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THE RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS

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CONTENTS

Introduction 279

1. Main stages in the development of theories of radiochemical processes in aqueous solutions 280
2. The concept of radicals as intermediate products in the radiolysis of water 283
   A. OH radicals as the oxidising component of radiolysis 283
   B. The participation of H atoms in radiolytic reactions 284
   C. The part played by HO_2 radicals 287
3. Ionised and excited water molecules in radiochemical reactions of dissolved substances 288
   A. Routes for the redistribution of the energy absorbed by a solution 288
   B. Proskurnin's concept of conjugate radiochemical reactions 291
   C. The participation of two types of excited water molecule in the reactions 292

INTRODUCTION

The study of the action of different forms of radiation on aqueous solutions is important chiefly because of the marked similarity in the behaviour of the primary products of the radiolysis of aqueous solutions and biological systems. On practical application is the construction of chemical dosimeters, which are not only air-equivalent but also simulate tissue behaviour. Moreover, the present development of atomic energy makes it important to take account of processes initiated by radiation and to examine possible methods of carrying out various redox reactions in inorganic and organic synthesis in aqueous solution. It is important to make maximum use of the energy absorbed when carrying out these processes.

These more general problems require the study of the nature of the primary products, the ways in which the energy absorbed by the solution can be transferred, and the mechanism of the reaction of the primary products with one another and with dissolved substances.

Although the effect of ionising radiation in aqueous solutions has been known for more than 50 years, there is as yet no single theory of the radiolysis of aqueous solutions. In this paper we have tried to show the main directions of development of the radiation chemistry of aqueous solutions, to examine modern theories of the mechanism of radiolytic changes, and to present what is in our opinion some of the most interesting effects of radiolytic reactions. We have taken into consideration the fact that the experimental material on the radiolysis of aqueous solutions has been presented fairly completely in a number of reviews on radiation chemistry[1-17].

1. MAIN STAGES IN THE DEVELOPMENT OF THEORIES OF RADIOCHEMICAL PROCESSES IN AQUEOUS SOLUTIONS

The decomposition of water to O_2 and H_2 when radium salts are dissolved in it was first observed in the nineteen-hundreds[18,19]. It was subsequently found that in aqueous solutions radium salts yield hydrogen peroxide as well as oxygen, the sum of the quantities of O_2 and H_2O_2 evolved being equivalent to the quantity of hydrogen formed[20,21]. At that time it was considered that radioactive elements (Ra, Rn) catalysed the decomposition of H_2O to H_2, O_2, and H_2O_2, but it was not suggested that radiation supplied the energy. In a review of data published up to 1907, Bragg[22] established that when the same quantity of radon acts on water and on air, the number of water molecules decomposed almost coincides with the number of ions formed in air. In 1913 Duane and Scheuer[23] studied the action of α-rays on water and formulated a general principle of radiation chemistry, according to which the main process in aqueous solutions is the action of the radiation on water. It was implied that all radiochemical reactions in solution take place as a result of the interaction of molecules of "activated water" with the dissolved substances. The nature of the activated water, however, remained unknown.

The formation of H_2 and H_2O_2 in pure, thoroughly degassed, water treated with X-rays and γ-rays remained undetected for a long time. This was apparently due to the low sensitivity of the analytical methods employed. Later Allen and Toulis showed that the steady-state concentration of these products is extremely small (10×10^{14} molecules $\times$ $\times$ ml^{-1} for the action of 2 MeV electrons and X-rays)[28,29].

Debierne (1914) and later Risse (1929) suggested that the action of ionising radiation on water produces H and OH radicals which participate in reactions[30,31]. In 1944, Weiss used the theory that H and OH radicals are formed when aqueous solutions are irradiated to explain the oxidation and reduction of a number of substances[32]. In 1948 Dainton analysed an aqueous solution of acrylonitrile irradiated with ultra-violet light, X-rays, and γ-rays, and detected the presence of OH groups in the polymer formed. Dainton concluded that in this case the OH radical is the chain initiator[33]. The existence of H atoms in liquid water has not yet been confirmed by direct experiment. Such data are available, however, for gaseous and solid phases, where the existence of atomic hydrogen has been shown. For example, the conversion of para-hydrogen to ortho-hydrogen under the influence of α-radiation takes place *via* H atoms[34].

In the nineteen-fifties, the e.p.r.† spectra of irradiated, frozen water and aqueous solutions were recorded at different temperatures. In some cases the presence of atomic hydrogen was established[35-41]. The e.p.r. spectra of frozen solutions are important in the chemistry of aqueous solutions since the form of the primary products of radiolysis (ions and excited molecules) and their distribution in the track of the ionising particle in the initial moment are evidently independent of the state of aggregation of the system (solid or liquid)[9].

All theories of the production of radicals during the radiolysis of water are based on the assumption that the formation of a pair of ions when the ionising particle and water molecule collide requires the same amount of energy in the liquid and gaseous phases. From mass-spectrometric data[42] it is known that when an electron collides with a water molecule, H_2O^+, OH^-, H^+, and H_3O^+ are formed, together with small quantities of O^- and H_2^+. A minimum of about 12.5 eV is required for the removal of an electron from a water molecule. After a thorough survey of all available data, Gray[43] took the average value of the energy necessary to form one pair of ions as 32.5 eV for X-rays and γ-rays and 35 eV for α-particles. This shows that approximately three pairs of ions are formed for every 100 eV absorbed by the solution.

