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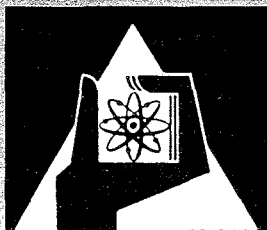
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Radiation Chemistry of Frozen Aqueous Solutions

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RADIATION CHEMISTRY OF FROZEN AQUEOUS SOLUTIONS

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Introduction

It is generally accepted that the following reaction intermediates play a role in the primary processes of water radiolysis: H_2O^+ , e^- , H_2O^* , H, and OH. The same intermediates are also important in frozen aqueous media.

In this paper the present state of our knowledge about the formation, identification and the reactivity of the electron and the hydrogen atom in frozen aqueous solutions is reviewed.

The electron (e^-)

In irradiated frozen alkaline aqueous solutions at 77 °K, trapped electrons were first observed early in 1962^{1,2}). The identification was based on the following facts. On γ -irradiation a blue colour appeared, which had an extinction maximum of 585 $\text{m}\mu$ ¹⁻³). Together with this visible absorption there appeared a singlet in the ESR spectrum with a line width of about 15 gauss and a g -factor approximately that of the free electron³⁻⁵). Recent work has been mainly concerned with two problems: first, the structure of the electron traps and secondly, the reactivity of the mobile and the trapped electrons.

Structure of the electron trap

Several ideas have been suggested to explain the structure of an electron trap in frozen alkaline solutions. These are (a) that the electron is located on an expanded orbital of a cation²), (b) that the electron is located on an expanded orbital of an O^- radical-ion^{6,7}), (c) that the electron is located in an anion vacancy^{4,8}), and (d) that the electron is trapped only by water molecules^{1,3,9}).

It is now clear that the nearest neighbours of the trapped electron are hydroxyl groups and not cations. This conclusion is based on the following experimental results:

(1) The position of the electron absorption maximum is hardly changed if the cation is varied, but the position is changed to a much larger extent if D₂O is used instead of H₂O as the solvent (table 1).

TABLE 1

Absorption maxima of trapped electrons in frozen solutions at 77 °K^{1,23}).

Solvent	Solute	Concentration (mol/l)	λ_{\max} (m μ)
H ₂ O	LiOH	4	blue
H ₂ O	NaOH	7	585
H ₂ O	KOH	7	585
H ₂ O	RbOH	7	585
H ₂ O	CsOH	7	585
D ₂ O	NaOD	7	560
CH ₃ OH	—	—	540
CH ₃ OH	CH ₃ ONa	3	540
CH ₃ OH	CH ₃ OK	3	540
CH ₃ CH ₂ OH	—	—	590

(2) The band width of the e_t^- singlet in the ESR spectrum is only slightly changed when the cations are varied. However, a strong reduction of the band width occurs when D₂O is used instead of H₂O as the aqueous component (table 2). Symons *et al.*⁴), Moorthy and Weiss⁶), Kevan¹⁰) and Bennett, Mile and Thomas¹¹) concluded that this result rules out the possibility that the electron is located on an expanded orbital of a cation, since in this case a larger interaction between the cations and the electrons should be observed. Equally, the term F-centre is not an ideal expression to designate a trapped electron in ice, if an F-centre is defined as an electron in an anion-

TABLE 2

Line width and g -factor of trapped electrons in irradiated alkaline ice at 77 °K after Moorthy and Weiss⁶).

System	g -factor	Line width (gauss)
LiOH/H ₂ O	2.0010	17.6
NaOH/H ₂ O	2.0006	15.9
KOH/H ₂ O	2.0003	14.7
LiOH/D ₂ O	2.0005	5.3
NaOH/D ₂ O	2.0003	6.3
KOH/D ₂ O	1.9999	5.5

vacancy surrounded by cations. Indeed, the presence of cations is not necessary to provide a trap in a frozen medium which contains hydroxyl groups, as is shown by the fact that electrons are trapped in glassy methanol at 77 °K during γ -irradiation with nearly the same efficiency as in 8 M aqueous alkaline glass⁹). The absorption spectrum of these trapped electrons is very similar to that of γ -irradiated alkaline aqueous glass, whereas the electrons trapped in frozen ethers have different optical properties. Moreover, if explanation (a) above were valid it would be difficult to account for Kevan's observation that the nature of the cation has no influence on the G -value of trapped electrons in alkaline ice¹²). Also, since irradiated methanol glasses contain no cations or O^- ions, the electron cannot be located at an expanded orbital of an O^- radical ion. Further support for the view that water molecules by themselves can form a trap for an electron is the observation of Marx, Leach and Horani¹³) that a blue colour appears in amorphous ice condensed from irradiated water vapour. It therefore seems reasonable to assume that the electron trap consists of a hole which is surrounded by oriented hydroxyl groups, the number of which has been estimated by Moorthy and Weiss, to be about 8⁶). Bennett, Mile and Thomas investigated the blue colour and ESR spectrum formed when sodium vapour is condensed on ice, and concluded that four protons are the nearest neighbours of the electron¹¹). Kevan estimated from ESR work that the diameter of the trapped electron in irradiated ice should be 6–8 Å¹⁰). This result is in rough agreement with a value of 5–6 Å estimated by Jortner for a e_{aq}^- in liquid water¹⁴).

