The Hydrated Electron

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Hydrated electrons are not easily distinguishable chemically from hydrogen atoms. Certainly in radiation chemistry and doubtless in other chemical studies (such as the reaction of sodium with water) they have been mistaken for hydrogen atoms. In fact hydrated electrons and hydrogen atoms constitute a conjugate acid–base pair, the former being the basic and more strongly reducing species. The recent discovery of the hydrated electron by radiation chemists is thus important not only in radiation chemistry but also to investigations on electron-transfer processes, novel mechanistic and synthetic reductions, redox phenomena, electrochemistry, and photochemistry. Because of its intriguing simplicity it is of some interest to theoreticians and spectroscopists.

Hydrated electrons are extra electrons solvated in liquid water. The process of solvation may be envisaged as the polarisation of the solvent molecules owing to electron-dipole interactions, the electric field of the extra electron inducing a potential well which then traps and stabilises the electron. It is thus bound in a self-induced stable quantum state of the polarised dielectric. It may be simply described as a polaron and is variously symbolised as $(H_2O)_n^-$ or e^-_{aq} but the latter will be employed here. The solvation energy, diffusion coefficient, and interaction distance indicate a charge distribution even larger than that of an iodide ion, probably extending 2·5–3·0 Å from the centre. Figure 1 naïvely

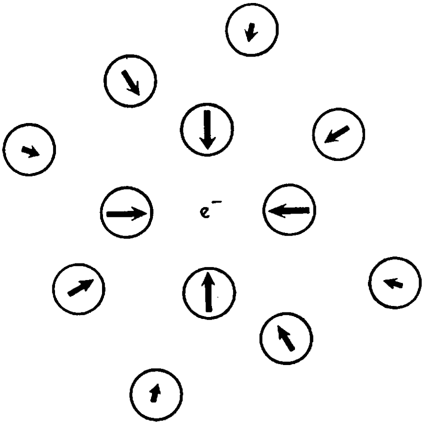

FIG. 1. *Diagrammatic representation of a solvated electron.*

depicts a solvated electron; the size of the arrows represents the extent of the electron–dipolar interaction and the degree of orientation of the water dipoles, both diminishing with increasing distance from the centre but extending well beyond the first solvation shell.

e^-_{aq} is intensely coloured and mobile. It is very reactive and hence short-lived, some of its reaction rates being among the fastest known. Its importance is manifest by the fact that since its discovery a few years ago the rates of reaction of e^-_{aq} with more than 300 molecules, ions, and radicals have been measured. This Review is concerned with the existence, detection, identification, stability, reactivity, and structure of e^-_{aq}. Almost all this information is derived from radiation chemistry.[1] Electrons solvated in media other than water are referred to briefly in the Introduction and for purposes of comparison in the section on theories of electron binding.

1 Introduction

A. Electrons Solvated in Various Media.—Electrons solvated or trapped in various media are characterised by blue colours, paramagnetism, and electrical conductivity. The optical absorption bands in the red or near infrared regions exhibited by these systems are invariably broad, intense, and without fine structure. The paramagnetic susceptibility and electron spin resonance absorption (e.s.r.) indicate free electrons having only weak interactions with neighbouring solvent nuclei. Equivalent conductivities of some of these systems are very high, being much larger than for ordinary ions in solution.

These properties characterise extra electrons stabilised in media as diverse as liquid ammonia,[2] crystalline salts,[3] low-temperature glassy ethers,[4] solutions of metals in fused alkali halides,[5] electrolysed tetralkylammonium salts,[6] and liquids and solids of great variety subjected to high-energy radiations. On some the information is prolific, on others scanty. More than a century ago Weyl[7] first showed that alkali metals dissolve in liquid ammonia to give blue solutions apparently perfectly stable when pure. These, and solutions of metals in amines and ethers, are widely used in organic chemical syntheses as reducing agents.[8] Indeed it is likely that any liquid having comparatively high dielectric constant and donor properties will dissolve alkali metals. Even an aprotic solvent, hexamethylphosphoramide, has recently been shown to form a blue reducing

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[1] For reviews on the radiolysis of water before the discovery of the hydrated electron see (*a*) A. O. Allen, 'The Radiation Chemistry of Water and Aqueous Solutions', Van Nostrand, New York, 1961; (*b*) E. J. Hart and R. L. Platzman, in 'Mechanisms in Radiobiology', Academic Press, New York, 1961, vol. I.

[2] M. C. R. Symons, *Quart. Rev.*, 1959, **13**, 99.

[3] (*a*) J. H. Schulman and W. D. Compton, 'Colour Centres in Solids', Pergamon, London, 1963; (*b*) M. C. R. Symons and W. T. Doyle, *Quart. Rev.*, 1960, **14**, 62.

[4] M. R. Ronayne, J. G. Guarino, and W. H. Hamill, *J. Amer. Chem. Soc.*, 1962, **84**, 4230.

[5] W. C. Fernelius and G. W. Watt, *Chem. Rev.*, 1937, **20**, 195.

[6] W. L. Jolly, *J. Amer. Chem. Soc.*, 1955, **77**, 4958.

[7] See C. A. Kraus, 'Solutions Metal-Ammoniac', Benjamin, Paris, 1964, p. 7.

[8] A. J. Birch and H. Smith, *Quart. Rev.*, 1958, **12**, 17.

solution stable for several hours.[9] When dissolved in alcohols, however, the alkali metals produce hydrogen fairly readily; when dissolved in water the reaction is vigorous. Any blue colour in aqueous solution, if it occurs, is extremely transitory. Despite an earlier report[10] of an optical absorption from potassium–water solutions some very careful recent work using a fast stop-flow technique showed that any colour was imperceptible on a sensitive spectrophotometer within 2 milliseconds.[11] This observation is in accord with the known rate of combination of hydrated electrons.

The increasing ease of dissolution of alkali and alkaline earth metals in ammonia and amines and increasing vigour with which these metals react with water to give hydrogen is also the order of increasing electropositivity. From conductivity and paramagnetic susceptibility measurements, from e.s.r. and the optical absorption data, the species responsible for the single broad absorption band centred at 15,000 Å in dilute ($<10^{-2}$M) metal–ammonia solutions has been fairly positively identified as the solvated electron.[2] In more concentrated ammonia solutions and in media of lower dielectric constant such as amines and ethers, other absorption bands appear which are generally attributable to monomers or quadrupolar ionic aggregates.[12] Electrons solvated in ammonia may be similar to the description given for e^-_{aq}, but from density measurements (a saturated solution of lithium in liquid ammonia being the least dense liquid known at 20°c)[13] and the e.s.r. line widths it is known that the electrons create and reside in large vacancies in the solvent, on average *ca.*10^2 Å^3, a volume otherwise occupied by about three ammonia molecules.

There are many features of electrons solvated in polar liquids beyond the scope of this Review that are relevant to discussions on e^-_{aq}. For instance, the order of relative stability for electrons solvated in ammonia, amines, alcohols, and water (as shown both by the rate of production of hydrogen in alkali-metal solution and the lifetime of the electron absorption spectrum in pulse radiolysis) is exactly converse to the depth of the potential well (if this is directly related to the energy of the absorption maximum or the dielectric constant). Consequently thermodynamic stability is not important. Thus it must be kinetic stability; but it is not governed by the protolytic power of the solvents. Although the concentration of H^+ in water is *ca.*10^8 higher than in ammonia, increases in the pH do not affect the stabilities very much, and the rates of the reactions of e^- with H^+ are known.

Perhaps the differences can be expressed by three equilibria (1)—(3), the third of which can be ignored but for the fact that dimeric species exist in amines and ethers.

$$M \rightleftharpoons M^+_s + e^-_s \qquad (1)$$

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[9] G. Fraenkel, S. H. Ellis, and D. T. Dix, *J. Amer. Chem. Soc.*, 1965, **87**, 1406.

[10] J. Jortner and G. Stein, *Nature*, 1955, **175**, 893.

[11] J. L. Dye, personal communication.

[12] (*a*) J. L. Dye and R. R. Dewald, *J. Phys. Chem.*, 1964, **68**, 135; (*b*) M. Ottolenghi, K. Bar-Eli, H. Linschitz, and T. R. Tuttle, *J. Chem. Phys.*, 1964, **40**, 3729.

[13] W. L. Jolly, 'Progress in Inorganic Chemistry', vol. I, Interscience, New York, 1959.

$$e^-_s + e^-_s \rightleftharpoons (e_2^{2-})_s \tag{2}$$

$$2e^-_s + 2M^+_s \rightleftharpoons (M_2)_s \tag{3}$$

Equilibrium (2) governs the stability of solvated electrons. If, as in water and alcohols, it is far to the right and $(e_2^{2-})_s$ readily forms H_2 gas which escapes then e^-_s is highly unstable. In NH_3 the $(e_2^{2-})_s$ species is only observed at concentrations of electrons much greater than 10^{-2}M and is stable, whereas reaction (2) occurs in irradiated water at $<10^{-6}$M. For media of low dielectric constant such as amines equilibrium (1) is to the left and (3) to the right, which is in accord with the expectation that on going to lower dielectric constant the tendency is for monomer or dimer to be formed in preference to isolated solvated ions.

The existence and relative stability of the $(e_2^{2-})_s$ species are rather intriguing. They also appear as F^1 centres in alkali halide crystals formed by the partial thermal or photolytic bleaching of *F*-centres and have been shown to be diamagnetic.[3] *F*-Centres, which are excess electrons trapped at anion vacancies in crystals, show absorption bands of similar shape to those of e^-_s in polar liquids and in these cases, since the cavity size is determined by the lattice parameters, the wavelength of maximum absorption (λ_{max}) and cavity size can be correlated through Ivey's rule.[14] Most glassy solids also show colouration when subjected to ionising radiations; Pyrex becomes brown and silica violet. Trapped electrons have been identified by their optical and e.s.r. spectra in low-temperature glasses of concentrated aqueous solutions,[15] organic ethers,[16] and alcohols.[17] Again $(e_2^{2-})_s$ species are in evidence. In liquid systems the absorption band of $(e_2^{2-})_s$ appears on the high-energy side of the e^-_s band whereas in solids they tend to be on the low-energy side, a difference which has been attributed[14] to the ability of the cavity in the liquids to adjust its size and shape to the constraint imposed by two electrons, presumably having paired spins.

B. Methods of producing e^-_{aq}.—Although the radiolysis of water is unquestionably the most direct and convenient method devised for generating e^-_{aq} it is valuable to compare the spectrum and reactivity so obtained with e^-_{aq} produced in other ways. Some possible method of producing e^-_{aq} are discussed.

(i) *From alkali metals.* The reaction of sodium with water is described classically by reaction (4) followed by the combination of two hydrogen atoms to form molecular hydrogen. If by analogy with ammonia the first step involves ionisation with the formation of e^- which survives long enough to become solvated then hydrogen will be formed by reactions (1*a*) and (5). As will be seen, the

$$Na + H_2O \rightarrow Na^+ + OH^- + H \tag{4}$$

$$Na \rightarrow Na^+ + e^-_{aq} \tag{1a}$$

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[14] M. J. Blandamer, R. Catterall, L. Shields, and M. C. R. Symons, *J. Chem. Soc.*, 1964, 4357.

[15] D. Schulte-Frohlinde and K. Eiben, *Z. Naturforsch*, 1962, **17a**, 445.

