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Electronic Processes Induced by Radiation in Solid Organic Systems

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We shall discuss the behaviour of charged particles produced by radiation and their role in physical and chemical processes (e.g. electrical conduction, recombination luminescence, and various optical properties). By analysing existing physico-chemical theories and concepts we can describe these processes quantitatively (at least to a first approximation) as well as gaining a deeper understanding of their mechanism. 402 references.

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I. INTRODUCTION

The fundamental importance of ion–molecule reactions during the radiolysis and photolysis of condensed phases was demonstrated during the late 1960's.[1-4] In particular, detailed studies were made of the electrical phenomena accompanying the radiolysis of hydrocarbons[1,5], such as induced electrical conductivity, recombination luminescence, and thermally stimulated and photo-stimulated processes in low-molecular hydrocarbon glasses previously irradiated at low temperatures. Since that work was reported much progress has been made in understanding the role of charged particles (and especially electrons) in the radiolysis of liquid, non-polar molecular systems[6,7], and the mobility and reactivity of excess electrons in liquid hydrocarbons have been fully investigated[8,9].

We have used the results of experimental and theoretical studies of organic (and inorganic) liquids to analyse the electronic processes induced by radiation in solid organic systems such as glasses and polymers. In this review we shall examine the experimental (and, to a lesser extent, the theoretical) work on charge generation, stabilisation, and recombination mechanisms which has been published since the end of the 1960's, as well as studies of charge transfer under the influence of an external or an internal (coulombic) electric field in solid organic systems. By analysing this information we have been able to assess the current level of understanding of these problems and to identify the topics to which more attention should be devoted.

II. CHARGE GENERATION

In this Section we shall discuss the theories by which the yield of free charges (and of charges contributing to electrical conduction) may be calculated for the radiolysis or photolysis of organic materials in a condensed phase with

allowance for the energy spectrum of the secondary electrons. This treatment explains both the changes in electrical conductivity of the medium produced by irradiation and the direction of the radiation-chemical reactions involving the charged particles. In some cases it is important to be able to calculate the total yield of charged particles (called the initial ionisation yield).

In flash photolysis the energy of the electron produced by the ionisation process is not usually sufficient to cause further ionisation of a molecule of the matrix: often it cannot even excite the molecule to an excited state. In this case we are dealing with the generation of isolated ion pairs. An analogous situation exists under radiolysis, but only for the secondary δ-electrons, whose energy is less than a few eV. However, in contrast to the photolysis case, during radiolysis with γ-quanta or fast electrons of 1–10 MeV energy the fraction of the energy expended in forming isolated pairs is quite low (a figure of ~30% has been suggested[10-13]). About 40% of the energy is spent in the generation of "spurs", containing 2 or more pairs of charges (up to 10), and 10% in the formation of spherical, multiply-charged ionisation regions containing 10–50 ion pairs. Lastly, the remaining 20% of the energy is dissipated in forming short cylindrical tracks with an ionisation density approaching that of 1–2 MeV protons but less strong than that of α-particles ($E_\alpha = 3-5$ MeV). Of course, the tracks of the δ-electrons are very much shorter than those of heavy charged particles[14-18].

The Onsager and the Poole–Frenkel' theory are often used to calculate the yields of free charges from isolated pairs. The yield of charges from the tracks of heavy charged particles and from spurs can be described in terms of the theoretical concepts developed by Jaffe and Lea.

Whereas in the radiation chemistry of water and other polar liquids the real structure of the track of a fast electron is allowed for in the calculation of the yield of charges into the bulk of the liquid, in the radiation chemistry of non-polar solid or liquid organic systems (mostly, hydrocarbons) all the calculations so far have assumed radiolysis by the ion-pair mechanism. However, the need to allow for the contribution of formations with multiple charges to the observed radiolytic effect is being increasingly recognised[6,7,19-21].

1. Ion Pair Generation

a) Onsager's theory

Onsager[22,23] considered the probability of dissociation of a pair of charges in thermal equilibrium with a medium of temperature T and static dielectric constant $\varepsilon\varepsilon_0$ in an electric field E_0 for an initial separation of the pair of charges r_0. The subsequent motion of the charges was assumed to be determined by diffusion (diffusion coefficient $D = D_+ + D_-$) and drift in the combined field $E_0 + E_C$ (where E_C is the coulombic field due to two unlike charges having a mobility $\mu = \mu_+ + \mu_-$). To solve this problem Onsager used Smoluchowsky's equation and expressed its stationary solution as a power series.

The problem was subsequently discussed many times[6,7,24-46], and for an isotropic initial distribution of thermalised electrons the probability of dissociation of a bound pair in the weak field approximation was shown to be

$$\Phi(r_0, E_0) = \Phi(r_0)\left[1 + \frac{e^3}{8\pi\varepsilon\varepsilon_0 k^2 T^2} E_0\right], \qquad (1)$$

where e is the electronic charge, k is Boltzmann's constant, T is the absolute temperature (K), and $\Phi(r_0) = \exp(-r_c/r_0)$, where $r_c = e^2/4\pi\varepsilon\varepsilon_0 kT$ is the Onsager radius. The coefficient $\beta_0 = e^3/8\pi\varepsilon\varepsilon_0 k^2 T^2$ has been called the Onsager field constant. In the presence of strong electric fields this approximation is not valid, and $\Phi(r_0, E_0) \to 1$ when $E_0 \to \infty$.

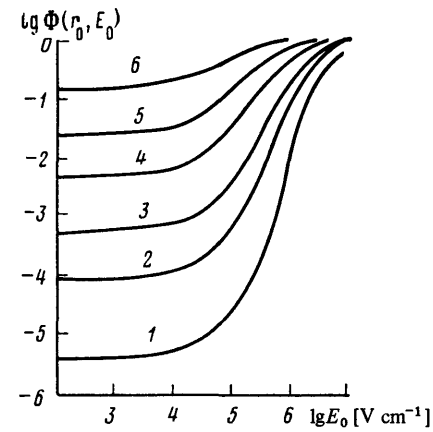


Figure 1. Dissociation probability Φ of a bound pair against E_0 for different initial distances: *1*) 1.5, *2*) 2.0, *3*) 2.5, *4*) 3.5, *5*) 5, *6*) 10 nm; $\varepsilon = 3.0$, $T = 300$ K[29].

For the typical values $\varepsilon = 3.0$ and $T = 300$ K the constants r_c and β_0 become 18.5 nm and 3.6×10^{-5} cm V^{-1} respectively. Numerical calculations of $\Phi(r_0, E_0)$ (Fig. 1) show a strong field and temperature dependence for small values of r_0 ($\lesssim 5.0$ nm).

If $g(r_0)$ is the probability density of the distribution of the bound pair with respect to initial separation ($\int_0^\infty g(r_0) 4\pi r_0^2 dr_0 = 1$) and G_0 is the initial ionisation yield it follows that the yield of free charges $G_{fi}(E_0)$ in the electric field E_0 can be expressed as

$$G_{fi}(E_0) = G_0 \int_0^\infty g(r_0)\,\Phi(r_0, E_0)\, 4\pi r_0^2 dr_0. \qquad (2)$$

Noting that $\Phi(r_0, E_0)$ in the weak field region is a linear function of E_0, and β_0 is independent of r_0, we can easily show that

$$G_{fi}(E_0) = G_{fi}(0)\,[1 + \beta_0 E_0], \qquad (3)$$

where $G_{fi}(0)$ is the yield of free charges in the absence of the electric field. Thus the dependence of G_{fi} on E_0 in the weak field region is linear, and therefore both $G_{fi}(0)$ and β_0 can be easily determined. This conclusion from the Onsager theory has been widely used as a test of the theory in concrete cases[47-49].

