FARADAY LECTURE*

The Electron as a Chemical Entity

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1 Introduction

When I heard that Council wished me to give the Faraday Lecture my reaction was compounded of delight and apprehension. The former was a stimulus to accept the invitation whilst the latter gave cause for refusal. My pleasure sprang from the very great honour that the Society had done me and from the fact that Faraday has been a life-long personal hero. I well remember preparing myself to go with a school party to view the solar eclipse of 29th June 1927 from the top of Ingleborough by studying the Ordnance Survey map of that district and seeing on it the words 'Faraday Ghyll'. I wondered if there were any connection between this topographical feature and the Laws of Electrolysis which an over-ambitious and enthusiastic master had brought to my tender and uncomprehending attention. Indeed there is; for although Michael was born in London in 1791, his father was born in Clapham Wood Hall about 1 mile west-south-west of Clapham Village. When I last visited it about a dozen years ago it was still standing and had a fine outlook over Burn Moor Fell. Somewhat fancifully – some would say extravagantly – I like to think that Michael's passion for long country walks (20 miles were a mere stroll to him) and some of his personal qualities – his respect for truth, his emphasis on self-education, his steadfastness – were derived from his West Riding ancestors. At all events I became interested in the man. I read his 'Chemical History of a Candle' and marvelled at the clarity of his exposition. Later I came to know and admire his scientific work and his ardent campaigning to ensure that natural philosophy should be an element in the education of all who lay claim to the title *educated*, a cause which, regrettably, still needs its champions today.

My countervailing feeling of apprehension stemmed from the hopelessness of trying to commemorate, by emulating, such a brilliant lecturer. I shall try to follow his precepts for lecturers, but I shall not reveal those to you until the end when you can judge as to whether his advice has been properly heeded by me.

Having accepted the invitation I had no hesitation about an appropriate topic. It just *had* to be concerned with electricity – Faraday's consuming passion, the etymology of which is based on the Greek for amber, *ηλεκτρον*. In his biography,[1] Pearce Williams draws attention to von Helmholtz' suggestion in

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[1] L. Pearce Williams, 'Michael Faraday', Chapman and Hall, London, 1965.

his 1881 Faraday Memorial Lecture that Faraday's second law of electrolysis combined with Dalton's Atomic Theory implied that 'at the atomic level each element received the same quantum of electricity. This quantum is what we would today call the electron'. Faraday missed this implication. Since his last work was concerned with electrical discharges in rarefied gases and since he also observed that these discharges were deflected by magnetic fields it is tempting to think that, with a little luck, Faraday might have identified the electron, in the *gas* phase at least, almost half a century before e/m was measured.

The idea that an electron in a condensed phase might have an importance in chemistry was not taken seriously for another half century. Of course the notion of redox potentials led to the writing of equations like

$$\mathrm{Fe_{aq}}^{2+} \rightarrow \mathrm{Fe_{aq}}^{3+} + \mathrm{e}^- \text{ and } \mathrm{I_{aq}}^- \rightarrow \tfrac{1}{2}\mathrm{I_2} + \mathrm{e}^- \qquad (1)$$

and it was suggested in the twenties by Franck and Scheibe[2] that such reactions could be stimulated by light, but the electron was thought to be unstable in water. I have a vivid memory of giving a lecture on the photo-ionization of aqueous bivalent ions of the first row of the transition elements at the Argonne National Laboratory in October 1952 and, after writing the first part of equation (1), being sternly and publicly rebuked by the late Professors James Franck and Robert Platzman who were confident that the aquated electron, $\mathrm{e_{aq}}^-$, would decompose according to equation (2) in a period comparable with the dielectric relaxation time of water, *i.e.* 10^{-11} s.

$$\mathrm{e_{aq}}^- \rightarrow \mathrm{H}\cdot + \mathrm{OH_{aq}}^- \qquad (2)$$

Such Olympian contumely was not to be disregarded and it was not until 1959 that I recovered sufficient self-confidence to carry out projected experiments to see if $\mathrm{e_{aq}}^-$ could exist long enough to take part in chemical reactions. I was encouraged to resurrect this experimental programme because in 1958 Weiss[3] and his collaborators and in 1959 Barr and Allen[4] (see Figure 1) had shown that the reducing entity in the radiolysis of water, then thought to be a hydrogen atom formed in a process written as

$$\mathrm{H_2O} \rightsquigarrow \mathrm{H}\cdot + \cdot\mathrm{OH} \qquad (3)$$

reacted in a different manner and at different rates with the same solute at $\mathrm{pH} \leqslant 2$ and at $\mathrm{pH} \geqslant 3$. This finding opened the possibility that at higher pH the reducing entity was $\mathrm{e_{aq}}^-$, convertible into $\mathrm{H}\cdot$ at low pH *via* reaction (4). (The alternative explanation that $\mathrm{H}\cdot + \mathrm{H_{aq}}^+ \rightarrow \mathrm{H_{2aq}}^+$ was the relevant reaction was thought less likely because $\mathrm{H_{2aq}}^+$ was expected to be an *oxidizing* agent.) Since the solute

$$\mathrm{e_{aq}}^- + \mathrm{H_{aq}}^+ \rightarrow \mathrm{H}\cdot \qquad (4)$$

concentrations used in these experiments were *ca.* 10^{-3} mol l^{-1} these results also

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[2] J. Franck and H. Scheibe, *Z. phys. Chem.* (*A*), 1928, **139**, 22.

[3] J. Weiss and E. Hayon, *J. Chem. Soc.*, 1960, 5091; E. Hayon and A. O. Allen, *J. Phys. Chem.*, 1961, **65**, 2181.

[4] N. F. Barr and A. O. Allen, *J. Phys. Chem.*, 1959, **63**, 928.

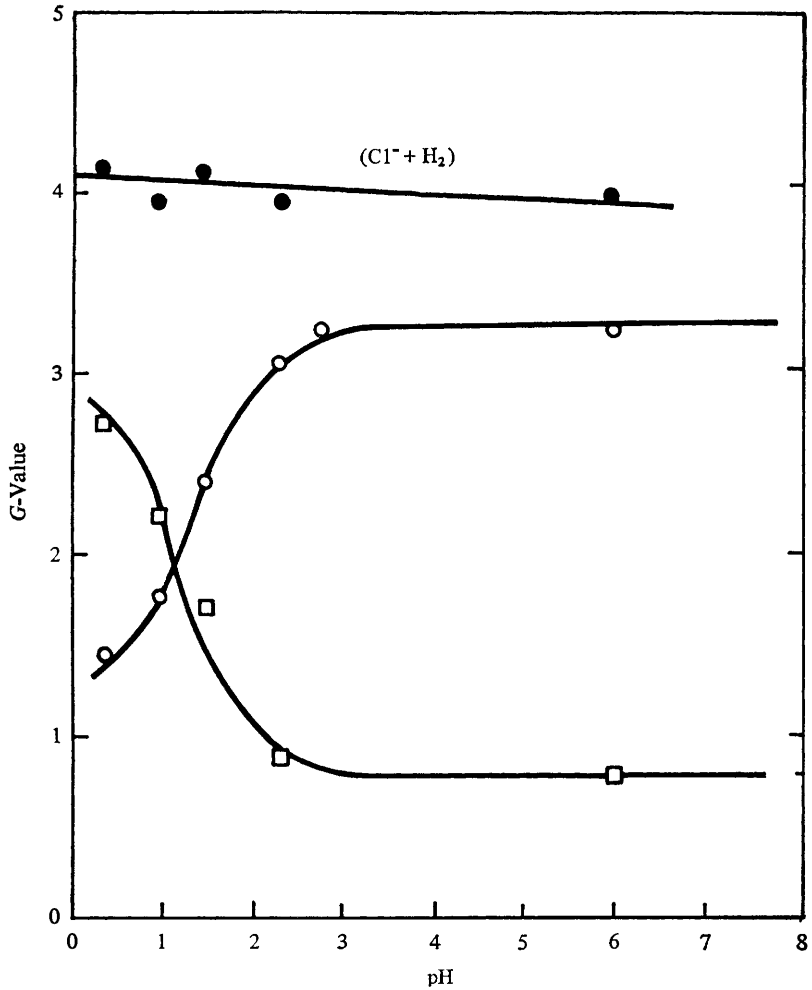

Figure 1 *Yields of hydrogen and chloride ion from the γ-radiolysis of* 0.1M *deaerated aqueous solutions of chloroacetic acid in the* pH *range* 0—6
(Reproduced by permission from *J. Phys. Chem.*, 1961, **65**, 2181)

implied that, unless the rates were *faster* than diffusion controlled reactions ($k \sim 10^{10}$ l mol^{-1} s^{-1}), then the lifetime of e_{aq}^- was at least 10^4 times greater than the dielectric relaxation time.

The next step was obvious. It was to find whether the reducing entity at pH $\geqslant$ 3 had zero or unit negative charge. This merely required a measurement of the effect of changing the ionic strength, μ, on the rate of the reaction of this entity with an ion A^{z_a}. However, there were no known fast reaction techniques available and we had therefore to have recourse to a competition method in which A^{z_a} and B^0 competed as shown in equations (5) and (6) and measuring the relative rates of these reactions at 25 °C. The Brønsted–Bjerrum Laws then

$$e_{aq}^- + A^{z_a} \rightarrow A^{z_a - 1} \tag{5}$$

$$e_{aq}^- + B^0 \rightarrow B^- \tag{6}$$

indicate

$$\frac{d[A^{z_a-1}]}{d[B^-]/dt} = \frac{k_5[A^{z_a}]}{k_6[B^0]}$$

where $\log_{10}[k_5/k_6] = \text{constant} + z_a(-1)f(\mu)$, and $f(\mu)$ is a function [under appropriate conditions approximating to $\sqrt{\mu}/(1 + \sqrt{\mu})$] of the ionic strength of the medium. Quite independently of this work at Leeds,[5] Czapski and Schwarz[6] were simultaneously doing similar experiments at the Brookhaven National Laboratories but using different A's and with B = H_2O_2. The results of both groups (see Figure 2) were concordant and conclusively showed that the reducing entity had unit negative charge and was probably the hydrated electron.

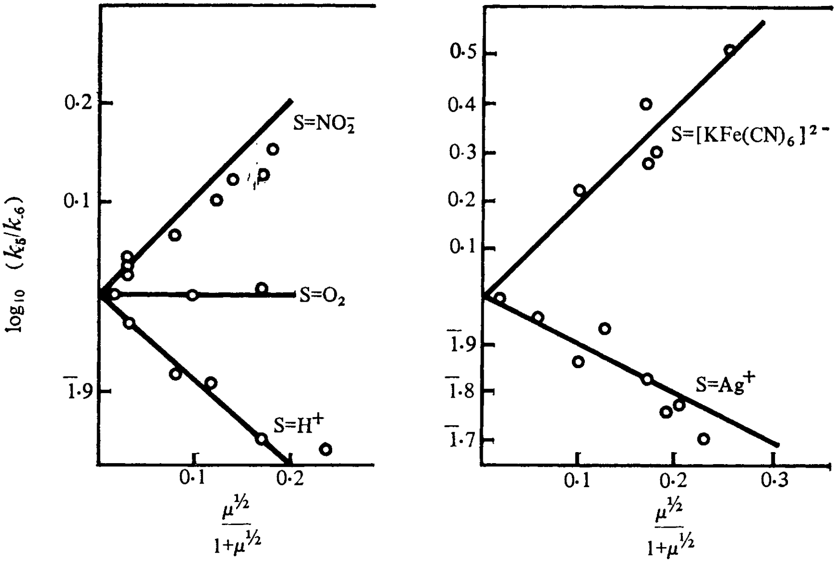

Figure 2 *The effect of ionic strength, μ, on the relative rate constants of reactions* (5) *and* (6) *in water at* 25 °C. *Plotted from data in refs.* 5 *and* 6

A^{z_a}	NO_2^-	O_2	H^+	Ag^+	$KFe(CN)_6^{2-}$
B°	H_2O_2	H_2O_2	H_2O_2	C_3H_6ON	N_2O

(Reproduced by permission from *Pure Appl. Chem.*, 1967, **15**, 21)

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[5] E. Collinson, F. S. Dainton, D. R. Smith, and S. Tazuke, *Proc. Chem. Soc.*, 1962, 140; F. S. Dainton and W. S. Watt, *Proc. Roy. Soc.*, 1963, **A275**, 447.

[6] G. Czapski and H. A. Schwarz, *J. Phys. Chem.*, 1962, **66**, 471.

In the past decade knowledge of this entity has grown apace and its properties are now more closely delineated than those of many chemicals. In pondering what to put in this lecture I considered there were two alternative approaches. On the one hand I could assume that much about the electron in condensed media was common knowledge and concentrate on some very recent developments of special interest to the cognescenti or, on the other hand, I could try to paint a broad-brush picture. I chose the latter course as being more appropriate to the occasion and as being more likely to interest a general audience. This decision inevitably means some sacrifice of rigour and precision of which Michael Faraday would certainly *not* have approved; but then he would probably have been rather shocked that the Faraday Lecture was given by a mere administrator who in the past few years has had to mix science and politics, because on 9 July 1849 Faraday wrote to Auguste de la Rive in these terms:[7] 'For me, who never meddled with politics and who thinks very little of them as one of the games of life, it seems sad that scientific men should be so disturbed by them and so the progress of pure philosophy be much and so often disturbed by the passions of men'.

What I shall do then is to describe in simple terms and in succession the theory of an electron in a condensed system, how this species may be prepared, and how its major physical and chemical properties have been elucidated, and conclude with some illustrations of its utility in chemistry.

2 On 'Dropping' an Electron into a Liquid or an Amorphous Solid[8]

An electron placed in an assembly of mono- or poly-atomic molecules of zero electron affinity will experience short-range repulsions and induce in them very rapid atomic polarizations which fluctuate as it moves through the medium. It is known as a 'quasi-free' electron and although its energy, V_0, will certainly be different from its energy in the gas phase there is no known experimental means of measuring it. This energy will change with changing medium density and is likely to decrease with increasing polarizability of the atomic constituents. As the density is increased a point will be reached at which the migrating electron will find itself in a spherical cavity, escape from which may be temporarily prevented by the symmetrical and close array of the molecules constituting the cavity wall. If it is confined long enough for translational and rotational displacements of the molecules to occur then, as described below, its energy may fall below V_0 when it is no longer 'quasi-free' but 'localized'.

Potential electron-trapping cavities of varying sizes will exist in amorphous solids and in fluids (including gases of more than a critical density) but not in perfect crystals or too attenuated gases. The energy of the confined electron relative to its quasi-free condition will then have two parts *viz*: *electronic* and *cavity reorganizational*. The latter has the following components: (i) that due to

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[7] See ref. 1 p. 357.

[8] There are many accounts of this theory. The latest, which contains references to most of the previous work, is to be found in 'Electrons in Fluids', ed. J. Jortner and N. R. Kestner, Springer, New York, 1973, pp. 1—25.

mechanical work involved in dilation or contraction of the cavity (this is not significant except at high pressure); (ii) that due to the change in surface free energy of the 'bubble' as dilation or contraction occurs; (iii) that due to rotation of the molecules of the cavity wall so that the positive ends point to the centre; (iv) the destabilization due to electrostatic repulsions of the permanent and induced dipoles aligned as in (iii); (v) inter-hydrogen-atom repulsions due to 'crowding' of these in the centre of the cavity: a destabilizing effect which increases in the order ROH, H_2O, NH_3; (vi) that due to polarization of molecules outside the cavity wall; these are usually treated as a continuum.

