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THE RADIOLYSIS OF FROZEN AQUEOUS SOLUTIONS

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INTRODUCTION

The great interest displayed recently in studying the action of ionising radiation on frozen aqueous solutions is due to the possibility in this case of recording and examining the primary products of the radiolysis of water, and also the possibility of elucidating the nature of the redistribution of the absorbed energy among individual components of the solutions. The present review constitutes the first attempt at a systematic survey of results published in this new branch of radiation chemistry. The first part of the paper discusses problems associated with the kinetics of the accumulation of the end-products of radiation-chemical changes in ice and solid aqueous solutions. The next two sections give data obtained from a study of the intermediate products of radiolysis by the methods of luminescence analysis and electron paramagnetic resonance. At the end of the review is a brief statement of some general conclusions which, in the writer's opinion, can be drawn at the present time from published results.

I. INVESTIGATION OF THE KINETICS OF THE ACCUMULATION OF END-PRODUCTS IN THE RADIOLYSIS OF ICE AND FROZEN AQUEOUS SOLUTIONS

The final products of the radiolysis of ice, as also of liquid water, are hydrogen, oxygen, and hydrogen peroxide. The first investigations by Duane and Scheuer in 1913 established that, when ice is exposed to α-rays at -180°, the yield of the stoichiometric mixture of oxygen and hydrogen which is formed is one-twentieth of that in the case of liquid water[1]. The yield of hydrogen peroxide on irradiation of ice with α-particles has only been halved compared with water (0.47 and 0.88†). The formation of molecular oxygen in the irradiation of ice, as also of water, is due to decomposition of hydrogen peroxide, and therefore the yield of oxygen is strongly dependent on the experimental conditions.

Investigation of the kinetics of the formation of H_2O_2, O_2, and H_2 under various conditions of exposure enabled Lefort and his coworkers[2-5] to establish the way in which the accumulation of the "molecular products" of the radiolysis of ice depended on the density of the ionising radiation‡ (α-rays and X-rays). In the case of densely ionising radiation (α-particles), raising the temperature of the ice from -196° to -40° had no effect on the yield of H_2 and H_2O_2. The absence of a temperature effect is probably due to the specimen's being warmed in the track of the particles to the liquid state (calculation shows that such "heated portions" exist for 10^{-9} sec) and to the radicals recombining (mean time of recombination of the radicals ~ 10^{-10} sec).

In the case of the radiolysis of ice by lightly ionising radiation, Bonet-Maury and Lefort[3,5] showed that the yield of hydrogen peroxide depends on the concentration of molecular oxygen dissolved in the water before it was frozen (X-rays). No H_2O_2 was detected in specimens of ice irradiated at between -192° and -116°.[3] It was established that H_2O_2 was formed at higher temperatures, its concentration increasing with rise in temperature of the specimen. Changing from the liquid to the solid phase is accompanied, as in the case of radiolysis by α-rays, by a diminished yield of hydrogen peroxide[3,5] and of molecular hydrogen[7]§. The change in the yield of hydrogen on passing to the solid phase is explained by differing conditions of diffusion of the intermediate species in water and in ice[7]. In the case of irradiation of ice with light ionising radiation at between -196° and -180°, $G(H_2)$ is of the order of 0.10-0.15.[8] The initial radiation yield of $2H_2 + O_2$ when ice is exposed to β-particles from tritium at -196° is 0.27.[9]

Ghormley and Stewart[10,11] investigated the kinetics of the formation of H_2, O_2, and H_2O_2 in the radiolysis of ice as a function of temperature and the presence of dissolved gases. Irradiation was carried out at temperatures between -269° and 0° with a cobalt source and with X-rays obtained by means of a van der Graaf accelerator (2 MeV). The products were analysed, as in the work quoted earlier, after fusion of the specimens. The initial yields of H_2O_2 and H_2 in ice containing dissolved oxygen were found to increase with rise in temperature. Molecular oxygen has no effect on the formation of H_2. In the case of the radiolysis of solutions of hydrogen peroxide, the rate of decomposition of the H_2O_2 was found to change sevenfold when the temperature was raised from -100° to -50°. It is interesting that, when specimens were irradiated at -196° with periodic interruption of the radiation and warming to 180° and above, the final concentration of hydrogen peroxide was lower than in specimens which had been continuously exposed at -196° until the same dose had been absorbed. In Ghormley and Stewart's opinion, the primary products of radiolysis (electrons, radicals, etc.[12]) "captured" at low temperatures by some kind of traps in the matrix are set free when the specimen is unfrozen, and enter into reaction with the dissolved substances, in particular with hydrogen peroxide.

Results obtained by Berger[13] indicate the possibility of the occurrence at low temperatures of chemical processes involving products of the radiolytic breakdown of components of the system, including water. According to these investigations, radiolysis with accelerated protons (energy 12 MeV, current 0.5 μA) of a mixture of methane, ammonia, and water frozen at 77°K results in the formation of urea, acetaldehyde, and acetone, the aggregate yield of the products being 1.39.

Investigations[14] on the ethyl alcohol–water system have established a definite correlation in the kinetics of the accumulation of H_2, H_2O_2, and acetaldehyde. These results indicate that the same chemically active species

† Here and subsequently the radiation yield G is given, as is customary in radiation chemistry, by the number of particles (molecules, radicals, etc.) formed calculated for 100 eV of radiated energy absorbed by the system.

‡ Günther and Holzapfel did not detect the formation of hydrogen on irradiation of ice with X-rays at -180°.[6]

§ Investigations made[7] on specimens irradiated with accelerated electrons (680–750 keV).