The positive and negative ions produced (after a number of collisions with water molecules, the velocity of the displaced electron falls to thermal values and the electron is captured by a water molecule with the formation of H_2O^-) can be hydrated (the energy evolved is sufficient for the rupture of an O–H bond) and converted to OH and H radicals in times of the order of 10^{-11} sec[44] according to the scheme‡:

$$\begin{aligned}
&\text{(a)} \quad H_2O \xrightarrow{\sim\sim\sim} H_2O^+ + e \\
&\text{(b)} \quad H_2O^+ + H_2O \rightarrow H_3O^+ + OH \\
&\text{(c)} \quad e + H_2O \rightarrow H_2O^- \\
&\text{(d)} \quad H_2O^- + H_2O \rightarrow OH^-aq + H \\
&\qquad\qquad H_2O \xrightarrow{\sim\sim\sim} H + OH
\end{aligned} \qquad (1)$$

According to this first theory of radical formation, they should be formed at some distance from one another (Dale, Gray, and Meredith[47] have estimated this distance as equal to 70 times the diameter of the water molecule).

According to the theory put forward by Magee and coworkers[48,49], the electron very rapidly gives up its energy to the surrounding water molecules and thus cannot overcome the force field of the H_2O^+ ion§. As a result of the subsequent neutralisation of the H_2O^+, the excited water molecule which is produced should "break down" into H and OH radicals. According to Magee, this neutralisation step takes not more than 10^{-13} sec. The energy evolved on neutralisation of the ions is sufficient to enable the H and OH radicals to overcome the cell effect and to move a considerable distance apart.

According to the second theory, any radiochemical reaction involves the reaction of excited water molecules, and the radicals formed by their dissociation, with the molecules of dissolved substances; ions do not take part in the reaction since their lifetime is extremely small (10^{-13} sec).

These theories of radical formation give different pictures of the initial distribution of the product radicals. According to the first theory, the H and OH radicals from ionised water molecules in an irradiated system are formed initially at a considerable distance from one another, and according to the second theory they are formed in the same place. According to the first theory, for strongly-ionising radiation (α-particles), the track after the hydration of the ions formed from the water molecules can be pictured as a beam of radicals (1000 per 1 μ of path) surrounded by a "diffuse" cloud of H atoms. For weakly-ionising radiation,

† Electron paramagnetic resonance.

‡ According to the most recent data[45,46], the lifetime of the H_2O^+ ion in the liquid phase is 1.6×10^{-14} sec. Reaction (1*b*) can take place in $\sim 10^{-13}$–10^{-14} sec.

§ Here no allowance is made for the fact that the movement of the electron takes place in the force field of polar molecules, which may weaken its interaction with the H_2O^+ ion.

the distance between the H and OH formed from one initially-ionised water molecule is greater than 15 mμ. These radicals are more uniformly distributed along the track (from 3 to 1 per 1 μ of path) and their concentration in the region of the axis of the beam does not exceed 10^{-4} M (for 60 kV electrons [50]).

According to the second theory, the OH and H radicals are uniformly distributed in the volume of the track, that is, the average concentration of H and OH is the same throughout its volume, irrespective of the form of the ionising radiation. It is difficult to verify either theory since our knowledge of the nature of the product radicals and the kinetics of their interaction is incomplete. To solve this complex problem various theories of the properties of the intermediate particles and their reactivity, based on the behaviour of free radicals in the gaseous phase, are being used. A further complicating feature is that an examination of the distribution of radicals in space and with time inside the spur¶ is required, with allowance for the distribution of the spurs relative to one another and for their interaction with one another with time. Thus it is necessary to allow for the fact that their distribution in the volume of the track changes with time as a result of diffusion and recombination of the radicals.

By limiting the conditions of the problem, results have been obtained which agree satisfactorily with experimental data only in a few cases. Thus Ganguly and Magee, starting from a model giving uniform distribution of radicals in the tracks and assuming that the distribution of radicals in the spurs remains unchanged during the reaction (a doubtful simplification), found that 80–100% of the radicals are removed in reaction with the acceptors† at acceptor concentrations of the order of 1–10 M for weakly-ionising radiation [51]. Schwarz and coworkers showed that Ganguly and Magee's calculations agree with the results of experiments on the determination of the number of recombining radicals and radicals removed in reaction with acceptors for the irradiation of aqueous solutions of KBr, KNO_2, and C_2H_5OH by γ-rays, deuterons, and helium ions [52,53]. This agreement between theoretical and experimental data is observed, however, only at intermediate values of the concentration of radical acceptors. At high and low acceptor concentrations, discrepancies between theory and experiment appear [54], indicating either that the model is not completely satisfactory or that the assumptions made in simplifying the problem are incorrect.

Armstrong, Collinson, and Dainton [55] established a difference in the values and in the directions of change in the yield of radical and molecular products of radiolysis on going from solutions of acrylamine in ordinary water to solutions in heavy water. This phenomenon may be related to a difference in the initial distribution of the oxidising and reducing components of radiolysis.

Filinovskii and Chizmadzhev solved the problem of the recombination of H and OH radicals in the track for the case of uniform distribution of these radicals in the track ($r \sim 1$ Å) and for the case of "broad" distribution of H radicals ($r \sim 100$ Å). They allowed for the change of the distribution of the radicals with time as a result of their recombination: in their calculations they assumed that the rates of radical reactions are identical [56]. Other workers [57] obtained a solution for the case of the Samuel–Magee–Burton model for the action of fast electrons on concentrated acceptor solutions.

Final verification of one or other of the theories of radical distribution in the track can be made by accumulating sufficient experimental data on the concentration dependence of the conversion yields of H and OH radical acceptors and balancing all the radiolysis products over wide ranges of radical acceptor concentrations.

Even at this stage, data from an analysis of the yields in the formation of the products of the "molecular decomposition of water" with change in the concentration of radical acceptor give interesting information on the geometry of the track. It has been established, for example, that the order of the reactions involved in the formation of the molecular products H_2 and H_2O_2 in solutions depends on specific features of the radiation (the density of ionisation and the energy of the ionising particles) and hence on the spatial distribution of the product radicals‡.