The electronic energy is evaluated from the usual equation

$$\psi_i(r)\,[V(r) - \tfrac{1}{2}\nabla^2] = W_i\,\psi_i(r) \tag{7}$$

assuming a particular binding potential $V(r)$, which will depend on the number, arrangement, and chemical nature of the molecules of the cavity wall, which of course also influence the reorganizational energy, especially through (ii), (iv), and (v). The optimum cavity size is then determined by minimizing the total energy for the $1s$ state of the electron. Calculations of this kind can be carried out for other states and the variations of energy with radius for $2s$ and $2p$ (*i.e.* optically combining) states are shown in typical cases in the *configuration diagrams.*

Such calculations enable the following predictions to be made: (i) whether a stable cavity exists, and, if so, the most probable number of molecules in the cavity wall; (ii) the optimum cavity size and therefore whether 'dropping' electrons into the medium will cause dilation or contraction; (iii) estimates of the heat changes accompanying trapping; (iv) because dilation involves structure loosening, it will be accompanied by a diminution of viscosity; (v) possible optical transitions, their energies and oscillator strengths, which in turn allow the form of the optical spectrum, the photoconductivity and photoelectric thresholds to be estimated. A typical configuration diagram is shown in Figure 3.

For stable cavities, the optical spectrum is the most important property and it is here that the first important discrepancy with experiment is found. The predicted $2p \leftarrow 1s$ lineshape is always narrower and more symmetrical (see Figure 4) than the observed spectrum which has a marked high-energy tail. Figure 5 shows the spectra of electrons solvated in different liquids which illustrate this point.[9] It also shows that small changes in chemical structure can cause significant shifts of λ_{max} which Dorfman has shown cannot be correlated with changes of the dielectric constant. As yet the theory cannot account quantitatively for these shifts but there are qualitative arguments to suggest that within the same homologous series component (v), *i.e.* lateral repulsions, is a dominant influence. Thus λ_{max} is greater for branched than straight-chain alcohols and for ethers than for alcohols, a result which may be interpreted by enforced greater cavity size due to repulsions of the increasing number of H atoms forming the cavity wall.

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[9] L. M. Dorfman, F. Y. Jon, and R. Wageman, *Ber. Bunsengesellschaft. phys. Chem.*, 1971, **75**, 681.

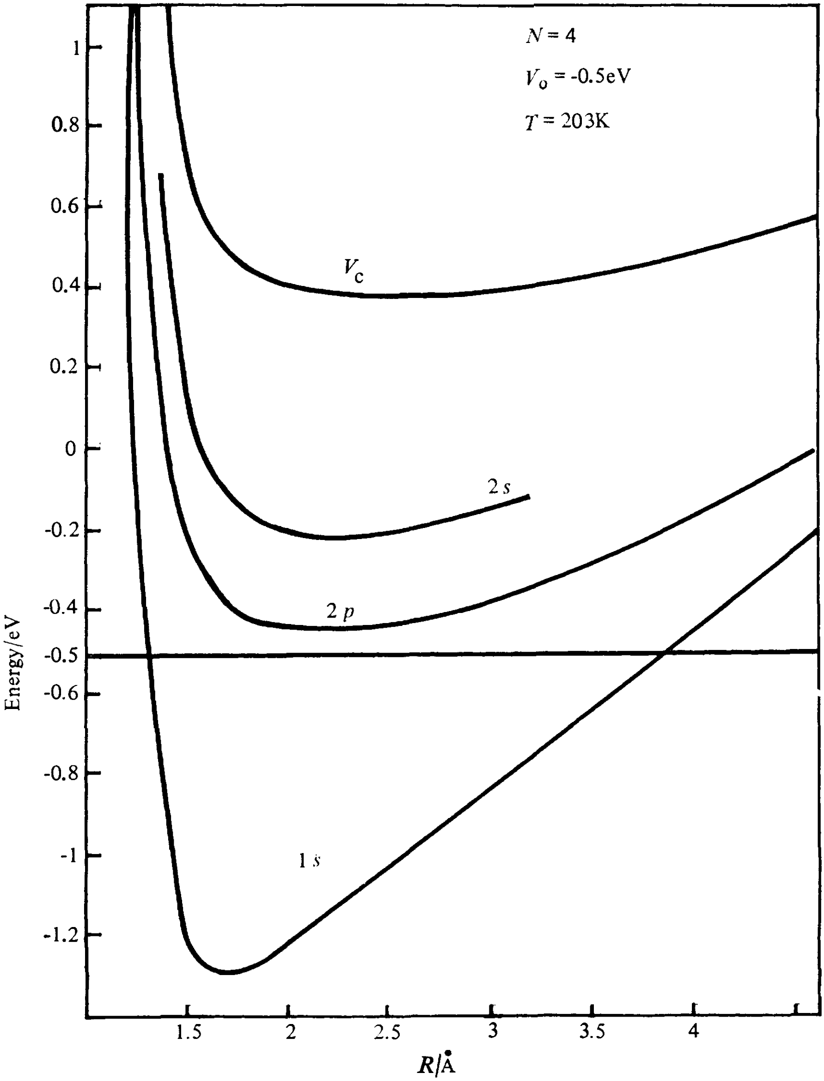

Figure 3 *Configuration diagrams for electron in liquid ammonia showing energy as a function of cavity radius for* 1*s and* 2*p states for four nearest neighbour* NH_3 *molecules* (Reproduced by permission from 'Electrons in Fluids', ed. J. Jortner and N. R. Kestner, Springer, New York, 1973)

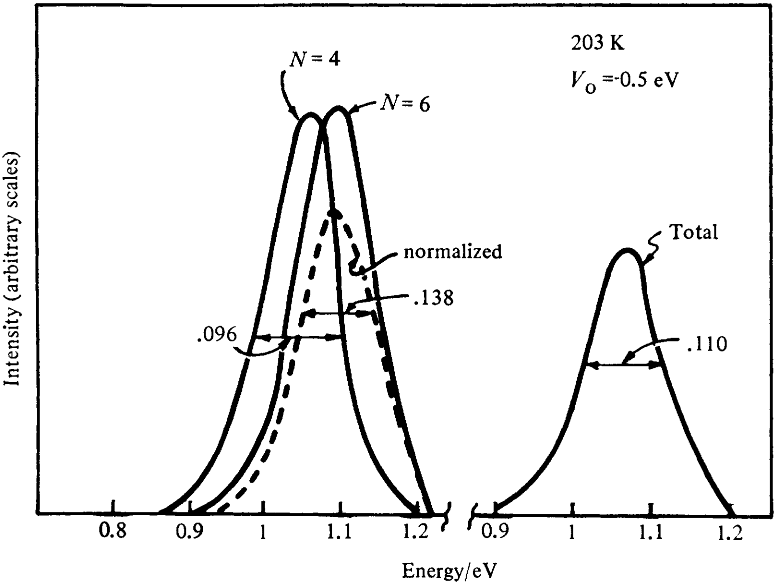

Figure 4 *Predicted spectrum for* e_s^- *in liquid ammonia at* 203 K. *Left-hand curves correspond to four and six nearest neighbours. Right-hand curve is an appropriately weighted composite. Taken from* Figure 4, p. 15 *of ref.* 8 *where underlying assumptions are explained* (Reproduced by permission from 'Electrons in Fluids'. ed. J. Jortner and N. R. Kestner, Springer, New York, 1973)

3 The Preparation of Solvated and Trapped Electrons in Condensed Media

A. Definitions.—It is useful to distinguish between a *solvated* electron, designated e_s^-, and a *trapped* electron, designated e_t^-. The former is an electron in a liquid which is either non-ionized or only very weakly so, such as water, ammonia, amines, ethers, alcohols, or hydrocarbons. It can move through the liquid by processes to be described and can be ascribed a numerical diffusion constant. The latter on the other hand, is an electron in an amorphous, non-ionic solid (*i.e.* glasses) and cannot move without gross disruption of, or detachment from, its cavity, becoming a *mobile* electron, e_m^-, which has higher energy than e_t^- and moves rapidly through the medium until it is retrapped at a suitable site which is an actual or potential cavity. As initially produced by any of the methods described below, an electron is, of course, unsolvated or untrapped and is progressively changed into the final fully solvated or trapped state. In the initial state it is sometimes alluded to as *dry* and in the intermediate state as *damp* or *moist* (a reference to water as the medium). These descriptions, though imprecise, are none-the-less useful because they describe realities.

B. Preparation.—The obvious method of preparation would be to bombard

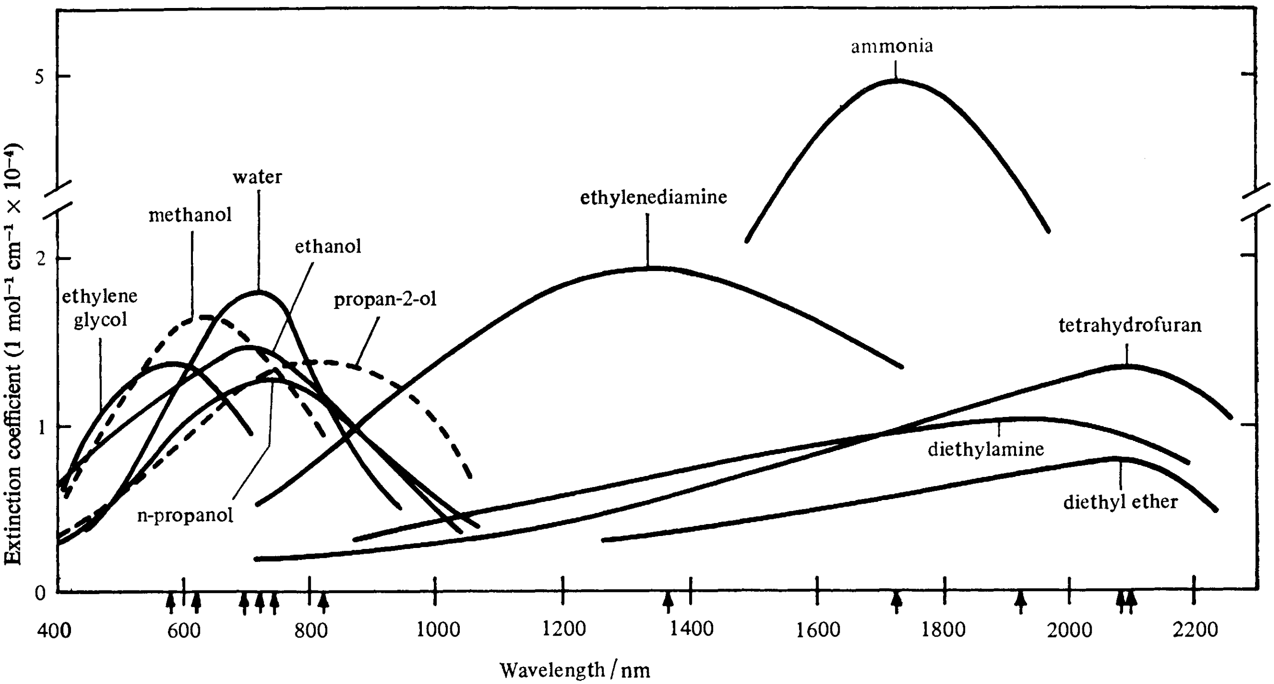

Figure 5 *Absorption spectrum of* e_s^- *in various solvents*
(Reproduced by permission from *Ber. Bunsengesellschaft phys. Chem.*, 1971, **75**, 681)

liquids or glasses with a stream of electrons from some external source. Although it is effective, as may easily be demonstrated by placing blocks of colourless plastics, such as poly(methyl methacrylate), in the beam of an electron accelerator when the characteristic colour of e_t^- becomes apparent, it is of little use because the whole material develops a negative potential. To avoid this it is usual to extract the electrons from molecules of the medium or from solutes by means of heat, light, or ionizing radiation (α-, β-, and γ-rays or fast charged particles delivered by an accelerator) or from solids in contact with the medium which are charged to a negative potential. The most useful methods are described below:

(*a*) *Spontaneous*. There are two kinds of thermal reaction. The first is the spontaneous loss of an electron from a substance, M, of low thermionic work function, ϕ_M, (or if the vapour is used, of low ionization potential, I_M) when it is brought into contact with an appropriate solvent.[10a] Equation (8) summarizes this process,

$$M_{solid} + S \rightarrow M_S^+ + e_S^-;\ \triangle H_8 = \phi_M - S_{M^+} - S_{e^-} \qquad (8)$$

where S denotes the enthalpy decrease on solvation. It is clear why the alkali metals, having low values of ϕ_M, so easily form e_S^- in contact with water, ammonia, or amines. They are less effective in less polar aprotic solvents such as the ethers and hydrocarbons where the solvation energies are much lower. However, it is possible to increase S_{M^+} by the use of small amounts of the cyclic ethers ('crowns' and 'cryptates') which co-ordinate and sequester in soluble form the cation and thus drive reaction (8) further to the right.[10b] This may cause a further complication in that M_S^- has a stability comparable to that of e_S^- and a spectrum which overlaps it, and so complex equilibria involving M, e_S^-, M_S^+, and M_S^- are established which are difficult to disentangle. For these reasons, and also because M is used as a metal mirror or in mercury amalgam and the concentration distribution of e_S^- initially produced is non-uniform, this method is not of high utility. When used in the rotating cryostat,[10c] in which jets of M atoms and solvent molecules are sprayed alternately onto a rotating glass cylinder at 77 K, reaction (8) does provide a means of obtaining good e.s.r. spectra of e_t^-.

The second method relies on the reversal of reactions of type (2) in protic solvents which dissolve freely the alkali-metal salt of the solvent. Thus if the solvent designated as H_2A is capable of ionizing into H^+ and AH^- it is possible to establish the reaction (9) by passing hydrogen atoms into or generating them within H_2A containing high concentrations ($> 10^{-2}$ mol l^{-1}) of NaAH. This was first established for water by Jortner and Rabani.[11a] The hydrogen atoms

$$H\cdot + AH^- \rightarrow e_S^- \qquad (9)$$

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[10] (*a*) See 'Solutions Metal-Ammonia', ed. G. Lepoutre and M. J. Sienko, Benjamin, New York, 1964, and 'Metal-Ammonia Solutions', ed. J. J. Lagowski and M. J. Sienko, Butterworths, London 1970; (*b*) J. L. Dye *et al.*, *J. Amer. Chem. Soc.*, 1970, **92**, 5226; *Ber. Bunsengesellschaft. phys. Chem.*, 1971, **75**, 659; *J. Phys. Chem.*, 1972, **76**, 2975; (*c*) J. E. Bennett, B. Mile, and A. Thomas, *Nature*, 1964, **201**, 919.

[11] (*a*) J. Jortner and J. Rabani, *J. Amer. Chem. Soc.*, 1961, **17**, 388; (*b*) W. L. Jolly in ref. 8, p. 169.

need not necessarily be free; it suffices if they are loosely bound to a molecule as in the radical $CH_3\dot{C}HOH$ when reaction (10) can take place:

$$CH_3\dot{C}HOH + C_2H_5O_s^- \rightarrow CH_3CHO + e_s^- \qquad (10)$$

In passing it may be noted that if the radical anion $A\cdot^-$ can be formed then reaction (11) is in principle possible and in the case of ammonia ($A\cdot^- = NH^-$)

$$H_2 + A\cdot^- \rightarrow e_s^- ; \qquad (11)$$

this is known as the Jolly reaction,[11b] though whether this proceeds as written or is two-stage, *i.e.* $H_2 + A\cdot^- \rightarrow H\cdot + AH^- \rightarrow e_s^-$, remains a moot point.