(probably H and OH radicals) are involved in the formation of "molecular products" of the radiolysis of water and of reaction products from the solute. A study of the dependence of the accumulated yield of these products on the concentration of the solution (the ethanol concentration was varied from 10^{-3} M to 15 M) led to the conclusion that at low temperatures (between -196° and -10°) ethanol can inhibit the recombination of H and OH radicals (at C_2H_5OH concentrations up to 5 M). This and other work[10,11,15] established that a rise in temperature of the frozen specimen is accompanied by an increase in the rate of radiolytic transformation of the dissolved substances.

As in the case of pure water and ice, the change from the liquid to the solid phase is accompanied, in the irradiation of aqueous solutions of some substances, by a decrease in their rate of conversion. Thus according to Haissinsky and Lefort[2,16] the efficiency of oxidation of the arsenite ion on exposure of its aqueous solutions (0.01 M, pH 7) to α-rays at -196° is half its value at ordinary temperatures. In the case of exposure to X-rays $G(AsO_2^-)$ at the temperature of liquid nitrogen is one-thirtieth of its value at room temperature (pH 10.5). A similar diminution in the efficiency of conversion of NO_3^- is observed in the radiolysis of the nitrate ion-water system[17,18].

The presence of molecular oxygen in frozen solutions greatly affects the yield of the accumulated final products[16-18]. In the nitrate ion-water system, for example, the inhibiting effect of O_2 has been shown to be due to its reaction with an intermediate product of the radiolytic transformation of the nitrate[19]. It has been suggested that the decrease in efficiency of radiolysis of the solutes on passing from liquid to frozen aqueous solutions should be used to estimate the direct effect of radiation on the solutes[20], on the hypothesis that the diffusion of intermediate products of radiolysis is a minimum in the case of frozen solutions, and that all the main effects of radiolysis are caused by the direct action of radiation (for example, see Cottin[21]).

However, the method of freezing the solutions cannot be regarded as acceptable for this type of estimate, since firstly the structure of the solution, and hence the conditions of radiolysis¶, change on passing from the liquid to the solid phase, and secondly it must be remembered that radiolytic changes in the specimen are recorded on the basis of an analysis of the specimen after fusion. In the course of fusion, however, intermediate products of radiolysis trapped in the lattice may undergo various reactions[2,22], and as a result the picture of the direct effect of radiation is confused.

Research in the 1960s has shown that radical involving H and OH may take place in frozen solutions even at very low temperatures (below -160°). It may be supposed, for example, that under these conditions H and OH migrate by a mechanism of relay transfer along hydrogen bonds. (The more "unwieldy" radicals formed from solutes react at temperatures in the vicinity of -90° to -100°[23].)

¶ Even in the case of frozen solutions, the peculiarities of the phase constitution must be taken into account in estimating the radiolytic effects. Thus Livingston and coworkers have shown (see Section III. 2) that the yield of atomic and molecular hydrogen in solutions of acids may vary by an order of magnitude depending on whether amorphous (vitreous) or crystalline specimens are subjected to radiolysis.

In spite of the great difference between the conditions of radiolysis of liquid and frozen solutions (resembling one another perhaps only in the initial distribution of ions and excited molecules) the laws governing the formation of the end-products of radiolysis in several cases, surprisingly, are identical. We have spoken earlier of the inhibiting effect of molecular oxygen on the reduction of the NO_3^- ion in liquid and frozen solutions of sodium nitrate[18]. We may also mention a definite correspondence in the yields of accumulated OH radicals[19].

When frozen concentrated solutions of a nitrate are irradiated in the presence of alkali, a lack of balance in the conversion products is observed, as in the case of liquid solutions, with respect to the oxidising (OH) and reducing (H) components of radiolysis, which is greater the higher the concentration of sodium nitrate. This phenomenon is explained by stabilisation of the OH radicals by the anion and formation of a compound which is not recorded by the usual methods (electron paramagnetic resonance and analysis for H_2O_2). Acidification of the solution to pH 2–3 was accompanied by a loss of nitrite, which was explained by interaction of this compound with the nitrite ion. The balance of conversion products of oxidising and reducing components of radiolysis then converges[19].

Work in which the kinetics of the formation of radical (H, OH, HO_2) and molecular (H_2, H_2O_2, O_2) products of the radiolysis of water were compared provided results[24-26] of considerable interest for an understanding of the mechanism of radiation-chemical reactions. They indicate that the final products of the radiolysis both of pure ice and frozen aqueous solutions result mainly from recombination of radical products†, but also from interaction of these radicals with solute molecules.

II. INVESTIGATION OF RADIOLYTIC EFFECTS IN FROZEN AQUEOUS SOLUTIONS BY THE LUMINESCENCE METHOD

Fluorescence

The first investigations of the luminescence of ice and water under the influence of ionising radiations were made during the late 1940s and early 1950s. In 1952 Grossweiner and Matheson[28] succeeded in observing, during the exposure of ice to X-rays (50 kV), a steady luminescence in the ultraviolet at temperatures between -170° and -100°. They established that the intensity of the steady luminescence varies linearly with the radiation dose (at rates of the latter of 400–100 000 r h^{-1}) and diminishes with rise in temperature. These workers also studied the luminescence of tritium ice at -196°; in this case the luminescence is due to absorption by the specimen of β-rays from the tritium. The efficiency of conversion into light of the energy absorbed by the specimen was found to be 3×10^{-5} quanta per ion pair[28].

Experiments on the luminescence of irradiated water and ice had also been made earlier[29-31], but then the possibility of estimating the luminescence effect in the visible region had been denied[30] on the grounds of the masking action of Čerenkov radiation.

† Glasel, for example, reaches the same conclusion from a study of the kinetics of the formation of D_2 in D_2O-ice by the action of electrons (of energy 2 keV)[27].