A number of other concepts have been put forward and are still used in one form or another to explain the nature and distribution of the products formed in the radiolysis of water.

The basis of theories of H atom formation is the assumption that a thermal electron (whose energy is lower than the excitation potential of water) is captured either by a water molecule (Lea *et al.*'s mechanism) or by the H_2O^+ ion from which it was "torn" (Magee, Samuel, *et al.*'s mechanism), in a time less than that required for reaction with dissolved substances. According to Platzman and Fröhlich's data [60], however, these two processes take place slowly. A free electron is assumed to have a lifetime of the order of 10^{-5} sec. In this time the electron can move from one water molecule to another (time of transfer 10^{-15}–10^{-14} sec; the dissociation of the H_2O^- ion requires $\sim 10^{-11}$ sec), since the energy levels of the electrons in the water molecules are close and overlap. In this case, the electron, when captured by a molecule of dissolved substance, would act as a weak reducing agent. This might explain the predominant oxidising action of irradiated water (since an OH radical is formed in the bulk of the solution at the same time as the electron). No convincing indications that this model is completely satisfactory have yet appeared, however.

From the conclusion that irradiated water has a high redox potential, Dainton and Collinson [2] suggested that the formation of H and OH radicals is accompanied by the formation of OH^+ radical ions which are hydrolysed in time. According to Weiss [61], the high redox potential is caused by reaction of atomic hydrogen with a proton to produce H_2^+. This, of course, could only be the case for acid solutions. It is known, however, that the predominant oxidising action of X-rays and γ-rays is independent of the pH of the solution [62] and therefore cannot be due to formation of H_2^+ according to the scheme

$$H + H^+ = H_2^+. \qquad (2)$$

¶ Spur — the track of the secondary electron, sometimes called the δ-ray (Editor).

† The term *scavenger* is used in place of *acceptor* by Western radiochemists (Ed. of Translation).

‡ This is reflected in the order of the equation giving the dependence of the yield of molecular products on the acceptor concentration. As pointed out by Magee and co-workers, [58,59], the order in acceptor concentration may vary from 0 to ½, depending on the density of ionisation and the energy of the particles. When γ-rays with energies of the order of 1 MeV are used, the order is 1/3.

According to Haissinsky and Magat[63], H atoms are not formed when aqueous solutions are irradiated (or at least do not exist independently) and the decomposition of the H_2O^- ion takes place according to the mechanism

$$H_2O^- \rightarrow O^- + H_2$$
$$O^- + H_2O \rightarrow OH + OH^- \quad (3a)$$

or

$$H_2O^- \rightarrow H^- + OH$$
$$\frac{H^- + H_2O \rightarrow OH^- + H_2}{H_2O^- + H_2O \rightarrow H_2 + OH + OH^-} \quad (3b)$$

This scheme for the radiolysis of water assumes the formation of two OH radicals for every hydrogen molecule (that is, eight OH radicals from four ionised water molecules) and might explain the high conversion yields for dissolved substances (~8 equiv /100 eV) reacting with the free hydroxyl.

The formation of molecular hydrogen from H_2O^- is inconsistent, however, with the experimentally observed dependence of the yield of molecular products H_2 and H_2O_2 on the concentration of H and OH radical acceptors[52,64-72]. Moreover, Proskurnin and coworkers have found conditions under which, as a result of a decrease in the yield of formation of molecular products, there is an increase in the yield of the products of conversion of the dissolved substances[73-76].

To illustrate the development of the theories of the formation of primary radical products, we must examine a recently proposed mechanism for the molecular decomposition of water.

In 1935, Fricke postulated the existence of two types of activated water molecule[77], $(H_2O)'_{act}$ and $(H_2O)''_{act}$, to explain conversion yield differences for substances in aqueous solutions when irradiated with X-rays. The first forms molecular products H_2 and H_2O_2 with a yield of 0.49, and the second type of activated water molecule exhibits the unique properties of activated oxygen and is formed with a yield of 1.96. By irradiating water with ultra-violet light corresponding to the absorption band of water below 2000 Å, Fricke and coworkers initiated reactions which they believed were characteristic only of $(H_2O)''_{act}$.

In 1948, Allen[28] suggested that the conversion of the products of the interaction between the ionising particle and the water molecule involved two processes which yield molecular products (H_2 and H_2O_2) and H and OH radicals§

$$H_2O \text{ —}\sim\sim\rightarrow {}^1/_2\, H_2 + {}^1/_2\, H_2O_2 \quad (F)$$
$$H_2O \text{ —}\sim\sim\rightarrow H_2 + OH\,. \quad (R)$$

At the points of intense ionisation (hot points), the molecules have energy in excess of that required for the formation of H and OH, so that the reaction H + OH = H_2O may be accompanied by recombination reactions

$$H + H = H_2 \quad (4)$$
$$OH + OH = H_2O_2\,. \quad (5)$$

The yield of "molecular" products changes on going from one system to another. Allen and Johnson[79] attributed the lack of agreement between the "molecular" yields for the irradiation of different solutions to a difference in the conditions for the back reactions

$$H + H_2O_2 \rightarrow OH + H_2O \quad (6)$$
$$OH + H_2 \rightarrow H + H_2O\,. \quad (7)$$

To explain the "high" yields of hydrogen peroxide observed in the radiolysis of acidic solutions of iron sulphate, Dainton and Sutton[80], in 1953, proposed a third general reaction (E) for the decomposition of water molecules

$$H_2O \text{ —}\sim\sim\rightarrow H + {}^1/_2\, H_2O_2, \quad (E)$$

which means essentially a new distribution of radical and molecular products. At the same time, Allen, on the basis of a critical survey of data obtained by different authors on the kinetics of the radiolysis of certain systems, also concluded that reactions F, R, and E take place[81].