(*b*) *Photochemical.* Electrons can be photo-detached from plates,[12] films,[13] cathodes,[14] and reducing solutes. The disadvantage of the first three methods is that the electrons are formed close to the emitting surface but the advantage is that the method can be used with any solvent towards which the surface is inert. If the surface is negatively polarized the drift velocity of the electrons released can be measured, so that it becomes possible to determine whether they are 'localized' or 'quasi-free'. By this means it has been shown[15] that in some cases neither of these descriptions is exclusive, *i.e.* the electrons show 'quasi-free' conduction between cavities in which they are localized for only a short time, τ, and from which they may be thermally ejected so that $\tau = \tau_0 \exp(\tilde{E}/RT)$ where $\tilde{E}$ is the average escape activation energy. If μ_{qf} is the mobility of the quasi-free electron between cavities in which the electron is immobilized then the observed mobility, μ, will be given by the equation

$$\mu = \mu_{qf}/(1 + n\tau)$$

in which n is the trapping frequency. In unsymmetrical hydrocarbons $n\tau \gg 1$, so that $\mu \simeq (\mu_{qf}/n\tau_0)\exp(-\tilde{E}/RT)$ and the values of $\tilde{E}$ are in the range 4—8 kJ, indicating very low binding of energy of e^- to the trap.

The most useful photochemical method, because it ensures a uniform distribution of e_s^- throughout the solvent, is that of detachment of an electron from a solute ion or molecule, D_s, according to equation (12). n may be unity,

$$D_s + nh\nu \rightarrow D_s^+ + 1e_s^- \qquad (12)$$

i.e. the process is monophotonic. This is true for many ions and molecules in aqueous solution[16] as is illustrated in Table 1. The biphotonic mode, *i.e.* $n = 2$, requires for effectiveness with light of moderate intensity, say, 10^{14} quantum $cm^{-2}\ s^{-1}$, that an intermediate state of some longevity such as a triplet state is

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[12] R. A. Holroyd and M. Allen, *J. Chem. Phys.*, 1971, **54**, 5014.

[13] F. W. Froben and J. E. Willard, *J. Phys. Chem.*, 1971, **75**, 35.

[14] G. C. Barker, *Ber. Bunsengesellschaft. phys. Chem.*, 1971, **75**, 728.

[15] H. T. Davis, L. D. Schmidt, and R. G. Brown, ref. 8, p. 393.

[16] Reviews of this method are to be found by G. Stein, 'Actions Chimiques et Biologiques des Radiations', Masson et Cie, Paris, 1969, **13**, 119; and H. I. Joschek and L. I. Grossweiner, *J. Amer. Chem. Soc.*, 1966, **88**, 3261.

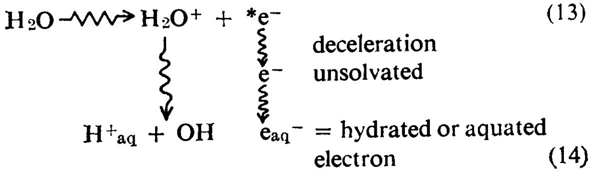
Table 1 *Quantum yields of* e_{aq}^- *formation from* D_{aq}

D_{aq}	Br^-	Cl^-	OH^-	SO_4^{2-}	I^-	$Fe(CN)_6^{4-}$	Fe^{2+}	$PhNH_2$	PhOH
λ/nm	185	185	185	185	254	254	254	254	254
Φ	0.34	0.43	0.11	0.71	0.23	0.67	0.06	0.16	0.02_5

readily accessible[17] and from which the ionization level may be reached by an allowed optical transition. It has the virtue that light of longer wavelength than is usually effective for monophotonic processes can be used but, clearly, high intensities such as those provided by laser sources are advantageous. Typical solutes capable of biphotonic photoionization are anthracene and TMPD (tetramethyl-*p*-phenylenediamine) and their derivatives in hydrocarbon solvents.

The advantage of the photochemical method is that it permits the use of flash photolysis to obtain both the spectra and rates of reaction of e_s^-. This is somewhat offset by the facts: (i) that the monophotonic quantum yields are not large (see Table 1); (ii) that D_s^+ is often an oxidizing agent and the reverse of reaction (12) may be rather fast; and (iii) that the absorption spectra of either D_s or D_s^+ or both may overlap that of e_s^-; *e.g.* when D = TMPD D_s^+ is the Würster's salt cation which absorbs strongly in the red end of the spectrum. Disadvantages (i) and (iii) cannot be eliminated but it is sometimes possible to convert D_s^+ by reaction with a molecule to form a non-absorbing product which does not react with e_s^- [see also (*c*) below].

(*c*) *Radiolysis of the Solvent.* When a fast charged particle is decelerated by passage through an assembly of molecules it loses energy by inelastic collisions in some of which the molecules are ionized. On average the energy lost from all causes per ionization event is *ca.* 30 eV and the indications are that the average energy of each ejected electron is *ca.* 10 eV, though this is the average of a wide distribution of actual values. This secondary electron is therefore decelerated in events which involve ionization only rarely and it is eventually thermalized some distance from its co-product, the ion derived from the parent molecule. The thermalized electron may then be solvated or trapped and the ion-molecule may decompose or react with another molecule(s) of solvent. For example in the case of water we may depict the process as:



in which the rates of formation of H_{aq}^+ and e_{aq}^- must both be limited by the dielectric relaxation rate.

The advantages of this method of generating e_s^- are numerous. In the first place, no solute is necessary and the complications inherent in (*b*) above are absent.

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[17] G. E. Johnson and A. C. Albrecht, *J. Chem. Phys.*, 1966, **44**, 3162, 3179; G. Beck and J. K. Thomas, *ibid.*, 1972, **57**, 3649.

Secondly, since the physics of the inelastic collision processes are not strongly influenced by the state of aggregation the primary act is insensitive to whether the molecular ensembles are solid, liquid, or gaseous. Thirdly, since the energy transferred to a molecule is primarily dependent on its proximity to the track of the fast charged particle, solutes in concentration $< 10^{-1}$ mol l^{-1} and are virtually immune from direct excitation by the electron. Finally, accelerator beams are readily pulsed to 10^{-9} s and therefore the analogue of flash photolysis, namely pulse radiolysis, is a valuable and now the major tool for elucidating the spectrum and reaction kinetics of e_s^-.[18]

Slightly offsetting these advantages is the fact that, as in the photochemical case, the co-product of the primary act or its breakdown product are free radicals which are therefore electron acceptors, *i.e.* oxidants, and also that both these species are distributed in 'spurs' and in isolated pairs in the close vicinity of the track of the fast charged particle. The first of these countervailing influences can often be removed by the addition of a substance from which the radical co-product can extract a hydrogen atom. Thus in the case of water, saturation with hydrogen gas or ethylene or the presence of 10^{-2} M ethanol is sufficient to capture all the hydroxyl radicals formed in reactions (13) and (14), provided the dose-rates and doses are not too large to use up most of the added solute. In each case the OH radical is converted into a reducing radical, respectively $H\cdot$, $HOCH_2CH_2\cdot$, and $CH_3\dot{C}HOH$, which does not react with e_s^- and which in the cases of $H\cdot$ and $CH_3\dot{C}HOH$ may be converted into e_s^- in highly alkaline solutions *via* reactions exemplified in equations (9) and (10), thereby augmenting the rate of formation of e_s^-.

The non-uniform, track-like distribution of the primary species is not so serious a handicap as might at first sight be presumed. This is not the occasion for a discussion of spur and track kinetics; suffice it to say that at dose-rates generally used in pulse radiolysis with >1 MeV electrons or using kiloCurie γ-ray sources and with radical scavenging solutes in the concentration range *ca.* 10^{-3} to 10^{-2} mol l^{-1} the kinetics of the subsequent reactions are adequately accounted for by assuming a uniform distribution of primary species.

For all these reasons the radiolysis method is the most convenient, controllable, and flexible means currently available for producing e_s^- or e_t^- in solids, liquids, and compressed gases.

(*d*) *Field Emission Methods.* Field emission from cathodes,[19] whilst leading in suitable circumstances to formation of e_s^-, is of limited utility because it needs high electric gradients, because it is restricted to media which are electrically insulating, and because it generates electrons in a highly non-uniform distribution.

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[18] See 'Pulse Radiolysis', ed. M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Academic Press, London, 1965; A. K. Pikaev, 'Pulse Radiolysis of Water and Aqueous Solutions', Indiana University Press, London, 1967; M. Anbar, M. Bambenek, and A. B. Ross, *Nat. Stand. Data Ref. Service* (*US*); 1973, **43**, 1—67; E. Watson and S. Ray, *ibid.*, 1972, **42**, 1—22.

[19] W. F. Schmidt and W. Schnabel, *Ber. Bunsengesellschaft phys. Chem.*, 1971, **75**, 654.

4 The Physical Properties of Solvated or Trapped Electrons

A. The E.S.R. Spectrum and Cavity Structure.—By definition, the free electron is the simplest free radical and paramagnetic species. Its e.s.r. spectrum would therefore be expected to be a singlet modified only by the number and type of atoms having non-zero nuclear spins with which it interacts, the precise form of which should therefore allow inferences to be drawn about the conformation of host molecules in the cavity walls. This expectation is fully realized. e_{aq}^-, e_{amm}^-,[20] and e_t^- in aqueous, ethereal, alcoholic, and amine glasses[21] all show strong singlet e.s.r. signals with no fine structure which, in the case of e_t^-, are markedly subject to power saturation. The only case for which it has been claimed that hyperfine structure is observable is when e_t^- is produced in the rotating cryostat,[22] and Bennett, Mile, and Thomas have used the weak satellite lines as a basis to argue about the number and arrangement of hydrogen atoms in the cavity wall. However, it must be remembered that in this technique alternate layers of solvent molecules and alkali-metal atoms are sprayed on to a rotating surface at 77 K and it is not certain how far the electrons are from the layer of alkali metal or to what extent the solvent layer is microcrystalline.

Much better evidence can be obtained in the case of hydrogen-containing glassy media by isotopic substitution with deuterium because the hyperfine splitting constant of the proton is 6.5 times that of the deuteron. This substitution would therefore be expected to cause line-narrowing, provided the molecules lining the cavity wall are oriented with the hydrogen atoms pointing towards the centre as would be expected from the permanent dipole moments of the OH bond in aqueous and alcoholic media. The linewidths for e_t^- in these glasses are given here[23a] and amply verify this prediction; this is further confirmed by the fact that the mean relaxation time $\sqrt{\tau_1\tau_2}$ depends on the hydrogen isotopic composition.

Host molecules	H_2O	D_2O	CH_3OH	CH_3OD	CD_3OH
Linewidth in glasses of e_t^-	14	6	11 ± 2	6	14

In passing it is important to recognize that these signals, like the optical absorption spectra of e_t^-, are light sensitive. Care must be taken to avoid this photo-bleaching which, when visible light is used, may be due to photo-decomposition of the traps. In methanolic glasses, for instance, this reaction is

$$e_t^- + h\nu\ (\text{visible}) \rightarrow \dot{C}H_2O^- + H_2 \qquad (15)$$

so that on exposure of the irradiated glass to visible light the singlet e.s.r. spectrum of e_{talc}^-, is replaced by the triplet of CH_2O^-.[23b]

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[20] E. C. Avery, J. R. Remke, and B. Smaller, *J. Chem. Phys.*, 1968, **49**, 951; C. A. Hutchison and A. C. Paston, *Rev. Mod. Phys.*, 1953, **25**, 255; *J. Chem. Phys.*, 1953, **21**, 7959.

[21] P. B. Ayscough, R. G. Collins, and F. S. Dainton, *Nature*, 1965, **205**, 965; F. S. Dainton and G. A. Salmon, *Proc. Roy. Soc.*, 1965, **A285**, 319; F. S. Dainton, G. A. Salmon, and J. Teply, *ibid.*, 1965, **A286**, 27; F. S. Dainton, G. A. Salmon, and C. von Sonntag, *ibid.*, 1969, **A313**, 31.

[22] See ref. 10*c*.

[23] (*a*) H. Zeldes and R. Livingston, *J. Chem. Phys.*, 1959, **30**, 40; (*b*) F. S. Dainton, G. A. Salmon, and P. Wardman, *Proc. Roy. Soc.*, 1969, **A313**, 1.

B. The Equivalent Conductance, Mobility, Diffusion Constant, and Stokes Radius of e_s^-.—These quantities are related by the equations

$$u\,(\text{mobility/cm s}^{-1}\text{ dyn}^{-1}) = 1.6 \times 10^{-12}\, D\,(\text{diffusion constant/cm}^2\text{ s}^{-1})/kT$$
$$= 1.04 \times 10^{-5}\,\lambda\,(\text{equivalent conductance/cm}^2\text{ ohm}^{-1}\text{ equiv}^{-1}) \qquad (16)$$

and $$r_s\,(\text{Stokes radius/Å}) = 0.82/(\text{viscosity/poise}) \times \lambda \qquad (17)$$

The measurement of λ_{e^-s}, is therefore important as the source of values of the diffusion constant, D_{e^-s}, and the Stokes radius, $r_{s,\,e^-s}$. This may be achieved by measurement of the changes in conductance during pulse radiolysis of pure liquids. Thus in the case of water the increment in equivalent conductance, $\Delta\Lambda_\infty$, is seen from equation (14) to be due to the formation of two additional conducting species, namely, H_{aq}^+ and e_{aq}^- and therefore

$$\Delta\Lambda_\infty = \lambda_{H_{aq}^+} + \lambda_{e_{aq}^-} \qquad (18)$$

Schmidt and Buck[24] were the first to carry out measurements of this kind and these were repeated with greater precision by Barker and Fowles[24] who also applied the method to e_{alc}^-. It is unnecessary to use pulse radiolysis conductivity when stable solutions of e_s^- are available and λ is known for the counter ion as in the case of ammoniacal solutions of alkali metals.

The results for the solvated electron in water and liquid ammonia at room temperature are shown here and illustrate the very high mobility of e_s^-, which

	u/cm^1 s^{-1} dyn^{-1}	D/cm^2 s^{-1}	r_s/Å
$_{aq}^-$	1.8×10^{-3}	4.8×10^{-5}	0.5
$e_{NH_3}^-$	10^{-2}	2×10^{-4}	0.35

in water is comparable with that of the hydroxide ion. Since r_s is much smaller than the radius of the cavity enclosing and defining e_s^- as calculated from existing models to account for λ_{max} for the $2p \leftarrow 1s$ optical transition (see Section 2), it seems unlikely that the whole solvation shell moves through the medium as an integral unit. More probably the motion of the charge is accompanied by a (partial?) disintegration of the cavity; perhaps a rotation of one or more molecules of the cavity wall enables the electron to jump to a downfield site where it is temporarily retrapped. This jump distance cannot be large in polar liquids but in non-polar liquids it is large, and in this phase of its migration the electron is to be regarded as probably quasi-free.[15,25]

C. The Ionic Atmosphere Relaxation Time, τ_{ia}.—The solvation of an electron by a solvent containing an electrolyte is followed by the build-up of the ion-atmosphere of e_s^- in which cations predominate. The sequence of these two processes in water is depicted in equation (19). If a solute S^z reacts with the hydrated

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[24] K. H. Schmidt and W. L. Buck, *Science*, 1966, **151**, 70; G. C. Barker P. Fowles, D. C. Sammon, and B. Stringer, *Trans. Faraday Soc.*, 1970, **66**, 1498.