The most detailed data on the luminescence of tritium ice were obtained by Jones[32], who found that the spectrum contains two maxima, near 400 and 550 mμ. At 77°K the specimens were found to have a colour, which disappeared on heating to 190°K.

When ice is irradiated at -196° with γ-rays from ^{60}Co, examination of the luminescence spectrum is prevented by the intense Čerenkov radiation[12,33]. When ice is exposed to 50 kV X-rays, *i.e.* under conditions such that Čerenkov radiation is absent, a luminescence band can be observed with a maximum at 395 mμ and a width of 75–90 mμ at half-height as well as an unresolved band with a maximum at 550 mμ. The intensity of the latter band is about one-quarter of the maximum intensity at 385 mμ[33]. When the specimen is heated, the intensity of the peak corresponding to 385 mμ decreases, and at -120° this peak completely disappears. The emission band in the region of 550 mμ remains roughly constant over this temperature range (between -196° and -120°)[33,34]. The luminescence completely vanishes at -100°.[34] Observations show[32,34] that, from the instant of exposure of the ice, there is a slow initiation of fluorescence, which follows a first-order law with rate constants of 0.086 and 0.31 min^{-1} at -196° and -145° respectively[34]. Over the range of rates of radiation dosage investigated (0–10^{17} eV g^{-1} min^{-1}) the intensity of fluorescence varies linearly with this rate over a wide temperature range[24,34].

With rise in temperature of the irradiated specimens from -196° to -70°, the intensity of fluorescence passes through a maximum at -180°.[33,34] With specimens irradiated for the first time, the curve relating intensity of luminescence with temperature shows a second peak in the region of -150°. After repeated cooling (to -196°) and irradiation of the specimen, the peak at -150° becomes smaller or disappears altogether. This effect is associated with radiolytic changes in the specimen.

Work on the effect of impurities on the fluorescence of ice is of interest for an understanding of the nature of the active fluorescence centres. The type of spectrum and also its intensity have found to depend on the nature of the cation[34].

Results on the effect of hydrogen peroxide and molecular oxygen on the luminescence of ice indicate that the chemical effects of radiolysis have a definite correlation with fluorescence and thermoluminescence. A hydrogen peroxide concentration of 2×10^{-5} M in a frozen solution appreciably diminishes the fluorescence when the specimen is first irradiated[34]. During subsequent exposures the intensity of the luminescence is restored to the values observed in pure ice. Hydrogen peroxide does not affect the temperature variation of the luminescence. Molecular oxygen, in contrast to H_2O_2, does not influence the intensity of the fluorescence[34].

Grossweiner and Matheson conclude that the species responsible for the steady fluorescence of ice are atoms formed by the capture of electrons by cations, the atoms then having undergone reionisation with subsequent capture of other electrons and emission of light.

Thermoluminescence

It has been found several times[10,33,34] that, when a specimen of ice is subsequently heated after being irradiated at the temperature of liquid nitrogen, it begins to emit light. The intensity of the luminescence passes through a series of maxima as the specimen is heated. The principal maxima occur at temperatures around -115° and -155°. In the first temperature range the emission band is almost entirely located in the visible region of the spectrum, but in the second range 90% of it is located in the ultraviolet[33]. The absorption spectrum at -196° is a broad line with a maximum at 2800 Å.[10] Ghormley[10,33] points out a correlation between the temperature characteristics of the thermoluminescence of ice (the appearance of an emission peak at -155°), the disappearance of the absorption band with a peak at 2800 Å, and also the decomposition of hydrogen peroxide in aqueous solutions of H_2O_2 which have first been irradiated at -196°. In his opinion the same stage of the process develops on heating the specimen in these three cases, and this can be represented either as the liberation of captured electrons or of positive holes, or else, finally, as the diffusion of free radicals. However, this last phenomenon, *i.e.* luminescence due to the "liberation" of radicals[10], is improbable in the opinion of other workers[12].

When the radiation dose is changed from 10^{18} to 10^{21} eV g^{-1} the intensity of the luminescence peak at -155° increases about hundredfold compared with that at -115° (rate of heating of specimen 10° min^{-1}). Grossweiner and Matheson found that the intensity of the main peak (at -118° according to them) at a rate of heating of 3° min^{-1} increases linearly with the dose[34]. The depth of the electron trap responsible for the glow has been estimated[34,35] as ~0.25–0.32 eV. A fairly intense luminescence peak is observed at -165°. Apart from the main peak at -118° and that at -165°, maxima have also been recorded[34] at -95° and -180°. Storing the specimens in air makes their luminescence more intense. The appearance and the intensity of the latter peaks are associated with the presence of molecular oxygen in the ice. When irradiated ice, prepared at 150 mm O_2 pressure, is heated, no distinct thermoluminescence peaks are observed over a wide range of temperature. Hydrogen peroxide also suppresses all the luminescence peaks. NaCl and HCl (0.05 M) appreciably depress the thermoluminescence.

Grossweiner and Matheson's information on thermoluminescence enabled them to suggest a model according to which an electron, originally captured by a "trap" and set free in the ice on heating, migrates to impurity centres, where radiation capture takes place. The nature of the trap was not established. Two main processes are postulated: (*a*) the electron is separated from the ion on activation, *i.e.* a process of the type $R^- \xrightarrow{h\nu} R + e$; (*b*) reaction takes place in the ice between neighbouring particles of the type: (1) $H + OH^- = H_2O + e$; (2) $OH + H^- = H_2O + e$, a process of type (2*b*) being regarded as the more probable. Apart from these schemes another possibility is, in the opinion of these workers, the capture of the electron by two protons with the formation of an ionised hydrogen molecule. However, they assume that the correctness of this or the other model should be carefully verified by magnetic measurements. In order to check the hypothesis that the fluorescing species may be an alkali metal ion, Matheson and Smaller[36] investigated the magnetic properties of irradiated samples of ice containing NaCl (concentration 0.01 M), on the assumption that in this case it is possible to record the presence of Na atoms, having a nuclear spin of $\frac{3}{2}$. Even in this case, however, only the species recorded in pure ice were detected.