The above approach has proved very fruitful in explaining various phenomena observed in liquid-phase radiolysis, quantitative as well as qualitative agreement with experiment being obtained in many cases[6,7,50-53]. In the absence of a strict theory of the retardation and thermalisation of electrons in a condensed phase[54-62] the experimental dependence of the yield of free charges on the temperature T or on the field E_0 is often used to determine the form of the distribution function $g(r_0)$ (usually in the one-parameter approximation). The following distribution functions are most commonly used[30]:

1) the δ-distribution

$$g(r_0) = \delta(r_0 - R)/4\pi r_0^2;$$

2) the undistorted Gaussian distribution (UG)

$$g(r_0) = \pi^{-3/2} R^{-3} \cdot \exp(-r_0^2/R^2);$$

3) the distorted Gaussian distribution (DG)

$$g(r_0) = (4\pi^{3/2}\sigma R^2)^{-1} \cdot \exp(-(r_0 - R)^2/\sigma^2),$$

with the usual assumption that $\sigma = 0.25\ R$, and R is the mean thermalisation length of the electron;

4) the exponential distribution (ED)

$$g(r_0) = (4\pi R r_0^2)^{-1} \cdot \exp(-r_0/R).$$

Table 1. Values of the parameter R for different $g(r_0)$ distributions and other characteristics of organic liquids at ~296 K.[6,30]

Compound	R, nm				ε	r_c, nm	$G_{fi}(0)$	μ, cm² V⁻¹ s⁻¹	$10^6\beta_0$, V⁻¹ cm	
	δ	UG	DG	ER					calc	exper
n-Pentane	9.03	7.13	8.28	6.23	1.842	30.6	0.14	0.16	6.00	—
Isopentane	9.50	7.58	8.70	6.76	1.84	30.6	0.17	—	—	—
Neopentane	19.71	17.82*	18.32	21.20	1.77	31.7	0.86	35.0	6.22	6.04
Cyclopentane	8.66	6.90	7.96	6.08	1.960	28.8	0.15	—	5.65	—
3-Methylpentane	8.78	6.95	8.08	6.06	1.901	29.65	0.15	—	5.81	—
n-Hexane	8.57	6.76	7.85	5.79	1.885	29.9	0.13	0.1	5.36	5.81
									10.7**	11.2**
Cyclohexane	8.28	6.56	7.60	5.75	2.022	27.9	0.15	0.35	5.47	—

* By applying a correction to Onsager's theory for the dependence of the mobility μ on the electric field E_0 (assuming $E_0 \geq E_{cr}$) Mozumder obtained[63] an R value of 7.7 nm for neopentane. This result is obviously controversial.
** At 219 K.

Numerical values of the parameters used to determine the yield of charges in various organic liquids at room temperature ($T = 296$ K) are given in Table 1. We note that the parameter R is much higher in neopentane than in n-hexane. Direct measurements[59] of the relaxation length (i.e. the distance over which the flow of photo-generated electrons decays by a factor of e) in films of these two compounds at low temperatures gave l_{rel} values of 3.0 and 15.7 nm respectively. Thus we can assume that the mobility of electrons is much greater in neopentane than in n-hexane.

In addition to describing accurately the stationary radiolysis ($t \to \infty$) results, Onsager's theory correctly interprets the kinetics of the process, and also the concentration dependence of the electron trapping processes[6,7]. Mozumder[64], using the prescribed diffusion method, obtained the following expression for the probability $F(t)$ which determines the relative number of bound pairs whose lifetime (before recombination) is $\geq t$:

$$F(t) = \exp\left\{-\frac{r_c}{r_0}\left[1 - \operatorname{erf}\frac{r_0}{(4Dt)^{1/2}}\right]\right\}. \quad (4)$$

As expected, $F(0) = 1$ and $F(\infty) = \exp(-r_c/r_0) = \Phi(r_0)$. Other approximate methods of calculating $F(t)$ are known[6,37,38]. A very simple method of estimating the recombination time of bound charges in a pair is an extension of the Stokes–Einstein relation to the case of the coulombic field of an ion, assuming that the terminal velocity is reached instantaneously[65]. This method leads to the "r_0^3" formula

$$t_{rec} = \frac{4\pi}{3}\frac{\varepsilon\varepsilon_0 r_0^3}{e\mu}.$$

For the distance $r_0 = r_c$ we obtain $t_{rec}^{max} = r_c^2/3D$.

A numerical solution of the non-stationary Smoluchowski equation is given in Ref. 66 for a model dielectric having the parameters $D = 9.27 \times 10^{-3}$ cm² s⁻¹, $\varepsilon = 2.023$, $r_c = 27.9$ nm, and $r_0 = 8.0$ nm. It is shown† that $t_{1/2} \cong 10^{-11}$ s irrespective of E_0 (as long as $E_0 \leq 10^5$ V cm⁻¹). The field E_0 begins to influence the recombination kinetics of the charges when $t \geq 2 \times 10^{-11}$ s.

The Laplace transform has been used[67,68] to establish the relationship between the concentration dependence of the trapping probability $F(c)$ and the probability density of the lifetime of the bound pairs $dF(t)/dt$, and experimental data on electron trapping in non-polar liquids have been fully analysed[69,70]. Since

$$1 - f(c) = \int_0^\infty \frac{dF(t)}{dt}\exp(-kct)\,dt \quad (5)$$

(where k is the rate constant of the reaction between an electron and the acceptor, and c is the concentration of the acceptor, $f(c) = (\alpha c)^{1/2}/[1 + (\alpha c)^{1/2}]$, and α is a constant), we can apply the inverse Laplace transform and obtain

$$dF(t)/dt = \lambda[(\pi\lambda t)^{-1/2} - \exp(\lambda t)\operatorname{erfc}(\lambda t)^{1/2}]. \quad (6)$$

In this expression $\lambda = k/\alpha$, and $\operatorname{erfc}(x) = 1 - \operatorname{erf}(x)$. Hence we arrive at

$$F(t) = \exp(\lambda t)\operatorname{erfc}(\lambda t)^{1/2},$$
$$F(t) \approx (\pi\lambda t)^{-1/2} \text{ for } \lambda t \geq 100. \quad (7)$$

Thus the initial decrease in the number of bound pairs in a non-polar liquid is very fast (with a half-life $t_{1/2}$ defined by the expression $\lambda t_{1/2} \cong 0.59$), but this is followed by a slower decay. According to Zador and coworkers[71] $t_{1/2} = 0.6 \times 10^{-12}$ s for cyclohexane at room temperature ($\lambda = 0.9 \times 10^{12}$ s⁻¹), but a later paper from the same laboratory[72] gives $t_{1/2} \cong 1.3 \times 10^{-12}$ s. At time $t = 10^{-8}$ s only 0.6% of the original number of bound pairs is still present ($G_0 = 4.0$), which is less by a factor of ~5 than the number of free charges in the liquid ($G_{fi}(0) \cong 0.12$).

In the general case we have, for non-polar liquids,

$$G(t) = G_{fi}(0) + [G_0 - G_{fi}(0)] \cdot F(t). \quad (8)$$

Several workers[73–75] have used the r_0^3 formula to calculate the distribution function $F(t)$ in liquid hydrocarbons, as well as the exponential form of the probability density distribution $g(r_0)$[73] or a similar expression[74]. It was shown that $t_{1/2}$ for n-hexane at room temperature is 3.5×10^{-12} s with $G_0 = 4.0$. On lowering the temperature $t_{1/2}$ is found to increase, reaching 0.13×10^{-9} s at −80 °C. The authors[74] point out that the expected diffusion-determined relationship $F(t) \propto t^{-1/2}$ at $t \to \infty$ is not obeyed; this is a consequence of using the r_0^3 formula, which ignores diffusion. However, at large values of r_0 (approaching r_c) the importance of diffusion increases, while the role of drift in the coulombic field of the ion becomes less important.

An analysis[76] of the validity of the Laplace transform for real liquids, in which the mobility is determined by trapping processes, suggests that Eqn. (5) is not applicable in general. However, the asymptotic behaviour of $F(t)$ at $t \to \infty$ or of $f(c)$ at $c \to 0$ is unchanged. We should also mention a series of papers[77–79] in which Onsager's theory is used to calculate the field dependence of the quantum yield of hot electrons injected into a dielectric by a metallic electrode. In the one-dimensional problem (but not in the three-dimensional problem) it is found that $G_{fi}(0) = 0$.

† $t_{1/2}$ is the time in which $F(t)$ decreases by a factor of 2 from 1.0 to 0.5.

The Poole–Frenkel' theory

The classical Poole–Frenkel' effect refers to the non-linear increase in electrical conductivity in strong electric fields (in the dark). One possible explanation of this effect relies on the lowering of the energy barrier opposing the ionisation of the neutral donor in the direction of the applied field E_0 by an amount $\Delta W = \beta E_0^{1/2}$, where $\beta = (e^3/\pi\varepsilon\varepsilon_0)^{1/2}$ is the Poole–Frenkel' constant. In this case the probability of thermal ionisation of the neutral donor in the field E_0 increases by a factor of $\exp(\beta E_0^{1/2}/kT)$. This simple model has been used to explain the non-linear behaviour of the photo-current in strong fields[80,81]. By allowing for the recombination of the pairs Tabak and Warter[81] obtained an approximate expression for the quantum yield of free charges:

$$\eta = \left[1 + (\nu t_{rec})^{-1} \exp\left(\frac{E_a - \beta E_0^{1/2}}{kT}\right)\right]^{-1}, \quad (9)$$

where ν is the frequency factor, E_a is the activation energy (height of the potential barrier), and t_{rec} is the mean recombination time.