[16] (*a*) Ref. 4; (*b*) F. S. Dainton and G. A. Salmon, *Proc. Roy. Soc.*, 1965, *A*, **285**, 319; (*c*) D. R. Smith and J. J. Pieroni, *Canad. J. Chem.*, 1965, **43**, 876.

[17] F. S. Dainton, G. A. Salmon, and J. Teplý, *Proc. Roy. Soc.*, 1965, *A*, **286**, 27.

$$e^-_{aq} + e^-_{aq} \rightarrow [(e_2^{2-})_{aq}] \rightarrow H_2 + 2OH^-_{aq} \qquad (5)$$

conversion of e^-_{aq} into hydrogen atoms by reaction (6) is very slow whereas

$$e^-_{aq} + H_2O \rightarrow H + OH^-_{aq} \qquad (6)$$

reaction (5) is rapid and will be dominant if the local concentration of e^-_{aq} close to the metal surface exceeds 10^{-7}M (since $k_6/k_5 > 10^{-7}$). Because of the magnitude of k_5 the spectrophotometric detection of e^-_{aq} under steady-state conditions is not feasible at present.[11] However, it should be possible to test for e^-_{aq} chemically. Indeed, the presence of N_2O in water to which dispersed sodium was added (in the form of sodium amalgam) inhibited the formation of hydrogen with the concurrent generation of nitrogen by reaction (7). From the known relative rates of

$$e^-_{aq} + N_2O \rightarrow N_2 + O^-_{aq} \qquad (7)$$

reaction of N_2O with e^-_{aq} and hydrogen atoms and the observed dependence of this inhibition on the pH of the water it was concluded that reactions (1*a*) and (5) rather than (4) occur.[18] In addition, Bennett, Mile, and Thomas[19] have reported depositing sodium atoms within an ice matrix at 77°K and from the line-width of the e.s.r. absorption concluded that electrons were produced and trapped at defects in the ice structure. They were also able to assign fine structure to the interaction of the electron with protons from four water molecules arranged tetrahedrally around the electron centre. Further, there is chemical evidence to suggest that e^-_{aq} is the precursor of hydrogen gas formed at the cathode when dilute solutions of Na_2SO_4 are electrolysed.[20]

(ii) *Photochemically.* An unsuccessful attempt has been made[20] to observe the absorption spectrum of e^-_{aq} in pure liquid water subjected to flash photoionisation from a windowless helium resonance lamp, the predominant light from which was believed to be at 584 Å, a photon energy well in excess of the ionisation potential of water. However, if a solute is added in dilute concentration, this may be readily photoionised by light transmitted by the water. Indeed, the flash photolysis of aqueous solutions of I^-, $Fe(CN)_6^{4-}$, phenol, cresol, etc.[21] has been shown to produce a transient species having the same absorption spectrum and reactivity as e^-_{aq}.

Photochemical electron-transfer reactions in general (or indeed any electron-transfer process) may involve hydrated electrons as intermediates. In 1938 Franck and Scheibe[22] supposed that the intense absorption bands in the region 2000—2500 Å which are characteristic of many anions in aqueous solution suggested that absorption of light was accompanied by the formation of a free radical and a hydrated electron. Then Dainton and James[23] much more recently

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[18] E. A. Shaede and D. C. Walker, *Chem. Soc. Special Publ.* No. 22, 1967, p. 277.

[19] J. Bennett, B. Mile, and A. Thomas, *Nature*, 1964, **201,** 919.

[20] D. C. Walker, unpublished work, and *Canad. J. Chem.* 1966, **44,** 2226.

[21] (*a*) L. I. Grossweiner, G. W. Swenson, and E. F. Zwieker, *Science*, 1963, **141,** 805; (*b*) G. Dobson, and L. I. Grossweiner, *Radiation Res.*, 1964, **23,** 290; (*c*) M. S. Matheson, W. A. Mulac, and J. Rabani, *J. Phys. Chem.*, 1963, **67,** 2613.

[22] J. Franck and G. Scheibe, *Z. phys. Chem.*, 1938, ***A*,139,** 22.

[23] F. S. Dainton and D. G. L. James, *Trans. Faraday Soc.*, 1958, **54,** 649.

showed that the energy of the charge-transfer spectral band of many bivalent transition-metal ions was linearly related to the redox potential of the M^{2+}/M^{3+} couple. Now there is chemical evidence for e^-_{aq} as the precursor of H_2 when U^{3+} salts react with and reduce water.[20]

(iii) *Chemically from the hydrogen atom.* The acid dissociation constant of the hydrogen atom can be obtained from equilibrium (6). k_{-6} has been evaluated[24]

$$e^-_{aq} + H_2O \rightleftharpoons H + OH^-_{aq} \qquad (6)$$

as $2{\cdot}2 \times 10^7$ l. moli^{-1} sec.$^{-1}$ while k_6 is the subject of some uncertainty (see later) but the best available value is 16 l. mole^{-1} sec.$^{-1}$ (ref. 25). Combination of these gives $pK_a = 9{\cdot}7$, hence e^-_{aq} should be fairly readily generated from hydrogen atoms in alkaline solution.

Reaction (-6), originally suggested by Baxendale and Hughes,[26] was subsequently confirmed by competitive studies with introduction of externally generated hydrogen atoms into alkaline solutions.[27] It has since been shown to be a fast non-rate-controlling step in the radiation-induced chain reaction between H_2 and N_2O at pH > 12.[28] Spectroscopic verification for this acid–base transfer was provided by the pulse radiolysis of alkaline water containing high pressures of hydrogen gas.[29] Under these conditions the radiation produced OH radicals reacted with H_2 to give hydrogen atoms which were then converted into e^-_{aq}, the optical absorbance of which was measured.

(iv) *By the radiolysis of water.* Despite the suggestion by Stein in 1952[30] and Platzman's theoretical prediction the following year,[31] the importance of hydrated electrons in aqueous radiation chemistry was not revealed and they continued to be mistaken for hydrogen atoms for almost a decade. Although hydrogen atoms and e^-_{aq} are fairly readily interconverted [$k_8 = 2{\cdot}3 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$ (ref. 32) and $k_{-6} = 2{\cdot}2 \times 10^7$ l. mole^{-1} sec.$^{-1}$ (ref. 24)] providing $3{\cdot}7 < \text{pH} < 14$,

$$e^-_{aq} + H^+_{aq} \rightarrow \text{'H'} \qquad (8)$$

interconversion cannot occur before their detection by the scavenging technique. This is because for normal scavenging of reactive species R, $k_{RS}[S] = ca.\ 10^7$ sec.$^{-1}$, where k_{RS} is the rate constant for reaction of R with scavenger S. Except in fairly acidic or very strongly alkaline solution the species existing about 10^{-7} sec. after the primary events leading to its formation will be scavenged.

Radiation chemistry is concerned with the interaction of high-energy radiations with chemical systems. Each high-energy electron, either from an external ion source or from Compton or photoelectric absorption of *X*- or γ-rays, will

[24] M. S. Matheson and J. Rabani, *J. Phys. Chem.*, 1965, **69**, 1324.

[25] E. J. Hart, S. Gordon, and E. M. Fielden, *J. Phys. Chem.* 1966, **70**, 150.

[26] J. H. Baxendale and G. Hughes, *Z. phys. Chem.* (*Frankfurt*), 1958, **14**, 323.

[27] J. Jortner and J. Rabani, *J. Amer. Chem. Soc.*, 1961, **83**, 3868.

[28] (*a*) F. S. Dainton and D. C. Walker, *Discuss Faraday Soc.*, 1963, **36**, 313; (*b*) C. H. Cheke and J. W. Swinnerton, *J. Phys. Chem.*, 1964, **68**, 1429.

[29] M. S. Matheson and J. Rabani, *Radiation Res.*, 1963, **19**, 180.

[30] G. Stein, *Discuss. Faraday Soc.*, 1952, **12**, 227.

[31] R. L. Platzman, N.A.S.-N.R.C. Reports, 1953, No. 305, p. 22.

[32] S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *Discuss. Faraday Soc.*, 1963, **36**, 193.

ultimately give rise to an additional ionisation for about every 30 ev of energy. Thus a 1 Mev electron generates about 33,000 other electrons in the irradiated material. Table 1 indicates the succession of events involving electrons that probably take place when a high-energy electron transfers its energy to liquid water. Very quickly the chain ionisation gives rise to a large number of sub-excitation electrons which become thermalised in *ca.* 10^{-13} sec. by vibrational and rotational and finally just collisional energy exchanges with the water molecules. If the electron then survives the dielectric relaxation time of water, 10^{-11} sec., it can become solvated and acquire the diffusion and interaction properties of chemical entities. This Review purports to show very good reasons for believing that e^-_{aq} survives for longer than 10^{-7} sec. and is the principal reducing species in the radiolysis of water. (In addition hydrogen atoms are formed in irradiated water but with about one quarter the yield of e^-_{aq}.)

TABLE 1

Time (sec)		
	α, β, γ, X-ray, etc.	High-energy particle or quantum
10^{-18}	↓	
	$e^-_{H.E.}$	High-energy electron (10^4—10^6 ev)
10^{-18}	↙ ↓ ↘	
	$e^-_{sec.}$	Secondary electrons (10—10^3 ev)
10^{-16}	↙ ↓ ↘	
	$e^-_{sub.}$	Sub-excitation electrons (<10 ev)
10^{-13}	↓	
	$e^-_{Th.}$	Thermalised electron (*ca.* 1kT)
10^{-11}	↓	
	e^-_{aq}	Solvated electron
ca. 10^{-8}	↓	
	e^-_{aq}	Survivor of intra-spur recombination reactions
$\geqslant 10^{-3}$	↓	
	$H + OH^-$	Possible decomposition products

Platzman[31] estimated that reaction (6), the conversion $e^-_{aq} \rightarrow H$, might occur within 10^{-9} sec. and an early attempt to observe e^-_{aq} spectroscopically failed.[33] (Had this estimation for the dissociation time been correct e^-_{aq} would not yet have been detected.) Samuel and Magee[34] developed an admirable diffusion model involving hydrogen atoms and hydroxyl radicals formed by the rapid neutralisation of thermalised electrons in a time too short for solvation to occur. Because the diffusion model explained the radical and molecular yields and their dependence on linear energy transfer, there was no cause before 1958 to doubt

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[33] H. Linschitz, N.A.S.-N.R.C. Reports, 1953, No. 305, p. 39.

[34] A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, 1953, **21**, 1080.

that radiation chemical affects in water resulted simply from the process

$$H_2O \rightsquigarrow H + OH$$

A need for the existence of e^-_{aq} in radiation chemistry then arose.

2 Chemical Evidence for e^-_{aq}

To distinguish chemically between hydrogen atoms and e^-_{aq} a reagent is required which reacts with each of these species either (i) at significantly different rates or (ii) to yield different products. (i) All of the reactions of e^-_{aq} are electron attachments and therefore reductions. Some of these are very rapid being just diffusion-controlled and in general e^-_{aq} reductions are faster than those of hydrogen atoms. With N_2O for instance there is a 10^4-fold difference, with O_2 only 2-fold, so relative rate determinations can distinguish them, as will be seen. When the reactant is a saturated organic compound with an abstractable hydrogen atom then the rate of reaction with hydrogen atoms greatly exceeds that with e^-_{aq} since the latter do not appear to participate in abstractions. Thus only hydrogen atoms produce H_2 by reaction with methanol. Further, because only one of them is charged the presence of inert salts in the solution will affect their rates of reaction with charged solutes differently. (ii) Occasionally an unstable intermediate of the electron-transfer reaction dissociates to give different stable products from those resulting from attachment or abstraction of hydrogen atoms. Monochloroacetic acid exemplifies this category of solute.