Data on the magnetic properties (obtained by the electron paramagnetic resonance method) of irradiated frozen solutions and of ice have not confirmed the above schemes.

According to recent experimental results the paramagnetic species, which have been identified with great reliability as H atoms and OH radicals, have different temperature parameters for their existence from those species which could have explained the thermoluminescence effects. Moreover, calculation shows that the yield of light quanta per 100 eV of absorbed energy is $\sim 10^{-4}$ in the case of the fluorescence of tritium ice at -196°,[28] and on irradiation with Co γ-rays it is $\sim 10^{-3}$ [33] (*i.e.* it has values differing by 2–3 orders magnitude from the yields of H and OH radicals[24,25]).

In the case of thermoluminescence the quantum yield is four orders of magnitude lower[33]. Comparison of the yields of photons and radicals shows that, in any case, not all the H and OH radicals can be involved in the formation of electrons which subsequently recombine with the active luminescence centres.

III. STUDY OF INTERMEDIATE RADICAL PRODUCTS OF RADIOLYSIS

The most important results, which are of great value for an understanding of the mechanism of the radiolytic transformation of dissolved substances and the nature of the intermediate products, have been obtained by examining the radiolysis of ice and of frozen solutions by the electron paramagnetic resonance (EPR) method. This is a very reliable method for investigating the nature and the kinetics of the accumulation of radical products of radiolysis, both primary and those resulting from secondary processes.

Research on the radical products of radiolysis can be divided into three groups. The first group of investigations relate to the identification and study of the properties of radical products of the radiolysis of ice, and also the kinetics of their accumulation. The second group comprises investigations on the effect of various additions on the behaviour of radicals formed from water. The third group deals with the study of radical products of the radiolysis of dissolved substances.

1. Identification and Properties of the Radical Products from the Radiolysis of Ice

The first work on the EPR spectra of irradiated frozen water was done by Livingston *et al.*[37] during 1953–1954. Their aim was to verify the hypothesis that H and OH radicals are formed by the action of radiation on water.

Identification and properties of H. This group of workers were able to detect atomic hydrogen in irradiated frozen solutions of acids ($HClO_4$, H_2SO_4, H_3PO_4). The spectrum of atomic hydrogen is a symmetrical doublet with a splitting of ~500 G and a g-factor close to that of a free electron (*i.e.* the spectrum is analogous to that of the free H atom in the gas phase)[38]. Such characteristics show that in this case the unpaired electron is well represented by the 1s wave function of atomic hydrogen. It was established that the intensity of the lines does not change when irradiated specimens are kept at 77°K.

When frozen solutions of H_2SO_4 in D_2O were irradiated, a triplet was observed caused by the presence of D atoms in the specimen.

Atomic hydrogen exists in frozen acids right up to -170° (H_2SO_4)[39] and -160° ($HClO_4$).[40] Kinetic investigations involving a comparison of the accumulation of atomic and molecular hydrogen on irradiation of an acid[8,24,29], and also an examination of the effect of ionisation density on the yields of radical and molecular products[40], showed that molecular hydrogen is formed in frozen acids mainly as a result of the recombination of hydrogen atoms.

Paramagnetic resonance in solutions of oxygen-containing acids irradiated with ^{60}Co γ-rays and tritium β-particles (βT), due to the presence of atomic hydrogen ($\Delta H \simeq 500$ Oe), has been observed also in other work[36,41–43]. The yield of H formed was found to depend on the nature of the anion of the acid and its concentration, as well as on the type of ionising radiation[40] (linear energy transfer, LET). There are indications in the literature that the EPR spectrum of atomic hydrogen has been recorded also in irradiated frozen solutions of hydrogen halides (HCl, HF)[39,40], fluorine derivatives of acids, and solutions of hydroxides of the alkali and alkaline earth metals (see Table 1).

Attempts to detect atomic hydrogen by the EPR method in pure ice irradiated at 77°K were unsuccessful. In 1958 a report appeared that the EPR spectrum of the hydrogen atom had been recorded when ice was irradiated at 4.2°K.[44] Subsequent investigations showed the initial radiation yield of H formed to reach values of ~0.5 (40-MeV electrons[45]) and 0.9 (^{60}Co γ-rays)[46]. The formation of atomic hydrogen in ice irradiated at 4.2°K has been regarded[47] as resulting from the capture of a "dislodged" electron by H^+ ions present in the matrix.

As ice irradiated at the temperature of liquid helium warms up[46,48,49], some of the hydrogen atoms disappear rapidly at 15°K, and the remainder more slowly at 60°K. The energy of "escape" of H atoms from the trap is less than 1.0 kcal mole^{-1} in the first temperature region, and rather more thane 2.5 kcal mole^{-1} in the second region[49]. These results were explained[46,48,49] on the basis of a model involving a postulated non-uniform initial distribution of H atoms in the irradiated ice.

TABLE 1. Properties of atomic hydrogen formed by the irradiation of frozen aqueous solutions.