The model has been developed further[82,83] (see also Refs. 31, 47, 84, 85). The thermalisation length of the electron has been calculated by the diffusion approximation (equating the rate of energy loss to $h\nu_p^2$, where ν_p is the phonon frequency and h is Planck's constant), so that $r_0 = (Dt)^{1/2}$. Allowing for the energy of the coulombic and of the externally applied field changes the form of Eqn.(9), since

$$E_a = e^2/4\pi\varepsilon\varepsilon_0 r_0 + eE_0 r_0;$$

and r_0 is given by the expression

$$\frac{h\nu_p^2}{D} r_0^2 = (\hbar\omega - E_g) + \frac{e^2}{4\pi\,\varepsilon\varepsilon_0 r_0} + eE_0 r_0,$$

where E_g is the width of the forbidden gap of the dielectric. With these corrections the expression for η gives a qualitatively correct description of the dependence of the photo-ionisation quantum yield on the photon energy ($\hbar\omega$) and on the strength of the externally applied field. However, a quantitative comparison of theory and experiment is complicated by the large number of undetermined parameters (t_{rec}, ν_p, ν) which cannot be obtained directly from experimental results.

In some recent publications the descriptions of the photolysis of various substances by the Onsager and the Poole–Frenkel' theory are compared[31–33,86–97]. In every case the Onsager theory is preferred. However, it has been pointed out[91,95] that both the Onsager and the Poole–Frenkel' mechanism may be operative in most cases. Depending on the value of r_0, and hence of the mean free path λ, either of these mechanisms could be predominant. When r_0 is much smaller than λ (and the diffusion of the electron within the Onsager sphere plays the major role) the yield of free charges from the bound pairs is directly described (for both radiolysis and photolysis) by the Onsager theory. On the other hand if r_0 is large (and of the same order as r_c) the decrease in height of the coulombic potential barrier under the influence of the external field (Poole–Frenkel' mechanism) becomes predominant. Furthermore, in the case of photo-excitation we should allow for surface recombination[89,92,93], which can cause large discrepancies in the yield of free charges at low field strengths from the values predicted by Onsager's theory[89].

2. Tracks and Multiply Charged Spherical Formations

Classical calculations of the yield of charges in the volume from tracks and from multiply charged spherical formations have been published by Jaffe and Lea[98–100] (see also the review articles in Refs.6, 7, and 19). In these calculations ions of opposite signs are assumed to be distributed in equal concentrations according to a Gaussian law with respect to the axis of the track or to the centre of the agglomerate (depending on the type of geometry). It is also assumed that the distribution curve remains Gaussian, but the width of the distribution changes with time as $r(t) = (b^2 + 4Dt)^{1/2}$, where b is the initial radius of the track (at the instant of formation). With these assumptions the authors calculate the decrease in the total number of charges as a function of time, which in the limit of $t \to \infty$ gives the relative number of charges reaching the volume of the sample. No allowance is made for polarisation by the external electric field. When the track is perpendicular ($\perp$) to the field E_0, and $t \to \infty$, the yield of charges from the tracks into the volume is given by

$$f_{tr}^{\perp} = \left[1 + \frac{k_r N_0}{8\pi D} (\pi/z)^{1/2} S(z)\right]^{-1}, \quad (10)$$

where

$$z = b^2\mu^2 E_0^2/2D^2, \text{ and } S(z) = \frac{1}{\pi^{-1/2}} \int_0^{\infty} \frac{\exp(-s)\,ds}{[s(1 + s/z)]^{1/2}};$$

$k_r = (e/\varepsilon\varepsilon_0)\mu$ is the recombination coefficient, and N_0 is the initial linear ionisation density in the case of the track.

Values of the function $(\pi/z)^{1/2}S(z)$ are given in graphical form in Refs.101–103. In the case of a short cylindrical track, with $N_0 = 5 \times 10^7$ cm^{-1} ($b = 10^{-6}$ cm) and $\mu = 10^{-5}$ cm^2 V^{-1} s^{-1} (say), we find that for E_0 values of 0, 10^2, 10^3, 10^4, 10^5, and 10^6 V cm^{-1} the $f_{tr}^{\perp}$ values are 0, 10^{-3}, 1.6×10^{-3}, 3.7×10^{-3}, 2.1×10^{-2}, and 19.4×10^{-2} respectively. For $r_0 =$ 5.0 nm we have $\Phi(r_0, E_0) \geq f_{tr}^{\perp}(E_0)$, the difference being largest in weak electric fields# ($E_0 \leq 10^4$ V cm^{-1}).

By using the prescribed diffusion method Mozumder[105,106] showed that Eqn.(10) is valid even on the assumption that the positive ions are distributed only along the axis of the track. He also showed that the rates of recombination of the charges in short tracks and spurs containing 10 pairs of charges are approximately equal, and that in a medium in which the diffusion coefficient of trapped electrons is $\sim 2 \times 10^{-3}$ cm^2 s^{-1} (i.e. $\mu_{dr} = 10^{-1}$ cm^2 V^{-1} s^{-1} at 300 K) the half-life $t_{1/2}$ is $\sim 3 \times 10^{-12}$ s (assuming an initial charge density in the tracks and spurs of $\sim 5 \times 10^{18}$ cm^{-3}). The yield of charges into the volume after irradiation with α-particles having energies of several MeV has been shown[107] to be ~ 10 times lower than after irradiation with fast electrons or γ-rays: this is because the N_0 parameter for δ-electrons of 1.0–5.0 keV energy is ~ 10 times lower than for the tracks of α-particles[19].

III. PROCESSES INVOLVING THE MOTION OF CHARGES UNDER THE INFLUENCE OF AN EXTERNAL(OR INTERNAL) ELECTRIC FIELD

As stated above, ionisation during radiolysis or photolysis is accompanied by the appearance of non-equilibrium (excess) charges whose motion in an external field is responsible for the induced conductivity. Extensive experimental investigations have shown that, in addition to the normal charge

The estimated values of $f_{tr}^{\perp}$ are probably much too high because no allowance was made for the polarisation of the track[104].

transfer and recombination processes, charge trapping can occur on relatively deep traps of physical or chemical origin. The trapped (stabilised) charges can persist for very long times, especially at low temperatures, thus giving rise to a whole series of new properties in the irradiated material (photo-stimulated conduction (PSC) in the visible and i.r. regions, thermally stimulated currents (TSC) when the sample is allowed to warm up, a sharp increase in recombination luminescence under i.r. illumination or on applying a strong electric field—the electro-photoluminescence phenomenon or Gudden–Pohl effect). The intensity of all these processes decreases with time to the initial values, characteristic of the non-irradiated materials. Therefore re-irradiation of the material is required each time one of these effects is to be observed.

1. Radiation-Induced Electrical Conductance

Measurements of electrical conductivity are one of the most direct methods of observing the charged particles during the early (physicochemical) stage of the radiolysis[108,109] §. In principle the method allows the properties of a quasi-free ("dry") electron to be studied before its solvation or capture by the medium. However, at the moment the time resolution of this method is greatly inferior to that of the optical method of detecting short-lived particles (0.2×10^{-9} s and 10^{-12} s respectively)[110–112].

Measurements of the radiation-induced electrical conductivity of polymeric dielectrics, using both pulsed and continuous radiation, are reported in Refs. 19, 102, and 113.

According to modern ideas, the instantaneous component (rise and fall time $\lesssim 1$ ns) of the radiation pulse electrical conductance (RPEC) in disordered solid systems is associated with the quasi-free state of the electron, characterised by a microscopic mobility μ_0 (1–100 $cm^2\ V^{-1}\ s^{-1}$). This interpretation is confirmed by the observation that the proportionality coefficient K_{inst} between the volume conductivity (γ_{inst}) and the dose of radiation absorbed (P) is independent of the intensity of the applied electrical field E_0 ($\lesssim 5\times10^5$ V cm^{-1}), and is only weakly dependent on temperature[19,102].

Table 2. Values of K_{inst} ($ohm^{-1}\ cm^{-1}\ Rad^{-1}\ s$) for some polymeric materials[114–120].