We therefore conclude that the electron is not spread over a large area of water molecules as is postulated in the original polaron model, but that the electron moves in the Coulomb field provided by the positively charged protons of the polar O–H groups. This picture shows that some analogy does exist between an F-centre in a crystal and a trapped electron in a hydroxyl-group-containing medium. This analogy was pointed out by Symons and co-workers⁸). From the analogy between F-centres in crystals and trapped electrons in ice, it follows that a defect or a vacancy should be present in the ice in order to trap an electron. Here the question arises as to whether the irradiation itself produces the trap, (e.g., an anion vacancy by the reaction $H^+ + OH^- \rightarrow H_2O$, where the proton comes from H_2O^+) or whether the trap is already present in the ice before irradiation.

Scavenger experiments show that the electron is trapped not less than 10 Å from the molecule from which it was ejected by the effect of the radiation. This makes it unlikely that the electron is trapped in an anion vacancy produced in the same spur. But the electron is also not trapped in an anion vacancy of another spur since $G(e_{tr}^-)$ for 8 M alkaline glasses is high ($G(e_{tr}^-) = 2.0 \pm 0.5$)^{9,12}) and does not depend on the dose received below the saturation region. From this consideration one can conclude that the traps are not formed by the irradiation, but must be present before irradiation. Since the traps can only consist of lattice defects, it follows that the sample with a higher degree of disorder and therefore with a higher concentration of defects should show in general a larger yield of trapped electrons than the corresponding crystals. One would expect further that the reactivity of the electrons in the solid matrix should be facilitated in a glassy phase, because some degree of reorientation and change in volume, assumed to be necessary for a reaction with electrons, should be much easier in the disordered glassy phase than in a perfect crystal. An example which shows the difference in the reactivity of electrons in a glassy and in a crystalline phase is discussed in the section, "Formation of H-atoms".

In order to show experimentally the influence of the lattice disorder on the trapping ability of ice, one has to compare the undisturbed ice lattice with an ice matrix in which the ice structure has broken down. The breakdown of the ice lattice can be obtained by adding ionic salts, e.g., alkali hydroxide, since the solvation shell and the volume of the ion disturb the ice lattice. It is expected from such an experiment that the $G(e_{tr}^-)$ value will increase with alkali hydroxide concentration up to a very high concentration, because each ion only perturbs its immediate environment. The experimental results show that this behaviour is indeed found by different authors^{6,9,10}).

Reactions of electrons in ice

Moorthy and Weiss found that univalent zinc and cadmium ions are formed on irradiation of frozen aqueous solutions containing the divalent cations⁷). The reduction proceeds by reactions with electrons in a similar manner to that observed in water at room temperature as found by Adams, Baxendale and Boag¹⁵).



Brown and Dainton studied similar reactions in frozen acid glass, measuring the absorption spectra of a number of metal cations formed in unusual valency states e.g., Mn^+ , Co^+ , Ni^+ , Ga^{2+} , Ag^0 , Cd^+ , In^{2+} , Tl^0 ¹⁶). The spectra of three of these are shown in fig. 1.