Material irradiated	Type of radiation and max. yield G, H atoms/100 eV	Temp. range of existence, °K	Ref.
Sulphuric acid (0.25 mole fraction), 77°K (glass)	1.62 (γ-rays)	up to 104°	24
Perchloric acid (0.125 mole fraction), 77°K	2.2 (γ) 1 ($T\beta$-rays)	up to 104° up to 119°	24 40
Phosphoric acid (0.45 mole fraction), 77°K (glass)	1.1 (γ)	up to 104°	24
$NaNO_3$ soln. (0.1 – 1 M) + CO_2, 84°–89°K	accelerated electrons (1.6 MeV)	up to 94°	42
Ice, 4.2°K	0.5 (e, 40 MeV)	disappears up to 77°	45
Ice, 4.2°K	0.9 (γ)	partly disappears at 15°, completely disappears at 60°	46
HF (16%), 77°K	0.06 (βT)	–	40
HCl (24%), 77°K	~0.006 (βT)	–	40
HF (48%), 77°K	"moderate" (γ)	–	39
NaOH, KOH, LiOH, Ba(OH)$_2$ (0.1 – 0.5 M), 77°K	"low" (γ)	–	40
Fluorosilicic and fluoroboric acids, 77°K	"high" (γ)	–	40

The "dislodged" electron may be stabilised [50,71] in frozen solutions containing alkali ($\geqslant 2$ M) and irradiated at 77°K. The g-factor of the singlet absorption line of this stabilised electron is close to that of a free electron.

In concluding this subsection we note that the nature of the traps which stabilise the H atoms is still unknown. The suggestion that hydrogen atoms are stabilised by their ability to form hydrogen bonds with the surrounding molecules of the matrix [39], is worthy of serious consideration.

Identification and properties of other radicals formed in the radiolysis of ice. The spectrum due to the presence of OH radicals in irradiated ice at 77°K was first observed by Smaller and Matheson during 1953–1954 [41]. However, they erroneously attributed the recorded paramagnetic resonance lines to atomic hydrogen [20,51–53]. The observed EPR spectrum [41] of the OH radical is a doublet with components of different intensities and a g-factor of ~2.0; the hyperfine splitting is approximately 30 Oe. D_2O–ice irradiated under the same conditions [41] gave a triplet spectrum with a line width of 2 Oe and a separation of ~5 Oe between the components of the triplet. The intensities of the lines were in the proportions 1:2:1. Further work on the radiolysis of ice and frozen aqueous solutions of hydrogen peroxide [25,36,40,41,43,45,46,54–61] and on the photolysis of these systems [62,63] (the latter work is not specially considered in this review) enabled the spectral and kinetic characteristics of OH radicals to be obtained with greater precision (see Table 2). The investigations of McMillan *et al* [52,54] on single crystals of ice irradiated at 77°K established that the OH radical in the matrix of ice possesses cylindrical symmetry and has a minimum hyperfine splitting of 35.5 Oe with $g_{\parallel} = 2.0127$ and $g_{\perp} = 2.0077$.

It was established that OH radicals exist in irradiated ice right up to -170° to -175° [36,40,55]. They disappear rapidly in the vicinity of -163°, according to the law [25,57,58]

$$-\frac{d(OH)}{dt} = k(OH)^{3/2} .$$

TABLE 2. Characteristics of OH and HO_2 radicals formed in the radiolysis of ice and of frozen aqueous solutions.

Irradiated material	g-Factor	Separation between components of hyperfine structure, Oe	Max. yield of radicals formed	Max. temperature of existence, °K	Suggested radical	Ref.
Ice, 4.2°K	2.008	~40	0.8	119°	OH	46
Ice, 77°K	2.008	~40	0.6 (γ)	119°	OH	25, 46, 55, 58
	2.01	~40	0.32 (β?)	119°	OH	40, 56
	2.0	~10	0.14 (γ) (overall)	146°	HO_2	25, 36, 41, 55
Ice, 77°K	—	41.5	(220-kV X-rays)	—	OH	61
Ice, single crystal, 77°K	2.0127 ($g_{\parallel}$)	35.5		—	OH	52
	2.0077 ($g_{\perp}$)				$H_3O^+ \cdot HO_2$	52
	2.00 ($g_{\parallel}$)					
	2.04 ($g_{\perp}$)			—		59
H_2O_2 (60–70%) 77°K	2.039 ($g_{\parallel}$)	13.5	10.3 (250-kV X-rays)	—		
	2.0055 ($g_{\perp}$)					
$NaNO_3$ soln. (neutral), 129°K	2.015	—	—	184°	$[OH \cdot NO_3^-]$ $[HOONO_2^-]$	19
$NaNO_3$ soln. (alkaline), 129°K	2.04	—		184°	$[O^- \cdot H_2O]$ $[O_3^-]$	19

Examination of the initial stages in the radiolysis of ice at 4.2° and 77°K showed that the radiation yields of accumulated OH radicals [25,46] and of atomic hydrogen are equal (0.8 and 0.9, ^{60}Co γ-rays) within the limits of experimental error. A close analogy has been noted [40] between these two species (and also between OD and D) in the kinetics of their accumulation and in their thermal stability. Analysis of the experimental results [25,26,58] shows that the destruction of OH radicals in irradiated ice is due mainly to their recombination with H atoms. A change in the density of the ionising radiation affects the accumulated yield and the steady-state concentration of OH radicals in the irradiated ice [59]. When β-particles from the tritium are used to irradiate ice, G(OH) is reduced to half compared with irradiation with γ-rays [40] (see Table 2).

Several papers on the thermal properties of radicals [36,40,55] report the appearance, in irradiated specimens of ice and in frozen solutions of H_2O_2 between -160° and -145°, *i.e.* after the spectrum of the OH radical has disappeared, of a fresh absorption line (an unsymmetrical spectrum, with a doublet hyperfine structure and a splitting of ~13.5 Oe), which disappears only in the vicinity of -130°. [55,63]. Like the spectrum of the OH radical, this absorption line exhibits anisotropy of the g-factor, with $g_{\parallel} = 2.039$ and $g_{\perp} = 2.0055$. Its structure is similar [25] to that of the EPR spectrum of O_2^-, observed in crystals of NaO_2. [64] The radical responsible for this spectrum was identified as HO_2. [59]

McMillan and coworkers examined the EPR spectra of an irradiated single crystal of ice [52,53], and found that the broad absorption line usually observed in polycrystalline specimens is split into at least two lines. Analysis of the results gave the spectral characteristics ($g_{\parallel} = 2.00$ and $g_{\perp} = 2.04$) and led to the conclusion that the observed paramagnetic species is symmetrical along the hydrogen bond of the crystal lattice. It was suggested that this species is the H_2O^+ radical.