A. Competition Studies.

—In 1958 Baxendale and Hughes[26] noted an extraordinarily large effect shown by Fe^{3+} and Cu^{2+} ions on the yield of hydrogen from irradiated acidified aqueous methanol solutions. Hydrogen gas produced in reaction (9) was reduced by

$$H + CH_3OH \rightarrow H_2 + CH_2OH \qquad (9)$$

Fe^{3+} to a much greater extent than competitive reaction (10) would predict,

$$H + Fe^{3+} \rightarrow Fe^{2+} + H^+ \qquad (10)$$

but this was understandable if e^-_{aq} was the precursor of H in acid solution [reaction (8)] and $k_{11} >> k_{10}$.

$$e^-_{aq} + Fe^{3+} \rightarrow Fe^{2+} \qquad (11)$$

At about the same time Hayon and Weiss[35] showed that an alteration of the pH of an aqueous solution of monochloroacetic acid gave rise to different products, so that discrimination was effected here because of condition (ii). In acid solution H_2 was the predominant product whereas Cl^- was favoured at $pH > 4$. Their results are reproduced in Figure 2 which shows the competition at $pH = 1$ between H^+ and $ClCH_2.CO_2H$ for e^-_{aq} by reactions (8) and (12). At low concentrations of chloroacetic acid reaction (8) predominates, e^-_{aq} are converted

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[35] E. Hayon and J. J. Weiss, 2nd Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva, 1959, vol. 29, p. 80.

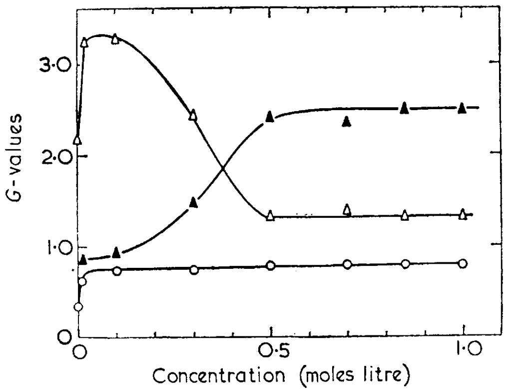

FIG. 2. *Dependence of radiation yields upon concentration of monochloroacetic acid in aqueous solution at* pH = 1.

▲$G(Cl^-)$; △$G(H_2)$; ○$G(H_2O_2)$

(Reproduced with permission from E. Hayon and J. Weiss[35])

$$e^-_{aq} + ClCH_2CO_2H \rightarrow Cl^- + \dot{C}H_2CO_2H \qquad (12)$$

into H-atoms, and H_2 is produced by reaction (13). It has subsequently been

$$H + Cl{\cdot}CH_2{\cdot}CO_2H \rightarrow H_2 + Cl\dot{C}H{\cdot}CO_2H \qquad (13)$$

shown that hydrogen atoms generated by an electrodeless discharge and passed into chloroacetic acid solution produce H_2 *via* reaction (13),[27] corroborating the designation of the acidic species as H and implying that at pH > 4 e^-_{aq} is produced. Also concurrently Barr and Allen[36] observed a discrepancy in the ratio of rate constants (k') for reaction with O_2 and H_2O_2 of 'H' atom species produced by irradiation or by reaction (14).

$$H_2 + OH \rightarrow H + H_2O \qquad (14)$$

k' had a value of *ca.* 500 with the product of reaction (14) whereas it was about unity for the radiation-produced species. Further, in the irradiation of acidified solutions k' was again *ca.* 500. Barr and Allen concluded that either e^-_{aq} was produced by radiolysis and H-atoms in (14), or H-atoms in radiolysis and an even more acid species such as H_2^+ in reaction (14). [In fact H_2^+ has been postulated to be so weakly reducing that it is itself reduced by iodide.[37]]

By discriminative competitive reactions many systems have now shown the principal reducing species in radiolysis to be the more basic form. Confirmation and final identification with the hydrated electron comes from the determination of the magnitude and sign of its charge and the spectroscopic evidence.

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[36] N. F. Barr and A. O. Allen, *J. Phys. Chem.*, 1959, **63**, 928.
[37] T. Rigg and J. Weiss, *J. Chem. Soc.*, 1952, 4198.

B. Effect of Ionic Strength.—From the Bronsted–Bjerrum theory of ionic reactions and the extended Debye–Hückel theory of electrolytes the rate constant k of reaction between two species of charge Z_A and Z_B in water at 25°c is given by eqn. (I).[38]

$$\log_{10}k = \log_{10}k_0 + 1{\cdot}02\, Z_A.Z_B\mu^{1/2}/(1 + a\mu^{1/2}) \qquad (I)$$

In this equation μ is the ionic strength of the solution, a is a parameter numerically close to unity, and k_0 is the rate constant at infinite dilution of ions. Thus k will increase, decrease, or remain constant depending respectively on whether the charges of the reactants are of the same sign, opposite signs, or one is zero. If Z_A for instance is known then a determination of the dependence of k on μ will permit an evaluation of the magnitude and sign of Z_B.

Because the reactions of e^-_{aq} are very rapid absolute values of k could not be determined in 1962 so it was necessary to compare the effect of μ on rate-constant ratios with a charged relative to an uncharged solute. Czapski and Schwarz[39] established in this way that the principal reducing species in irradiated water had unit negative charge. They observed the rate of reaction of e^-_{aq} with H_2O_2 compared with H^+, O_2, and NO_2^- as a function of ionic strength, their results being shown in Figure 3. In this figure K represents the ratio $k_{(e^- + H_2O_2)}/k_{(e^- + x)}$ (where x is H^+, O_2, or NO_2^-) at ionic strength μ and K_0 is that ratio when $\mu = 0$. The lines drawn with slopes of $+1{\cdot}02$, O, and $-1{\cdot}02$ show that Z for $e^-_{aq} = -1$. The same conclusion was reached by Collinson, Dainton,

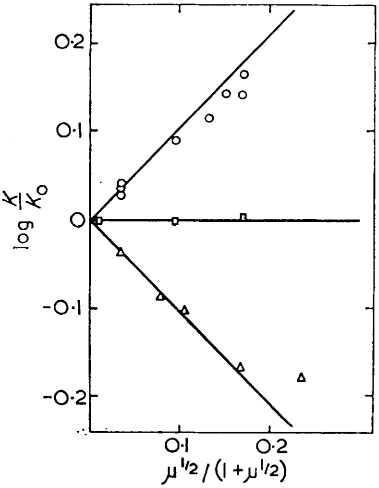

FIG. 3. *Effect of ionic strength* (μ) *upon the relative rate constants for reactions of* e^-_{aq} *with various solutes.* ONO_2^- *relative to* H_2O_2; □O_2 *relative to* H_2O_2; △H^+ *relative to* H_2O_2. K *is the relative rate at ionic strength* μ, K_0 *when* $\mu = 0$.

(Reproduced with permission from G. Czapski and H. A. Schwarz[39])

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[38] G. Scatchard, *J. Amer. Chem. Soc.*, 1930, **52**, 52.

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

Smith, and Tazuki[40] using Ag^+ ions in competition with acrylamide as the charged and uncharged solutes and recently[41] measurements on the absolute value of k_{15} have shown it to vary with ionic strength according to eqn. (I).

$$e^-_{aq} + Fe(CN)_6^{3-} \rightarrow Fe(CN)_6^{4-} \qquad (15)$$

Equation (I) is valid only if species A, B, and the transition complex have at all times the equilibrium distribution of ionic atmospheres. This will be true for the transition complex even if its lifetime is less than the ionic relaxation time, if the ion atmospheres of A and B are united when the complex is formed. Coyle, Dainton, and Logan[42] have discussed the implications to the Brønsted treatment if B, in this case the electron, is suddenly generated in a solution of A so concentrated that the formation of the transition complex is complete before the electron could acquire an ion atmosphere. Under these circumstances the complex will have a charge of $(Z_A + Z_B)$ but an ion atmosphere initially equivalent to that of A. The 1·02 in eqn. (I) is then replaced by 0·51 which means that an ion having charge -2 without an ionic atmosphere cannot be distinguished from an ion of unit charge in equilibrium with the ions constituting the medium. Coyle, Dainton, and Logan have shown that the radiation and photochemically produced hydrated electron establishes its ion atmosphere in less than 3×10^{-9} sec. Thus the e^-_{aq} scavenged some 10^{-7} sec. after its formation resembles a univalent negative ion in being solvated and in equilibrium with an appropriate ion atmosphere.

There is substantial chemical evidence for the existence of e^-_{aq} in irradiated water. In a series of classic experiments Hart and Boag[43] showed by a fast spectrophotographic technique that a strong absorption band in the visible could be identified with e^-_{aq} and this permitted direct, precise measurements of the reactivities of hydrated electrons.

3 Spectroscopic Evidence for e^-_{aq}

In 1953 Platzman[31] remarked 'irradiated water turns blue, we just don't see it'. This was a consequence of his postulation that e^-_{aq} should exist in irradiated water, that it should have a broad absorption maximum at a photon energy of about 2 ev, and that it should have a very transient existence. Linschitz[33] had earlier failed to detect an absorption not because his time resolution, which only permitted observations to be made 10^{-5} sec. after a short pulse of *X*-rays, was inadequate (as was thought at the time) but because the sensitivity of detection was too low. In 1960 Keene[44] reported an unidentified absorption in the visible region of the spectrum in water irradiated with a 2 μsec. pulse of 4 Mev electrons which Matheson suggested may be due to e^-_{aq}.[45] In 1962 Hart and Boag observed and identified the absorption spectrum of e^-_{aq}.

[40] E. Collinson, F. S. Dainton, D. R. Smith, and S. Tazuki, *Proc. Chem. Soc.*, 1962, 140.

[41] S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *J. Amer. Chem. Soc.*, 1963, **85**, 1375.

[42] P. Coyle, F. S. Dainton, and S. R. Logan, *Proc. Chem. Soc.*, 1964, 219.

[43] E. J. Hart and J. W. Boag, *J. Amer. Chem. Soc.*, 1962, **84**, 4090.

[44] J. P. Keene, see *Radiation Res.*, 1964, **22**, 1, ref. (1).

[45] M. S. Matheson, *Ann. Rev. Phys. Chem.*, 1962, **13**, 90.

A. The Technique of Pulse Radiolysis.—Owing to the availability of accelerators which provide very short pulses (0·01 to 5 μsec.) of high-energy electrons (1·5 to 30 Mev) the radiation analogue of the photochemical technique of flash photolysis, namely pulse radiolysis, has been most fruitfully applied in recent years. The electron beams are sufficiently intense to initiate enough reaction during the short pulse either to measure the rate of formation of a product or the decay of a reactive intermediate immediately afterwards, or even to study the build-up or steady-state concentration during the pulse. The first applications of absorption spectroscopy to pulse radiolysis in 1960[46] quickly led to a perfection of the technique. Figure 4(*a*) shows the type of apparatus used by Hart and Boag[43] to obtain the spectrum of e$^-_{aq}$ in sodium carbonate solution and then in pure water. A uranium-spark spectroflash was triggered simultaneously with, or at a measured time delay after, an electron pulse from a 1·8 Mev electron accelerator, the absorption spectrum being photographed on a spectrograph. In their initial experiments a 0·5M-Na$_2$CO$_3$ solution showed a well-defined maximum at about 7000 Å which decayed completely within 25 μsec. In pure water the e$^-_{aq}$ absorption was much shorter lived; indeed, the carbonate solution was an extremely favourable environment for this first observation, not only because of the extended lifetime of e$^-_{aq}$ owing to the pH, but also owing to the removal of OH radicals by CO$_3^{2-}$ to give CO$_3^-$ which absorbs slightly in the same region.