From the above it may be concluded that the action of rapid particles on water and aqueous solutions leads to the formation of ionisation products and excited states of the water molecules, both of which may produce H and OH radicals. Thus, although the nature of the primary products has not yet been established by direct experiments, we can, when considering radiolytic processes, speak of the primary chemical interaction of H and OH radicals with one another and with dissolved substances leading to the formation of molecular products H_2 and H_2O_2 and products of conversion of the dissolved substances. The subdivision of the processes involved in the formation of the products into reactions F, R, and E, and the mechanism proposed by Haissinsky, should, in our opinion, be regarded merely as a method of balancing the radiolytic products, since $G(H_2)$ and $G(H_2O_2)$ change on going from one system to another. These considerations can also to some extent be applied to cases of radiolysis under the influence of α-radiation. There is no fundamental difference between the processes involved in the formation of the primary product radicals on ionisation by α-rays and by γ- and X-rays. The only difference is in the density of ionisation in the track in α-ray radiolysis, where the recombination processes (4) and (5) have a higher probability.

H and OH radicals are formed in water in equivalent quantities and may initiate both oxidation and reduction. The fact that irradiated water has a predominantly oxidising action is apparently due firstly to the difference between the "effective" concentrations of the OH and H radicals, arising from the difference in the distribution of these radicals in the track of the ionising particle¶, and secondly to the difference between the reactivities of the H and OH radicals. For a long time no allowance was made for the effect of the reverse reaction, which increases with increase in the radiation dose, and the attainment of equilibrium between the original substances and the products of their conversion in a number of systems (for example, nitrate, nitride[82], was attributed to the definite redox potential of irradiated water (+0.96 V)[2]. It was assumed that a reversible equilibrium exists between the hydrogen atoms and OH radicals.

§ A number of workers[48,78] believe that molecular hydrogen and hydrogen peroxide, together with H atoms, are formed as a result of changes in the excited water molecules in the spurs, according to the following reactions:

$$H_2O^* + H_2O^* \rightarrow H_2 + H_2O_2 \quad (8)$$
$$H_2O^* + H_2O^* \rightarrow 2H + H_2O_2 \quad (Ea)$$
$$H_2O^* + H_2O \rightarrow 2H + H_2O_2 \quad (Eb)$$

¶ In the estimation of the oxidising properties of irradiated water in early studies on solutions saturated with air, no allowance was made for the fact that the O_2, an energetic H atom acceptor, facilitates the removal of the reducing component of the radiolysis of water from the reaction and thus prevents the reduction of other dissolved substances[2,5].

This theory excludes the possibility of formation of reduction products whose potential is more negative than +0.95 V. Moreover, it is inconsistent with experimental observations on the conversion of a number of substances (for example, methylene blue) which are capable of being oxidised and reduced under conditions where competing acceptors (oxygen) are absent[2]. As a result of the absence of reversible equilibrium between the oxidising and reducing components of the products of the radiolysis of water, it is possible, using selective electrodes, to obtain values for the redox potentials of the products of the conversion of each of these components[83,84]. It has been found that the potential of a platinum electrode in irradiated 0.8 *N* H_2SO_4, corresponding to the appearance of the products of conversion of H atoms, is close to that of the normal hydrogen electrode[83].

It has been shown[74,76,83-86] that when one of the radicals, for example H, is removed by an acceptor, the conversion yield of another substance which is an acceptor of the conjugate radical (OH) increases. The absence of reversible equilibrium between the products of oxidation and reduction of a given acceptor (for example, in the case of the nitrate–nitrite system) means that the ratio of the concentration of its oxidised and reduced forms depends on the experimental conditions. The decrease in the accumulated yield of products with time of irradiation in such systems is due to an increase in the rate of the reverse processes. With the introduction of conjugated acceptors it is possible to suppress the reverse processes completely, in which case the conversion yield of one of them reaches a value equivalent to the utilisation of the products of conversion of all the radiolysed water molecules[75]. The reactivity of the radical products of radiolysed water molecules will now be considered.

2. THE CONCEPT OF RADICALS AS INTERMEDIATE PRODUCTS IN THE RADIOLYSIS OF WATER

A. OH Radicals as the Oxidising Component of Radiolysis

As we have seen, OH radicals are evidently formed in the dissociation of H_2O^+ to H^+ and OH as a result of hydration of the positive hydrogen ion, since the time necessary for this process has been calculated[46] to be much less than the time required for the neutralisation of H_2O^+†. The OH radicals have not yet been detected by direct methods in irradiated water. However, in a number of radiolyses[89-91] of frozen aqueous solutions, the e.p.r. method and luminescence analysis have established the existence of intermediate products at temperatures below -160° (one type of radical) and -120°, and in a number of cases it may be assumed that OH radicals have been observed[36,90,92]. It has not yet been possible, however, to identify OH radicals precisely from these spectra. Kaitmazov and Prokhorov[93] have described an attempt to obtain the e.p.r. spectrum of the OH radical during the photolysis of aqueous H_2O_2 solution. The identification of the OH spectrum reported cannot be taken as conclusive, since OH radicals react readily with H_2O_2 to form HO_2, whose spectrum is superimposed on that of the OH. It was not until 1959 that the OH radical was identified in irradiated ice and the kinetics of its conversion in the temperature range 77°–108°K studied by the e.p.r. method[94,95].