Thus the EPR method has provided an experimental proof of the formation of H and OH radicals in the radiolysis of aqueous solutions, which had been postulated by chemists 16–18 years previously. These primary radical products of the radiolysis of water give rise to the formation of the molecular products of radiolysis, H_2 and H_2O_2, and produce various changes in the dissolved substances, as will be seen from the subsequent account.

2. Effect of Additions on the Behaviour of Radicals Formed in the Radiolysis of Ice.

The influence of additives on the behaviour of radicals formed by the irradiation of water is important in connection with the possible direct control of radiolytic reactions by varying the paths for the redistribution of the absorbed energy among the components of the irradiated system. Most such information has been obtained by examining systems containing hydrogen peroxide and an acid in addition to water.

Matheson and Smaller [36,41] noted an increase in the intensity of the spectral lines due to the OH radical in solutions of hydrogen peroxide. They also observed that the distance between the peaks in this spectrum as well as the intensity of the latter increase with increasing concentration of H_2O_2. At the same time the distance between the components in the spectrum of the OH radical increases, and its lines diminish in intensity. The change in the distances between doublet peaks is linked, in the opinion of

these workers, with changes in the environment of the radicals, which become increasingly noticeable as the hydrogen peroxide concentration is raised. The antibathic changes in the peaks of the two doublets can probably be attributed to the conversion of one type of radical into another by the reaction $HO + H_2O_2 = HO_2 + H_2O$. These workers found that the yield of radicals is 2–3 times greater in the presence of 0.02 M hydrogen peroxide (or D_2O_2), and becomes still higher in more concentrated solutions. An investigation[59] of the decomposition of H_2O_2 (250 keV X-rays, 90°K) showed that the yield of radical products (mainly HO_2) formed increases by a factor of 10 with increase in the H_2O_2 concentration from 0 to ~45 wt.%, then remains constant over the range 45–85%, and diminishes to about half its value on passing to still more concentrated solutions. This work established also that the linear energy transfer (LET) greatly influences the yield of radicals formed in H_2O_2 solutions (see Table 3), which falls appreciably with growth in density of ionisation in the track.

This indicates that the diffusion and the recombination of radicals play an important part at low temperatures too.

The literature contains many facts on the effects of additions on the kinetics of the formation of the reducing component, H radicals, in radiolysis. The work of Livingston and his coworkers (for example, Ref. 24) has established that such compounds as acids tend to extend the temperature range of existence of atomic hydrogen in ice (Table 1). The yield of H atoms formed depends, as already noted, on the nature of the anion and also on the structure of the specimen[24].

The nature of the anion in the acid influences also the maximum steady-rate concentration of H atoms. Thus the latter is an order of magnitude greater in $HClO_4$ than in H_2SO_4 solution (2.9×10^{19} atoms g^{-1}). A study of the width of the lines due to atomic hydrogen yields interesting results. Thus when the concentration of $HClO_4$ is increased from 0.02 to 0.25 mole fraction, the line width (the distance between the heights of semi-maximum intensity) first increases from 2 to 4.2 G (at a mole fraction of 0.15), then increases to a still greater extent on passing to 0.16 mole fraction (to 5.0 G) and to 0.18 (to 5.8 G), and decreases to 4.8 G (at the mole fraction 0.25). With specimens containing sulphuric acid, a change in concentration from 0.02 to 0.8 mole fraction is accompanied by a continuous decrease in line width (from 4.8 to 3.6 G), but in the case of H_3PO_4 there is only a slight change in the lines. These data may be useful in elucidating the nature of the traps in frozen specimens and the character of the interaction between them.

Examination of the effects of such additions as O_2, H_2O_2, etc. on $G(H)$ under the stabilising influence of acids makes it possible to study the interaction of the radicals with acceptors and the capture of radicals in traps. Whereas molecular oxygen has no effect on the kinetics of H formation in irradiated frozen solutions of acids, hydrogen peroxide lowers the value of $G(H)$ on irradiation at the temperature of liquid nitrogen‡. For example, the value of $G(H)$ in sulphuric-acid solution is diminished by 80% and more at a hydrogen peroxide concentration of ~0.7 wt.%. The yield of molecular hydrogen then drops sharply over the range of H_2O_2 concentrations up to 0.15 wt.%. These data indicate that hydrogen peroxide successfully "intercepts" H atoms even before the stage of H capture by a trap.

TABLE 3. Yields of radicals in H_2O_2 solutions (~ 65 wt.%) with different types of radiation.

Type of radiation	Mean LET, keV μ^{-1}	Yield of radicals, spins/100 eV
250 kV X-rays	0.6	10.3
15 MeV deuterons	14	6.3
5.7 MeV α-particles	86	2.1

As already noted, increasing the acid concentration (sulphuric, perchloric, and phosporic) first involves a growth in the accumulated yield of atomic hydrogen, after which it passes through a maximum and then falls. This phenomenon is easily explained if it is supposed that the increased content of the anion in the solution changes the conditions under which recombination of H and OH radicals and their capture by traps (or stabilisation by anions) take place[19]. In the radiolysis of concentrated solutions (>0.15–0.3 mole fraction) of the acids $HClO_4$, H_2SO_4, and H_3PO_4, the recombination of H atoms obviously becomes less probable — this follows from a comparison of the curves for the variation of the changes in $G(H)$ and $G(H_2)$ with the acid concentration§. It must again be stressed that this concentration dependence of the yields of H and H_2 is general in character, and extends to the anions of oxo-acids (SO_4^{2-}, ClO_4^-, PO_4^{3-}, NO_3^-, CO_3^{2-}).