Material	$10^{19}K_{inst}$	ε (Ref. 121)
Poly(tetrafluoroethylene) (PTFE)	31	2.0
Low-pressure polyethylene (LPPE)	11	2.2–2.4
High-pressure polyethylene (HPPE)	3.0	»
Polypropylene	3.0	2.15–2.35
Poly(ethylene terephthalate) (PETP)	2.0	3.10–3.40
Polystyrene	1.4	2.6
PM-1 polyimide	1.2	4.0
Crystalline poly(chlorotrifluoroethylene) (F-3)	0.4	3.0
Poly(vinylidene fluoride) (F-3)	0.20	3.0
Poly(vinylidene fluoride) (F-2)	0.16	9.5
Poly(vinylidene chloride)	0.20	2.85
Poly(vinyl chloride) (PVC)	0.12	3.05
Poly(methyl methacrylate) (PMMA)	0.16	3.20

§ See also the recently published monograph: A.K.Pikaev, S.A.Kabakchi, I.E.Makarov, and B.G.Ershov, "Impul'snyi Radioliz i Ego Primenenie" (Pulse Radiolysis and Its Applications), Atomizdat, Moscow, 1980, p. 279.

The K_{inst} values for a number of polymeric materials at room temperature are given in Table 2. We note that the K_{inst} values for non-polar polymers are higher than those for polar polymers (for example, two orders of magnitude higher for PTFE than for PMMA). Furthermore, an increase in the degree of crystallinity of a given material produces a slight increase (approximately 2-fold) in K_{inst}.[114,120]

The parameter K_{inst} is defined by the equation

$$G\mu_0\tau_s\,(cm^2\ V^{-1}) = \frac{10^7}{\rho}K_{inst}\,(ohm^{-1}\ cm^{-1}\ Rad^{-1}\ s), \qquad (11)$$

where τ_s is the life time of the quasi-free electron, and ρ is the density of the dielectric (g cm^{-3}). Taking $G = 1.0$ (for $E_0 = 5\times10^5$ V cm^{-1}) and $\mu_0 = 10\ cm^2\ V^{-1}\ s^{-1}$ we find that $\tau_s = 2\times10^{-13}$ s for PTFE (and an even smaller value for PMMA). This estimate confirms that the lifetime of the quasi-free charge carriers is comparable with the thermalisation time (10^{-13}–10^{-14} s). It has even been suggested[120,122–127] that the life time could be shorter than the thermalisation time.

The experimentally observed lack of dependence of K_{inst} on the dose per pulse (in the range 1–10^5 Rad)[128] suggests a very high concentration of electron (or hole) traps (10^{18}–$10^{21}\ cm^{-3}$). Somewhat different results were obtained by Hughes[129–132] after a study of the RPEC of amorphous (fused) SiO_2 (quartz). By using very pure amorphous SiO_2 he was able to determine μ_0, τ_s, and G_0 independently (20 $cm^2\ V^{-1}\ s^{-1}$, 14 ns, and 3.6 respectively). The dependence of G on E_0 predicted by Onsager's theory was observed for $r_0 = 10.0$ nm.

In contrast to pulse irradiation, for which K_{inst} is independent of E_0 ($< 5\times10^5$ V cm^{-1})[117–119], in the case of continuous irradiation the electrical conductivity increases with E_0[133] as predicted by the Onsager theory.

Systematic studies of the relaxation of RPEC in polymers and in ceramic materials[116,134,135] have confirmed previous reports of the independence of the kinetics on the dose of radiation. Thus, changes in the dose per pulse of more than three orders of magnitude had no effect on $\tau_{1/2}$ for PTFE and the UF-46 ceramic[134,135]. Similarly, in the case of polystyrene an increase in the dose from 1 to 4×10^6 Rad (Refs. 136 and 137 respectively) caused an increase in $\tau_{1/2}$ from 3 to 8 μs, probably due to the change in pulse length from 0.1 to 4.0 μs.

These results suggest that the recombination of charge carriers is inhomogeneous at short irradiation times. This conclusion is confirmed by the kinetics of photocurrent decay in hydrocarbons previously subjected to radiolysis at 77 K.[138]

Explanations of two types have been proposed for these features of the process (the dose-independent, hyperbolic decay of the RPEC, and the lack of dependence of K_{inst} on E_0). In the first approach the inhomogeneity of the recombination kinetics is ascribed to the neutralisation of charged particles in isolated bound pairs, and the induced electrical conductivity to the motion of electrons under the influence of the external field and of the coulombic field of the parent ion (E_C).[138–146] This model also explains the decay kinetics of the i.r.-stimulated current in frozen and irradiated hydrocarbons. The conditions for the validity of this model are defined by the inequalities $\mu_0\tau_s \lesssim 10^{-10}\ cm^2\ V^{-1}$ and $G_g \geq G_{fl}$ (where G_g is the yield of bound charges).

Of course, electric currents involving these non-dissociated pairs are self-polarising. Unlike the classical types of dielectric polarisation (electronic, ionic, and Maxwell–Wagner polarisation) this polarisation should produce (after the irradiation) negative currents in spite of the presence of an external field[127]. However, the present writers doubt whether negative currents can ever be observed in real systems because of the slowness of the pair recombination process.

The second approach[104,116,134,135] relates the inhomogeneity of the RPEC decay kinetics to the recombination of charge carriers in track-like formations (mainly, in short cylindrical tracks), and it assumes that the contribution from electrons in bound pairs to the electric current is much smaller than that of free electrons, so that the recombination kinetics of charges in the pairs are not reflected in the decay of the radiation-induced current. The yield of charges able to contribute to the electric current is determined not only by the yield of free charges from bound pairs as a result of thermal dissociation and separation in an electric field (as in Onsager's theory), but also by the total yield of charges in the short tracks. The ratio of the yields of triplets and singlets in the irradiation of tetracene by α-particles was found to be 3 : 1, which is characteristic of the recombination of random partners[147,148]. This means that no correlation exists within the tracks between the electron and the parent ion, i.e. the track can be treated as a dense solid-state plasma region. The polarisation of the track in an electric field by the motion of its constituent charges is of the classical Maxwell–Wagner type, and should not cause the appearance of negative currents after completion of the irradiation in the presence of the electric field E_0.

However, a consequence of this model is that in strong electric fields ($\sim 10^6$ V cm^{-1}) the yield of free charges from isolated pairs may be greater than the yield of charges in the short cylindrical tracks. Thus we would expect an increase in K_{inst} in very strong fields[117]. Furthermore, the model can be used to calculate (using experimental data on the delayed component of the RPEC) the initial density of charges in the short cylindrical track and μ_{dr}. In the case of polyimides these two parameters were found[118] to be 4.5×10^{18} cm^{-3} and 3.6×10^{-7} cm^2 V^{-1} s^{-1} (for $E_0 = 10^6$ V cm^{-1}), in good agreement with published data[149,150].

2. Recombination Luminescence

Recombination luminescence (RL) is one of the most fully investigated effects accompanying the radiolysis or photolysis of solid organic systems. A detailed discussion of the results obtained up to 1970 can be found in a number of monographs and review[1-3,151,152]; more recent results have also been included in review articles[153-158].

The emission of light has been shown to be a direct consequence of the evolution of energy attending the recombination of opposite charges (whether free, or bound), the intensity of the luminescence being proportional to the rate of disappearance of charges through recombination[159-161]. (Some anomalies in this proportionality are considered in Ref. 156.) Although the quantum yield of RL is usually small, the method is extremely sensitive ($\sim 10^7$ quanta, as compared to 10^{11}–10^{13} spins in the ESR method and 10^{15}–10^{16} molecules in the absorption spectroscopy method), and therefore it has been widely used to study charges stabilised in a condensed phase. The following are the main areas of research in which the method has been most successfully applied: 1) studies of charge recombination mechanisms, and estimates of the relative contributions of diffusional and tunnelling transport to the process; 2) influence of the nature of the medium on the ionisation potential of an impurity; 3) studies of the mechanism of elementary reactions leading to the emission of light quanta; 4) studies of the effect of various external factors (temperature, electric field, illumination) on the recombination process.

The diffusion approach to the calculation of the decay kinetics of isothermal recombination luminescence (IRL) during photo-ionisation of aromatic amines in polar solvents (water, methanol, glycerol, or their mixtures) at 77 K was used in Ref. 162 without allowance for the effect of the coulombic field of the parent ion on the diffusional motion of the electron. By selecting a suitable initial distribution of the electrons in pairs with respect to the distance (r_0) from their corresponding ion a relationship similar to that observed experimentally was calculated between the IRL intensity (L_{IRL}) and the time elapsed after the end of the u.v. irradiation:

$$L_{IRL} = Kt^{-m}, \tag{12}$$

where K and m are constants, with $m \cong 1.0$.