By recombining with one another, OH radicals are able to form hydrogen peroxide, whose steady-state concentration[96] cannot exceed 10^{-3} M. Increase in the pH of the solution from ~0 to 12 decreases $G(H_2O_2)$ by a factor of 2.5–3, in irradiation by X-rays[97]. A sharp decrease in the H_2O_2 concentration at pH ~2.5 and a slight increase in the H_2O_2 concentration at pH ~12 has been reported[98,99]. This phenomenon is attributed to the possibility of dissociation of the OH radical to O^- and H^+ under these conditions and its removal from the reverse reaction of peroxide oxidation (6). The possibility of dissociation of OH radicals in alkaline medium and the stability of O^- at pH 13.9 has been reported by other authors[100-103]. The e.p.r. spectra of frozen nitrate solutions has revealed that on going from alkaline solutions (1 M and 0.1 M NaOH) to neutral solutions, one radical disappears and another is produced, which may correspond to the process

$$\underset{\text{(I)}}{OH} + OH^- = \underset{\text{(II)}}{O^-H_2O} \quad (9)$$

The radicals (I) and (II) can exist only at temperatures ≤ -160°.[104]

It is generally assumed that the fate of the free hydroxyl in the radiolysis of water is its dimerisation with the formation of hydrogen peroxide, but it is also necessary to allow for the possibility of disproportionation of OH radicals to H_2O_2 and O_2.[105] Kazarnovski and coworkers, using potassium ozonide as a source of free hydroxyl radicals, showed that the disproportionation of OH in aqueous solutions should play a more important role than the dimerisation process.

The OH radicals have a high electron affinity (free energy = 40 kcal mole^{-1}[106,107]) and hence may act as oxidising agents. The electron affinity plus the solvation energy is 147.6 kcal mole^{-1}.[108] This may explain the radiolytic oxidation of, for example, halide ions‡ Cl^-, Br^- and I^-, salts of uranium(IV),[111-117] tin(II),[117-119] and iron(II),[120,121] oxy-anions such as SeO_3^-, TeO_3^-, AsO_2^-, NO_2^-, and PO_3^{3-},[122-127] the gases CO, NH_3, H_2S, N_2O, and N_2 dissolved in water[128-132] (Table 1), and a large number of organic compounds (alcohols, acids, ketones, aldehydes, aromatic compounds, etc.). The oxidising power of OH radicals is determined by the redox potential of the system and depends on the acidity of the medium, decreasing with increase in pH.[132-135]

It has been observed in a number of cases (the radiolysis of solutions of ferrous salts, the dye methylene blue, etc.) that there is a sharp decrease in the conversion yield of the substances in the pH range 2–3, due to a decrease in the oxidising power of the OH radicals[111,136,137]. In approximately the same pH range there is an increase in the reducing power of H radicals[134]. Since these two radicals can be considered to have opposing effects, and both are always present in solution, it is possible that the apparent decrease in the oxidising power of OH and reducing power of H is due to the same factor. It would be interesting to examine this question for a large number of systems with the action of the conjugated radical excluded in each case.

† Weiss and coworkers[87,88] believe that in strongly acidic medium H_2O^+ exists for a longer period (up to 10^{-11}–10^{-10} sec), as does H_2O^- in alkaline medium. These ions may react with dissolved substances if the concentration of the latter is sufficiently high.

‡ The reaction of ordinary OH radicals with Cl^- would be accompanied by an increase in free energy (17 kcal mole^{-1}), so that it is assumed that excited OH radicals take part in this reaction[106,109,110].

A number of workers believe that OH radicals may exhibit reducing properties towards strong oxidising agents. Thus, Haissinsky and Lefort[138] consider that the reduction of Ce^{4+} and $Cr_2O_7^{2-}$ [138-140] involves reaction between OH and these ions. It must be remembered, however, that the reduction of these compounds is caused not by the direct action of OH radicals but by the formation and decomposition of intermediate compounds of the peroxide type produced as a result of the addition of hydroxyl to these ions[131]. Proof of this is provided by the fact that apparent participation of OH radicals in reduction processes are characteristic only of compounds capable of forming more highly oxygenated derivatives.

B. The Participation of H Atoms in Radiolytic Reactions

H atoms, formed in aqueous solutions as a result of reaction (1*d*) and also, in acid medium, by the reaction[53,141]

$$H_3O^+ + e = H + H_2O, \qquad (10)$$

are able to reduce a number of substances (Tables 1 and 2).

There is every reason to suppose that atomic hydrogen (H radicals) in the condensed phase are present in the hydrated state, that is, as H_3O. We must also remember that the hydrogen atom is able to form hydrogen bonds. This may explain the rapid displacement of H and OH radicals within the volume by the so-called relay mechanism of active particle transfer and may thus explain the absence from the e.p.r. spectrum of H atoms and OH radicals in irradiated frozen aqueous solutions at low temperatures (above -196° and -160°) when diffusion of the radicals is hindered[142]. It is only comparatively recently that the e.p.r. method has made it possible to detect H atoms in pure frozen water at the temperature of liquid helium[35]. In frozen solutions of oxy-acids, the doublet belonging to H can be observed at higher temperatures[37-39]. No attempt has been made to observe directly H radicals in the liquid phase, since their steady-state concentration during irradiation is extremely low.

Zalkind and Veselovskii suggested that the decrease in the electrode potential of a smooth platinum electrode in acidified irradiated water was caused by the setting-up of a redox potential corresponding to a definite concentration of H atoms in the solution[83,84,143]. Assuming that the lifetime of the H atoms in water is of the order of several minutes, it is possible to estimate the steady-state concentration of H atoms in the volume, the value found being $\sim 3 \times 10^{-5}$ M;[143] when an oxidising-component acceptor (oxalic acid) is present in the solution, the steady-state concentration of H is several times greater. This conclusion for liquid solutions at ordinary temperatures, however, is inconsistent with the diffusion picture of the track of the ionising particles and the recombination reactions of H atoms. From a study of the isotopic exchange between H_2 and D_2 in aqueous solutions, initiated by γ-rays, and assuming that the rates of the processes

$$H + H_2 = H_2 + H \qquad (A)$$

$$H + D_2 = HD + D, \qquad (B)$$

in the liquid phase are the same as in the gaseous phase, Friedman and Zeltmann[144] estimated the steady-state concentration of H atoms and obtained the value 2×10^{-8} M for a dose power of 10^{18} eV cm^{-3} sec^{-1} §. In our opinion, this value for the steady-state concentration of H corresponds more closely to the real value, although the assumption that the rate constants of processes (*A*) and (*B*) in the gaseous and liquid phases are equal is a considerable simplification.