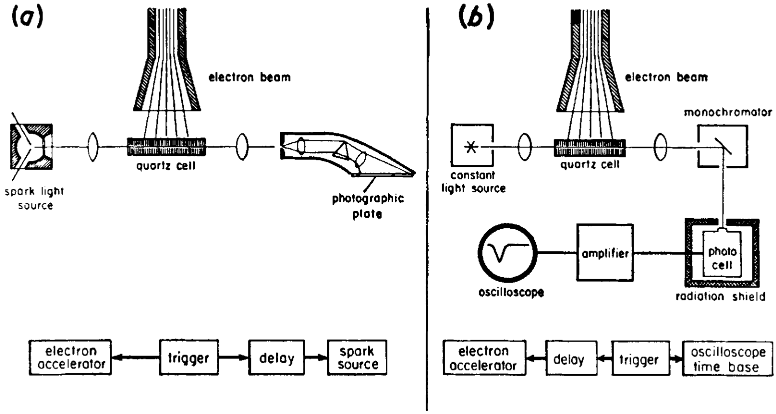

FIG. 4. *Schematic diagrams of apparatus used in pulse radiolysis;* (*a*) *synchronised flash spectrographic technique;* (*b*) *kinetic spectrophotometric technique.*

(Figure 4*a* reproduced with permission from J. W. Boag[58])

This synchronised flash absorption spectrophotographic method can give complete spectra at a variety of time intervals after the electron pulse and can be used to obtain kinetic results. It has a number of disadvantages however. First,

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[46] (*a*) R. L. McCarthy and A. MacLachlan, *Trans. Faraday Soc.*, 1960, **56**, 1187; (*b*) M. S. Matheson and L. M. Dorfman, *J. Chem. Phys.*, 1960, **32**, 1870; (*c*) J. P. Keene, *Nature*, 1960, **188**, 843.

the time resolution is limited by an integrated time-intensity factor during the period of the spectroflash (usually a few μsec.); secondly, the sensitivity is governed by the speed and contrast of the photographic plates; and finally, optical density measurements have to be calculated from densitometer traces and compared with blanks showing the sensitivity of the emulsion and spectroflash to various spectral regions. The spectrum obtained by Hart and Boag thus showed certain structural features and secondary bands not observed by the use of the rapid spectrophotometric recording technique though both have similar resolving power (*ca.* 100 Å).

The kinetic spectrophotometric method is now more generally used and is depicted schematically in Figure 4(*b*). Light from a stabilised source passes through the irradiation cell, is monitored by a photomultiplier on the exit slit of a monochromator, and the resulting signal is fed onto the *Y*-plates of an oscilloscope to which a suitable time base is applied just before the electron pulse. The oscilloscope screen is photographed and thus a time-dependence of the absorption is recorded for each wavelength setting of the monochromator. This optical detection system compares the transmission of the irradiation cell before the pulse with that during and after the pulse. The smallest change in transmission which can be detected is governed only by fluctuations in the lamp output (very small over a few tens of microseconds) resulting in much greater sensitivity than is possible in the dual-cell systems of conventional spectrophotometry. Shot noise in the photomultiplier is the principal limitation over very short times[47] and since this is inversely proportional to the square-root of the light flux through the cell an efficient optical system and high intensity lamp yield enormous sensitivities. Optical-density measurements of 0·002 are common[47] and 0·00002 is reported to be possible.[48] With this sensitivity concentrations of 2×10^{-9}M can be measured in cells 1 cm. in depth for species having $\epsilon = 10^4$ l. mole^{-1} cm.$^{-1}$. Multiple-reflection cells further increase the effective sensitivity of the optical detection and have been used successfully with the higher energy electron beams.[49]

B. Absorption Spectrum of e^-_{aq}.—Figure 5 shows the absorption spectrum of e^-_{aq} in pure deaerated water obtained by Keene[50] using a spectrophotometric method. The band has an absorption maximum at 7200 + 100 Å which corresponds with an energy of 1·72 ev. It is a very broad band, having a half-height width of about 1·0 ev, and is asymmetric on the high-energy side when represented on a linear energy scale; but there is no discernible fine structure to the band between 8000 and 3000 Å on instruments capable of 100 Å resolution. Rabani, Mulac, and Matheson[51] have determined the extinction coefficient without the need to measure the radiation intensity or assume a chemical yield of

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[47] J. P. Keene, *J. Sci. Instn.*, 1964, **41**, 493.

[48] I. A. Taub, Proc. Manchester Symposium on Pulse Radiolysis, 1965, Academic Press, London.

[49] L. M. Dorfman, *Science*, 1963, **141**, 493.

[50] J. P. Keene, *Discuss. Faraday Soc.*, 1963, **36**, 304.

[51] J. Rabani, W. A. Mulac, and M. S. Matheson, *J. Phys. Chem.*, 1965, **69**, 53.

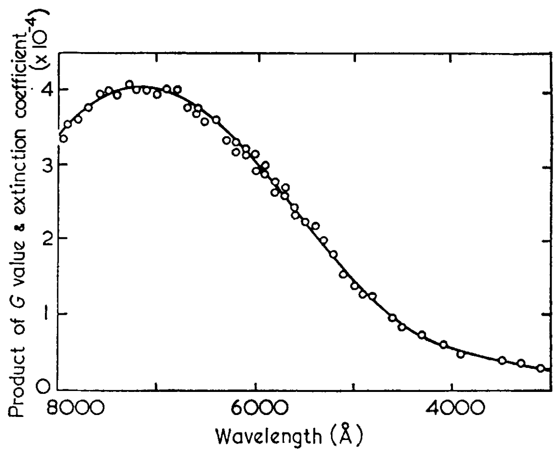

FIG. 5. *Absorption spectrum of* e^-_{aq}.
(Reproduced with permission from J. P. Keene[50])

e^-_{aq}. They observed the decay of e^-_{aq} concurrent with the formation of the tetraform ion produced in reaction (16).

$$e^-_{aq} + C(NO_2)_4 \rightarrow C(NO_2)_3^- + NO_2 \qquad (16)$$

From the known ϵ of $C(NO_2)_3^-$ the molar decadic extinction coefficient of e^-_{aq} at 7200 Å was computed as 15,800 l. mole$^-$ cm.$^{-1}$ and from this and Figure 5 an oscillator strength for the optical transition of about 0·8 can be estimated. So far a full spectral analysis in the near infrared has not been reported and it may prove important in discussions on the optical transitions giving rise to the absorption band to know if fine structure on the low-energy side of the peak exists.

Studies with deuterium oxide[52] show a small isotopic shift in the absorption maximum to higher energies and probably a very significant increase in extinction coefficient and oscillator strength. [This assumes that the radiation yield of solvated electrons is not more than 30% larger in D_2O than in H_2O. In this regard it would be valuable to measure the extinction coefficient of e^-_{aq} in D_2O by the tetranitromethane method as a direct check on both ϵ and $G(e^-_{aq})$.] Anbar and Hart[53] have shown the absorption band of e^-_{aq} in concentrated solutions of inert electrolytes such as $MgCl_2$, KF, NaOH, $NaClO_3$, etc. to be shifted to shorter wavelengths accompanied by a small reduction in the absorbance, probably owing to a tightening of the solvent shell by the ionic atmosphere. Decreasing

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[52] D. M. Brown, F. S. Dainton, J. P. Keene, and D. C. Walker, *Proc. Chem. Soc.*, 1964, 266.
[53] M. Anbar and E. J. Hart, *J. Phys. Chem.*, 1965, **69**, 1244.

temperature also causes a shift in the absorption band to higher energies.[54]

Although e^-_{aq} is very short-lived its intense absorption band spanning the readily accessible region of the spectrum enables its reactions to be studied unambiguously, accurately, and kinetically.

C. Identification of the Absorption Band.—Evidence for the assignment of the transient absorption band shown in Figure 5 to e^-_{aq} is rather convincing. (i) The energy of λ_{max} agrees reasonably closely with the early prediction,[31] the current theoretical estimates,[55] and the solvation energy determined from thermochemical data.[56] (ii) The band's shape, proportions, and asymmetry are analogous to those of electron bands in metal–ammonia solutions, *F*-centres and other trapped electron species which have been identified by their e.s.r. absorption. (iii) Additives which are known to react with e^-_{aq} such as H^+, O_2, H_2O_2, N_2O, CO_2, Cu^{2+}, etc. suppress the absorption band, whereas reagents which do not react rapidly with e^-_{aq}, such as CH_3OH, NH^{4+}, Na^+, etc. do not affect the absorption. (iv) The rate of disappearance of the e^-_{aq} band is exactly complemented by the rate of formation of the $C(NO_2)_3^-$ absorption band when $C(NO_2)_4$ is the additive.[51] (v) An absolute value for the yield, $G = 2{\cdot}6 + 0{\cdot}2$,[51] of species responsible for the absorption equals the best estimates of $G(e^-_{aq})$ by chemical methods.[57] (vi) Measurements of transient electrical conductivity by Boag[58] on pulse-irradiated water showed that a charged species was produced which decayed at the same rate as the optical absorption in the presence and absence of additives. (vii) Kinetic ionic-strength effects have shown that the band was due to a species having unit negative charge.[41] (viii) A transient species having the same absorption spectrum and reactivity was obtained by flash photolysis of certain aqueous solutions which are believed to undergo photochemical charge-transfer-to-solvent processes involving e^-_{aq}.[21] (ix) A strengthening in the e^-_{aq} band is observed when H_2 and OH^- are in sufficient concentration for the radiation-produced OH radical to be transformed to e^-_{aq} *via* reactions (14) and (−6).[29]

Measurements of the e.s.r. absorption of e^-_{aq} are not feasible at present on account of its very transient existence. Since the modulated magnetic field cannot be scanned rapidly enough it may only be possible to obtain the e.s.r. spectrum of e^-_{aq} by a sampling technique. Further, because of the long time-constant required for good signal-to-noise ratios, the decay characteristics may have to be studied by an intermittancy technique similar to that used by Fessenden for hydrocarbon radicals.[59] Clearly e.s.r. measurements on e^-_{aq} are vital in elucidating the nature of the electron binding and the size, shape, and orientation of the solvent sheath and would corroborate the optical studies on the reactivity of e^-_{aq}.

[54] J. H. Baxendale and J. P. Keene, unpublished work.
[55] J. Jortner, *Radiation Res.*, 1964, Suppl. 4, 24.
[56] J. H. Baxendale, *Radiation Res.*, 1964, Suppl. 4, 139.
[57] M. S. Matheson, *Radiation Res.*, 1964, Suppl. 4, 1.
[58] J. W. Boag, *Amer. J. Roentgenol.*, 1963, **40**, 896.
[59] R. W. Fessenden, *J. Phys. Chem.*, 1964, **68**, 1508.

4 Reactivity of e^-_{aq}

A. Reactions in Irradiated Water.—The radiolysis of pure deærated water by high-energy electrons can be described by the following equation

$$H_2O \rightsquigarrow e^-_{aq}(2{\cdot}5) + OH(2{\cdot}3) + H(0{\cdot}6) + H_2(0{\cdot}45) + H_2O_2(0{\cdot}85) + H_3O^+(2{\cdot}5)$$

where the numbers in parentheses are the yields per 100 ev of energy absorbed. e^-_{aq} reacts rapidly with all these species except H_2 and possibly, albeit slowly, with water.