Subsequently the diffusion model (modified by the inclusion of a term for the coulombic interaction between charged particles) was used successfully to explain a wide range of phenomena.

Abell and Mozumder[163] concluded from an exact solution of the Smoluchowski equation that Eqn. (12) can be applied only over a narrow range of t values (no more than 1.5–2 orders of magnitude), whatever the initial distribution $g(r_0)$ of the electrons in the pairs: this conclusion differs from that of Debye and Edwards[162], who did not impose any limits on their range of t. The expression for L_{IRL} becomes

$$L_{IRL} \propto t^{-1/2}, \tag{13}$$

which follows directly from Eqn. (7). Under these conditions the diffusional recombination process should be activation-limited, and therefore strongly temperature-dependent. However, neither of these predictions of the diffusion theory is fulfilled in practice. The IRL decay kinetics are independent of temperature over times between 10^{-6} and 10^3 s[164,165]: the decay curve is accurately described by the expression

$$L_{IRL}(0)/L_{IRL}(t) = 1 + K_1(t-t_0). \tag{14}$$

Similar results have been obtained by other workers[166-181]. The hypothesis that charge recombination (especially at low temperatures) is the result of a tunnelling transition of the electron from the anion to the cation has been put forward increasingly in recent years. It is suggested[182] that the tunnel effect can extend over relatively large distances (up to 50 Å), by analogy with the recombination of an F-centre electron in alkali halide crystals[183]. Approximate theories of this phenomenon have been proposed by many workers[184-206].

It has been shown[207-209] that the presence of a slight activation energy ($E_a \cong 0.02$ eV) is not inconsistent with a predominantly tunnelling transfer mechanism, since the many possible equilibrium configurations of a trapped electron in frozen organic systems probably have a finite spread in energy.

By assuming an exponential distribution function $g(r_0)$ (see Section I) the following expression for L_{IRL} has been obtained[187,189]:

$$L_{IRL} = \alpha\nu \frac{a}{b} \Gamma\left(1 + \frac{a}{b}\right) N_0 (\nu t)^{-(1+a/b)}, \quad \nu t \gg 1, \tag{15}$$

where a is the damping parameter of the wave function, b is the parameter of the distribution function $g(r_0)$, ν is the frequency factor, N_0 is the initial concentration of isolated pairs, α is a constant, and $\Gamma(x)$ is the gamma-function. Since $a \ll b$ Eqn. (15) reduces to (12) for $m = 1.02$. The frequency factor is very large, and therefore the condition $\nu t \gg 1$ is always satisfied. The time dependence of $g(r_0, t)$ is illustrated in Fig. 2.

It is thought[184] that the tunnel mechanism of recombination can explain the very low limiting concentrations of ions which are stabilised during low-temperature radiolysis (10^{17}–10^{18} cm^{-3}, which is only a small fraction of the total number of traps[1,143]). The limiting concentrations of free radicals for

similar doses of radiation are substantially higher (10^{19}–10^{20} cm^{-3}).

The tunnelling hypothesis has allowed satisfactory explanations to be proposed for a number of experimentally observed features of electron trapping in frozen matrices which could not be explained by the classical diffusion theory[171,186,195,200,202,210–213].

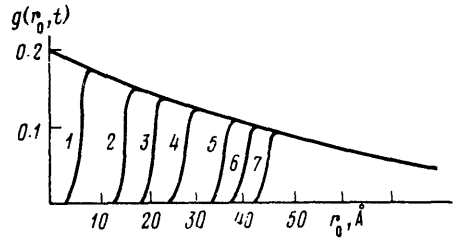


Figure 2. Plots of $g(r_0,t)$ for different times (*1*) 1 ps, *2*) 1 ns, *3*) 1 μs, *4*) 1 ms, *5*) 1 s, *6*) 1 min, *7*) 1 h) in the tunnelling mechanism for the recombination of bound pairs during low-temperature radiolysis or photolysis; $\nu = 10^{15}$ s^{-1}, $a = 1$ Å, $b = 50$ Å.[189]

It was established that the decay kinetics of L_{IRL} are relatively insensitive to the type of radiation (photolysis, or radiolysis)[214,215]. In photolysis studies a more uniform ionisation density over the thickness of the initial matrix is often achieved by using additives[152,156,216] requiring two quanta for ionisation of the molecule. The commonest of these additives are *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and tryptophan. The physical characteristics of the TMPD–methylpentane (3-MP) solid solutions which have been used[217–222] at 77 K are summarised below:

Parameter	Value
Concentration range of TMPD in 3-MP	(1.0–3.0) × 10^{-3} M; (0.6–2.0) × 10^{18} cm^{-3}
Density	0.88 g cm^{-3}
Viscosity	10^{12} Pa s
Glass formation temperature	77 K
Static dielectric constant	2.3
Onsager radius r_c	95 nm
Field constant β_0	5.7 × 10^{-4} cm V^{-1}
Red absorption edge TMPD	360 nm (3.44 eV)
Ionisation potential of TMPD in the gas phase	6.7 eV
Ionisation potential of TMPD in the solid solution	5.9 eV
Lifetime of the triplet state	2.3 ± 0.3 s

As we have already pointed out, the photo-ionisation of the TMPD molecules takes place in two steps: initially the molecule is excited into a singlet state ($\lambda \leq 360$ nm), from which it passes into the triplet state by intersystem crossing, and the absorption of a second light quantum ($\lambda \leq 400$ nm) in the triplet state causes ionisation of the molecule. Two-quantum ionisation of commercial polyethylene under u.v. irradiation has been reported also in Ref. 223.

Characteristic decay curves of L_{IRL} of a TMPD–3-MP solid solution after u.v. irradiation ($\lambda = 313$ nm) for different times (τ_1, $2\tau_1$, $20\tau_1$) are shown in Fig. 3. On the linear portion of the plot of L_{IRL} against exposure time τ the slope is proportional to the square of the intensity of u.v. radiation, as expected for a two-quantum ionisation process. For $\tau \leq 2\tau_1$ (≤ 30 s) the charges are generated mainly as bound pairs, and the yield of free charges is very small. In this range of exposures the TMPD–3-MP solution displays electrophotoluminescence (EPL)[224,225]: the application of a strong electric field ($> 2.2 \times 10^5$ V cm^{-1}) produces a flash of recombination radiation, and a second application of a field of equal strength but opposite polarity produces another flash. Further observation of the effect is possible only if the sample is irradiated again. The amplitude of the RPL flash is exponentially dependent on the strength of the electric field:

$$L_{EPL}(0) = A \exp(\alpha E_0/kT), \qquad (16)$$

where $\alpha \approx 0.9$–1.7 Å. (An explanation of the EPL phenomenon with allowance for electron tunnelling is given in Refs. 196 and 226–230.)

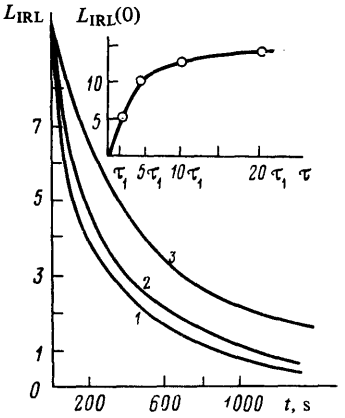


Figure 3. Intensity of isothermal recombination luminescence (L_{IRL}) against time; $\tau_1 = 15$ s, $T = 77$ K[152]; $\tau = \tau_1$ (*1*), $\tau = 2\tau_1$ (*2*), and $\tau = 20\tau_1$ (*3*).

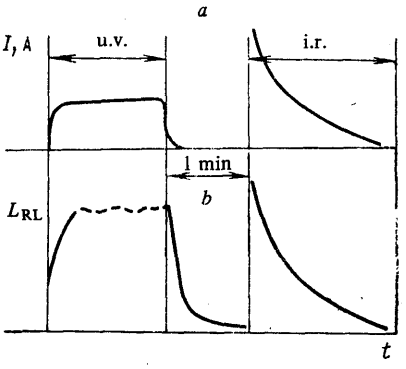


Figure 4. Comparison of the kinetics of photo-stimulated conduction (*a*) and recombination luminescence (*b*) in TMPD–3-MP at 77 K; $\lambda_{u.v.} = 313$ nm, $\lambda_{i.r.} = 694$ nm.[234]

By using a distorted Gaussian distribution centred on $\bar{r}_0 = 32$ Å, with a dispersion parameter of 6.2 Å and a life time for a trapped electron of 10^3 s, the kinetics of the decay in frozen TMPD–3-MP solutions have been described quantitatively[231–233] to an accuracy of 3%. It has been suggested that the lifetime of the trapped electrons decreases exponentially as the strength of the external field increases, thus increasing the probability of a tunnelling transition to the parent ion[196].