The decrease in the electrochemical potential of a platinum electrode in an irradiated acid may be due to the accumulation of molecular hydrogen in the solution and resultant supersaturation, or to the accumulation in the solution of intermediate products (whose formation is possibly related to the fate of the H atoms) which exist for a comparatively long time.

The hydrogen atoms take part in recombination reactions with one another and with OH radicals, forming H_2 and H_2O. For the action of strongly-ionising radiation (for example, α-particles) on water and aqueous solutions, G_{H_2} remains almost constant, irrespective of the composition of the solution in the range of intermediate values of the concentrations. This is due to the high values of the local concentrations of radical products in the track. In the case of γ-radiation, the introduction of H-atom acceptors into the irradiated water in comparatively small quantity may lead to a sharp decrease in G_{H_2} through competition for H atoms in the recombination process H + H.[75] In the presence of the conjugate OH-radical acceptor, the conversion yield of the H-atom acceptor increases and remains constant over a wide dose range, through a decreased recombination of H with OH radicals[75] and the reverse oxidising processes[73,86,132,137]. In this case G_{H_2} shows almost no change compared with its value in the absence of OH acceptor, if the concentration of H-atom acceptor ensures removal of the latter from the recombination reaction H + H, that is if it is equal to or greater than ~ 1 M.

The reducing power of the H atoms is determined by the reactivity of the H-atom acceptor, and also by the pH of the medium in which the reaction takes place. However, the dependence of the reactivity of the dissolved substance on the pH of the solution must be taken into account. This dependence may be more clearly defined than in the H atom case and the effect may exceed that in the latter, as, for example, in the reduction of dichromate ion[123,135]. The reducing power of the H atoms increases with increase in the pH of the solution[145-147].

Some workers[148] attribute oxidising properties to the H atom in acid solutions. For example, Weiss suggests that in acid medium, H atoms present in the form H_2^+ take part in the oxidation of iron(II) ions and organic compounds according to the scheme

$$RH_2 + H_2^+ \rightarrow RH + H^+ + H_2 \qquad (11)$$

The theory that H atoms have an oxidising action is supported by experiment[149-151]. Atomic hydrogen, prepared by electrical discharge in H_2, was passed into acidic solutions of Fe^{2+} and Fe^{3+}, and the kinetics of the oxidising and reducing reactions of the Fe^{2+}–H_2O and Fe^{3+}–H_2O systems were studied. Under these conditions, however, the data[149] show that intermediate products of the conversion of sulphuric acid and H atoms, and not H_2^+, may take part in the reactions.

Cottin studied the oxidation of phosphite and considers that H atoms are capable of oxidising phosphite ions by the formation of an H–H bond, which is stronger than the H–HPO bond[127].

The question of the existence of the molecular hydrogen ion H_2^+ in acid medium (pH = 1 – 4) is of interest since in

§ The effective lifetime of the H atoms under these conditions, according to Friedman and Zeltmann, is 0.2 sec.

TABLE 1. Examples of radiolytic processes involving oxidation and reduction of inorganic compounds in aqueous solution.