By adjusting the electron current of the accelerator the dose per pulse can be varied up to *ca.* 5000 rads. Typical oscilloscope traces obtained by the kinetic spectrophotometric technique are shown in Fig. 6 for samples of neutral water irradiated with 2 μsec. pulses of 4 Mev electrons (*a*) corresponds to the deposition of *ca.* 50 rads, (*b*) *ca.* 500 rads, and (*c*) *ca.* 5000 rads. At the highest dose, the concentration of e^-_{aq} at the end of the pulse is *ca.* 10^{-5}M and the rate of decay of e^-_{aq} is presented approximately by second-order kinetics. e^-_{aq} can undergo the following reactions with radiation products:

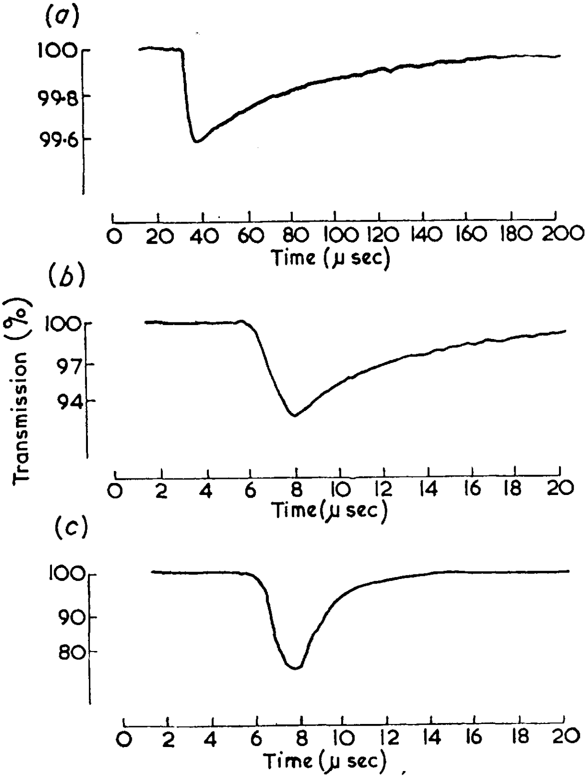

FIG 6. *Oscilloscope traces showing the variation of percentage light transmission as a function of time for* (*a*) *low,* (*b*) *intermediate, and* (*c*) *high-intensity electron pulses.*

$$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2OH^-_{aq} \tag{17}$$
$$e^-_{aq} + OH \rightarrow OH^-_{aq} \tag{18}$$
$$e^-_{aq} + H \rightarrow H^-_{aq} \tag{19}$$
$$e^-_{aq} + H_3O^+ \rightarrow H + H_2O \tag{20}$$
$$e^-_{aq} + H_2O_2 \rightarrow OH + OH^-_{aq} \tag{21}$$

Since e^-_{aq}, OH, and H_3O^+ are produced in comparable amounts reactions (17), (18), and (20) should be truly of the second order, but with different rate constants. Since H and H_2O_2 are produced with smaller yields than e^-_{aq} reactions (19) and (21) will contribute to a complex and time-variable extent to the decay of e^-_{aq}; in fact, since H_2O_2 is a stable product, (21) may be the dominant process in the later stages of the decay. The initial slope of a high-dose second-order plot would thus give a composite rate constant k given by eqn. (II).

$$k = 2k_{17} + k_{18}\frac{[OH]_0}{[e^-_{aq}]_0} + k_{19}\frac{[H]_0}{[e^-_{aq}]_0} + k_{20}\frac{[H_3O^+]_0}{[e^-_{aq}]_0} + k_{21}\frac{[H_2O_2]_0}{[e^-_{aq}]_0}\,. \tag{II}$$

where $[\;\;]_0$ corresponds to the concentrations of the various species at the end of the pulse. If reaction were not occurring during the pulse the concentration ratios would be given by the ratio of radiation yields. Gordon, Hart, Matheson, Rabani, and Thomas[32] obtained a series of theoretical curves by numerical computation on the basis of these reactions for selected values of rate constants and radiation yields and compared their experimental curves with the closest-fitting calculated curve to obtain the values k_{17}—k_{22} quoted in Table 2. Dorfman and Taub[60] have shown unambiguously that the combination of two hydrated electrons in reaction (17) give rise to molecular hydrogen, not hydrogen atoms. This was done by the pulse radiolysis of 0·5M-C_2H_5OD in D_2O which gave yields of D_2 and HD, $G(D_2) = G_{D2} + \frac{1}{2}G_{e^-aq}$ and $G(HD) = G_D$, expected on the basis of reaction (17).

B. Lifetime of e^-_{aq} in Water.—At doses per pulse less than 50 rads, when the concentration of e^-_{aq} is less than 10^{-7}M, first-order decay rates are prevalent. At 10^{-7}M however, the rate of reaction (20) with respect to the H^+_{aq} present in neutral water resulting from the ionic dissociation of water should follow second-order kinetics because this ionic dissociation is extremely slow. For smaller doses, when $[H_3O^+]$ is essentially constant, reaction (20) imposes an upper limit of 300 μsec. on the lifetime of e^-_{aq} in neutral water, so that the pH of the water must be adjusted appropriately for studies of reaction (6).

Early estimates of k_6 from first-order decay plots at doses of *ca.* 50 rads surprisingly gave values of similar magnitude in different laboratories [2—4 × 10^4 (ref. 32), $\leqslant 4{\cdot}4 \times 10^4$ (ref. 60), $2{\cdot}7 \times 10^4$ (ref. 61*a*), $\leqslant 5{\cdot}5 \times 10^4$ (ref. 61*b*), $4{\cdot}3 \times 10^4$ sec.$^{-1}$ (ref. 61*c*)], equivalent to a half-life for e^-_{aq} of 20—25 μsec. It

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[60] L. M. Dorfman and I. A. Taub, *J. Amer. Chem. Soc.*, 1963, **85**, 2370.

[61] (*a*) J. P. Keene, *Radiation Res.*, 1964, **22**, 1; (*b*) J. Rabani and G. Stein, *J. Chem. Phys.*, 1962, **37**, 1865; (*c*) G. Dobson and L. I. Grossweiner, *Trans. Faraday Soc.*, 1965, **61**, 708 (from flash photolysis).

was subsequently shown[52] that this half-life ($t_{\frac{1}{2}}$) could be increased to 47 μsec. by more rigorous purification, particularly complete elimination of CO_2 and by pre-irradiation. An increase in the pH to 9·8 increased $t_{\frac{1}{2}}$ further to 58 μsec. and a dose effect noted whereby $t_{\frac{1}{2}}$ increased as the dose per pulse was diminished. Thus values of 100—300 μsec. were obtained for $t_{\frac{1}{2}}$ for 10 rad pulses with chemically purified water.[62] Very recently Hart, Gordon, and Fielden[25] have examined reaction (6) using hydrogen-saturated solutions (to alleviate the build-up of H_2O_2 during the pre-irradiation purification) at pH = 8·3 (high enough to eliminate reaction (20) but not sufficiently alkaline to involve reaction (−6)) and at very low doses where $[e^-{}_{aq}] < 10^{-8}$M. They obtain an ultimate limit of $t_{\frac{1}{2}} = 800$ μsec, giving $k_6 = 16$ l. mole^{-1} sec.$^{-1}$.

Dewald, Dye, Eigen, and DeMaeyer[63] have made some most interesting measurements on the decay of the electron absorption when water is added to a dilute solution of electrons solvated in ethylenediamine. They find a first-order decay of e$^-$ after mixing is complete, the reaction rate being proportional to the water concentration used, and conclude from their results that $k_{22} = 20$ l. mole^{-1} sec.$^{-1}$.

$$e^-{}_s + H_2O \rightarrow H + OH^-{}_s \qquad (22)$$

It has been pointed out[25] that this value is very close to the best value obtained from pulse radiolysis for k_6, but some ambiguity exists because the nature of e$^-$ in reaction (22) is unknown. If (22) is the reaction of H_2O with electrons solvated in ethylenediamine, as seems likely since the kinetic results come from the rate of decay of this species, then it is probably not pertinent to compare k_6 with k_{22}. Because of the large variation in water concentration studied it is unlikely that the conversion $e^-{}_s \rightarrow e^-{}_{aq}$ is a non-rate-controlling step in this experiment and hence its relevance to reaction (6) is unknown.

Since in neutral water reactions (17) or (20) will predominate over (6) the latter will have no practical significance. Reaction (6) is, however, of fundamental importance in the estimation of thermodynamic data and because it determines the relative stability of $e^-{}_{aq}$ and hydrogen atoms in neutral water. Does $e^-{}_{aq}$ decay spontaneously or react with water, *i.e.*, does reaction (6) occur? The evidence for its occurrence is based solely on the fact that under conditions of great purity and at very low concentrations the first-order decay plots are linear. This may be unsubstantial evidence because, first, the concentration-dependence of the initial rates is in general a better test of the order of a reaction than the time-dependence of the rate and indeed the initial rate has been shown to be concentration-dependent, decreasing with decreasing dose per pulse.[25,62] Secondly, because of the inhomogeneity of primary radiation absorption in spurs and δ-rays, at very low doses the rate of reaction will not be uniform throughout the sample so that second-order plots of reactions (17), (18), and (20) would be non-

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[62] J. H. Baxendale, M. Ebert, J. P. Keene, and A. J. Swallow, Proc. Manchester Symposium on Pulse Radiolysis, 1965, Academic Press, London.

[63] R. R. Dewald, J. L. Dye, M. Eigen, and L. DeMaeyer, *J. Chem. Phys.*, 1963, **39**, 2388 (value of k_{22} revised slightly recently; personal communication from J. L. Dye).

linear anyway. Further, since the number of species per spur is small (2 to 20) many intraspur combinations will show first-order kinetics, and their contribution to the overall decay should increase continuously with diminishing doses. At 2 rads per pulse, for instance, the mean separation of spurs is *ca.* $1{\cdot}6 \times 10^4$ Å so that about 400 μsec. must elapse before the electron concentration can be considered uniform at 5×10^{-9}M and hence the actual local concentrations initially are not given simply by the dose and radiation yields.

An evaluation of the Arrhenius parameters for the supposed reaction (6) might resolve the dilemma. If the steric factor for all e^-_{aq} reactions is close to unity then an activation energy of some 12 kcal. mole^{-1} can be expected if $k_6 = 16$ l. mole^{-1} sec.$^{-1}$, whereas a typical activation energy for diffusion of 2—3 kcal. mole^{-1} might apply if the bimolecular reactions predominate or reaction with impurity is the limiting factor. Further, if reaction (6) does occur then its effect should be curtailed and the lifetime of e^-_{aq} extended by increasing the pH of the water to 12—14 whereupon equilibrium (6) will be well to the left.

C. Reactivity with Solutes.—If a solute S, which reacts with e^-_{aq} according to the generalised reaction (23), is added in sufficient concentration so that e^-_{aq} generated by pulse radiolysis react almost exclusively by reaction (23) then,

$$e^-_{aq} + S \rightarrow [S^-] \rightarrow \text{stable products} \qquad (23)$$

provided $[S] >> [e^-_{aq}]$, pseudo-first-order decay kinetics are observed. k_{23} is hence obtained directly from the observed half-life of e^-_{aq}. Because of the intense broad absorption band of e^-_{aq} and the sharp time resolution of the pulse characteristics a vast wealth of rate results pertaining to e^-_{aq} is readily obtained and now available. Anbar and Neta[64] have tabulated absolute rate constants for 280 reactions represented by reaction (23), including 164 with organic solutes. In Table 2 a few of these are presented principally to exemplify the diversity and trends in the reactivity of e^-_{aq}.