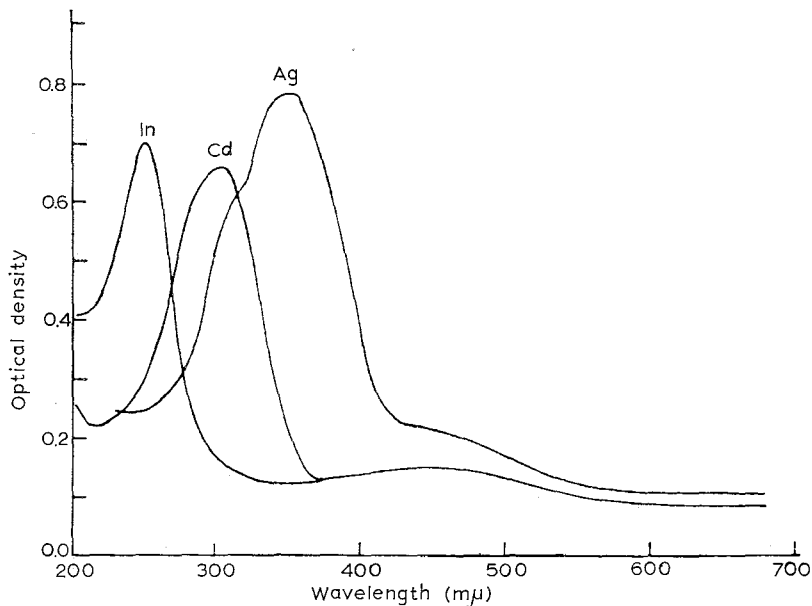
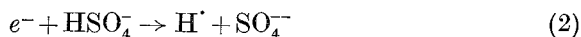


Fig. 1. Absorption spectra produced by γ -irradiation at 77 °K of deaerated 5.4 M H_2SO_4 containing 10^{-2} M Ag^+ , 10^{-2} M Cd^{2+} and 10^{-2} M In^{3+} ¹⁶).

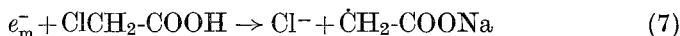
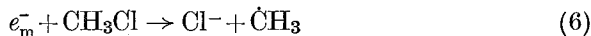
Electrons can react also with Brønsted acids such as HSO_4^- as Kevan, Moorthy and Weiss have found¹⁷). In this reaction H-atoms are formed in the following manner:



The reactions of mobile electrons with organic-halogen-containing compounds have been observed by Ayscough, Collins and Dainton, Dainton and Gopinathan^{18,21}) and Schulte-Frohlinde and Eiben in Karlsruhe⁵).

If methylechloride or chloroacetic acid is added to alkaline ice in concentrations lower than 10^{-2} M/l, neither the ESR spectrum nor the blue colour is influenced. However on illumination with white light the blue colour disappears and at the same time the ESR spectrum

changes. The line of the trapped electron (line A, fig. 2) vanishes and a new signal appears, which is, in the case of methylchloride, a quartet, and, in the case of chloroacetic acid, a triplet (fig. 2). The reactions occurring can be described by the following sequences:



where m=mobile and t=trapped.

It is interesting to note that in these experiments a mobile, i.e., a quasi-free, electron undergoes the reaction and not a solvated electron as usually in liquid water.

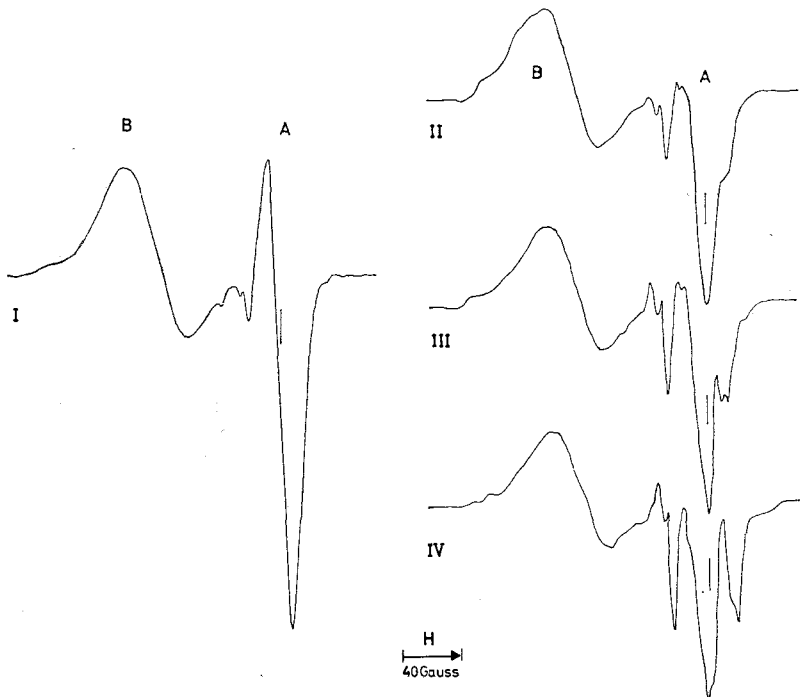


Fig. 2. ESR spectra of γ -irradiated alkaline ice at 77 °K. 6 M KOH/NaOH + 10^{-2} M ClCH₂COOH. I: after γ -irradiation (dose 1.3×10^{18} eV/ml); II and III: after γ -irradiation and during illumination with white light; IV: after bleaching of the blue colour⁵).