[25] See ref. 12, ref. 8 p. 393, and W. F. Schmidt and A. O. Allen, *J. Chem. Phys.*, 1970, **52**, 4788

$$e_f^- \xrightarrow{\tau_s} e_{aq}^- \xrightarrow{\tau_{ia}} e_{aq}^- + \begin{matrix}\text{ion}\\ \text{atmosphere}\end{matrix} \qquad (19)$$

electron the half-life of the hydrated electron, $t_{\frac{1}{2}}$, will be $0.7/k_{20}[S^0]$ and if this

$$e_{aq}^- + S^z \rightarrow S^{z-1} \qquad (20)$$

reaction is diffusion controlled, the value of D in the preceding table indicates that by varying $[S^z]$ from 10^{-4} to 1 mol l^{-1}, $t_{\frac{1}{2}}$ can be reduced from 10^{-6} to 10^{-10} s. Since Debye and Falkenhagen have shown that, at 25 °C

$$\tau_{ia} = 10^{-10}\ D/\mu\Lambda_\infty \qquad (20)$$

it is evident that by adjusting $[S^z]$ the hydrated electron can react either *after* establishing its ion-atmosphere *i.e.* $t_{\frac{1}{2}} > \tau_{ia}$, when k_{20} will depend upon ionic strength according to the Brønsted-Bjerrum equation (this is the basis of the proof of the existence of e_{aq}^-; see Section 1) or *before*, *i.e.* $t_{\frac{1}{2}} < \tau_{ia}$. In the latter case the activity coefficient of e_{aq}^-, *i.e.* f_e, will be unity and independent of μ, whilst the transition state $[S^z \ldots e^-]^{\ddagger}$ with a charge $z - 1$ will have an ion-atmosphere appropriate to an ion of charge z provided it changes to product before it has time to establish the ion-atmosphere appropriate to charge $z - 1$. This problem has been fully treated by Logan[26] and in the case of $z = -1$ a more simple treatment involving putting $\log_{10} f_{\ddagger} = -0.51z\,(z - 1)f(\mu)$, leads to the result that, at 25 °C in water,

$$\text{when } t_{\frac{1}{2}} > \tau_{ia}, \log_{10} k_{20} = \text{constant} + 1.02f(\mu) \qquad (21)$$

$$\text{when } t_{\frac{1}{2}} < \tau_{ia}, \log_{10} k_{20} = \text{constant} + 0.51f(\mu) \qquad (22)$$

Hence if the ionic strength is kept constant and the concentration of a reactive univalent anion is increased the apparent rate constant should diminish by an amount of $0.51\,f(\mu)$. This was observed by Logan and Dainton[26] for the case $S^- = I_3^-$ and is illustrated in Figure 6 using as the reference competitive substrate the uncharged molecule N_2O. It is obviously desirable to test this idea more rigorously by using ultra-fast pulse techniques and single solutes of different charge.

D. The Thermodynamic Properties of e_s^-.—If the rate constants for the decomposition of e_s^- into H and HA^- and for the reverse reaction, *i.e.* k_{23} and k_{-23},

$$e_s^- \rightleftharpoons H + HA_s^- \qquad (23)$$

can be measured and if the ionic product $[H^+_s]\,[HA_s^-]$ and the free energy of solvation of the proton are known, then $\triangle G^0{}_{24}$ and hence the redox potential on the hydrogen scale can be calculated. Combining these data with values of

$$\tfrac{1}{2}H_{2,g} \rightarrow H_s^+ + e_s^- \qquad (24)$$

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[26] F. S. Dainton and S. R. Logan, *Proc. Roy. Soc.*, 1965, **A287**, 281; S. R. Logan, *Trans. Faraday Soc.*, 1967, **63**, 3004, 3009.

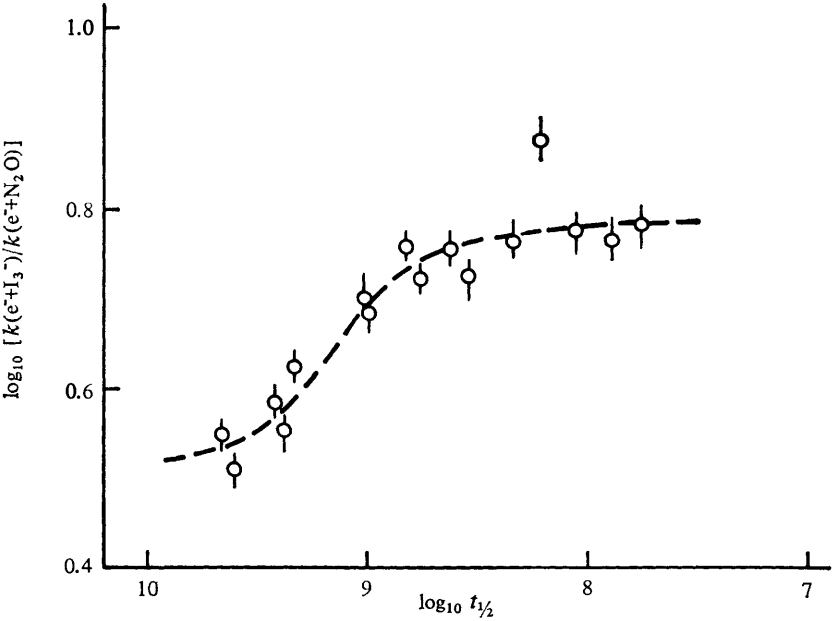

Figure 6 *To illustrate the smaller rate constant of the reaction* $e_{aq}^- + I_3^-$ *when the electron reacts with* I_3^- *before forming its ion-atmosphere*, i.e. $t_{\frac{1}{2}} < \tau_{ia}$
(Reproduced by permission from *Proc. Roy. Soc.*, 1965, **A287**, 281)

Table 2 *Significant thermodynamic quantities*[a] *for* e_s^-

Reaction	*Ammonia*				*Water*			
	ΔH_0^0	ΔS_0^0	ΔG_0^0	E_h^0	ΔH_0^0	ΔS_0^0	ΔG_0^0	E_h^0
$\frac{1}{2}H_2 \rightarrow H_s^+ + e_s^-$	157	−101	187	1.58	260	−57	277	2.87
$e_g^- \rightarrow e_s^-$	−97	48	−111	—	−160	−8	−157.5	—

[a] $\triangleleft H$ and ΔG in kJ mol^{-1}; ΔS in J mol^{-1} deg^{-1}; E_h^0 in volts.

the standard entropy of solution of H_2, H·, and e_s^-, the last of which can be obtained by semi-empirical relations connecting ΔS^0 of univalent anions and their radii, the thermodynamic quantities in Table 2 are obtained.[27a] These have a number of interesting features. Firstly, metals with a potential >2.87 V would be expected to form hydrated electrons on contact with water whilst those having values less than this would be expected to be unaffected or to react only slowly or on warming. This is exactly consonant with what is known of the alkali and alkaline earth metals' behaviour. Secondly, the enthalpy and free energy increments on desolvation of e_s^- in both solvents are only slightly greater than ch/λ_{max} of the optical absorption spectra of e_s^-, which suggests that optical excitation of e_s^- brings the electron to a level which is close to and may

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[27] (*a*) G. Lepoutre and J. Jortner, *J. Phys. Chem.*, 1972, **76**, 683 where references to earlier work are also given; (*b*) R. R. Hentz and D. W. Brazier, *J. Chem. Phys.*, 1971, **54**, 2777.

overlap the conduction band, a fact which has implications for the photoconductivity of e_t^- in aqueous and ammoniacal glasses (see Section 5). Thirdly, ΔS^0 for the solvation of e^- in ammonia is positive which suggests that in this solvent the solvation process is also structure breaking.

In principle, estimates of the partial molal volume of e_s^- can be made by studying the effects of pressure on k_{23} and k_{-23}. In practice, indirect methods have to be used[27b] and these lead to a value for e_{aq}^- between -1.7 and 2.7 cm^3, which, provided allowance is made for electrostriction, is not inconsistent with a cavity radius of *ca.* 1 Å for e_{aq}^-.

5 Spectroscopic and other Evidence concerning the Cavities

A. The Effects of Pressure and Temperature on the Spectrum.—The configuration diagrams show that the smaller the cavity radius the larger the energy gap, ΔE, between the 1*s* and 2*p* levels. The distribution of 1*s* states of different radii can easily be calculated from the form of the configuration diagram and the assumption that the cavities are in thermal equilibrium with their surroundings *i.e.* $N_{r_i} = N_{r_j} \exp[(E_{r_j} - E_{r_i})/kT]$. Combining these two pieces of information with the transition probabilities leads to the expectation that the absorption spectrum will be slightly unsymmetrical about ch/λ_{max} and show a *low*-energy tail. In fact a *high*-energy tail is always observed. This indicates that either one or both of the 1*s* and 2*p* energy–radius theoretical relationships is incorrect. If this conclusion is rejected then a non-Boltzmann distribution of 1*s* states must be presumed and can be found empirically so that the observed spectrum is reproduced. This has been carried out for e_{amm}^-.

Any change of an external variable which causes a diminution in the average size of the cavities is, because of the relationship between ΔE and *r*, likely to cause λ_{max} to move to shorter wavelengths. This 'blue shift' is observed in both liquid ammonia[28] and in liquid aqueous[29] and alcoholic systems[30] when the temperature is reduced or the system compressed, as illustrated in Figures 7 and 8. If the configuration diagrams are accepted the data allow crude estimates to be made of the isothermal compressibility and isobaric thermal expansibility of the cavities, and the indications are that the cavities are 'softer', *i.e.* more compressible and expansible, than the bulk liquids.

B. Direct Evidence for a Range of Trap Sizes for e_t^-.—The point has been made that if the electron trapped in a glass is not decomposed by light [*cf.* reaction (15)] the absorption of a quantum may drive an electron from its trap. If therefore the incident light has a wavelength span covering only a portion of the absorption spectrum due to the whole distribution of traps present in the system, the population of those traps which absorb the light will be depleted selectively. The

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[28] R. Vogelsgesang and U. Schindewolf, *Ber. Bunsengesellschaft phys. Chem.*, 1971, **75**, 651.

[29] F. S. Dainton, *Ber. Bunsengesellschaft phys. Chem.*, 1971, **75**, 608.

[30] R. R. Hentz, Farhataziz, and E. M. Hassan, *J. Chem. Phys.*, 1971, **55**, 4974; M. G. Robinson, K. N. Jha, and G. R. Freeman, *ibid.*, 1971, **55**, 4933.

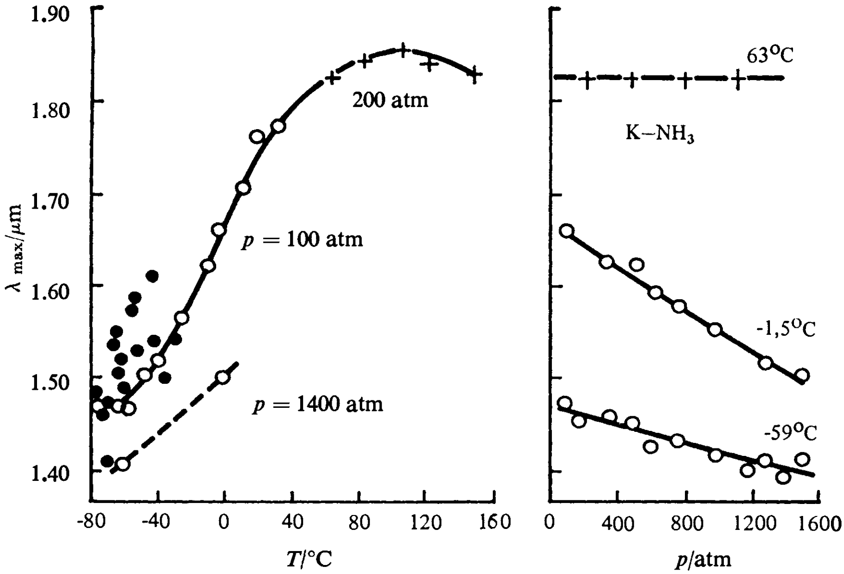

Figure 7 *The effect of temperature and pressure on* $\lambda_{\max}$ *of the absorption spectrum of* e_s^- *in ammonia*
(Reproduced by permission from *Ber. Bunsengesellschaft phys. Chem.*, 1971, **75**, 651)

electrons then liberated may then fall into holes forming e_t^- species which do not absorb the incident light, in which case they will remain and augment the light absorption in the wavelength range outside that of the incident light. The result should therefore be a photodistortion of the initial spectrum and, in principle, this process should be reversed by re-illumination with light different in wavelength from that of the initial incident light. This *photo-shuttle* process is represented in equation (25). Furthermore, if there is no possible fate for a

$$e^-{}_{t,\,i} \underset{h\nu_j}{\overset{h\nu_i}{\rightleftharpoons}} e^-{}_{t,\,j} \tag{25}$$

photoexcited electron other than retrapping, the total number of trapped electrons will remain constant and throughout all photo-shuttle processes which distort trap distributions the absorption spectrum should satisfy the condition $\int \mathrm{OD}\,\mathrm{d}\nu$ = constant. This photo-shuttle under this fully compensatory condition has been realized[31] for an assembly of trapped electrons in alkaline aqueous glasses at 77 K and is displayed in Figure 9.

The view that photo-shuttling perturbs the trap depth and size distribution is confirmed by the observation[31] that the e.s.r. signal field strength saturation characteristics change when the optical absorption spectrum is displaced. Moreover, when the spectrum is blue-shifted, with concomitant increase of the

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[31] G. V. Buxton, F. S. Dainton, T. Lantz, and P. Sargent, *Trans. Faraday Soc.*, 1970, **66**, 2962.

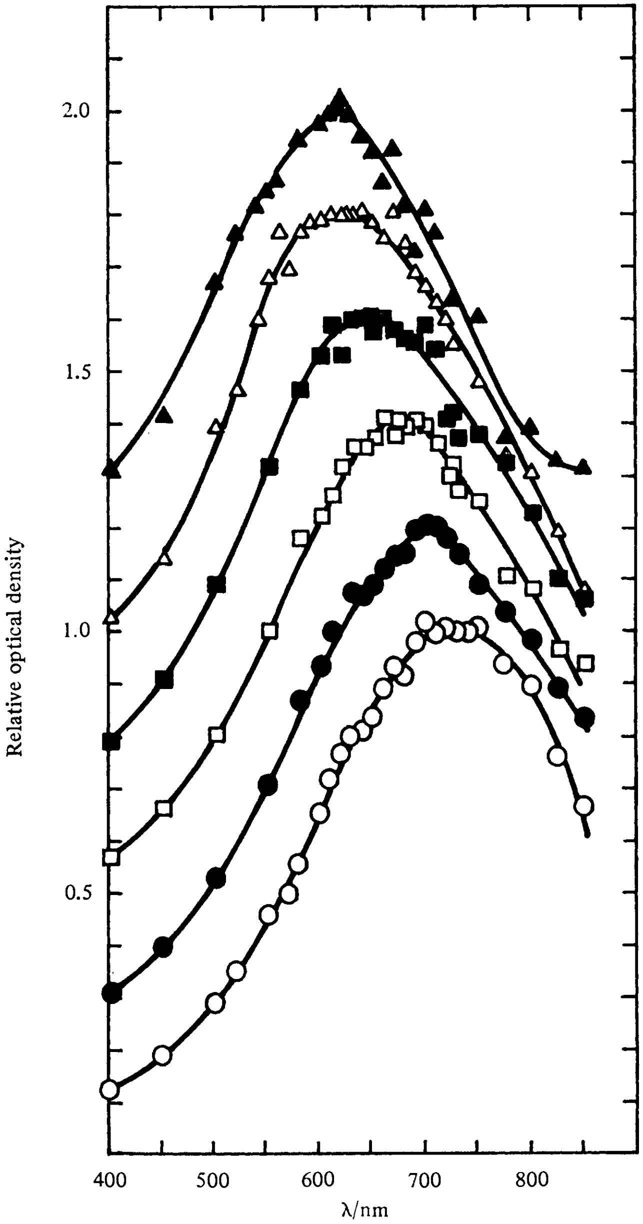

Figure 8(a) *The effect of pressure on the absorption spectrum of* e_{aq}^-. ○, 1 atm; ●, 1.10 kbar; □, 2.13 kbar; ■, 3.53 kbar, △, 4.88 kbar; ▲, 6.26 kbar. *For each pressure increase the spectra have been displaced* 0.2 *units vertically upward*
(Reproduced by permission from *J. Chem. Phys.*, 1971, **55**, 4974)

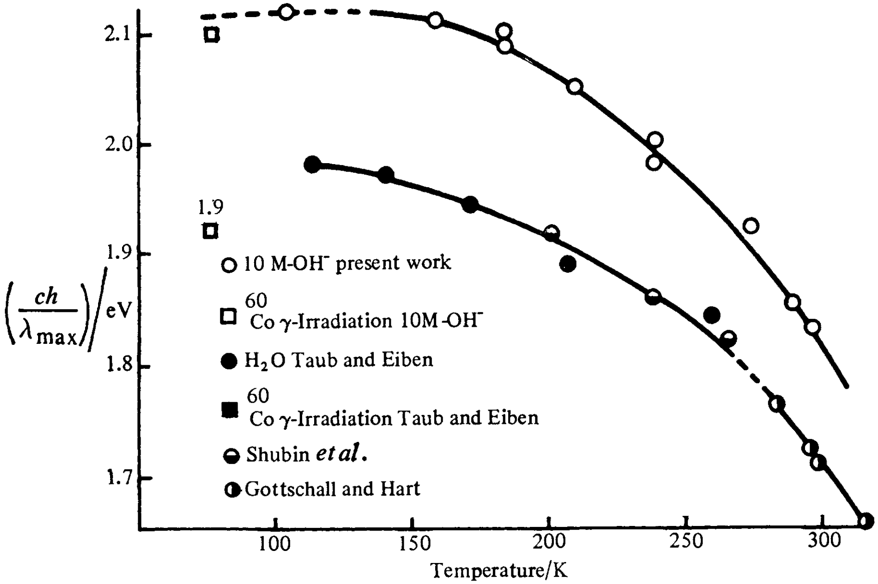

Figure 8(b) *The effect of temperature on* ch/λ_{max} *of* e_{aq}^-
(Reproduced by permission from *Ber. Bunsengesellschaft phys. Chem.*, 1971, **75**, 608)

average trap depth and therefore decrease in the trap radius, the mean relaxation time $\sqrt{\tau_1\tau_2}$ decreases; a result which is consistent with shortened spin-lattice relaxation time to be expected from the greater proximity to the electron of the nuclei in the cavity wall.