Since all reactions of e^-_{aq} are either electron-attachment or dissociative electron-transfer processes one might expect that the availability of a suitable low-energy molecular orbital governs the reactivity of a solute. Although a number of reaction rates involving e^-_{aq} appear to be limited only by the encounter rate, such as that with $Co(CN)_6{}^{3+}$, this is not so for k_{20}, the reaction between e^-_{aq} and H^+_{aq}, since the diffusion-controlled limit should be *ca.* 5×10^{10} l. mole^{-1} sec.$^{-1}$ for this charge-neutralisation process. If this is an electron-transfer reaction then the product of reaction (20) will be either H_3O or H_9O_4 (depending on the nature of H^+_{aq})[65] but not H immediately. There are other reasons for believing H_3O (or H_9O_4) to have a chemical importance.[66]

There are striking differences in the reactivity of e^-_{aq} with various organic

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[64] M. Anbar and P. Neta, *Intern. J. Appl. Radiation*, 1965, **16**, 227.

[65] M. Eigen and L. DeMaeyer, in 'The Structure of Electrolytic Solutions' (ed. W. J. Hamer), Wiley, New York, 1959.

[66] (*a*) H. J. Bernstein, *J. Amer. Chem. Soc.*, 1963, **85**, 484; (*b*) E. J. Hart, *Science*, 1964, **146**, 19; (*c*) M. Anbar and D. Meyerstein, *J. Phys. Chem.*, 1965, **69**, 698; (*d*) T. J. Sworski, *J. Amer. Chem. Soc.*, 1964, **86**, 5034.

TABLE 2 *Reactivity of various chemical species* (×) *with* e^-_{aq} *in dilute aqueous solution at* pH 7 (*values taken from ref.* 64)

×	(l. mole^{-1} sec.$^{-1}$)	×	k(l. mole^{-1} sec.$^{-1}$)
e^-_{aq}	5×10^9	$Co(CN)_6^{3+}$	$9·0 \times 10^{10}$
OH	3×10^{10}	$Fe(CN)_6^{3-}$	$3·0 \times 10^9$
H	$2·5 \times 10^{10}$	$C(NO_2)_4$	$4·6 \times 10^{10}$
H^+_{aq}	$2·3 \times 10^{10}$	Ethanol	$< 10^5$
H_2O_2	$1·3 \times 10^{10}$	Naphthalene	$3·1 \times 10^8$
H_2O	< 16	CH_3CO_2H (pH 5·4)	$1·8 \times 10^8$
O_2	$2·0 \times 10^{10}$	$CH_3CO_2^-$ (pH 10)	$< 10^6$
N_2O	$8·7 \times 10^9$	Benzene	$< 7 \times 10^6$
Cu^{2+}	$3·0 \times 10^{10}$	Nitrobenzene	3×10^{10}
Cd^{2+}	$5·2 \times 10^{10}$	Glycine	$<10^7$
Na^+	$< 10^6$	Ribose	$< 10^7$
NH_4^+	*ca.* $2·5 \times 10^6$	Purine	$1·7 \times 10^{10}$

solutes. Saturated hydrocarbons, alcohols, ethers, and amines, having no low-lying vacant orbitals, react sparingly, $k < 10^7$ l. mole^{-1} sec.$^{-1}$. Compounds containing unsaturated groups or halogens have high reactivities many showing rate constants well in excess of 10^{10} l. mole^{-1} sec.$^{-1}$. There is often a striking dependence on the extent of ionic dissociation; thus undissociated acetic acid has a comparatively high reactivity whereas the acetate ion is virtually unreactive. Amino-acids and sugars on the whole are unreactive whereas the pyrimidine and purine bases present in nucleic acids and other biologically important media are extremely reactive. Since e^-_{aq} is the predominant radiation-produced reducing species in aqueous systems and since the phenomenon of indirect action will apply in most biological material consisting of 80—90% water, these rate-constant data are clearly apposite to an elucidation of the biological effects of high-energy radiations. e^-_{aq} is unreactive towards benzene, phenol, and toluene and in general behaves as an efficient and sharply discriminating nucleophilic reagent.[67] Indeed its reactivity towards aromatic compounds is related to the electron density of the π orbitals in the ring as expressed by Hammett's σ-function.

5 Structure of e^-_{aq}

Although much information is available pertaining to the kinetic and thermodynamic properties of e^-_{aq} its nature and structure are still the subject of conjecture. Jortner has drawn comparisons with models of electron binding in other media to make approximate quantum mechanical calculations of the cavity size and of the energy levels and oscillator strength corresponding to the optical transition, all with reasonable success. This section deals with the variety of theories on electron binding.

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

A. Electron Binding in Various Media.—Whereas many gross similarities exist between the properties of electrons trapped in widely differing environments, certain detailed features seem to mitigate against an enveloping structural model. Different theories seem preferable for systems intrinsically very similar, as for excess electrons in the non-polar liquids helium and argon. In liquid helium short-range repulsions between the electron and helium atoms strongly suggest a large cavity or bubble structure containing the electron,[68] whereas strong long-range attractions in liquid argon lead to a quasi-free electron model in which the core–electron interactions are neglected.[69] Sometimes the data are conflicting. For instance, Anbar and Hart[53] have observed a single absorption band centred at 9200 Å attributable to the solvated electron in pulse-irradiated ethylenediamine whereas the absorption band corresponding to this species in solutions of metals in ethylenediamine occurs at 12,600 Å.[70]

Excess electrons in various liquids may be free or localised. When the electron moves too freely the liquid structure may not be perturbed as seems to be the case for liquid argon. Localisation in cavities, however, may arise from local fluid dilation as a result of short-range repulsions between the extra electron and electrons of the medium. This may be very short-lived, as in liquid helium, or long-range polarisation effects may provide some stability. If the polarisation is merely electronic then it can occur in both polar and non-polar media but for orientational polarisation the molecules of the medium must have a dipole moment and the time required for molecular rotation is necessary for solvation.

In 1933 Landau[71] suggested a model for *F*-centres in ionic crystals, suggesting the electron was trapped in the crystal structure by the polarisation of the dielectric medium induced by the presence of the extra electron. This 'polaron' model is now untenable for *F*-centres because the latter are best described as electrons at anion vacancies, where clearly there is no electrostatic discontinuity and hence no extraneously induced polarisation. However, Landau's polaron theory has been applied to explain electron binding by self-trapping in metal–ammonia solutions by Davydov,[72] Deigen,[73] and Platzman and Franck,[74] and these theories are discussed by Jortner, Rice, and Wilson.[75]

(i) *Metal–ammonia solutions.* Both the diminution of density and hyperfine splitting of the e.s.r. absorption indicate that the electron is located in a vacancy of some 3 Å radius in metal–ammonia solutions. This species is responsible for the absorption band centred at 15,000 Å. In estimating the energy levels available to the electron within such a cavity one could consider it to be either an electron-in-a-box problem, the electron being confined to a spherical volume of uniform field with infinitely steep potential walls, or nearly hydrogen-atom like, the field

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[68] W. T. Sommers, *Phys. Rev. Letters*, 1964, **12**, 271.

[69] H. T. Davis, S. A. Rice, and L. Meyer, *J. Chem. Phys.*, 1962, **37**, 2470.

[70] R. R. Dewald and J. L. Dye, *J. Phys. Chem.*, 1964, **68**, 121.

[71] L. Landau, *Physik Z. Sowietunion*, 1933, **3**, 664.

[72] A. S. Davydov, *Z. eksp. theor. Fiz.*, 1948, **18**, 913.

[73] M. F. Deigen, *Trudy Inst. Fizik. A. N. Ukrain. S.S.R.*, 1954, **5**, 105.

[74] R. L. Platzman and J. Franck, *Z. Physik*, 1954, **138**, 411.

[75] J. Jortner, S. A. Rice, and E. G. Wilson, in 'Solutions M'tal-Ammoniac' (ed. Lepoutre and Sienko), Benjamin, Paris, 1964.

decreasing coulombically from the central point. An electron-in-a-box calculation by Ogg[76] led to the result that for minimum energy the cavity would have to be 10 Å in radius, though subsequent refinements including those of electronic polarisation and surface-tension considerations yielded a cavity radius of *ca.* 4 Å.[77] An LCAO calculation was attempted,[78] the electron being assumed to have 1*s* and 2*p* wave functions centred on hydrogen atoms forming the walls of the cavity, but this model is invalidated by the observation that the appropriate proton chemical shift in the nuclear magnetic resonance (n.m.r.) spectrum was absent.[79]

The compromise model depicts the electron as incompletely confined to a cavity of uniform field and thus experiencing a coulombic fall-off outside. Although the energy levels will then be essentially hydrogenic, because of the penetration of the electron into the surrounding medium bulk properties, such as the polarisation energy of the medium regarded as a continuous dielectric, can be used instead of coulombic or exchange interactions. This forms the basis of the continuum treatments based on Landau's polaron concept. Jortner, Rice, and Wilson[75] have pointed out that *a priori* calculations of charge distribution and electron energy levels are not yet possible but that two approximations can be applied. The first of these, the electronic adiabatic approximation, assumes that the extra electron is much more loosely bound and therefore of lower mean velocity than the valence and core electrons of the medium; consequently the extra electron is affected by the potential resulting from the average charge distribution of the electrons of the medium. Jortner's quantum mechanical treatment of this, using a one-electron wave function, leads to an expression for the potential which at large interaction distances is proportional to $(1/D_{\mathrm{op}} - 1/\mathrm{D_S})$, where D_{op} and D_{s} are the high-frequency and static dielectric constants respectively. In the limit, then, this treatment gives the same results obtained in the earlier polaron models.[72,73,74]

Whereas in a crystal lattice the binding energy of an extra electron may be only 0·1 ev and the adiabatic approximation reasonably valid, in polar liquids this may be 1 to 2 ev and hence the extra electron is not substantially more weakly bound than valence electrons. Consequently electronic polarisation should be considered in estimating the binding energy since the electrons of the medium will be affected by the mean charge distribution of the extra electron. Jortner[80] has discussed this second approximation which treats the extra and medium electrons on an equal basis. Since the solution of the potential functions depends on the charge distribution of the electron itself this treatment is a self-consistent field (S.C.F.) approximation. Using wave functions for a 1*s* ground state and 2*p* excited state, Jortner has applied the S.C.F. method with considerable success to metal–ammonia systems. He computes a value for the energy of the $(2p \leftarrow 1s)$ transition of 0·93 ev when a cavity radius of 3·2 Å is taken. This

[76] R. A. Ogg, *Phys. Rev.*, 1946, **69**, 668.
[77] R. A. Stairs, *J. Chem. Phys.*, 1957, **27**, 1431.
[78] J. H. Simpson, *Proc. Roy. Soc.*, 1949, *A*,**197**, 269.
[79] J. V. Acrivos and K. S. Pitzer, *J. Phys. Chem.*, 1962, **66**, 1963.
[80] J. Jortner, *Mol. Phys.*, 1962, **5**, 257.

compares favourably with the experimental value of 0·80 ev for the energy of $\lambda_{\max}$ in ammonia.[81]

(ii) *F-Centres.* For *F*-centres the e.s.r. data show the electron to be largely confined to the vacancy but interacting to some extent with the first shell of cations.[82] For these systems too a semi-continuum model, termed a point-ion-lattice approximation,[82] has been developed in which it is assumed that the dipoles of the ions surrounding the *F*-electron point toward the centre of the cavity rather than following the detailed motion of the electron. Thus the absorption band is again described approximately by a $(2p \leftarrow 1s)$ transition.

