Gauthier, Canad.J.Chem., 55, 1821 (1977).
52. A.A.Balakin, I.A.Boriev, and B.S.Yakovlev, Canad.J.Chem., 55, 1985 (1977).
53. I.A.Boriev, A.A.Balakin, and B.S.Yakovlev, Khim.Vys.Energ., 12, 20 (1978).
54. K.Fueki, D.F.Feng, and L.Kevan, Chem.Phys. Letters, 13, 616 (1972).
55. R.G.Brown and H.T.Davis, Chem.Phys.Letters, 27, 78 (1974).
56. H.A.Gillis, N.V.Klassen, G.G.Teather, and K.H.Lokan, Chem.Phys.Letters, 10, 481 (1971).
57. J.T.Richards and J.K.Thomas, Chem.Phys. Letters, 10, 317 (1971).

58. J.H.Baxendale, C.Bell, and P.Wardman, Chem. Phys.Letters, **12**, 347 (1971).
59. N.V.Klassen, H.A.Gillis, and G.G.Teather, J.Phys.Chem., 76, 3847 (1972).
60. M.A.Krivoglaz, Uspekhi Fiz.Nauk, 111, 617 (1973).
61. R.Schiller, J.Chem.Phys., 57, 2222 (1972).
62. H.Hammer, W.Schoepe, and D.Weber, J.Chem. Phys., 64, 1253 (1976).
63. B.Halpern and R.Gomer, J.Chem.Phys., 51, 1031 (1969).
64. P.G.Le Comber, J.B.Wilson, and R.J.Loveland, Solid State Communs., 18, 317 (1976).
65. A.P.Buchikhin, V.I.Gol'danskii, A.O.Tatur, and V.K.Shantorovich, Zhur.Eksper.Teor.Fiz., 33, 615 (1971).
66. G.F.Novikov and B.S.Yakovlev, Int.J.Radiat. Phys.Chem., 7, 479 (1975).
67. Landolt-Bornstein, Springer-Verlag, Berlin, 1951. pt.1, p.506.
68. J.Lekner, Phys.Rev., 158, 130 (1967).
69. M.H.Cohen and J.Lekner, Phys.Rev., 158, 305 (1967).
70. L.S.Miller, S.Howe, and W.E.Spear, Phys.Rev., 166, 871 (1968).
71. H.T.Davis, L.D.Schmidt, and R.M.Minday, Chem.Phys.Letters, 13, 413 (1972).
72. H.T.Davis, L.D.Schmidt, and R.M.Minday, Phys.Rev., **A3**, 1027 (1971).
73. J.-P.Dodelet and G.R.Freeman, Canad.J.Chem., 53, 1263 (1975).
74. J.-P.Dodelet, K.Shinsaka, and G.R.Freeman, J.Chem.Phys., 63, 2765 (1975).
75. N.R.Kestner and J.Jortner, J.Chem.Phys., 59, 26 (1973).
76. J.M.Ziman, J.Phys., **C1**, 1532 (1968).
77. S.Kirkpatrick, Rev.Mod.Phys., 45, 574 (1973).
78. M.H.Cohen, J.Non-Cryst.Solids, **A**, 391 (1970).
79. Y.Maruyama and K.Funabashi, J.Chem.Phys., 56, 2342 (1972).
80. L.Kevan, J.Phys.Chem., 76, 3830 (1972).
81. T.Huang and L.Kevan, J.Chem.Phys., 61, 4660 (1974).
82. W.F.Spear, Advances in Physics, 23, 523 (1974).
83. B.S.Yakovlev, I.A.Boriev, and L.I.Novikov, Optika i Spektrosk., 33, 889 (1972).
84. L.V.Lukin and B.S.Yakovlev, Int.J.Radiat.Phys. Chem., 7, 677 (1975).
85. L.V.Lukin and B.S.Yakovlev, Chem.Phys.Letters, **42**, 307 (1976).
86. J.M.Warman, K.D.Asmus, and R.H.Schuler, Adv.Chem.Ser., 82, 25 (1968).
87. B.S.Yakovlev, I.A.Boriev, L.I.Novikova, and E.L.Frankevich, Int.J.Radiat.Phys.Chem., 4, 395 (1972).
88. G.O.Beck and J.K.Thomas, J.Chem.Phys., 60, 1705 (1974).
89. I.A.Boriev and B.S.Yakovlev, Khim.Vys.Energ., 10, 327 (1976).
90. I.A.Boriev and B.S.Yakovlev, Khim.Vys.Energ., 8, 247 (1974).
91. J.H.Baxendale, J.P.Keene, and E.J.Rasburn, J.Chem.Soc., Faraday Trans.I, 70, 718 (1974).
92. G.Bakale, E.G.Gregg, and R.D.McCreary, J.Chem.Phys., 57, 4246 (1972).
93. J.H.Baxendale and E.J.Rasburn, J.Chem.Soc., Faraday Trans.I, 70, 705 (1974).
94. L.V.Lukin and B.S.Yakovlev, Dokl.Akad.Nauk SSSR, **224**, 381 (1975).
95. R.A.Holroyd, T.E.Gangwer, and A.O.Allen, Chem.Phys.Letters, 31, 520 (1975).
96. J.H.Baxendale, B.P.H.Geelen, and P.H.G.Sharpe, Int.J.Radiat.Phys.Chem., 8, 371 (1976).
97. L.V.Lukin, Summary of Candidate's Thesis, Moscow Physicotechnical Institute, Moscow, 1975.
98. L.V.Lukin and B.S.Yakovlev, Khim.Vys.Energ., 11, 419 (1977).
99. G.Bakale, U.Sowada, and W.F.Schmidt, J.Phys. Chem., 79, 3041 (1975).
100. J.H.Baxendale and P.H.G.Sharpe, Chem.Phys. Letters, 41, 440 (1976).
101. A.A.Balakin and B.S.Yakovlev, Khim.Vys.Energ., 9, 29 (1975).
102. J.Jortner, Ber.Bunsenges.Phys.Chem., 75, 607 (1971).
103. L.V.Lukin and B.S.Yakovlev, Khim.Vys.Energ., 12, 125 (1978).
104. J.K.Baird, Canad.J.Chem., 56, 2133 (1977).
105. J.R.Miller, Chem.Phys.Letters, 22, 180 (1973).
106. K.I.Zamaraev and R.F.Khairutdinov, Chem.Phys., 4, 181 (1974).
107. E.J.Marshall, M.J.Pilling, and S.A.Rice, J.Chem.Soc., Faraday Trans.II, 71, 1555 (1975).
108. M.J.Pilling and S.A.Rice, J.Chem.Soc., Faraday Trans.II, 71, 1563 (1975).
109. W.H.Hamill, J.Phys.Chem., 73, 1928 (1969).
110. T.Sawai and W.H.Hamill, J.Chem.Phys., 52, 3843 (1970).
111. V.M.Byakov, V.I.Gol'danskii, and V.P.Shantarovich, Dokl.Akad.Nauk SSSR, 219, 633 (1974).
112. J.E.Aldrich, M.J.Bronskill, R.K.Wolff, and J.W.Hunt, J.Chem.Phys., 55, 530 (1971).
113. E.Hayon, Nature Phys.Sci., 238, 76 (1972).
114. K.Y.Lam and J.W.Hunt, Int.J.Radiat.Phys.Chem., 7, 317 (1975).
115. V.M.Byakov, Int.J.Radiat.Phys.Chem., 8, 253 (1967).
116. O.A.Anisimov, Summary of Candidate's Thesis, Institute of Chemical Kinetics and Combustion, Novosibirsk, 1976.
117. O.A.Anisimov, A.M.Raitsimring, and Yu.N.Molin, Proc.IV Int.Conf.on Positron Annihilation, Helsingor, Denmark, 1976, p.32.
118. U.Sowada, G.Bakale, K.Yoshino, and W.F.Schmidt, Chem.Phys.Letters, 34, 466 (1975).
119. G.Bakale, U.Sowada, and W.F.Schmidt, J.Phys. Chem., 80, 2556 (1976).
120. K.Funabashi and J.L.Magee, J.Chem.Phys., 62, 4428 (1975).
121. A.Henglein, Ber.Bunsenges.Phys.Chem., 79, 129 (1975).
122. G.J.Schulz, Rev.Mod.Phys., 45, 423 (1973).
123. J.C.Y.Chen, Adv.Radiat.Chem., 1, 245 (1969).
124. L.G.Christophorou, Chem.Rev., 76, 409 (1976).
125. R.P.Blaunstein and L.G.Christophorou, J.Chem. Phys., 49, 1526 (1968).
126. E.L.Frankevich, Uspekhi Khim., 35, 1161 (1966) [Russ.Chem.Rev., No.7 (1966)].
127. G.R.Freeman, Adv.Chem.Ser., 82, 339 (1968).
128. Kh.S.Bagdasar'yan, 'Dvukhkvantovaya Fotokhimiya' (Two-quantum Photochemistry), Izd.Nauka, Moscow, 1976.
129. A.Mozumder, J.Chem.Phys., 48, 1659 (1968).
130. A.Hummel, J.Chem.Phys., 48, 3268 (1968).
131. Yu.A.Berlin and V.L.Tal'roze, Int.J.Radiat.Phys. Chem., 3, 97 (1971).