Whilst experiments of this kind demonstrate the reality of the distribution of traps of different depths they do not answer the question as to whether the light absorption process detraps the electrons, making them capable of moving to other sites where they can be retrapped or whether the electrons remain in their cavities and the effect of light absorption is merely to change the shape of the cavities and thereby alter both ΔE for $2p \leftarrow 1s$ transition and the observed spectrum. In the case of e_t^- in alkaline aqueous and MTHF (2-methyltetrahydrofuran) glasses this question has been conclusively answered by showing that when electrodes are inserted in the glass photo-conductivity can be established.[32] It must therefore be presumed that photo-excitation makes the electron mobile, at least to the degree of bringing it to any conduction band, and equation (26) in which e_m^- represents a mobile electron is a better representation of actuality than equation (25)*. An interesting feature of the photo-conductivity

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*There is no *a priori* reason why the only effect of light absorbed in the wavelength range of the e_t^- absorption spectrum should be to mobilize the electron. In alcohols for instance, at wavelengths less than λ_{max}, reaction (15) occurs and it has been shown by Bernas *et al.*[32] that in hydrocarbon glasses the detrapping excitation is shifted 0.2 eV relative to the absorption spectrum.

[32] I. Eisele and L. Kevan, *J. Chem. Phys.*, 1970, **53**, 1867; K. F. Baverstock and P. J. Dyne, *Canad. J. Chem.*, 1970, **48**, 2182; A. Bernas, D. Grassel, and J. B. Trueny, *J.C.S. Chem. Comm.*, 1972, 759.

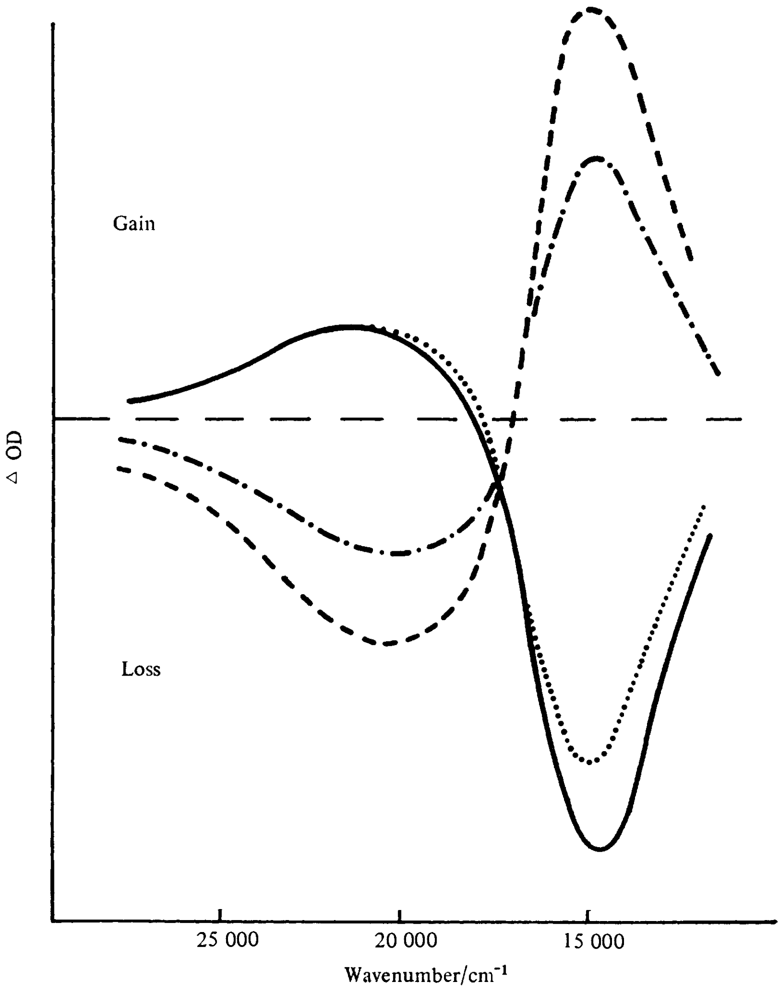

Figure 9 *The 'Photoshuttle'*, i.e. *changes in optical density at different wavelengths caused by selective illumination of* e_t^- *in* 10M *hydroxide glasses at* 77 K. *Full line after illumination with* $\lambda > 640$ nm, *broken line after subsequent illumination with* $\lambda < 500$ nm *of* e_t^- *formed by* γ*-radiolysis. Lines with dots refer to the corresponding experiments with* e_t^- *formed by photolysis of* $Fe(CN)_6^{4-}$
(Reproduced from *Trans. Faraday Soc.*, 1970, 66, 2962)

$$e^-_{t,\,i} \overset{h\nu_i}{\rightleftharpoons} e_m^- \underset{h\nu_j}{\rightleftharpoons} e^-_{t,\,j} \qquad (26)$$

is that, as shown in Figure 10, it may be super-ohmic. When this is the case it must be concluded that the higher the energy gained by e_m^- from the higher

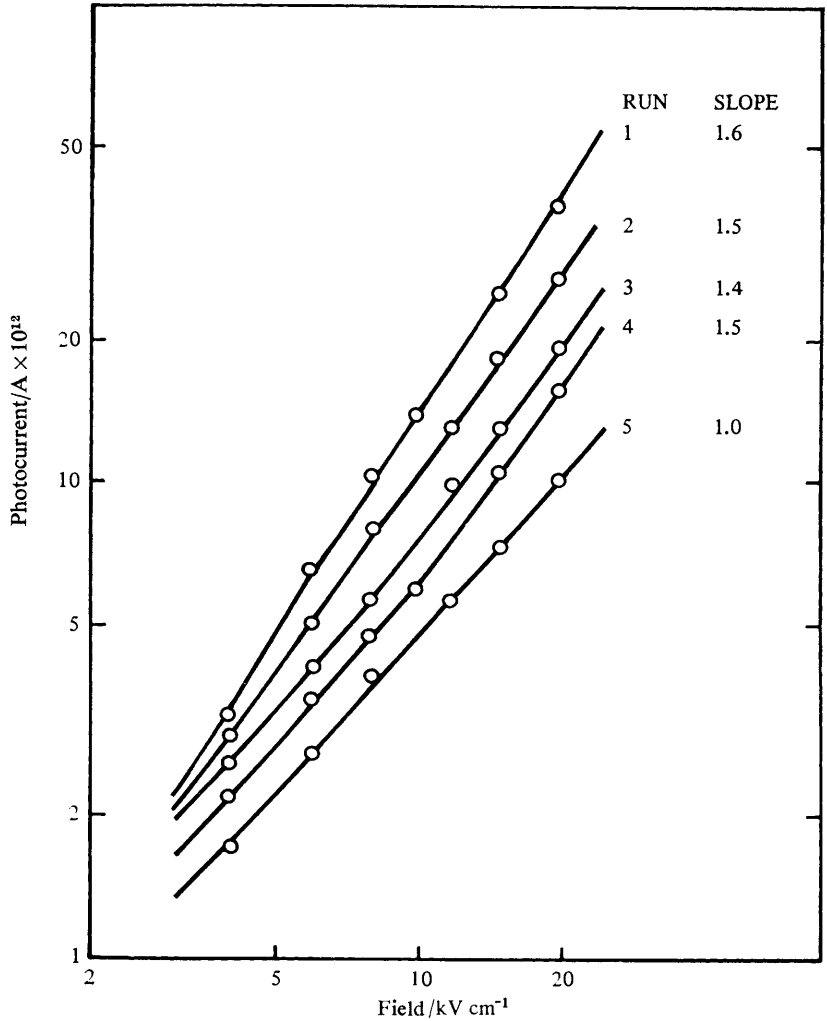

Figure 10 *Photoconductivity of* e_t^- *in* 10M *hydroxide glass at* 77 K. *Current–voltage curves are plotted bilogarithmically and are for successive doses of* 0.6 Mrad (Reproduced by permission from *J. Chem. Phys.*, 1970, **53**, 1867)

electrical field, the less likely it is to be retrapped. This is interesting in that it is the only direct evidence supporting the theoretical argument that the higher the energy of an electron ejected from a molecule in the primary radiolytic act the further it will travel before solvation in a liquid or trapping in a glass.

When e_t^- is produced in a system by a method which leaves the glass with no net charge, there are balancing cations or radicals or both. These latter can capture and destroy electrons mobilized by light and whose trajectories before retrapping intersect the site of the cations or radicals. *Photobleaching* therefore occurs, but since the electrons first removed will be those bound to traps closest to the cations and radicals the number of 'jumps' and retrapping and detrapping events before an electron is finally destroyed continually increases as photobleaching proceeds. Hence, even though the quantum yield for photomobilization remains constant the apparent quantum yield for photobleaching progressively diminishes.[31] This is shown in Figure 11 for alkaline aqueous glasses at 77 K. There are three interesting consequences of this mechanism. First, if the chance of retrapping increases with the ease of reorientation of molecules in the walls of potential cavities, then it will increase with increasing temperature and the quantum for photobleaching should decrease with increasing temperature. Figure 11 shows that this prediction is fulfilled. Secondly, if efficient electron capturing solutes are added the photobleaching rate should increase and this too is observed. Finally, it will be obvious that the compensatory conditions can never be absolutely attained but are more nearly realized after those electrons

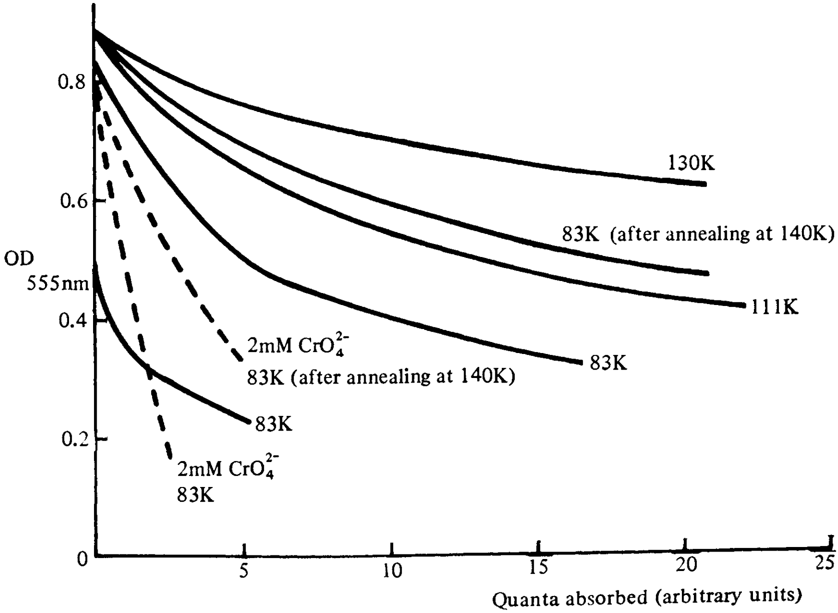

Figure 11 *The photobleaching of* e_t^- *in* 10M *hydroxide glass at various temperatures in the presence or absence of chromate ions as scavenger*[31]
(Reproduced by permission from 'Reactions of Solvated Electrons', MTP International Review of Science, Physical Chemistry, Series One, Volume 9, Chapter 9, Butterworths, London, 1972)

trapped very close to the sites of their formation have undergone geminate recombination either by preliminary thermal- or photo-bleaching.

6 The Trapping and Solvation Mechanism

All liquids and glasses contain 'holes'; in liquids they fluctuate in size and position but in rigid glasses these fluctuations are so slow as to be negligible on the time-scale of most experiments. It is highly unlikely that the number and distribution of these 'holes' will, before occupancy, accord exactly with those necessary to accommodate an unspecified number of electrons in a thermal equilibrium distribution. The observed final distribution of configurations of cavities each containing an electron will be determined by the balance achieved between the cavity stabilization forces described in Section 2 and the disruptive forces of thermal agitation. An adjustment of the shapes of holes after they have captured electrons will therefore take place and the rate of this adjustment will be regulated by the ability of the solvent molecules to rotate and translate, which, in turn, will depend on temperature. In addition the solvation process is itself exothermic and the extent of relevant molecular reorientation will be influenced by this variable amount of heat released per hole and the rate at which it can be conducted away. Consequently two distinct experimental situations can be envisaged. Firstly, in *liquids* where mobility is unrestricted or in 'soft' glasses, the spectroscopic changes accompanying the adjustment to the final equilibrium distribution might be detectable and, secondly, in *glasses* at a sufficiently low temperature the rigidity and higher local temperature gradients favouring heat loss may be sufficient to prevent the attainment of the true equilibrium distribution and a metastable distribution will be permanently preserved.

A. Isothermal Optical Changes associated with Solvation.—The change from the initial distribution to the ultimately stable one implies a cavity deepening and narrowing and therefore a net enhancement of absorption at shorter wavelengths and a diminution at longer wavelengths taking place on a time-scale comparable with the dielectric relaxation time of the medium. To observe this phenomenon conveniently it is therefore usual to cool the liquid in order to lengthen the relaxation time. The phenomenon has now been observed in several systems but one of the clearest is that observed when alcohols are pulse-radiolysed. Figure 12 displays some of the data obtained by Baxendale and Wardman[33] for n-propanol at 152 K using 5 ns pulses. Evidently at 10 ns only about half the electrons are not in holes of their final configuration and the remainder, which are in shallow 'red' traps, adjust in a half-life of *ca.* 60 ns. The authors point out that this time is substantially shorter than the known dielectric relaxation time for this temperature and it must therefore be presumed that the local heating can contribute to the acceleration of local molecular movement.

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[33] J. H. Baxendale and P. A. Wardman, *Nature*, 1971, **230**, 448; *J.C.S. Faraday Trans.*, 1973, **69**, 586.