Experimental results reported in Refs. 221 and 234 (Fig. 4) give additional information on the possible contribution from electrons in bound pairs to the observed electric current. It has been established that during i.r. irradiation ($\lambda = 694$ nm) only ~50% of the bound pairs initially formed by u.v. irradiation are able to recombine (higher-energy radiation is needed to cause annealing of the remaining pairs). Since at 77 K the number of bound charges is much greater than the number of free charges, the photo-current produced by u.v. irradiation should be due to the polarisation of the bound pairs in the external electric field E_0 ($\ll E_C$).[139] However, in that case the net charge flowing in the external circuit as a result of the current stimulated by i.r. radiation should be negative, since the current is produced by the depolarisation of the bound pairs and is equal to one-half of the charge flowing through the external circuit in the case of u.v. illumination. Furthermore, the kinetics of the negative current (Fig. 4a) should be similar to the kinetics of the photo-stimulated IRL (Fig. 4b), as is found experimentally. However, the sign of the photocurrent observed in practice is the opposite to that predicted by the theory. It is also found that the recombination time of a bound isolated pair after the trapped electron has been set free by i.r. light is not greater than ~1 ns.[235]

On the assumption that only free charges can contribute to the photocurrent under u.v. irradiation[152,234], and noting that the lifetime of these charges before capture by a trap is less than 1 μs,[221] we can resolve the above inconsistency. By the same argument we can explain also the experimental finding[140] that i.r. irradiation of 3-MP previously exposed to low-temperature (77 K) radiolysis in the presence of an external electric field E_0 causes a negative current to flow when $E_0 = 0$. Thus, the appearance of a negative current can be ascribed to depolarisation of the short tracks (see Section II and Ref. 127).

As we have already pointed out, under u.v. irradiation the formation of free charges giving rise to the observed photocurrent is due to the ionisation (with a very low probability) of excited triplet molecules of TMPD, and in the case of i.r. irradiation it is due to optical ionisation of stabilised bound pairs (again, with a very low probability). In order to describe the experimental results quantitatively as well as qualitatively (Fig. 4) we have to postulate a relatively high drift mobility for the free electron formed as a result of u.v. or i.r. irradiation (a low-energy electron with energy ≤ 1 eV).

It is found[236] that the type of radiation used (light, or X-rays) has no effect on the decay kinetics of the recombination-induced phosphorescence of tryptophan in a frozen mixture of water and ethylene glycol, or on the thermo-luminescence curve. Similar results have been reported for less polar matrices[214,215,237]. However, there are regions of high local concentration of charge[238,239] produced by electron irradiation of the material: in strongly polar matrices these regions begin to disappear[240] only at times $> 10^{-9}$ s. The need to allow for these effects in studies of the kinetics of IRL is stressed.

Recently published work[241] shows that the recombination probability of charges produced by u.v. irradiation is higher (by approximately 2) than when γ-radiation is used, at least in the case of a frozen solution of tryptophan in a mixture of ethylene glycol and water. It is also reported that the type of radiation (α or β radiation) can affect the decay kinetics of L_{IRL} in methylcyclohexane at 77 K, so that Eqn. (14) does not apply[242] at times between 1 and 500 ns (see also Refs. 243–245).

Neither the type of emitting centre nor the nature of the luminescence is yet fully understood. It is usually assumed that the recombination (followed by light emission) involves the scheme

$$\begin{aligned} A^+ + B^- &\rightarrow A^* + B, \\ A^* &\rightarrow A + h\nu, \end{aligned} \qquad (17)$$

where B^- could be a trapped electron or an anion, and A is a molecule of solvent, solute, or radiolysis product. In some polymeric materials (polyethylene, polystyrene, PTFE, polypropylene) the luminescence centres can be carbonyl groups attached to the ends of molecular main chains or side chains[167]. However, the energy set free by the recombination process can be transferred to the impurity acting as a recombination centre[219,246]. It has been suggested[166,201] that radiative recombination by the scheme

$$A^+ + B^- \rightarrow A + B + h\nu, \qquad (18)$$

can explain the RL in pure alkenes during radiolysis. According to this mechanism photon emission and recombination occur simultaneously. The excited state of the luminescence centre is assumed to be formed by transfer of the recombination energy of the charges in the initial matrix[247–256].

Studies of the recombination-induced emission generated by the scheme (17) have shown that both fluorescence and phosphorescence of the molecule A can occur in non-polar matrices[165,170,219], but in strongly polar solvents only phosphorescence is possible[170] (see also Refs. 257 and 258).

Photo-excitation may occur through the ejection of a bound electron from a trap, and its recombination, or by a tunnelling transition of the electron from the excited state in the trap[177] at longer wave lengths ($\lambda > 900$ nm). In the former case we can expect both the triplet and the singlet level of the molecule A to be excited, whereas in the latter case the triplet state is preferentially excited. A study[180] of the effect of short illumination periods ($\lambda > 450$ nm), repeated at 20 s intervals, on the IRL curve of polybutadiene failed to detect a significant change in the population of the traps responsible for the isothermal decay of L_{IRL} at 90 K. However, a longer period of illumination (~7 min) can markedly increase the RL intensity observed as the sample is allowed to warm up to room temperature (especially at low temperatures). These experiments have confirmed the hypothesis that traps are present in large numbers, and with a depth distribution. Other workers came to a similar conclusion[223].

When a sample exposed to low-temperature hydrolysis is allowed to warm up the $L_{IRL} = f(T)$ curve contains several peaks whose position on the temperature scale can be correlated with the type of molecular motion which becomes "unfrozen" in this temperature range[256,259,260] or with structural changes associated with that motion[261–267]. The correlation can be explained by assuming a proportionality between the probability of setting the charge carriers free from their traps and the frequency factor of the appropriate molecular motion (note that thermal emission from a trap is accompanied by partial or total collapse of the trap as a result of the structural changes involved). An alternative explanation is possible: the softening of the matrix associated with the temperature rise allows faster diffusion of the trap (containing a captured electron) in the field of the cation. A 10 Å change in the distance between the two species is equivalent to an increase of 10^4–10^5 times in the probability of electron tunnelling[175], which can easily account for a strong peak in the radiothermoluminescence curve.

IV. STABILISATION AND CHARGE TRANSFER

The energy spectrum of the charged particles formed in a condensed phase during radiolysis is extremely broad, extending from the primary electron energy (several MeV)

to a few hundredths of an electron-volt. In the case of photolysis the energy spectrum is very much narrower ($E_e \leq 10$ eV).

It is usually assumed that as a result of collisions the electron rapidly loses its excess energy (in $\sim 10^{-14}$ s) to the level of 1–5 eV, and somewhat more slowly (in 10^{-13}–10^{-12} s) to the level of kT. This excess electron in the process of losing energy (or being thermalised), also known as a "dry" or quasi-free electron, is responsible for a number of physical and chemical processes in the condensed phase[8,108,110]. In the majority of condensed media the quasi-free state of the excess electron is unstable, and the electron is captured (solvated) by the medium. Early capture theories such as the Pekar–Deigen–Davydov polar theory and the "cavity" capture theory are reviewed in Ref.3. More recently the total energy (E_t) of the system (medium + excess electron) has been defined[268,269] as $E_t = E_c + E_m$, where E_c is the electronic component of the total energy, and E_m is the reorganisation energy of the medium (≥ 0). For the quasi-free state, which is described by a plane wave being scattered by the atoms and molecules of the medium, $E_m = 0$, and therefore $E_t = V_0$, where V_0 is the energy level of the bottom of the conduction band of the medium measured from the vacuum level, determined by the relative magnitude of the short-range repulsive forces and the long-range polarisation interaction forces. In the case of a localised electron the wave function is $\psi(R) \propto \exp(-R/R_0)$, where R is the configurational coordinate and R_0 is the radius of the coordination sphere (or cavity). The stability of this state is defined by two necessary conditions:

1) $\partial E_t/\partial R = 0$ for $R = R_0$ (configurational stability), and

2) $E_t(R_0) < V_0$ (energy stability).

Exactly analogous arguments can be applied to the stability of the excited states of a trapped electron. V_0 values of 1.32 and −0.63 eV have been calculated[269] for liquid ^{4}He and Ar respectively, as compared with experimental values of 1.05 and −0.33 eV. According to these values the drift mobility of electrons in these liquids should be 2.2×10^{-2} and 470 cm^2 V^{-1} s^{-1} (in the latter case the electron is, obviously, quasi-free). The satisfactory agreement between calculation and experiment for the parameters of the bound state of an electron in liquid helium is illustrated in Table 3.