System studied (suggested reactant in brackets)	Experimental conditions	Concentration range studied, M*	Maximum value of conversion yield of original substance, molecules (or ions) / 100 eV	References**
$Fe^{2+} \rightarrow Fe^{3+}$ (OH)	acid medium in the presence of O_2	$2\cdot10^{-6}$—$1\cdot10^{-2}$ (10^{-4}—10^{-2})	15.6 (15.6)*	136,181—197,80 67,120
$Fe^{3+} \rightarrow Fe^{2+}$ (H)	acid medium, without O_2	$1\cdot10^{-4}$—$1\cdot10^{-2}$	~8	136,182,155
	pH = 0.8 (without O_2)	$1\cdot10^{-3}$	0.07	140,147
	pH = 2.46 (with O_2)	$2.2\cdot10^{-4}$—$3.86\cdot10^{-4}$	15	198,199
$Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-}$ (OH)	pH = 2—11 (without O_2)	$1\cdot10^{-4}$—$1\cdot10^{-1}$ (10^{-4}—10^{-1})	1.02 (1.02)	122
$Fe(CN)_6^{3-} \rightarrow Fe(CN)_6^{4-}$ (H)	pH = 0.5—7 (with O_2)	$2\cdot10^{-4}$—$5\cdot10^{-3}$	5 4	133
	pH = 12 (without O_2)		0.95	133
Fe^{2+} 2, 2′-bipyridyl (OH)	0.8 N H_2SO_4	$1\cdot10^{-3}$	15.6	200
Fe^{3+} 2, 2′-bipyridyl (H)	pH ⩽ 7	$1\cdot10^{-3}$	9.4	200,201
Fe^{3+} 1, 10-phenanthroline (H)	pH = 0.4—3.5	$1\cdot10^{-4}$	9.6	201
	pH = 6 (with O_2)	$1\cdot10^{-4}$	4.0	198
$Ce^{4+} \rightarrow Ce^{3+}$ (H)	0.8—1 N H_2SO_4 in the presence of O_2	$1\cdot10^{-4}$—$4\cdot10^{-3}$ ($1\cdot10^{-3}$—$4\cdot10^{-3}$)	2.2—2.4 (2.36)	203,199,202,82,204,205
		$2\cdot10^{-4}$—$1\cdot10^{-3}$	5.2	140
$Ce^{3+} \rightarrow Ce^{4+}$ (OH)	3 M K_2CO_3 (alkaline solution)	$1\cdot10^{-3}$	1.7—1.9	138
$Cl^- \rightarrow Cl$ (OH*)	pH = 11	$1\cdot10^{-2}$—7	3.2	109,206—208
$Br^- \rightarrow Br$ (OH)	pH ≃ 7	$1\cdot10^{-5}$—4.5 ($1\cdot10^{-3}$—$1\cdot10^{-1}$)	0.66	111,66,109,207,122
$I^- \rightarrow I$ (OH)	pH = 2—11	$1\cdot10^{-7}$—5 ($1\cdot10^{-5}$—$1\cdot10^{-3}$)	3 (3)	111,122,112,209
$BrO_3^- \rightarrow Br_2 + O_2$ (H)	0.1 N H_2SO_4	$6\cdot10^{-4}$	2.0	202,210
$IO_3^- \rightarrow I_2$ (H)	pH = 12.5	$5\cdot10^{-4}$—$1\cdot10^{-3}$	~1.7	211,209,202
	pH ≃ 0	$5\cdot10^{-4}$—$1\cdot10^{-3}$	~0.6	211
$Sn^{2+} \rightarrow Sn^{4+}$ (OH)	4 N HCl, 1 N NaOH	$1\cdot10^{-2}$—1 ($1\cdot10^{-2}$—$1\cdot10^{-1}$)	0.5; 0.6 (~0.5)	118,119
	pH ≃ 0.1	$3.6\cdot10^{-1}$	0.49	212
$Sn^{2+} \rightarrow Sn^0$ (H)	weakly alkaline medium, vacuum	$1\cdot10^{-2}$	~0.03—0.01	119
$Ti^{3+} \rightarrow Ti^{4+}$ (OH)	1—4 N HCl	$1\cdot10^{-2}$—$1\cdot10^{-1}$ ($1\cdot10^{-2}$—$1\cdot10^{-1}$)	5 (5)	119
	1—4 N H_2SO_4	$1\cdot10^{-2}$—$1\cdot10^{-1}$	4.2 (4.2)	119
$Co^{3+} \rightarrow Co^{2+}$ (H)	pH ~ 0.4	$1\cdot10^{-3}$	2.3	82
$Tl^{3+} \rightarrow Tl^+$ (H)	pH ~ 0.4	$1\cdot10^{-4}$—$2\cdot10^{-3}$ ($1\cdot10^{-4}$—$2\cdot10^{-3}$)	1.18 (1.18)	213,82,214
$U^{4+} \rightarrow U^{6+}$ (OH)	3 N H_2SO_4	$5\cdot10^{-4}$—$5\cdot10^{-2}$ ($2\cdot10^{-2}$—$5\cdot10^{-2}$)	2,0 (2.0)	113—116
$SeO_3^{2-} \rightarrow SeO_4^{2-}$ (OH)	pH = 2÷11	$1\cdot10^{-4}$—$1\cdot10^{-1}$ ($1\cdot10^{-4}$—$1\cdot10^{-1}$)	0.6 (0.6)	122,111
$TeO_3^{2-} \rightarrow TeO_4^{2-}$ (OH)	pH = 2÷11	$1\cdot10^{-4}$—$1\cdot10^{-1}$ ($1\cdot10^{-4}$—$1\cdot10^{-1}$)	0.6 (0.6)	122
$AsO^{-}{}_2 \rightarrow AsO^{-}{}_3$ (OH)	pH = 2.5; 7	$1\cdot10^{-4}$—$1\cdot10^{-2}$ ($1\cdot10^{-3}$—$1\cdot10^{-2}$)	1.75; 2.2 (with O_2) (1.75)	124,111,122,215
	pH = 10.5	$1\cdot10^{-4}$—$1\cdot10^{-2}$ ($1\cdot10^{-2}$—$5\cdot10^{-2}$)	3.25; 15 (O_2) (3.25)	124
$H_2PO^{-}{}_3 \rightarrow PO_4^{2-}$ (OH)	pH = 0.4; 3	$2\cdot10^{-5}$—$1\cdot10^{-1}$ ($5\cdot10^{-3}$—$1\cdot10^{-1}$)	3.8; 3 (3.8; 3)	127,216
$PuO_2^{2+} \rightarrow Pu^{4+}$ (H)	0.5 N H_2SO_4	$2.8\cdot10^{-5}$—$9\cdot10^{-3}$ ($1\cdot10^{-3}$—$9\cdot10^{-3}$)	1.7 (1.7)	217,218
$VO^{+}{}_2 \rightarrow VO^{2+}$ (H)	pH ~ 0.4	$3\cdot10^{-4}$—$1\cdot10^{-2}$ ($3\cdot10^{-4}$—$1\cdot10^{-2}$)	2.7 (2.7)	134
$HClO_4 \rightarrow ClO^{-}{}_3 + Cl^-$	acid medium (with and without O_2)	$1\cdot10^{-3}$—8.4	1.34	127,219
$NaClO_4 \rightarrow ClO^{-}{}_3 + Cl^-$	pH = 5.4—4.6 (with and without O_2)	1—8	~2.42	127
$NH_2OH \rightarrow N_2 + NH_3 + N_2O + H_2$	pH = 4, vacuum	$1\cdot10^{-3}$—$5\cdot10^{-3}$ ($1\cdot10^{-3}$—5.10^{-3})	6.8 (6.8)	111,220
$NH_2OH \rightarrow NH_3 + NO^{-}{}_3$	pH = 3.3 in the presence of O_2	$1\cdot10^{-3}$	3.5	111
$N_2H_4 \rightarrow NH_3 + N_2 + H_2$ (H + OH)	pH = 0.3—12.3	$5\cdot10^{-5}$—$5\cdot10^{-2}$ ($1.5\cdot10^{-2}$—$5\cdot10^{-2}$)	5.2 (5.2)	221,111
$NH_3 \rightarrow NO^{-}{}_2$ (OH)	pH = 6.9—9.6 (with O_2)	$5\cdot10^{-4}$ $1\cdot10^{-1}$	1.3 (pH = 12.5)	129
$NO^{-}{}_3 \rightarrow NO^{-}{}_2$ (OH)	pH = 2—11 (vacuum)	$1\cdot10^{-4}$—1.11^{-4} ($1\cdot10^{-4}$—$1\cdot10^{-1}$)	0.91 (0.91)	122,126,132
$NO^{-}{}_2 \rightarrow NO^{-}{}_3$ (OH)	pH = 6 (vacuum)	$1\cdot10^{-4}$—$1\cdot10^{-3}$	1.6	112
$NO^{-}{}_3 \rightarrow NO^{-}{}_2$ (H)	pH = ~ 1.5—14	10^{-7}—5 ($5\cdot10^{-1}$—10^{-2}); (2—6)	4.4 (2,2: 4.4)	75,70,208,222
Reduction of MnO_4^- (H + OH)	pH = 0.4—12	$7.7\cdot10^{-4}$—$2.6\cdot10^{-1}$	8.5 (pH = 0.4); G (—Mn^{VII})	223—226, 205
Reduction of $Cr_2O_7^{2-}$ (H + OH)	pH = 1—12	$1\cdot10^{-4}$—$1\cdot10^{-3}$ ($1\cdot10^{-4}$—$1\cdot10^{-3}$)	3.8	139,135,140
	pH ≃ 0.4, with O_2	$2\cdot10^{-4}$	0.78 (Cr^{3+})	226
$CO \rightarrow CO_2$ (OH)	pH = 3.5	$1\cdot10^{-6}$—$1\cdot10^{-4}$	4	128
$H_2S \rightarrow S$ (OH)	acid medium in the presence of O_2	$2.4\cdot10^{-3}$—$6\cdot10^{-3}$	high	111,25,130