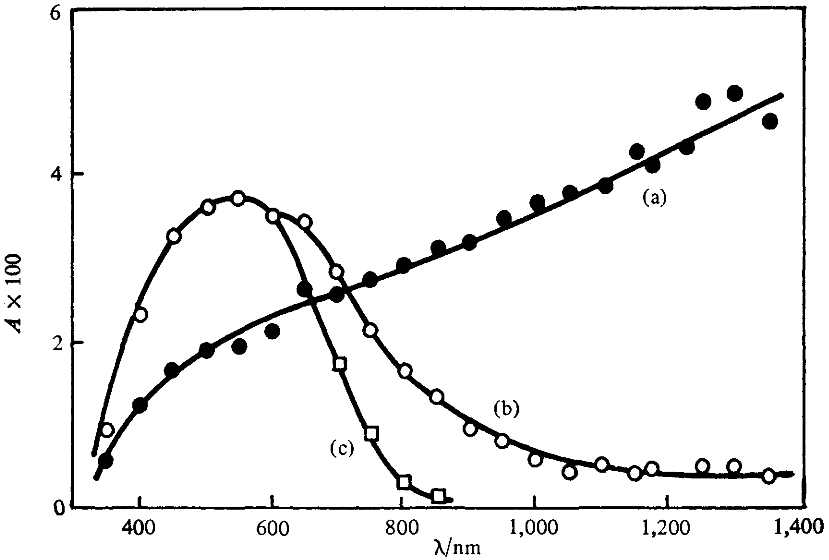

Figure 12 *Spectra observed following a* 5 ns, 600 krad *pulse absorbed by n-propanol at* 152 K, (*a*) *immediately after the pulse,* (*b*) 200 ns *later,* (*c*) 1 μs *later*
(Reproduced by permission from *Nature*, 1971, **230**, 448)

Attempts to detect solvation of e_s^- at room temperature have not been very successful. Even using 10 ps time resolution no changes have been observed in the spectrum of e_s^- in water, glycol, or C_1 to C_4 alcohols.[34]

B. Metastable Distributions of e_t^- and their Thermal Relaxation.—When alkaline aqueous glasses which have been γ-irradiated at 77 K are subsequently warmed, then, as shown in Figure 13, the absorption band narrows; the width at half height shrinking from 0.99 to 0.92 eV and a blue displacement of λ_{max} of *ca.* 120 Å is observed which is accompanied by an increase in absorption around λ_{max}. This enhancement of absorption is mainly at the expense of the absorption at the red and, to a lesser extent, at the blue end of the original spectrum. Whatever pretreatment a γ-irradiated sample receives, warming to 150 K results in an ultimate spectrum which is always the same[31] and therefore is likely to be that corresponding to the equilibrium trap distribution at this temperature. Since a rise in temperature normally produces a *red* shift in the equilibrium spectrum at temperatures above 140 K the inference must be that metastable distributions are possible and can persist if the system is sufficiently refrigerated.

Although some of the trapped electrons are destroyed in this warming process, most are not and since some of these changes occur below 135 K, where it has been shown that bulk diffusion cannot occur, it must be presumed that most of

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[34] M. J. Bronskill, R. K. Wolff, and J. W. Hunt, *J. Chem. Phys.*, 1970, **53**, 4201.

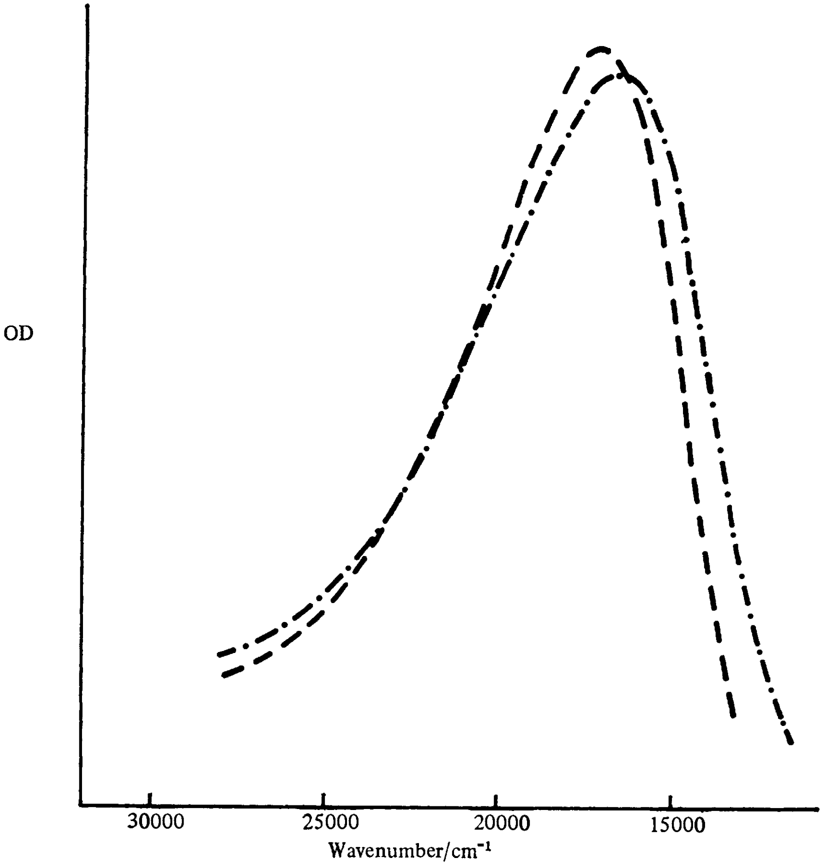

Figure 13 *The spectrum of* e_t^- *in* 10M *hydroxide glass:* —· —· — *after irradiation at* 77 K *and* — — — *annealing to* 150 K *and re-cooling*
(Reproduced from *Trans. Faraday Soc.*, 1970, **66**, 2962)

the traps which change shape do so by rotation without translation of cavity molecules. A few electrons, particularly those close to a spur or positively charged centres and therefore in a high electrostatic field do migrate, and it must be presumed that this is by a tunnelling mechanism facilitated by rotation of one or more cavity wall molecules which destabilize the original site whilst predisposing an adjacent site to receive the electron.

The most striking evidence for metastable trap distribution has been obtained by Higashimura and his colleagues[35,36] for a variety of alcoholic, ethereal, and water–glycol glasses irradiated at 4 K. A typical example is shown in Figure 14

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[35] H. Hase, M. Noda, and T. Higashimura, *J. Chem. Phys.*, 1971, **54**, 2975; 1972, **57**, 1029.
[36] H. Yoshida and T. Higashimura, *Canad. J. Chem.*, 1970, **48**, 504.

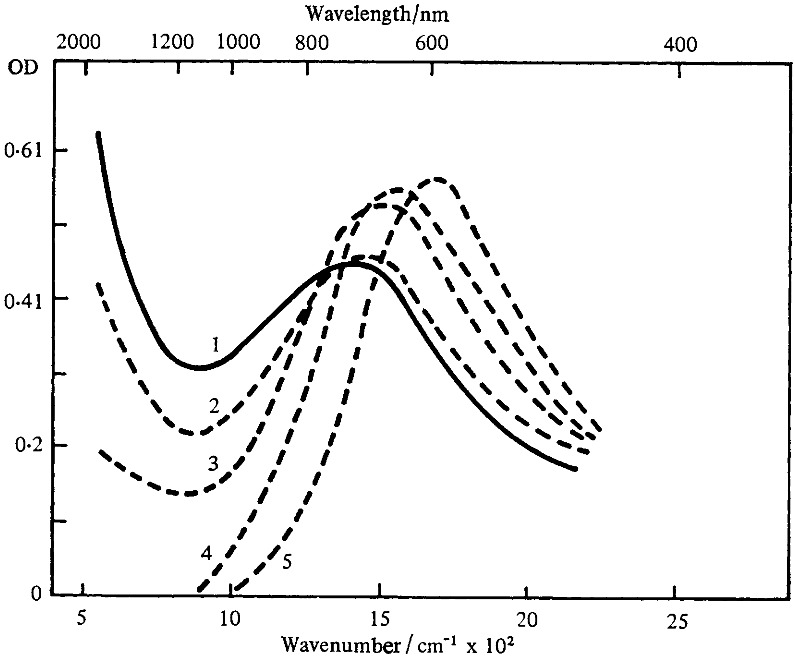

Figure 14 *The spectrum of* e_t^- *in equivolume water–glycol glass* γ*-irradiated at* 4 K (1) *and after warming to* 20 K (2); 30 K (3); 40 K (4); *and* 77 K (5)
(Reproduced by permission from *J. Chem. Phys.*, 1971, **54**, 2976)

for which the long-wave i.r. absorption disappears irreversibly on warming to 77 K with concomitant intensification of absorption in the visible region. Changes of this kind are usually accompanied by a broadening of the e.s.r. signal attributed to e_t^- which, if the argument given in Section 5B is correct, indicates that the cavities are both deepening and narrowing.

7 The Chemical Reactions of e_s^-

The reality of the solvated and trapped electron as a discrete physical entity cannot be doubted. We must now inquire into the kinds of chemical reactions in which it may participate and the factors which determine the rates at which these reactions can proceed.

A. Reaction Types.—The electron is the simplest free radical and the archetypal reducing agent and nucleophile and all the reactions of e_s^- and e_t^- except their decomposition derive from these characteristics. Thus it will combine with other free radicals such as •OH and H• and with itself (see Table 3). The last reaction is particularly interesting in that in aqueous systems the gross chemistry suggests that the ultimate products are $H_2 + 2OH^-$ but leave open the interesting question

Table 3 *Types of reactions of* e_{aq}^- *and their room temperature rate constants*

Type	*Equation*	*Rate constant at room temperature*
Decomposition	$e_{aq}^- \rightarrow H\cdot + OH_{aq}^-$	$14\,s^{-1}$
	$2\,e_{aq}^- \rightarrow H_2 + 2\,OH_{aq}^-$	$5 \times 10^9\,l\,mol^{-1}\,s^{-1}$
With acids	$e_{aq}^- + H_{aq}^+ \rightarrow H\cdot$	$2 \times 10^{10}\,l\,mol^{-1}\,s^{-1}$
	$e_{aq}^- + HCO_2H \rightarrow H\cdot + HCO_2^-$	$8 \times 10^7\,l\,mol^{-1}\,s^{-1}$
	$e_{aq}^- + HOAc \rightarrow H\cdot + OAc^-$	$8 \times 10^7\,l\,mol^{-1}\,s^{-1}$
	$e_{aq}^- + H_2PO_4^- \rightarrow H\cdot + HPO_4^{2-}$	$\sim 10^6\,l\,mol^{-1}\,s^{-1}$
Capture (non-dissociative)	$e_{aq}^- + O_2 \rightarrow O_2^-$	$2 \times 10^{10}\,l\,mol^{-1}\,s^{-1}$
	$e_{aq}^- + CO_2 \rightarrow CO_2^-$	$8 \times 10^9\,l\,mol^{-1}\,s^{-1}$
	$e_{aq}^- + I_2 \rightarrow I_2^-$	$5 \times 10^{10}\,l\,mol^{-1}\,s^{-1}$
	$e_{aq}^- + Cd^{2+} \rightarrow Cd^+$	$5 \times 10^{10}\,l\,mol^{-1}\,s^{-1}$
Capture (dissociative)	$e_{aq}^- + PhCl \rightarrow Ph\cdot + Cl^-$	$5 \times 10^8\,l\,mol^{-1}\,s^{-1}$
	$e_{aq}^- + PhBr \rightarrow Ph\cdot + Br^-$	$4 \times 10^9\,l\,mol^{-1}\,s^{-1}$
	$e_{aq}^- + PhI \rightarrow Ph\cdot + I^-$	$1.2 \times 10^{10}\,l\,mol^{-1}\,s^{-1}$
	$e_{aq}^- + N_2O \rightarrow N_2 + O\cdot^-$	$9 \times 10^9\,l\,mol^{-1}\,s^{-1}$
	$e_{aq}^- + C(NO_2)_4 \rightarrow NO_2 + C(NO_2)_3^-$	$5 \times 10^{10}\,l\,mol^{-1}\,s^{-1}$
	$e_{aq}^- + BrO_3^- \rightarrow BrO_2 + O^{2-}$	$4 \times 10^9\,l\,mol^{-1}\,s^{-1}$

as to whether an intermediate state is the solvated, spin-paired, and therefore diamagnetic, dielectron shown in equation (27). Some interesting pointers may

$$2\,e_{aq}^- \rightarrow e_{2,aq}^{2-} \rightarrow H_2 + 2OH^- \qquad (27)$$

be obtained from subjecting alkaline aqueous glasses at 77 K to prolonged γ-irradiation. It has long been known that initially this causes an intensification of the characteristic purple colour but that doses in excess of 6 Mrad bring about a bleaching. Kevan and Zimbrick[37] and Pikaev *et al.*,[38] by studying the changes of e.s.r. signals caused by such massive doses have shown (see Figure 15) that whilst the $\cdot OH + O\cdot^-$ radical concentration grows throughout the irradiation, the singlet signal ascribed to e_t^- passes through a maximum and declines in a manner similar to the colour. This is consonant with increasingly complete occupancy of all potential e_t^- sites after which any additionally generated electrons can only combine with $\cdot OH$ (which clearly does not happen) or spin-pair with existing e_t^- forming dielectrons. Kevan has further shown that $e_{2,t}^{2-}$ gives rise to a broad absorption band with $\lambda_{max} \simeq 10\,000$ Å and decomposes when the glass is either warmed to 135—145 K or illuminated by light of $\lambda > 7000$ Å.

Non-dissociative capture of electrons by a wide range of molecules, *e.g.* $O_2 \rightarrow O_2^-$, $CO_2 \rightarrow CO_2^-$, $R_2CO \rightarrow R_2\dot{C}O^-$, quinones $\rightarrow Q^-$, polynuclear aromatic compounds, and by ions, *e.g.* Cd^{2+}, $Fe(CN)_6^{3-}$, NO_2^-, CrO_4^{2-}, is

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[37] J. Zimbrick and L. Kevan, *J. Amer. Chem. Soc.*, 1967, **89**, 2483; L. Kevan in ref. 16.

[38] O. F. Khodzhaw, B. G. Ershov, and A. K. Pikaev, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1967, 1882, 2253.

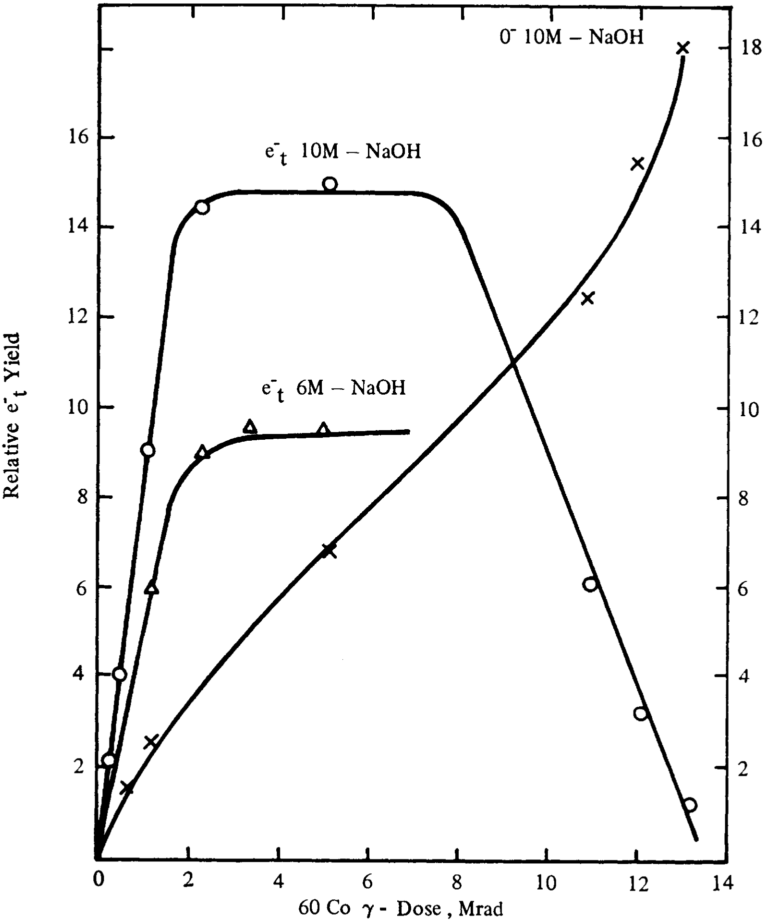

Figure 15 *Relative* e_t^- *and* $\cdot O^-$ *yields as measured by e.s.r. spectroscopy for γ-irradiated* 10M *hydroxide glass at* 77 K
(Reproduced by permission from *J. Amer. Chem. Soc.*, 1967, **89**, 2483)

often a very facile process. Since many of the product species are coloured the pulse radiolysis method can be used to study not only the decay of e_s^- but the synchronous build-up of the product and any subsequent reactions which the product may undergo. Much new chemistry has been revealed in this way.