B. Jortner's model for e^-_{aq}.—By analogy with the metal–ammonia solutions Jortner[55] has performed a variational calculation using hydrogenic-type wave functions for the ground and excited states based on the continuum model with the approximations applied previously. Since the binding energy of the extra electron in water should be higher than in ammonia because of the greater dielectric constants one may expect the S.C.F. to be the better approximation. Choosing appropriate one-electron wave functions for the ground, 1*s*, and first excited state, 2*p*, Jortner calculates the energy of the optical transition $h\nu = E_{2p} - E_{1s}$. Difficulties of non-spherical charge distribution in the excited 2*p* state are disregarded (as if the state were triply degenerate) and in addition it is a non-equilibrium state. This arises because the Franck–Condon restriction on electronic transitions allows the electronic polarisation but not the orientational polarisation to adjust itself to the charge distribution of the excited state. The orientational polarisation in the 2*p* state is consequently given by the potential function of the 1*s* charge distribution, f_{1s}. Thus Jortner describes the energy of the transition by the differences in the zero-point, orientational, and electronic polarisation energies of the two states according to eqn. (III)

$$\begin{aligned} h\nu = {} & \left[\int \psi_{2p}\left(-\frac{h^2}{8\pi^2 m}\nabla^2\right)\psi_{2p}\,d\tau - \int \psi_{1s}\left(-\frac{h^2}{8\pi^2 m}\nabla^2\right)\psi_{1s}\,d\tau\right] \\ & + e\left(\frac{1}{D_{\mathrm{op}}} - \frac{1}{D_{\mathrm{s}}}\right)\int \psi^2_{2p} f_{1s}\,d\tau - e\left(\frac{1}{D_{\mathrm{op}}} - \frac{1}{D_{\mathrm{s}}}\right)\int \psi^2_{1s} f_{1s}\,d\tau \\ & + \frac{e}{2}\left(1 - \frac{1}{D_{\mathrm{op}}}\right)\int \psi^2_{2p} f_{2p}\,d\tau - \frac{e}{2}\left(1 - \frac{1}{D_{\mathrm{op}}}\right)\int \psi^2_{1s} f_{1s}\,d\tau \qquad \text{(III)} \end{aligned}$$

where the symbols have their usual meaning in quantum mechanics. The wave functions ψ_{1s} and ψ_{2p} contain variational parameters which are related to the mean charge distribution of the state through a function governed by the cavity radius *R*. Jortner thus computes $h\nu$ for various values of *R* and finds that $h\nu =$ 0·93 ev when $R = 3{\cdot}3$ Å (as for electrons solvated in NH_3) whereas $h\nu = 1{\cdot}35$ ev when $R = 0$. Since the experimental value for $h\nu$ is 1·7 ev the cavity radius of e^-_{aq} appears to be vanishingly small. However, it should be noted from these

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[81] M. Gold and W. L. Jolly, *Inorg. Chem.*, 1962, **1**, 818.
[82] B. S. Gouray and F. J. Adrian, *Solid State Phys.*, 1960, **10**, 127.

calculations that the mean radius specifying the charge distribution in the ground state is 2·5—3·0 Å and in the excited state is 4·9 Å, so that although the size of the cavity is trivial the electron is rather widely spread out over the surrounding water molecules. The value of 2·5—3·0 Å should thus be appropriate for the evaluation of the diffusion coefficient and collision radius of e^-_{aq}. A success of the model is that values for these parameters so obtained show reasonable agreement with those from kinetic data.[32] On the basis of the larger surface tension, density, and dipole moment of water than of ammonia one would certainly have expected the electron to be associated with a much smaller and deeper trap in water.

Despite the evident success of Jortner's theoretical treatment there remain a few factors requiring consideration.

(i) Whereas one may qualitatively conjecture that the spectral band derives its broadness from variations in the size and shape of the cavities owing to disorder from thermal motions, it is not only very broad (half-width *ca.* 1 ev) but has similar proportions to the band in ammonia despite the exceptional differences in cavity size calculated for the two solvents. In both solvents there is asymmetry on an energy scale on the high-energy side but no discernible second band corresponding to ($3p \leftarrow 1s$) transitions. Nor does e^-_{aq} show signs of a convergence limit at 5400 Å. Perhaps this fine structure is masked by the broadness but accounts for the asymmetry. On this basis, at lower temperatures some of the thermal disorder should be removed but Dorfman[83] reports there to be no fine structure or narrowing of the solvated-electron band in irradiated liquid ethanol even at − 78°C. However, using the transition dipole moment, Jortner calculates the oscillator strength of the ($2p \leftarrow 1s$) transition to be $f = 1{\cdot}1$ when $R = 0$. This compares with the experimental value of *ca.* 0·8. If this can be regarded as a normal one-electron system in which $\Sigma f = 1{\cdot}0$ for all transitions from any one energy level then the oscillator strength for higher excited transitions might indeed be too small to observe.

(ii) In these calculations the excited state is assumed to be a bound state. Consequently e^-_{aq} should show neither photoconductivity nor photobleaching when illuminated with light corresponding to the wavelength of maximum absorption (λ_{max}). Such an experiment is difficult to perform on e^-_{aq} and analogies with other electron systems is conflicting. Irradiated glasses at low temperatures readily undergo photobleaching of the electron bands[16] whereas metal–ammonia solutions do not show photoconductivity.[84]

(iii) The shift of the absorption band with temperature should be mainly due to changes in the cavity size rather than in D_s or D_{op}.[55] Consequently Jortner predicts that $d(h\nu)/dT$ for metal–ammonia solutions should be 2 to 3 times greater than for e^-_{aq}. This is quite contrary to the experimental findings. $d(h\nu)/dT$ has values of 10·5 cm.$^{-1}$ deg.$^{-1}$ for solutions of sodium in ammonia[85] and 1·5 cm.$^{-1}$

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[83] L. M. Dorfman, 'Advances in Chemistry', Series 50, 1965, American Chemical Society.

[84] R. L. Potter, R. G. Shares, and J. L. Dye, *J. Chem. Phys.*, 1961, **35**, 1907.

[85] (*a*) H. Blades and J. W. Hodgins, *Canad. J. Chem.*, 1955, **33**, 411; (*b*) R. C. Douthit and J. L. Dye, *J. Amer. Chem. Soc.*, 1960, **82**, 4472.

deg.$^{-1}$ for potassium in ethylamine[86] but 25 cm.$^{-1}$ deg.$^{-1}$ for e^-_{aq}[54] and 29·2 cm.$^{-1}$ deg.$^{-1}$ for e^- in ethanol.[83]

(iv) Jortner's model appears to predict a ($2p \leftarrow 1s$) transition energy for electrons solvated in aliphatic alcohols intermediate between water and ammonia. In fact λ_{max} for methanol appears at *ca.* 2·1 ev.[83]

C. Alternative Models.—If the spherically symmetric potential well of the electron solvation sheath contains various energy levels these must be quantised. If the potential function is hydrogenic then the separation between successive levels diminishes towards the convergence limit and the first transition, $2p \leftarrow 1s$, is three-quarters of the well depth. This is demonstrated in Figure 7(*a*). Baxendale[56] has calculated the hydration energy ($\triangle H_S$) of e^-_{aq} to be 1·72 ev, exactly equal to $E_{\lambda_{max}}$. This may or may not be fortuitous. If the polarisation energy of the medium, E_P, is substantial then the energy required to remove the electron from the well, the ionisation potential I_P, will be different from $\triangle H_S$ as indicated in Figure 7(*b*). If the coincidence $E_P \approx \frac{1}{4}E_{\lambda_{max}}$ then $\triangle H_S$ will be given by $E_{\lambda_{max}}$. Figure 7(*b*) may represent the Jortner model, the asymmetry arising from weak but significant transitions to higher excited levels than $2p$.

On the other hand, if the disparities cited above are substantiated, particularly regarding the photobleaching at λ_{max} which occurs for the low-temperature glasses (similarities between solvated and trapped electrons being discussed later) then perhaps λ_{max} corresponds to the release of the electron from the trap. At wavelengths less than λ_{max} the electron may be excited into a conduction band giving rise to a continuum on the high-energy side. This is depicted in Figure 7(*c*), the absorption band corresponding to an ionisation-efficiency profile representing the transition probability of excitation to levels above the ionisation potential. The ill-defined low-energy cut-off may result from the numerous structural variations of the potential well and perhaps sub-ionisation excitation levels within the trap such as E_{λ_a} in Figure 7(*c*). A combination of ionisation continuum and symmetrical charge-transfer absorption band is also a possibility, particularly if neighbouring unexpanded cavities exist as Freeman and Fayadh have suggested even for non-polar liquids.[87]

If optical absorption corresponds to the release of an electron from a potential well, the broadness, asymmetry, and shape could alternatively result from the occurrence of many orientations of solvent molecules giving rise to wells of differing depths. Figure 7(*d*) shows this, λ_{max} merely corresponding to the most probable but comparatively tenuous trap. If the distribution of traps is not in thermal equilibrium, photolysis at λ_{max} would cause the absorption maximum to shift to higher energies since only traps of energy $\leqslant E_{\lambda_{max}}$ would be affected. Photolysis at λ_{max} in the case represented by Figure 7(*c*) would lead to a diminution of the absorbance without altering the shape of the band.

Despite enormous differences in stability, electrons caught in the polarisation fields of polar liquids or glassy or crystalline solids all have very similarly shaped

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[86] L. R. Dalton, J. D. Rynbrandt, E. M. Hansen, and J. L. Dye, personal communication.
[87] G. R. Freeman and J. M. Fayadh, *J. Phys. Chem.*, 1965, **43**, 86.

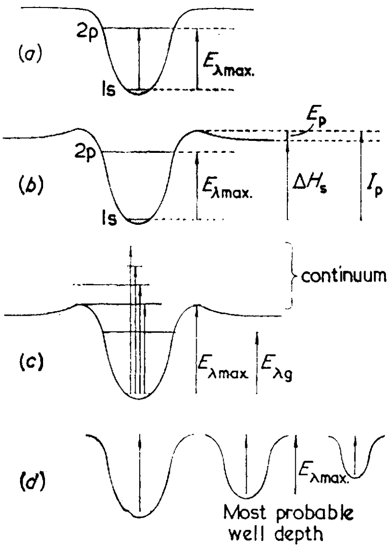

FIG. 7. *Energy levels corresponding to possible absorption processes (see text for details).*

absorption bands. Whether it is metal–ammonia solutions peaking at 15,000 Å or *F*-centres with band maxima in the visible region, the shape and proportions are analogous. Are these 'trapped' or 'solvated' electrons?