Phase effect

Dainton and Jones¹⁹⁾ and Dainton and Gopinathan²⁰⁾ studied the reactivity of mobile electrons in frozen 5 M sulphuric acid in the presence of the electron scavengers N_2O and $ClCH_2COOH$. The results for N_2O show that there is a large phase effect (fig. 3). In the glassy phase the $G(N_2)$ value is high, whereas in the crystalline state it is

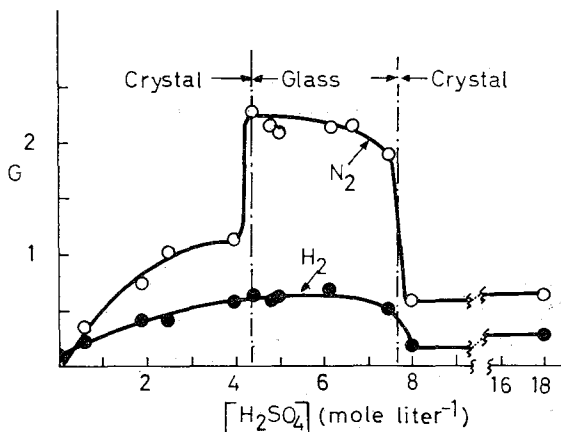


Fig. 3. The effect of acid concentration on the radiolysis at 77 °K of aqueous systems containing 0.0116 M N_2O ¹⁹⁾.

smaller. At present it is not clear whether this is due to a real phase effect or whether in the crystalline state some segregation of the N_2O from the lattice occurs. Since the N_2 is the product of the reaction of electrons with N_2O , it follows that the reaction of $e^- + N_2O$ is faster in the ice than the reaction $e^- + H^+$, if the concentration of H^+ is the same in the ice as in the corresponding liquid.

Thermal disappearance of electrons

Dainton and Gopinathan²¹⁾ studied the disappearance of trapped electrons upon heating of irradiated alkaline ice. The interesting result is that the blue colour of the electrons does not decay in a kinetically uniform way. There are three distinct temperature ranges, each having a distinct extent of decay and kinetic order: a high temperature region where the decay is clearly first order. In the low temperature range the bleaching is incomplete after five hours and neither $\log OD$ nor OD^{-1} is a linear function of time (OD = optical density). In an intermediate temperature range the decay appears to

be precisely of second order. There is no evidence of these effects being associated with electron traps of different depths. In the first place λ_{\max} and the general shape of the absorption spectrum are unchanged as the bleaching proceeds, and in the second place the decay constant is unaffected by the dose received. A possible explanation is the following.

Two radicals are present in the irradiated alkaline glass, e_t^- and O^- . These two radicals disappear together on warming (reaction 8).



Reaction (9) competes with this process, yielding hydrogen. However, hydrogen is formed only in a very low yield ($G=0.14$). Therefore reaction (8) is the most important.

The complex kinetics are explained on the assumption that a set of different first-order reaction rate constants exist for reaction 8). One of the suggested reasons for this assumption is that the e^- and O^- radicals are not distributed uniformly. The distance between e_t^- and O^- is estimated from scavenger experiments to be about 20–25 Å whereas the distance in the case studied should be 200 Å, if uniform distribution is assumed. These results also imply that the electron travels distances of at least 20–30 Å in solids before being trapped and that the spur size may be in this region.

The H-atom

As first found by Livingston, Zeldes and Taylor²²), hydrogen atoms are produced by γ -irradiation of acid ice at 77 °K. The ESR spectrum consists of a doublet with a g -factor of nearly that of a free electron and a hyperfine splitting of 504 gauss. This large splitting is charac-

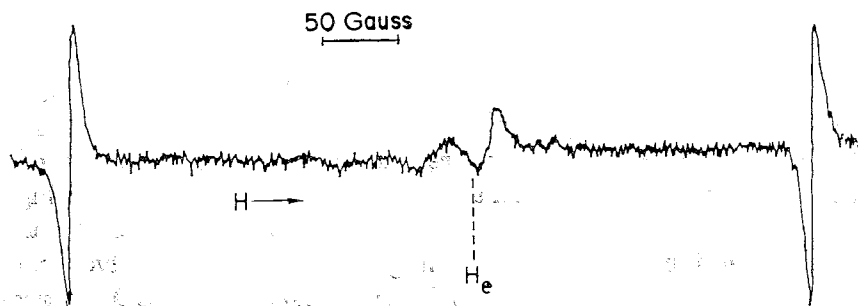


Fig. 4. ESR spectrum of ice γ -irradiated and observed at 4.2 °K²³).

teristic of the H-atom. The doublet is replaced by a triplet, if D_2O is used instead of H_2O . Later, it was found that H-atoms are formed by irradiation of pure neutral ice at the temperature of liquid helium ^{23,24}).