Many examples are known of *dissociative* electron capture. Indeed the high rate of reaction of e_{aq}^- with some species [equations (28), (29), and (30)] was responsible for the earliest evidence for the existence of the hydrated electrons.[3,39]

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[39] F. S. Dainton and D. B. Peterson, *Proc. Roy. Soc.*, 1962, A267, 443.

$$e_{aq}^- + H_2O_2 \rightarrow HO\cdot + OH^- \qquad (28)$$

$$e_{aq}^- + RCl \rightarrow R\cdot + Cl^- \qquad (29)$$

$$e_{aq}^- + N_2O \rightarrow N_2 + O^- (\rightarrow \cdot OH + OH^-) \qquad (30)$$

Reaction (30) is especially important because nitrogen is inert and therefore a permanent product and the accompanying radical is the simplest and most powerful oxidizing radical. Provided it is present in concentrations greater than *ca.* 2×10^{-3} mol l^{-1}, nitrous oxide is therefore an excellent titrant for electrons however these are produced,[39] and it is used for this purpose and for providing, in conjunction with the radiolysis of water, a reliable and controllable source of hydroxyl radicals. Of course other electron scavengers are used as titrants in other media. For example tetranitromethane is useful in alcoholic media

$$e_s^- + C(NO_2)_4 \rightarrow \cdot NO_2 + C(NO_2)_3^- \qquad (31)$$

(equation 31) because the nitroform anion is stable and highly coloured.

Reactions (28)—(31) have been described as dissociative processes but presumably the capture and dissociation are not necessarily simultaneous and the primary electron adduct may have a finite life. This certainly is the case for N_2O^- in non-polar solvents[40] and is probably true for RCl^-.

The acid of which e_s^- is the conjugate base is the hydrogen atom (with a pK = 9.6) and it may be formed by reaction with the solvated proton or with undissociated acids, *e.g.*

$$e_s^- + H_s^+ \text{ (or } H_3A^+) \rightarrow H_s\cdot \text{ (or } + H_2A) \qquad (32)$$

$$e_s^- + H_2PO_4^- \rightarrow H_s\cdot + HPO_4^{2-} \qquad (33)$$

Here again, whether the mechanism is an instantaneous dissociative capture or involves an adduct of finite life as an intermediate is often uncertain. There is, for example, some evidence for the existence of $H_3O\cdot$ as the first product of reaction (32) in water. But what is certain is that the rate constants of these reactions cover a wide span. Reaction (32) is fast in water, alcohols, and ethers but slow in liquid ammonia. It is also the case that, although the hydrogen atom is a reducing agent, it is less effective than e_s^- as an electron donor and can also act as an abstractor of hydrogen atoms from C—H bonds and is much less reactive to nitrous oxide than is e_s^-. A striking consequence of this is that, as shown in Figures 2 and 16, varying $[H_s^+]$ has a dramatic effect on the distribution of products.[41] In general, if e_s^- reacts with substrate A to give product $\overline{Pr_a}$ (rate constant k_a) and the hydrogen atom reacts only with A or some other substrate to form Pr_b, then product yields *vs.* pH curves strongly resembling pH titration curves are obtained, *e.g.* Figure 16. In these circumstances the relationship (34) is obeyed, and before pulse radiolysis was available this was the principal

$$(\text{yield of } Pr_a)^{-1} = \text{constant } (1 + k_{22}[H_s^+]/k_a[A]) \qquad (34)$$

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[40] F. S. Dainton, P. O'Neill, and G. A. Salmon, *J.C.S. Chem. Comm.*, 1972, 1001.
[41] P. L. Airey and F. S. Dainton, *Proc. Roy. Soc.*, 1966, **A291**, 478.

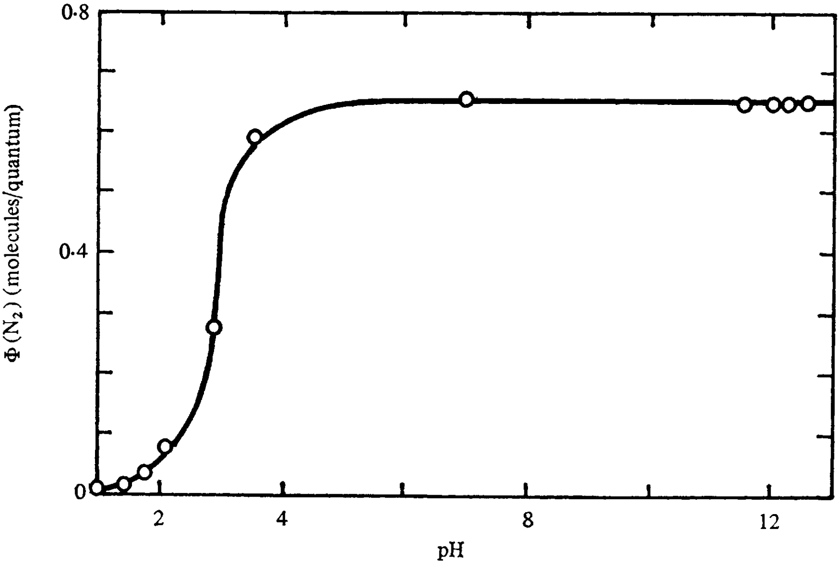

Figure 16 *The effect of changing* pH *on the quantum yield of nitrogen produced by the photo-detachment of electrons from* $Fe(CN)_6^{4-}$ *ions dissolved in* 0.005M *aqueous solutions of nitrous oxide and illuminated by* 254 nm *light*
(Reproduced by permission from *Proc. Roy. Soc.*, 1966, **A291**, 479)

method of obtaining relative rate constants of reaction of e_s^- with different solutes.[42]

Little is known about the mechanism of decomposition of e_s^- as represented by equation (23). In the case of e_{aq}^- the first-order rate constant depends on temperature in a way which suggests a considerable *negative* entropy of activation[43] implying a structure-making process as rate-determining, which is presumably that of full hydration of the hydroxide ion product. It is also associated with a negative volume of activation of 16 ml mol^{-1} which is also consistent with structure-making and cavity collapse. The solvated electron in ammonia is at least 10^8 times longer-lived than e_{aq}^- and here there is clear evidence that the negative volume of activation is even larger, a fact which is in accord with the theoretical view that the cavity in e_{amm}^- is much larger than that of e_{aq}^-.

B. Factors Regulating Bimolecular Reaction Rates.—Bimolecular reactions in solution are distinguished from their gaseous counterparts in two ways. Firstly, the solvent impedes the movement of the dissolved reagents and, secondly, when the reagents encounter one another they are 'caged' by solvent molecules thus ensuring that they collide several times before they are able to separate. If the

[42] See for example, p. 457 of F. S. Dainton and W. S. Watt, *Proc. Roy. Soc.*, 1963, **A275**, 447.
[43] R. Olinger and U. Schindewolf, *Ber. Bunsengesellschaft phys. Chem.*, 1971, **75**, 693.

probability of reaction at any collision is high the reactants are always destroyed when both are within the same cage and the rate-determining step of the reaction is the rate of encounter. Such processes are called *diffusion-controlled.* If, on the other hand, the reaction rate within the cage is low, then only very rarely are the reactants consumed. Most of them escape, their concentration remains uniform and the impedance of the solvent to the diffusion together of the reactants is no longer the limiting factor. Such processes are often referred to as *activation-controlled* because it is so frequently necessary for the collision pair to power a minimum activation energy as a pre-condition for reaction. For bimolecular reactions of e_s^- which come into the latter category treatment by the collision or transition-state theory is as adequate (or inadequate?) as it is for any bimolecular reactions and similar types of correlation are observed. For example the rate constants of reactions of e_{aq}^- with substituted phenoxide ions follow Hammett-type relations[44] and the slow reactions of e_{aq}^- with acids

$$e_{aq}^- + HB \rightarrow H\cdot + B^- \qquad (35)$$

[equation (35)] obey the Brønsted relationship,[45] $k_{35} = \zeta K_{HB}^{0\cdot51}$. However, the chance of reaction on collision can also be slight because the entropy of reaction is sufficiently negative. This is expected to be the case for reactions of e_s^- in which, probably because of collapse of the cavity, the volume of activation is negative. This is true for the reaction of e_{aq}^- with, for instance, saturated amides, where measurements of the effects of high pressures on the rate of reaction[46] have led to values of $-\Delta V^{\ddagger}$ in the range 7—10 ml mol^{-1}.

As illustrated in Table 3, there are many reactions of e_{aq}^- which have rate constants $\geqslant 10^{10}$ l mol^{-1} s^{-1}. In these cases there is a *prima facie* case for considering these reactions to be diffusion controlled. The Einstein–Schmoluchowski treatment leads to expression (36) for the diffusion-controlled rate

$$k_{ss} = 4\pi r\ D\ \delta/(e^{\delta} - 1) \text{ where } \delta = -z_a/\epsilon\ r\ kT \qquad (36)$$

constant k_{ss} (for definition see next section) between e_s^- and an ion of charge z_a. In this expression r is the interaction distance and will usually be a few Å, D is the sum of the diffusion constants of e_s^- and of the other reactant (for reagents other than H_{aq}^+ which has a specially high mobility, $D \sim 5 \times 10^{-5}$ cm^2 s^{-1}), ϵ is the static dielectric constant of the solvent so that for aqueous solutions and when $z_a = 0$, k_{ss} is expected to be *ca.* 2×10^{10} l mol^{-1} s^{-1}.

The effects of pressure and temperature on these reactions will depend on how sensitive r, D and ϵ are to changes in these variables. In general, D is far more sensitive than either r or ϵ and therefore the magnitudes of the activation energy and activation volume for diffusion, which are properties of the solvent should be the major factors controlling the temperature and pressure dependence of

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[44] M. Anbar and E. J. Hart, *J. Amer. Chem. Soc.*, 1964, **86**, 5633.

[45] J. Rabani, 'Solvated Electron', American Chemical Society, Washington, p. 242.

[46] R. R. Hentz, Farhataziz, and E. M. Hassan, *J. Chem. Phys.*, 1972, **57**, 2959.

k_{ss}. It has been established that, for many reactions in water and methanol,[47] $d\ln k_{ss}/dT$ equals $d\ln \eta/dT$, where η is the viscosity of the solvent. Similarly for the reaction of e_s^- with nitrobenzene, acetone, and naphthalene in ethanol $RT\,d\ln k_{ss}/dP$ corresponds to activation volumes in the range 5.6—7.5 ml mol^{-1}, which is about the value of $-RT\,d\ln \eta/dP$ for this solvent.[48]

8 Some Applications of our Knowledge of e_s^-

Faraday is reported to have justified his work on electromagnetic induction to an enquiring well-born lady with the riposte 'Of what use is a new-born baby, Madame?' Modern paymasters of scientific research require less rhetorical answers and it is perhaps appropriate to conclude with some brief mention of the usefulness of knowledge of the chemistry of the electron. Disregarding the importance of knowing about a particle of such intrinsic chemical significance as the electron, its utility rests on its intense colour and high reactivity. These make it possible to produce rapidly and in a completely controlled and measurable way a wide variety of new chemical species and if, as is often the case the latter are also coloured, their reactions may be investigated. Typical examples of these, in addition to those already mentioned, are the following.

1. The hydrodimerization of vinyl compounds effected either cathodically or by using metal amalgams is important industrially. By pulse radiolysis of aqueous solutions of vinyl monomers, denoted by m_1, it is possible to measure directly not only the rate constant of additions of e_{aq}^- to the monomer but also that of the dimerization of the protonated adduct.[49a] When m_1 = acrylonitrile and $(m_1H)_2$ is succinodinitrile

$$2\,m_1H \rightarrow (m_1H)_2 \qquad (37)$$

$k_{37} = 1.2 \times 10^9\ l\ mol^{-1}\ s^{-1}$. It is also possible to obtain the rate constants of the first propagation step in the free-radical addition polymerization step of such monomers and of inhibition reactions caused by, for example, O_2 and metal ions.

2. Mechanistically allied to this is the industrially important coupling of pyridine to form dipyridyls the mechanism of which can be shown to follow the course[49b]

$$e_s^- + C_5H_5N \rightarrow C_5H_5N^- \rightleftharpoons \tfrac{1}{2}(C_5H_5N)_2^{2-} \xrightarrow{\frac{1}{2}O_2} \tfrac{1}{2}(C_5H_4N)_2 + OH^-$$

3. The electron is such a powerful reducing agent and so easily converted into $\cdot OH$ in N_2O–containing solutions that it can be used to form a whole range of new species including O_2^-, O_3^-, and their acids HO_2 and HO_3; unstable halogen oxides such as BrO and BrO_2; metal ions in unusual valency states *e.g.* Cd^+ and In^{2+}. Moreover, when these reactions are diffusion-controlled, tests can be

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[47] M. Anbar, Z. B. Alfassi, and H. Bregman-Reisler, *J. Amer. Chem. Soc.*, 1967, **89**, 1263; J. K. Thomas, S. Gordon, and E. J. Hart, *J. Phys. Chem.*, 1964, **68**, 1524; and unpublished results of I. Janowsky and F. C. Cattell.

[48] K. N. Jha and G. R. Freeman, *J. Chem. Phys.*, 1972, **57**, 1408.

[49] (*a*) K. Chambers, E. Collinson, and F. S. Dainton, *Trans. Faraday Soc.*, 1970, **66**, 142; (*b*) Unpublished work cited by J. D. Rose, *Proc. Roy. Soc.*, 1969, **A312**, 314.

made of the reactivity of these new labile compounds. In this way it was shown that the reducing power of some univalent ions of Group II diminishes in the order $Zn^+ > Cd^+ > Pb^+$,[50] and whether the species MO_2^+ formed by reactions (38) and (39) are identical

$$M^+ + O_2 \rightarrow MO_2^+ \tag{38}$$

$$M^{2+} + O_2^- \rightarrow MO_2^+ \tag{39}$$

4. Most living cells have a high water content and pH > 5, and therefore e_{aq}^- is likely to be a primary product of radiolysis. Depending on the degree of anoxia, the e_{aq}^- will persist or be converted into O_2^-. Consequently it is now possible to investigate *in vitro* some of the reactions likely to occur *in vivo* when living substances are irradiated and to lay the foundations of a molecular radiobiology.

The list is far from exhaustive, but I will not complete the catalogue, because I am mindful of one of Faraday's famous aphorisms: '[The audience] wish for something they can comprehend. This may be deep and elaborate for the learned but for those who are as yet tyros and unacquainted with the subject must be simple and plain.' I hope I have met the needs of the tyros. Let me conclude with two matters for those more learned in physical chemistry.