Table 3. Calculated and experimental physical parameters of trapped electrons in liquid ^{4}He.[269]

Property	Experiment	Theory
Radius of cavity (0 atm), A	16	15.5
Radius of cavity (20 atm), A	10.5	11.5
Mobility, cm^2 V^{-1} s^{-1}	0.02	0.01
Photo-ionisation threshold, eV	0.9—1.0	0.92
Critical density of liquid for transition to the bound state ($E_t < V_0$), mole cm^{-3}	$(1.5—2.0)\cdot 10^{-3}$	$1.0\cdot 10^{-3}$

The properties of trapped electrons in metal–ammonia solutions, in polar liquids, and in glasses have also been explained successfully[153,155,269–271]. Calculations show that the cavities in which the electron is stabilised have diameters of several Ångstroms. In the theoretical calculations for non-polar alkanes the dipole moment of the C–H bond is used[153,272–274] in place of the dipole moment of the whole molecule (as in the case of polar matrices). In other respects the method of calculation is standard. In polymeric materials the cavities are larger than in alkane glasses, because the width of the singlet in the ESR spectra (which characterises the interaction between the captured electron and the surrounding protons on the surface of the cavity) is narrower in these materials, and the spin–lattice relaxation time is longer.

Experimental and theoretical results on the mobility of electrons in non-polar liquids are reviewed in Refs.8, 9, and 275, in polar liquids in Ref.276, and in solid matrices in Ref.277.

Table 4. Characteristics of an excess electron in non-polar liquids[9].

Liquid	T, K	V_0, eV	μ, cm^2 V^{-1} s^{-1}
Methane	109	0.0	400
Neopentane	293	−0.43	50—70
Ethane	120	0.22	0.01
n-Pentane	293	−0.01—0.04	0.14
Cyclopentane	293	−0.21	1.1
Tetramethylsilane	293	−0.59	90—100

As was pointed out above, the main characteristics of an excess electron in the quasi-free state are the energy of the state with respect to the vacuum level (V_0) and the mobility of the electron (μ). Theoretically, a correlation between these two characteristics can be expected. As a rule, higher values of μ correspond to negative values of V_0 (see Table 4). Mobilities $\mu \geq 10$ cm^2 V^{-1} s^{-1} indicate a stable quasi-free state, whereas lower values ($\mu \leq 1$ cm^2 V^{-1} s^{-1}) indicate stability of the bound (localised) state of the excess electron.

A correlation between V_0, μ, and the yield of free charges G_{fi} has also been demonstrated[278]: for $\mu \geq 50$ cm^2 V^{-1} s^{-1} we find $G_{fi} \cong 1.0$ (see Refs.8 and 279).

Two theoretical models have been used to allow for the thermal energy responsible for the transfer of an electron from a localised state (in systems where such a state is stable) into a quasi-free state. The first model (partial localisation model)[280,281] assumes an equilibrium between electrons in the bound and in the free state. The relationship between the observed value μ and the true mobility μ_0 is given by the formula

$$\mu = \mu_0(1-P), \tag{19}$$

where P is the probability of localisation. The second model[282] treats the medium as a complex conglomerate of two different types of region, one transparent and one opaque to excess electrons, and assumes that the volume fraction of the transparent region is a function of V_0 (see Ref.8).

Experimental measurements[283–286] of μ and V_0 in mixtures of alkanes (neopentane/n-hexane) can be explained satisfactorily by both these models.

Experimental data on μ and V_0 in the solid phase are scarce. The main method of determining V_0 in a solid solution is an indirect (complicated, and laborious) measurement of the ionisation potential of TMPD or tryptophan in different solvents[287–293], using the formula

$$\Delta I = I_g - I_s = -P^+ - V_0, \tag{20}$$

where I_g and I_s are the ionisation potentials in the gas and the solid phase, $P^+ = -e^2/2r_0(1-1/\varepsilon_{opt})$ is the polarisation energy of the cation (and r_0 is its radius), and ε_{opt} is the optical dielectric constant. Tentative results obtained in this way for various glasses frozen at 77 K are given in Table 5.

These results suggest a very high mobility for ice and for the 10 M KOH–H_2O alkaline glass, as has been found experimentally[295]: the Hall (i.e. the true) mobility in these media is $\mu_0 \cong 5$ cm^2 V^{-1} s^{-1}. The increase in mobility at low temperatures is consistent with the motion of electrons by the band mechanism. Unfortunately, mobility measurements by the Hall effect are impossible for the majority of frozen hydrocarbons, and experimental results are confined to the drift mobility.

Table 5. Experimental data used to determine V_0 for some glasses at 77 K.[294]

Glass	ΔI, eV	ϵ_{opt}	$-P^+$, eV	V_0, eV
Methylcyclohexane	0.85	2.28	2.09	1.24
3-Methylpentane	0.85	2.22	2.05	1.20
2-Methyltetrahydrofuran (MTHF)	1.08	2.23	2.06	0.98
Ethanol	1.70	2.08	1.94	0.24
Methanol	1.85	1.97	1.84	−0.01
Ice	2.0	1.78	1.64	−0.36
10 M KOH–H_2O	2.2	1.96	1.83	−0.37

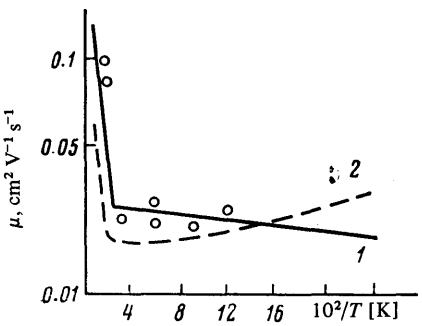


Figure 5. Temperature dependence of mobility: *1*) 3-MP,[296] *2*) MTHF.[297]

Experimental results[296,297] on the mobility of charge carriers in 3-MP and 2-methyltetrahydrofuran (MTHF) are shown in Fig.5. The measurements were by photo-injection of electrons[296] from a TMPD film electrode, or by pulse photolysis[297] of previously γ-irradiated MTHF. The results for the 35–77 K range are interpreted in terms of the Holstein hopping model[298], and those for temperatures below 35 K by the band model. It has been suggested[299] that the transition from hopping conduction to band conduction should occur at the Debye temperature (see Refs.300–302), which for 3-MP and MTHF is close to 35 K, i.e. to the break point in the curves of Fig.5. The reported[296,297] values of μ cannot be compared with the (much lower) values given by the trap-controlled diffusion mechanism for the motion of the carriers[303–306]:

$$\mu = \mu_0 \tau_3 / (\tau_B + \tau_3), \qquad (21)$$

where $\tau_3 \cong 10^{-12}$ s, $\tau_B \cong 10^3$ s at 77 K, and $\mu_0 \cong 1$ cm^2 V^{-1} s^{-1}.

In Ref.307 the drift mobility of electrons in 3-MP at 77 K, measured by injection of high-energy electrons, is given as $\sim 10^{-15}$ cm^2 V^{-1} s^{-1}, which formally agrees with the trap-controlled diffusion mechanism if we take $\mu_0 \tau_3 = 10^{-12}$ cm^2 V^{-1} [138] and $\tau_B = 10^3$ s[138,231,232]. These large discrepancies between the mobility values of a given material require an explanation.

Large discrepancies between experimental values of μ are observed also in polymeric materials. Thus, in the case of polyethylene, which has been investigated intensively[149,150,308–313], μ values between 10^{-4} and 10^{-14} cm^2 V^{-1} s^{-1} have been reported. The higher values (10^{-4}–10^{-6} cm^2 V^{-1} s^{-1}) are usually observed when the chosen measurement method involves the injection of low-energy, "cold" electrons (≤1 eV). Furthermore, the activation energy of the drift mobility (E_a) for these high mobility values is much lower (~0.2 eV) than for the low values of μ obtained after injection of high-energy, "hot" electrons ($E_a \geq 0.5$ eV). These differences between the μ values for hot and for cold electrons are probably associated with the chemical and physical features of the structure with which the excess electrons are interacting. For example, large differences between hot and cold electrons are not observed in PTFE[309,314], whereas in PMMA drift mobilities differing by several orders of magnitude have been reported for the injection of cold[315] and of hot electrons[316], the values being higher for the cold electrons.