3. Study of Intermediate Radical Products of the Radiolysis of Dissolved Substances

In spite of the ever increasing use of the EPR method in studying intermediate products of radiolysis, only two or three papers have yet appeared reporting more or less detailed investigations of intermediates formed from dissolved substances. The EPR spectra of many irradiated frozen aqueous solutions are characterised by extreme complexity owing to the superposition of absorption lines due to several radicals. Difficulties also arise in the identification of radical products from their spectra because no data are yet available on the influence of intracrystalline fields on the structure of these spectra. The first papers on the complicated EPR spectra recorded in irradiated frozen acids (H_2SO_4, H_3PO_4, $HClO_4$) date from 1954.[36,39] It was noted that the EPR spectrum of irradiated sulphuric acid clearly shows two absorption lines, narrow and broad, in the vicinity of $g = 2$. Their intensities depend on the acid concentration, dilution weakening the narrow line, which completely disappears at the ratio H_2O : acid = 2 : 1. The central lines of the

‡ An analogy suggests itself between the mechanism of the inhibiting action of H_2O_2 on the yield of H formed and its effect on the luminescence of irradiated specimens (Section II). It is reasonable to assume that the same process — interception of the electrons from the traps by the hydrogen peroxide — develops in these cases. Hence it can also be concluded that the H atoms are formed as a result of the addition of the electron to H^+.

§ It is interesting that, in pure water at 77°K, $G(H) = 0$, whereas $G(H)_2 \simeq 0.1$. It may be supposed that molecular hydrogen is formed by the interaction of species which are not recorded by the EPR method. The yield of the molecular end-products of radiolysis was also found to exceed that of the intermediate radical products in a study of the kinetics of the radiolysis of dissolved substances[19].

EPR spectra for the acids H_3PO_4 and $HClO_4$ differ considerably from one another and from the lines for sulphuric acid. The H_3PO_4 spectrum contains two broad lines, whereas that of irradiated perchloric acid consists of several lines of varying intensity and width. All the lines become wider on dilution of the acids. In sulphuric acid the central line remains at temperatures of the specimen right up to -110°. It is stressed[8] that the complicated line spectrum is an obstacle to identification of the radicals. Livingston and Weinberger[24] point out that the concentration of these paramagnetic species far exceeds that of hydrogen atoms. Although the latter disappear at lower temperatures, they are relatively inert towards the radical products under consideration here. Later in this paper a curious experimental fact is reported. As an acid-containing specimen is irradiated, the concentration of atoms increases, and reaches a limiting value when a certain dose has been received. With further irradiation of the specimen, however, the width of the lines due to H atoms again increases. Livingston and Weinberger link this phenomenon with dipole – dipole interaction between H atoms and other paramagnetic species having an unpaired electron. When it is remembered that in several cases $G(H) > 2G(H_2)$ (in the acids $HClO_4$ and H_3PO_4), the conclusion suggests itself that under these conditions (at the temperature of liquid nitrogen) some of the H atoms can probably react with components of the solution to form radical products. The addition of such radical-acceptors as hydrogen peroxide and nitric acid can be used to control reactions involving H atoms (for example, the formation of H_2). Unfortunately, no further details are given.

As a possible mode of formation of a paramagnetic species in irradiated solutions of sulphuric acid[65] Livingston and Weinberger suggested a scheme analogous to Allen's scheme for the liquid phase, according to which OH radicals form with the acid a complex which is also a radical but less reactive than the OH radical.

Investigations on the radiolysis of frozen solutions of sodium nitrate by Molin, Buben, and the present writer[42] showed, apart from the identified main products of the radiolysis of a nitrate (the radicals NO_2, HNO_3^-), the presence of a radical to which was assigned the structure $OH.NO_3^-$. It was suggested (as a possibility) that the nitrate ion stabilises the oxidising component in the radiolysis of water, *i.e.* the OH radical (narrow absorption line, $g = 2.015$), by forming the complex radical¶. Such a radical disappears at temperatures close to -100° to -90°. This radical was not detected in alkaline solutions; instead, a paramagnetic species was formed, whose spectrum was a wider line having $g = 2.04$. This spectrum could be due to the presence of a radical of the type $O^-.H_2O$, formed under the influence of alkali: $OH + OH^- = O^-.H_2O$.

An absorption line with analogous spectral characteristics (g, ΔH) was recorded also in irradiated frozen alkali solutions at 77°K, and was attributed to the radical $O^-(nH_2O)$.[50]

The possible existence of compounds of the type "OH.acid" has also been deduced[40] in the radiolysis of the $HClO_4$–H_2O system. It is assumed that OH radicals form a complex with an acid by hydrogen bond formation. The present writer and Yanova[60] were able to observe that the position of the absorption line in the EPR spectrum due to the OH radical stabilised by the anions ClO_4^-, SO_4^{2-}, and NO_3^- depends on the nature of the anion. They suggested that the g-factor of the absorption line may emerge as an indirect measure of the stability shown by the OH ... anion bond in the series of oxygen-containing anions examined.

In a study of the thermal stability of radical products of the radiolysis of frozen perchloric acid, it has been established[40] that the disappearance of both atomic hydrogen and stabilised OH radicals is accompanied by the accumulation in the system of other, as yet unidentified radicals.