Formation of H-atoms

Livingston and Weinberger ²⁵) showed that there is a strong phase effect on the G -value for the formation of H-atoms. In rapidly frozen glassy sulphuric acid the $G(H)$ -values are much higher than in crystalline samples, which are obtained by annealing of glassy samples. In this case, segregation of the components is unlikely because, for instance, the monohydrate of H_2SO_4 is known to be a fairly stable compound.

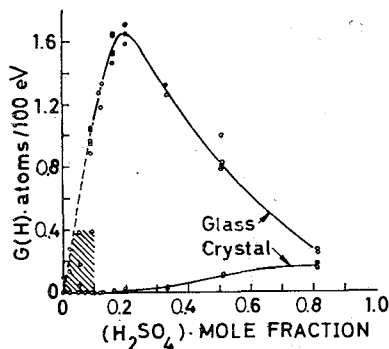


Fig. 5. Atomic-hydrogen initial yields from aqueous sulphuric acid irradiated with γ -rays and examined at 77 °K ²⁵).

It is more reasonable to assume that the large disorder in the glassy state facilitates the production and trapping of hydrogen atoms and that the differences found must be due to a real phase effect.

This result is an example of the fact that usually the G -values in crystalline phases are smaller than in glassy phases or liquids. The question then arises as to what happens to the electrons in a crystalline phase in which neither intermediates nor products are formed. The answer must be that the electrons return to the sites in which they were generated, which may be because they do not escape the Coulomb field of the counter-ion. This back-reaction does not give products or intermediates because of a large cage effect in a perfect crystal which prevents that dissociation becoming apparent.

The chemical nature of the reactions to H-atoms has been studied by Kevan, Moorthy, and Weiss ^{7,17}). As already mentioned, the authors assume that the main reaction leading to H-atoms even in acidic ice is the reaction of electrons with Brønsted acids. They have found further that H-atoms are formed also in neutral ice in the presence of added salts. The $G(\text{H})$ -values appeared to be very small, and from the concentration dependence and other considerations it is concluded that the H-atoms are trapped in the solvation shell of the ions. The formation of the H-atoms in this case does not include electrons, since electron scavengers have no effect on the yield. Moorthy and Weiss suggest, therefore, that the H-atom in this case is formed by dissociation of the excited water molecules.

Thermal disappearance of H-atoms

Flourney *et al.*²⁶) studied the disappearance of H-atoms in pure neutral ice at temperatures between 4.2 °K and 77 °K. They found that the decay did not follow a simple order. At a fixed temperature some of the H-atoms disappeared very rapidly, while the rest disappeared much more slowly. These results may be explained by assuming either that there are traps of different depths, each having different characteristic activation energies of release, or that spur effects may be important. In the light of the new results of Dainton and Gopinathan on the decay of electrons in alkaline ice, the last

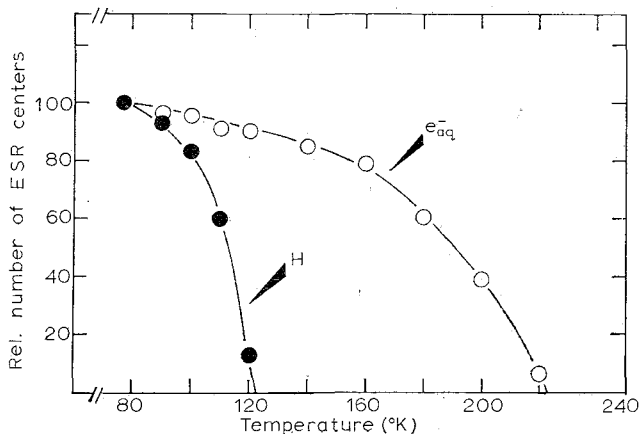


Fig. 6. Effect of stepwise heat treatment on the number of H-atoms and solvated electrons in 10 M NaOH/H₂O ice at 77 °K ²⁷).

explanation is the more likely. In ice containing 12.9 Mol/% sulphuric acid, H-atoms disappear according to a second-order kinetic law. Since the G -value for the formation of the molecular hydrogen is nearly one half of the G -value for the H-atoms, Livingston and Weinberger²⁵) assume that the H-atoms disappear by dimerisation. During the disappearance of the H-atoms the concentration of the other radicals present (mainly SO_4) does not alter considerably. In comparison with the trapped electron, the H-atom disappears at a much lower temperature (fig. 6).

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