132. S.J.Rzad, P.P.Infelta, J.M.Warman, and R.H.Schuler, J.Chem.Phys., **52**, 3971 (1970).
133. P.P.Infelta and R.H.Schuler, J.Phys.Chem., 76, 987 (1972).
134. G.W.Klein and R.H.Schuler, J.Phys.Chem., 77, 978 (1973).
135. I.A.Boriev and B.S.Yakovlev, Int.J.Radiat.Phys. Chem., 8, 511 (1976).
136. K.Fueki, J.Chem.Phys., 63, 4085 (1975).
137. J.Kroh and J.Piekarska, Bull.Acad.Polon.Sci., **22**, 167 (1974).
138. A.A.Arshakuni, V.M.Byakov, V.I.Pichuzhkin, and V.V.Saraeva, Khim.Vys.Energ., 9, 203 (1975).
139. J.Kroh, E.Hankiewicz, and J.Piekarska, Int.J. Radiat.Phys.Chem., 8, 289 (1976).
140. J.K.Thomas, K.Johnson, T.Klippert, and R.Lowers, J.Chem.Phys., 48, 1608 (1968).
141. Yu.A.Berlin, Int.J.Radiat.Phys.Chem., 8, 305 (1976).
142. A.Mozumder and M.Tachiya, J.Chem.Phys., 62, 979 (1975).

Branch of the Institute of Chemical Physics,
Academy of Sciences of the USSR,
Chernogolovka