Henriksen studied the radiolysis of frozen aqueous solutions of glycine[61] (220 kV X-rays), and traced the conversion of the primary radical product of radiolysis, OH, into secondary radicals. The type of spectrum characteristic of the OH radical, recorded at the temperature of liquid nitrogen, changed considerably when the specimen was annealed at about -90° for 15 sec. On further annealing at the same temperature the spectrum of the species recorded became of the type observed in irradiated polycrystalline glycine, and this spectrum did not disappear right up to temperatures close to the melting-point of the solution. This spectrum, characterised by a triplet hyperfine structure, was attributed to radicals of the type $^{\cdot}CH_2COO^-$, $^{+}NH_3\dot{C}HCOO^-$.

As can be seen from the above results, the EPR method in combination with other physicochemical methods of investigation, opens up great opportunities for the study both of the formation of the primary products of radiolysis and of the further processes which they undergo, and will thus provide direct information on the mechanism of radiochemical reactions in frozen aqueous solutions.

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As an analysis of data on the kinetics of the accumulation of radical products of radiolysis shows, the mechanism of the reactions undergone by the products of radiolysis cannot yet be regarded as entirely clear. Although a certain analogy is observed between the laws governing the formation of the end-products of radiolysis in liquid and in solid (frozen) aqueous solutions (for example, accumulation of reaction products of oxidising component as function of pH, effect of O_2 on accumulated yield of end-products, etc.), account must be taken of the changes occurring in the medium on passing from one phase to the other (quite apart from the effect of temperature on the reaction velocity). In the frozen phase itself, moreover, a change in temperature results in substantial changes both in the structure of the specimen and in the kinetics of the accumulation of radical and molecular products, as is shown by data obtained by different methods of investigation. It has already been noted that the degree of crystallinity of the

¶ It was established that the formation of this radical is in fact linked with the fate of the OH radicals. This was proved by the absence of its spectrum in $NaNO_3$ solutions (1 M) to which had been added small quantities (0.1 M) of an active acceptor for OH radicals, glycerol, or ethanol[19].

specimen (the size of the crystals) influences the radiolysis, perhaps because the principal reactions, which depend on the diffusion of active species, take place on the surfaces of these crystals. Further difficulties in considering the radiolytic effects result from the necessity for taking into account the peculiarities of energy transfer between crystallites in polycrystalline specimens. For these reasons it is not yet possible to describe quantitatively radiolytic processes in frozen aqueous solutions (and still less to transfer the results to the liquid phase), and opportunities for their elucidation must be sought from data obtained by various methods of investigation. Some information has already been obtained[23,66] from a simultaneous examination of changes in several properties of frozen solutions. Thus the disappearance of radicals varying in nature (EPR method)[23] at temperatures between -100° and -90° and changes in the structure of ice (X-ray method of investigation)[67] at these temperatures, together with a study of the dielectric properties[68], indicate, it is assumed[23], that these phenomena are interrelated. The EPR data and X-ray examination show that a similiar phenomenon occurs at lower temperatures: the disappearance of radicals formed by the irradiation of ice and a change in the structure of the latter at -160° to -150°.[23,40] A study of products formed by an electric discharge in the vapours of H_2O_2 and H_2O and frozen at various temperatures led to the conclusion[69] that the transition from amorphous to crystalline ice creates conditions which facilitate the recombination of HO and HO_2 radicals frozen out at lower temperatures. It must be emphasised, however, that X-ray examination reveals differences in the structure of ice (which probably determine which radical traps are involved, and in which temperature ranges, in the setting free of active products), not only associated with its temperature but also depending on its mode of formation (by rapid cooling of water or by condensation of the vapour)[23,67]. The results obtained by different methods of investigating radiochemical reactions in frozen specimens must therefore be compared on samples of ice obtained under identical conditions. Nevertheless, it must again be stressed that a definite link exists between several properties of these systems, although ice and frozen solutions are formed under different conditions. Thus there is obviously[66,70] a connection between phase transformations in ice and in frozen aqueous solutions of hydrogen peroxide: the regions of destruction of frozen radicals formed from H_2O and H_2O_2 practically coincide with the phase transformation points (-116° for the start of the endothermic transformation, and -53° for the exothermic transformation). The suggestion made by several workers[69,70] can be accepted that in both cases, independently of the mode of preparation of the ice, a change in temperature produces reorientation of the water molecules and an associated redistribution of hydrogen bonds; as a consequence of this, the conditions of interaction of active products of radiolysis, in particular radical products, are changed.

In conclusion we may underline some fundamental generalisations which have now been established experimentally, and on which future research may be based: (1) at low temperatures there is a movement of active species, which affects the yield of radiolysis products in frozen solutions; (2) the formation of H and OH radicals in the radiolysis of aqueous solutions has been demonstrated, and the reactions of these species with dissolved substances determine the nature of the changes undergone by the latter; (3) it has been established that the radicals formed from water are stabilised by solute anions, and the influence of various radical-acceptors on the yield of radical products has been examined.

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ANALYSIS OF TRACE IMPURITIES BY GAS CHROMATOGRAPHY

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1. INTRODUCTION

The extensive and varied advances made in gas chromatography range from analytical studies on mixtures of several constituents on the one hand to trace analysis of minor constituents in various systems on the other hand. The latter type of problem is of great importance in the polymer industry, where high-purity monomers are often required. In some cases, even very small traces of certain impurities in the monomer can alter the course of the polymerisation reaction and mar the final product.

Whereas high precision is the foremost requirement in the analysis of complex mixtures, trace analysis relies primarily on high-sensitivity methods. Present-day gas chromatography techniques in their conventional, unmodified form can detect components present at a level of a few hundredths of one per cent. We shall therefore apply the term "trace constituent" to substances whose concentration in the sample is of the order of 0.001% or less.

Chromatographic methods of trace analysis are reviewed in the present article. The chromatographic analysis of complex organic systems has been previously discussed[1] by one of us.