It has been found[317] that benzene as the acceptor of a dry electron lowers the yield of solvated electrons (e_s^-) in methanol caused by the two-quantum ionisation of anthracene (or pyrene), but it has no effect on processes induced by laser radiation of wave length corresponding to the absorption band of e_s^-. The authors[317] conclude that the dry electron is not formed in the latter case. Nevertheless we can again postulate that benzene is an effective acceptor of hot dry electrons (two-quantum ionisation of anthracene) but does not react with thermal electrons (see Ref.318). Similar conclusions follow from the work of Kostin and coworkers[319,320].

In general the mobility of an electron in a disordered system depends on the energy of the electron. At some threshold energy E_C' ($E_C' > E_C$) the mobility suddenly increases to a terminal value[321,322] determined only by phonon scattering; under these conditions $\mu_0 \cong 3\lambda$ (where λ is the mean free path of the charge carrier), so that for $\lambda = 30$ Å we have $\mu_0 \cong 100$ cm^2 V^{-1} s^{-1}. For electron energies higher (by ~0.2 eV) than the bottom of the conduction band E_C but not higher than E_C' the motion of the electron can be highly hindered, because some of the space is not available for its motion[323–326]. In this case we are dealing with the continuum problem of the theory of flow[327], in which the mobility is determined by the expression[328]

$$\mu_0 = \frac{eD}{kT} = \frac{1}{6}\left(\frac{e}{kT}\right) a^2 \nu,$$

where a is the lattice parameter. For $a = 3$ Å, $\nu = 10^{15}$ s^{-1}, and $T = 300$ K we obtain $\mu_0 \cong 1$ cm^2 V^{-1} s^{-1}. According to the theory of flow, characteristic mobility values for this mechanism of motion should be in the range 0.01–1.0 cm^2 V^{-1} s^{-1}. Lastly, for electron energies $E_e < E_C$ the motion of the electron takes the form of a series of jumps from trap to trap in the forbidden gap (the hopping conduction mechanism), and $\mu \leq 10^{-5}$ cm^2 V^{-1} s^{-1}.

In disordered systems such as amorphous or partly crystalline glasses and polymers, energy bands are always assumed to be present[321,322,329], because these materials show short-range order in the relative position of atoms and molecules. However, the band edges can be diffuse in this type of material, i.e. they can have tails in which the electrons exist mostly in localised states. Because of the high density of these states their wave functions are able to overlap, and the electron can move by jumping from one localised state to another as a result of interaction with the thermal

fluctuations of the matrix energy. At low temperatures (below the Debye temperature) barrierless tunnelling transitions between localised states become predominant[277,321], causing a sharp change in the temperature dependence of the mobility (see Fig. 5).

In recent years important developments have taken place in the theory of the motion of current carriers in solid amorphous materials (including polymers) in the presence of an external electric field. These developments have been aimed mainly at explaining some special aspects of the drift mobility of electrons and holes determined by the crystal counter method[330-342]. The theory is being developed along two main directions. The earlier approach[343-346] relies on the jump (hopping) mechanism of motion of the electron in amorphous dielectrics, assuming the following distribution of jump times:

$$\psi(t) \propto t^{-(1+\alpha)}, \qquad (22)$$

where α is a constant ($0 < \alpha < 1$). This is the Scher–Montroll stochastic jump model[343]. The function (22) is quite different from the exponential function $\psi(t) \propto \exp(-at)$, used in the classical (diffusion) jump theory, in which the average jump time is assumed to be $t_{aver} = a^{-1}$. A not very convincing account of this theory is given in Refs. 347 and 348. Several critical comments on the Scher–Montroll model are made in Refs. 349–354.

In the second approach the motion of the electron is treated by the classical band model in the presence of a continuous distribution (in energy) of charge traps[355-364]. The equivalence of these two approaches has been demonstrated by several workers[345,359,361,365]. The special features of the non-gaussian diffusion and drift of charge carriers in amorphous matrices are extremely important, because they give a correct formulation of the early stages in the recombination of isolated ion pairs[367] as well as explaining the shape of the initial portion of the current decay curve after irradiation[118,119,368].

Perlman and Bamji[369] stress the need for the utmost care in interpreting experimental results obtained by the crystal counter method in polymers (especially in polyethylene).

One of the models proposed for the motion of a solvated electron e_s^- in a liquid may also find application in the solid state. This is the so-called configuration coordinate model of the motion of e_s^- by diffusion[370-372]. According to this model the orientation polarisation function is arbitrarily fixed, and the total energy E is calculated. A diffusion jump between states with an orientation polarisation function for which the total energy E is a minimum is treated as a continuous change in the polarisation P between the values P_0 and P_1, such that

$$P_u(r) = (1-u)P_0(r) + uP_1(r),$$

where u can vary from 0 to 1.

In full agreement with experiment, the calculated activation energy for the motion of the electron in ice is 0.16 eV. This model avoids the discrepancy with experimental values of the activation energy for electrical conduction found in the earlier models. Thus, in the transition

$$e_s \rightarrow e^- + \text{full orientation relaxation}$$

the activation energy for water is ~0.5 eV. If on the other hand we assume a vertical transition (i.e. a transition in which the orientation is not perturbed) the activation energy is even higher, and coincides with the energy of the optical transition (usually ≥ 1 eV).

The above model is based on the rotation of the molecular dipoles. It is difficult to believe that this rotation can take place at 77 K. However, at room temperature the mechanism may be generally applicable, especially in the case of polymeric materials. The presence of dipoles (due to various structural imperfections and chemical impurities) even in non-polar polymers has been demonstrated by measurements of pyroelectric properties[373]: it is now accepted that substantial changes in dipole orientation can occur even below the glass transition temperature. Thus the conditions in polymers at room temperature are not inconsistent with the proposed mechanism of the drift mobility of a trapped electron in a condensed phase.

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During the preparation of this review several new publications have appeared, with critical comments on many of the topics discussed above. We shall briefly discuss the most important of these.

The validity of the classical ideas on the diffusion and drift of charged particles in interpreting the results of electron trapping measurements and pair recombination in a condensed phase is challenged[374], in spite of the allowance for non-gaussian diffusion of electrons in amorphous matrices[367,375-383]. An attempt is also made[379,380,382] to explain the kinetics of the disappearance of ion radicals in frozen organic glasses in terms of the Scher–Montroll model rather than by the tunnel effect.

A study of the photo-ionisation of TMPD in non-polar solvents has led to the conclusion[384,385] that the precursor of the free electron is not an ion pair but an excited state of the solute molecule. This result is directly relevant to the problem of the contribution of electrons from isolated pairs to the electric current (see Refs. 104, 127, 386).

The influence of the dose ($\leq 10^3$ Rad) on the induced electrical conductivity during pulsed (~50 ns) irradiation of crystalline ice is discussed in Ref. 387, mainly in terms of the formation of free OH radicals. These results agree very well with those of Nikol'skii and coworkers[262], who showed that in polyethylene electron capture (mainly on radicals) begins at doses as low as $\sim 10^5$ Rad. It is suggested that the formation of stabilised electrons, characterised by the i.r. absorption spectrum, involves electron capture by pre-existing traps not only in solid[388] but also in liquid polar matrices[389]. The possibility of explaining the "blue" shift of the absorption spectrum of a trapped electron in terms of its motion within the ion pair is discussed[390]. However, Rice[391] believes that in molecular frozen glasses the migration of trapped electrons is unlikely, though such migration has been demonstrated experimentally in frozen alcohols[392] with observation times ≤ 750 ns (see also Ref. 393).

The lowest reported values ($\leq 3 \times 10^{-13}$ cm^2 V^{-1}) of $G\mu_0\tau_3$ have been observed in polar polymers[114,120]. This has been interpreted[126] as evidence that the conduction is due to hot electrons with energy ≤ 10 eV, and a far-reaching analogy between RPEC and electrical breakdown in dielectrics has been proposed[394] (see also Refs. 104 and 120). Vaisburd's model of the electrical conduction induced in dielectrics by powerful electron beams[395,396] should also be mentioned here.

We have been unable, through lack of space, to deal adequately with the generation of current carriers from excited neutral states of the polymer molecule or from complexes, which plays a fundamental role in photolysis[397] and may also be important in radiolysis. The study of these states has been made much easier by our improved understanding of spin effects in the elementary processes of high-energy chemistry, due mainly to the work of Frankevich and coworkers (see review articles in Refs. 398 and 399). The energy structure of ionised and excited states in organic molecular crystals is now known in great detail[400-402].

Therefore we can hope for similar advances, in the near future, in our understanding of disordered organic matrices, including polymers.

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