D. Trapped and Solvated Electrons.—An arbitrary distinction between trapped and solvated electrons could be whether or not the potential well existed before the arrival of the electron at the site. This seems to be more meaningful than simply distinguishing solids from liquids or orderly from randomly polarised centres. On this basis *F*-centres are clearly trapped electrons. Crystalline solids in general because of the orderliness and immobility, particularly at temperatures much below their melting points, may only 'trap' electrons and then only at crystal defects of which *F*-centres are a type. Thus Ghormley and Stewart[88] did not observe any colour due to e^-_{aq} in irradiated clear ice at 77°K. As Platzman[31] has pointed out the relaxation time of ice at low temperature could be several years and hence the electron moves rather freely. The structure of ice apparently does not contain potential wells capable of trapping electrons except when the crystal is distorted or defective, nor can orientational polarisation occur.

Liquids at room temperature cannot normally give rise to stable traps either. Since in water for instance the dipolar relaxation time is about 10^{-11} sec. a potential trap formed by the random orientation of neighbouring molecules cannot exist much longer than 10^{-11} sec. in the absence of a stabilising influence

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[88] See C. J. Hochanadel, N.A.S.-N.R.C. Reports 1953, No. 305, pp. 43–44.

such as the arrival of an electron. It might be pertinent to ask if e^-_{aq} is a solvated electron and formed entirely by self-induced dipolar orientations, or if the electron is trapped in an existing polarised site resulting from random orientations. A thermalised electron in water at room temperature will pass a molecule in a period too short for orientational polarisation and may therefore only cause self-induced electronic polarisations. Orientational polarisations may then follow in fluid media; but at 77°K rotations will be extremely sluggish if possible at all. Despite this, however, the absorption spectra of electrons stabilised in low-temperature glasses are virtually identical with spectra obtained in the liquid phase at room temperature. Since water does not readily form a glass comparisons in pure water are not currently possible, but two very closely related systems, namely a concentrated aqueous solution and methanol, are compared in Figure 8. Curve (*c*) shows the electron absorption band in pulse-irradiated 15M-sodium hydroxide in water at 25°C[53] whereas curve (*d*) was obtained by γ-irradiation of 6M-sodium hydroxide aqueous glass at −196°C.[89] These curves are identical except for the shift of the whole spectrum owing to the temperature change. Similarly, curve (*a*) shows the electron-absorption band at 6500 Å in pulse-irradiated liquid methanol at 25°[90] whereas curve (*b*) was obtained by γ-irradiation of methanol glass at −196°.[90] Again the spectra are identical but for a normal temperature shift. (The value of $G\epsilon$ reported was three times larger for the low-temperature irradiation. This could possibly result from an alteration of the extinction coefficient but is more probably a yield effect.)

To have identical solvent orientations and distribution of orientations in fluid and rigid phases suggests that the electrons are not in fact polarons but are trapped in existing potential wells resulting from the mean instantaneous distribution of molecular orientations, this distribution being frozen-in when glassy solids are made. When cooling produces crystallisation on the other hand an ordered pattern of molecular orientations results which seldom permits the occurrence of electron stabilisation, except at defect sites. Thus electron yields in glasses are invariably larger than in the corresponding crystalline phase.[91]

The mobility of e^-_{aq}, and indeed electrons in other polar media, could consequently arise from jumping or tunnelling between existing potential traps. This may account for the facts that the rate of reaction of e^-_{aq} with many solutes is governed more by the solvation energy of the activated complex than that of the electron[53] and that electrons solvated in water, ethanol, and methanol react with H^+ at similar rates.[66b] On this basis too the absorption spectrum would correspond to a charge-transfer-to-solvent phenomenon. Recently a linear relationship has been noted between the energy of λ_{max} for the charge-transfer spectra of iodide ions and that for electrons solvated in the various media, corroborating the prediction made by Platzman and Franck.[74]

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[89] F. S. Dainton and N. Gopinathin, unpublished work.

[90] F. S. Dainton, J. P. Kenne, T. J. Kemp, G. A. Salmon, and J. Teply, *Proc. Chem. Soc.*, 1964, 265.

[91] (*a*) F. S. Dainton and F. T. Jones, *Trans. Faraday Soc.*, 1965, **61**, 1681; (*b*) T. Henriksen, *Radiation Res.*, 1964, **23**, 63; (*c*) R. Livingston and A. J. Weinberger, *J. Chem. Phys.*, 1960, **33**, 449.

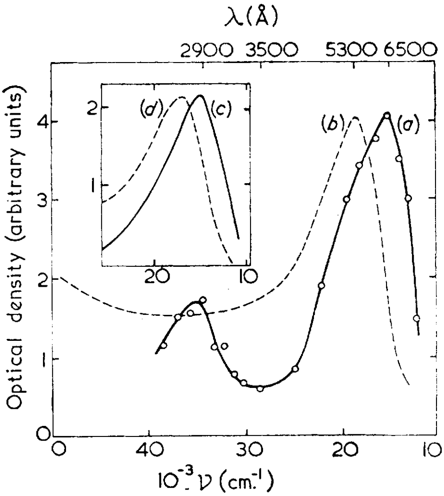

FIG. 8. *Comparisons of absorption spectra of solvated and trapped electrons. (a) Methanol at* 25°,[90] *(b) Methanol at* −196°,[90] *(c)* 15M-NaOH *in water at* 25°,[53] *(d)* 6M-NaOH *glass at* −196°,[89]

6 Conclusions

Whereas the chemical distinction of hydrated electrons and hydrogen atoms is rather esoteric they are readily distinguished spectroscopically, in both the optical and microwave regions. e^-_{aq} has been shown to have a broad intense absorption spectrum throughout the visible region whereas hydrogen atoms absorb only in the far vacuum ultraviolet at ordinary temperatures. Also, because of the weak interactions with protons forming the walls of the cavity shown by stable solvated electrons, one would expect similar very narrow splittings of the e.s.r. absorption in the case of e^-_{aq} in marked contrast to the enormous hyperfine splitting shown by hydrogen atoms.

This Review is concluded with a summary of the principal structural, kinetic, and thermodynamic parameters pertaining to e^-_{aq}. and the knowledge of many of the fundamental properties of e^-_{aq} is summarised in Table 3.

Combining the value quoted for the diffusion coefficient of e^-_{aq} with the rate constant for reaction (17), $k_{17} = 5 \times 10^9$,[64] one calculates an effective reaction diameter for e^-_{aq} of *ca.* 5 Å which agrees well with the calculated charge distribution of the 1*s* ground state, corroborating the Jortner model. The thermodynamic results were calculated by Baxendale[56] with subsequent small corrections applied for the more recent value of k_6.[25] For equilibrium (6) one can calculate the

$$e^-_{aq} + H_2O \rightleftharpoons H + OH^- \qquad (6)$$

standard free-energy change $\Delta G° = +8{\cdot}4$ kcal. mole^{-1} from the values of $k_6 = 16$ l. mole^{-1} sec.$^{-1}$ and $k_{-6} = 2{\cdot}2 \times 10^7$ l. mole^{-1} sec.$^{-1}$. Combining this with $\Delta G°$ for the reactions $H \rightarrow \frac{1}{2}H_2$ and $H^+_{aq} + OH^-_{aq} \rightarrow H_2O$ one obtains for the reaction $e^-_{aq} + H^+_{aq} \rightarrow \frac{1}{2}H_2$, $\Delta G° = -61{\cdot}8$ kcal. mole^{-1}. On the conventional

TABLE 3

		Ref.
Absorption maximum (λ_{max})	7200 Å (1·72 ev)	50
Estimated heat of solution (ΔH_S)	$\geqslant$ 1·72 ev	*a*
Calculated first excitation energy (Jortner model)	1·35 ev	55
Molar extinction coefficient at λ_{max}	15,800 l. mole^{-1} sec.$^{-1}$	51
Oscillator strength, obs.	*ca.* 0·8	43
calc.	1·1	55
Calculated cavity size	*ca.* 0	55
Calculated mean radius of charge distribution: In ground state (1*s*)	2·5—3·0 Å	55
In first excited state (2*p*)	4·9 Å	55
Diffusion coefficient	4·5 × 10^{-5} (+ 15%) cm.^{2} sec.$^{-1}$	*b*
Ge^-_{aq} in neutral water	2·5 + 0·1	57
Lifetime with respect to ($e^-_{aq} + H_2O \rightarrow H + OH^-$)	$t_{\frac{1}{2}} \geqslant 800\ \mu$sec.	25
Lifetime in neutral water (H_3O^+ *ca.* 10^{-7}M)	$t_{\frac{1}{2}} = 300\ \mu$sec.	
Standard electrode potential	< 2·67 v	*a*
pK_a for $H \rightleftharpoons e^-_{aq} + H^+_{aq}$	< 9·7	*a*

[a] Baxondale's results (ref. 56) adjusted for the recent value of k_8 = 16 l. mole^{-1} sec.$^{-1}$
[b] Personal communication quoted in ref. 66^b.

scale therefore the hydrated electron has a standard electrode potential of 2·67 v. Baxendale makes the comparison with the value of 2·1 v for the hydrogen atom from which it is evident that e^-_{aq} is the stronger reducing agent. He suggests in addition that, since the convention of quoting standard potentials is based on the arbitrary assumption that $\Delta G° = 0$ for the standard hydrogen electrode [reaction (24)], it is now possible to adopt an absolute scale which would thus

$$H^+_{aq} + e^- \rightarrow \tfrac{1}{2}H_2 \tag{24}$$

require all potentials to be 2·67 v more negative. However this suggestion neglects differences in free energy between the electron of reaction (24) which is an electron (free) on the surface of an electrode, and e^-_{aq} for which the above result was evaluated. These will differ by at least the solvation energy of e^-_{aq} (1·72 v).

The solvation energy (ΔH_S) of e^-_{aq} was evaluated by Baxendale from the cycle shown below, a value of −260·5 kcal. mole^{-1} being used for the abso-

$$\begin{tikzcd}
e^-_{aq} \arrow[d, "\Delta G_S"'] & + & H^+_{aq} \arrow[d] & \rightarrow & (\tfrac{1}{2}H_2)_{aq} \\
{} & & {} & & & {} \arrow[ul]
\end{tikzcd}$$

Baxendale compares this with the free energy of hydration of halide ions and notes that for I^- ($\triangle G_s = 57$ kcal. mole^{-1}), which is closest to $e^-{}_{aq}$, the contribution made by the entropy of hydration can be neglected. Thus the enthalpy and free energy of hydration are equated so that $\triangle H_s = -39{\cdot}7$ kcal. mole^{-1} or 1·72 ev. Since the hydration energy is a function of the ionic radius this small hydration energy implies a distribution of charge of $e^-{}_{aq}$ certainly greater than the 2·2 Å radius of the iodide ion,[92] a further endorsement of Jortner's calculations.

$\triangle H_s$ calculated in this way must however be regarded as approximate since its evaluation requires an absolute value for a thermodynamic function of an individual ion for which there is no strict thermodynamic basis.[92] It should also be noted that since $k_6 = 16$ l. mole^{-1} sec.$^{-1}$ is an upper limit the values quoted for the standard potential and pK_a are maxima and the value of $\triangle H_s$ is a minimum. If the value for pK_a falls much further (to *ca.* 8) any studies of the lifetime of $e^-{}_{aq}$ with respect to its reaction with water (reaction 6) will be impossible since for any pH reactions (−6) or (20) will predominate. The hydrogen atom is evidently a stronger acid than is water and consequently $e^-{}_{aq}$ is a weaker base than OH^-. It is not surprising then that $e^-{}_{aq}$ abstracts a proton from H_2O very slowly, *i.e.*, that k_6 is small.

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[92] K. B. Harvey and G. B. Porter, 'Introduction to Physical Inorganic Chemistry', Addison-Wesley, 1963.