A. Glass-forming Liquids and Time-Dependent Rate Constants.—In liquids which on cooling increase in viscosity and pass smoothly into a rigid amorphous solid there must be a finite temperature at which transport processes become infinitely slow. It follows that η^{-1} for the liquid and the diffusion constant of solutes in it cannot follow the Arrhenius Law which prescribes a dependence on temperature of these two quantities which is incorporated in a term $\exp(-E_t/RT)$, where E_t is the activation energy for transport. It is difficult to test the correctness of this statement because D, η, and the related quantity, the reciprocal of the dielectric relaxation time, can only be measured over a few orders of magnitude variation. No such limitation applies to the determination of the rate constants of diffusion-controlled reactions of e_s^- in which time resolution down to nanoseconds can be achieved and the concentration of the substrate can be varied, so that variations of k over eight orders of magnitude can be investigated. For reactions of e_s^- in aqueous glass-forming liquids or in MTHF with various solutes, the Arrhenius plot is non-linear and the apparent activation energy, *i.e.* $RT^2\ \mathrm{d}\ln k_{ss}/\mathrm{d}T$, increases with decreasing temperature.[51] The inadequacy of the Arrhenius equation is shown by the fact that the frequency factor and apparent activation energy can reach absurd values at low temperatures;[52] thus, in MTHF, values of $10^{34}\ \mathrm{l\ mol^{-1}\ s^{-1}}$ for A and 59 kcal for E_a are obtained, and in alkaline aqueous

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[50] G. E. Adams, J. H. Baxendale, and J. W. Boag, *Proc. Chem. Soc.*, 1963, 241.

[51] (*a*) G. V. Buxton, F. C. Cattell, and F. S. Dainton, *Trans. Faraday Soc.*, 1971, **67**, 687; (*b*) K. Kawabata, S. Okabe, S. Fujita, H. Horii, and S. Taniguchi, *Ann. Reports Rad. Centre Osaka Prefecture*, 1968, **8**, 70.

[52] See F. S. Dainton and A. K. Pikaev in 'Progress and Problems in Contemporary Radiation Chemistry', Czech. Acad. Science, Prague, 1971, vol. 2.

solutions the corresponding values at 150 K are 5×10^{21} and 15. Almost 50 years ago Tamman and Hesse[53] found that the fluidity of glasses above their softening points fitted a different equation:

$$k_{SS} = A_{SS} \exp[-B/(T-T_0)] \tag{40}$$

Figure 17 shows that this equation applies to the rate of reaction of e_{aq}^- with

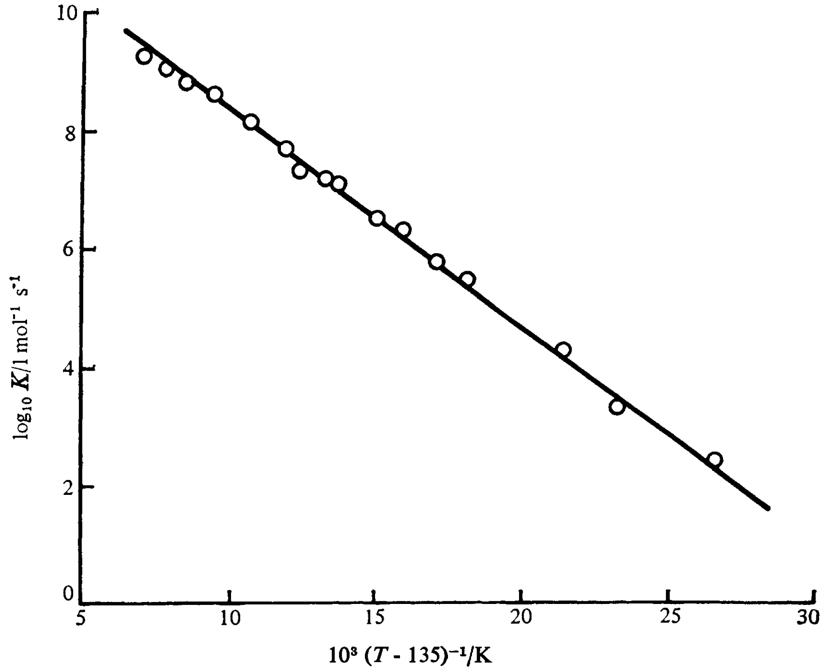

Figure 17 *The dependence of k on temperature for the reaction of* e_{aq}^- *with* $NO_{2,aq}^-$ *in* 10M *aqueous hydroxide solution. The straight line corresponds to equation* (40), i.e. $\log_{10}k = 12.02 - 890/(T - 135)$
(Reproduced from *Trans. Faraday Soc.*, 1971, **67**, 697)

an oxyanion in aqueous glass-forming liquids. Experiments with other solutes which react with e_{aq}^- show that A_{SS}, B, and T_0 are characteristic of the solvent and largely independent of the nature of the solute. The fact that the diffusion constant of oxygen and the ionic mobilities of Na^+ and OH^- in the same medium fit a similar relationship with similar values of B and T_0 supports the view that the temperature dependence of D far outweighs those of r and ϵ [see equation (36)].[51a]

This point can be tested by using the theory of diffusion-controlled bimolecular

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[53] G. Tamman and W. Hesse, *Z. anorg. Chem.*, 1962, **156**, 245.

reactions as elaborated by Noyes.[54] He pointed out that if, to a solution of one reagent, the second reagent could be instantaneously introduced in uniform concentration, the true bimolecular rate constant, k_r, would only be observed at $t = 0$. As the reagent concentrations in the immediate vicinity of each solute were depleted by reaction, so average concentration gradients would be set up and k_{obs} would fall from k_r, to the diffusion-controlled value k_{ss} according to equation (41), where $x = (Dt)^{\frac{1}{2}} (1 + k_r/k_{ss})/r$. For $x > 4$, $e^{x^2} \text{erf}x$ is close to

$$k_{obs} = (1 + k_r \, e^{x^2} \, \text{erf}x/k_{ss}) \, k_{ss}/(1 + k_{ss}/k_r) \qquad (41)$$

$\sqrt{\pi} \, x$. By pulse radiolysis the instantaneous introduction of the second reagent, e_{aq}^-, is possible and it can be shown that, for glass-forming aqueous solutions, the second condition is also readily satisfied. Consequently the optical density of e_{aq}^-, OD, should decline with time according to equation (42), where [S] is the solute concentration.

$$\ln (OD_0/OD) = [S] \, k_{ss}\{t + k_{ss} \, t^{\frac{1}{2}}/2 \, (\pi D)^{3/2}\} \qquad (42)$$

This has been confirmed by experiment the results of which enable k_{ss} and D to be independently derived at any temperature, and hence from equation (36) $r\delta/(e^{\delta} - 1)$ may also be obtained.[54] The results show that D does indeed obey the Tamman–Hesse equation with values of B and T_0 independent of the nature of the solute and that, as shown in Table 4, A_{ss} is close to 10^{12} l mol^{-1} s^{-1} but that r, the interaction distance, is highly dependent on the nature of the solute. Evidently the larger and more oxygenated the anion the larger r, and it may be that the very large value of r for S = CrO_4^{2-} is, at least in part, due to tunnelling of the electron through its cavity and a small number of hydrogen-bonded water molecules to the hydration shell of the anion.

Table 4 *Values of A_{ss}, B, T_0, and r for reactions of e_{aq}^- in aqueous glass-forming liquids*

Medium	*Reagent*	$\log_{10} A_{ss}$	B	r/nm[a]
	Acetone	10.7	613	0.6
9.5M-LiCl	H^+	10.5	557	0.7
T_0 = 129 K	NO_2^-	11.0	666	0.4
	NO_3^-	11.3	716	0.8
	CrO_4^{2-}	11.3	655	1.7
10M-OH^-	NO_2^-	11.8	905	0.8
T_0 = 135 K	NO_3^-	12.1	956	1.0
	CrO_4^{2-}	11.9	824	2.0

[a] The quantity in this column contains a factor dependent on temperature and electrostatic energy of the interacting solute and e_{aq}^- which is however not thought to differ much from case to case.

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[54] R. M. Noyes, *Progr. Reaction Kinetics*, 1971, **1**, 129.

B. Selective Solvation in Two-component Liquids.—Figure 5 illustrates the marked dependence of the optical spectrum of e_s^- on the nature of the solvent. Subject only to the effects of the 'blue-shift' (see Section 6) these differences are preserved at low temperatures. Moreover, when the liquids form glasses the e.s.r. spectrum is generally narrower the greater λ_{max}. Therefore an examination of these spectra of e_s^- in binary mixtures which are sufficiently different in chemical nature should reveal whether the mixtures are truly homogeneous in the liquid and glassy states.

Such a pair of miscible substances are ethanol and MTHF. In 1965, Shields[55] found from e.s.r. evidence on γ-irradiated glasses that, as shown in Figure 18, the cavities containing e_t^- consisted, surprisingly, largely of alcohol molecules down to a mole fraction of 0.35 alcohol, and that there appeared to be little evidence of the presence of e_t^- in cavities the walls of which contained both alcohol and ether molecules. This at once raised the question as to whether the

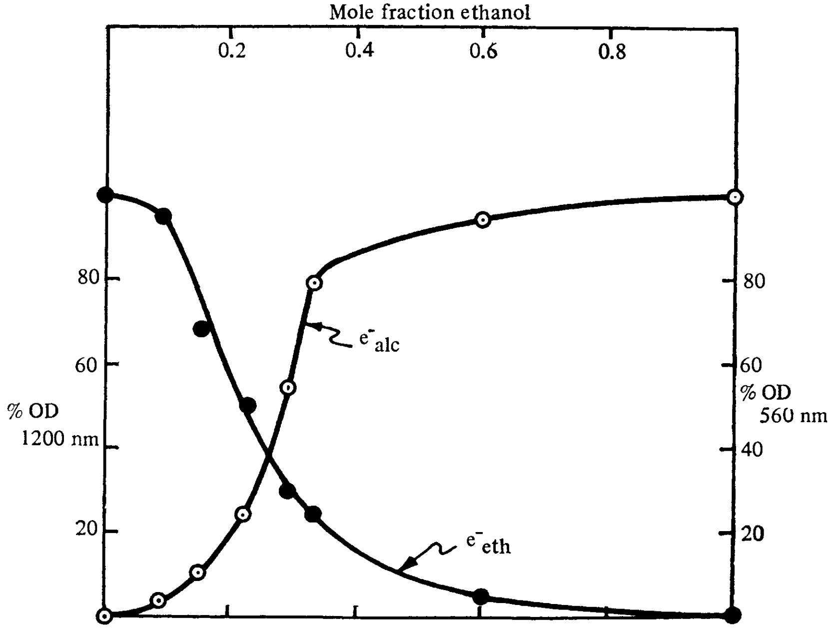

Figure 18 *The nature of the immediate environment of* e_t^- *generated by radiolysis at* 77 K *of glasses containing ethanol and MTHF in varying proportions.*[56] *The ordinates correspond to the optical densities ascribable either to* e_{alc}^- *or* e_{eth}^- *expressed as a percentage of the optical density produced by the same radiation dose absorbed by the pure alcohol or pure ether*

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[55] L. Shields, *J. Phys. Chem.*, 1965, **69**, 3186.

[56] G. V. Buxton, F. C. Cattell, and F. S. Dainton, *J.C.S. Faraday Trans.*, 1975, **71**, 115.

mixture was inhomogeneous, comprising a sea of MTHF containing islands of ethanol to which the electrons preferentially migrated and were solvated or whether, on the other hand, the mixture was homogeneous and ethanol molecules were drawn in to solvate e^- preferentially. In view of the rigidity of the glass at the experimental temperature the latter hypothesis seemed less likely than the former.

This question was conclusively settled by Dainton and Whewell[57] who studied the spectroscopic changes following 0.2 μs pulse radiolysis of low-temperature, *liquid* mixtures of these two substances. As may be seen from Figure 19, even in a mixture containing only 0.3 mole fraction of ethanol, the species initially produced is predominantly e_{eth}^-, but this decays and is synchronously replaced by e_{alc}^-. Moreover, the temperature dependence of this reaction follows the Tamman–Hesse equation which also holds (with the same value of T_0 = 80 K)

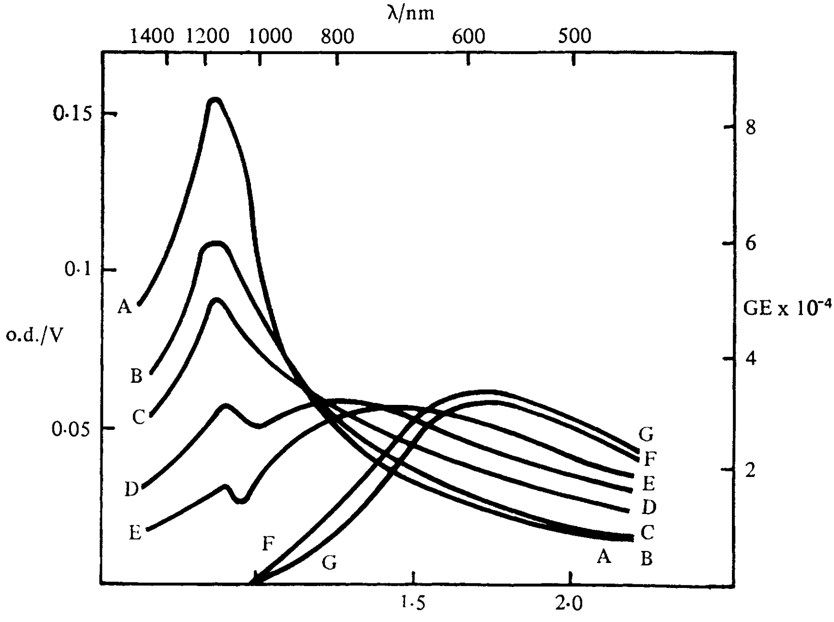

Figure 19 *Spectroscopic evidence for the progressive conversion of* e_{eth}^- *into* e_{alc}^- *in* 0.28 *mole fraction ethanol in MTHF at* 107 K. *The decay of absorption at* 1200 nm *and the growth of absorption at* 560 nm *are synchronous and increase with temperature proportionately to* $\exp[302/(T - 80)]$. *Curve* A *immediately after* 0.2 μs *pulse*; B, *after* 3 μs; C, *after* 10 μs; D, *after* 20 μs; E, *after* 30 μs; F, *after* 100 μs; *and* G *after* 180 μs (Reproduced from *J.C.S. Chem. Comm.*, 1974, 494)

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[57] F. S. Dainton and R. J. Whewell, *J.C.S. Chem. Comm.*, 1974, 493.

for the diffusion-controlled combination of benzyl radicals in this mixture. These results point unmistakeably to the conclusion that, before irradiation, the mixture is homogeneous and the environment of e^- when first solvated is predominantly that of the molecules in numerical excess, but that these are progressively displaced by ethanol molecules in a diffusion-controlled process leading to the thermodynamically more stable e_{alc}^-. This latter species can decompose spontaneously to $C_2H_5O^-$ and $H\cdot$ and it is significant that this unimolecular reaction, which does not involve translation of any molecules through the liquid, shows a normal Arrhenius dependence on temperature.

It would be unwise to generalize this result for all binary liquid mixtures and it is notable that, when less compatible compounds such as an alkane and an alcohol are used, this behaviour is not observed. Thus Hentz and Kenney-Wallace[58] have found that, in the pulse radiolysis at room temperature of such a mixture containing only 0.1M alcohol, only e_{alc}^- species can be detected in as short a space of time as $2\mu s$. This finding suggests that clusters of alcohol molecules pre-exist in the unirradiated liquid.

In my opening remarks I foolishly gave hostages to fortune by inviting you to judge whether I had followed the precepts laid down by Faraday. I have already mentioned one of his aphorisms and must now give you the others. They are: '1. One hour is enough for anyone. 2. Listeners expect reason and sense whilst gazers only require a succession of words. 3. The most prominent requisite of a lecturer, though perhaps not the most important, is a good delivery. 4. The lecturer should give the audience full reason to believe that all his powers have been exerted for their pleasure and instruction.'

I would like to express my indebtedness to many un-named former colleagues and students without whom much of this work bearing my name and referred to in this lecture could not have been accomplished.

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[58] R. R. Hentz and G. Kenney-Wallace, *J. Phys. Chem.*, 1972, **76**, 2931.