* The figures in brackets in column 3 give the concentration range (M) with the observed constant conversion yield of acceptor given in brackets in column 4.

** The first references are to papers giving the most complete data.

this range of pH values reaction (7) is possible, and this is associated with "conversion" of OH radicals to H atoms and participation of the latter in reactions involving oxidation, for example, of Fe^{2+} ions[136], or reduction, for example, of V^V and Ce^{4+}.[82,134]

Let us examine this question briefly.

In a study of the kinetics of radiolytic reactions in systems containing H_2O, H_2, O_2, and H_2O_2 in various combinations, Allen *et al.*[152,153] generalised the results of a series of investigations and concluded that two forms of H, differing in chemical character, exist. The H atom formed directly during radiolysis appears rather to be a solvated electron. The H atom exists in acidic or basic form, depending on the pH of the medium; this can be represented as follows

$$e \underset{}{\overset{H^+}{\rightleftarrows}} H \overset{H^+}{\rightleftarrows} H_2^+. \qquad (2a)$$

The solvated electron (H_2O^-) can be captured by an atom, molecule, or radical with a high electron affinity (for example, O_2 or OH). It has been suggested[87] that at a sufficiently high pH, H_2O^- exists in solution for at least 10^{-11}—10^{-10} sec and may react with a dissolved substance if the concentration of the latter is sufficiently high. Allen[144] suggests that the H atom is able to take part in one of the reactions (6) or (7), which decrease the accumulation yield of molecular products

$$H + H_2O_2 = H_2O + OH \qquad (6)$$

$$OH + H_2 = H_2O + H + 11.6 \text{ kcal mole}^{-1} \text{ ¶} \qquad (7)$$

A characteristic feature of the second form of H atom produced according to reaction (7) is that kinetic data[152,153] shows them to react more readily with oxygen than with

¶ From data given by Kondrat'ev[154].

TABLE 2. Characteristics of some conjugated radiation-chemical reactions.

Type of reaction and conditions	Conjugated acceptors		Accumulation yield, molecules 100 eV	Number of H_2O molecules converted	Note: increase in yield compared with conditions when one of the conjugated acceptors is absent	References
	of H atoms	of OH radicals*				
Reduction of Ce^{4+} ions in the presence of air 0.1 *N* H_2SO_4	Ce^{4+} ($\sim 3\cdot10^{-4}$)	benzene (0.02) acetic acid (2×10^{-2}–1×10^{-1})			$\sim$ 2.3 times greater than without acceptors	202
Reduction of Ce^{4+} ions in the presence of NO_3^- and Tl^+ 0.8 *N* H_2SO_4	Ce^{4+} ($4\cdot10^{-4}$) $NaNO_3$ (0.5)		11	11		228
Reduction of Ce^{4+} ions 0.8 *N* H_2SO_4	Ce^{4+} ($10^{-4}\div10^{-2}$)	benzene (10^{-6})	8.2	8.2	3.4 times	82
Reduction of Tl^{3+} ions 0.8 *N* H_2SO_4	Tl^{3+} ($1\cdot10^{-3}$)	benzene (10^{-6})	8.1	8.1	3.5 times	82
Reduction of Cr^{6+} ions 0.8 *N* H_2SO_4	$Cr_2O_7^{2-}$ ($1\cdot10^{-3}$)	benzene (10^{-6})	8.2	8.2	3.4 times	82
Decomposition of AET** in neutral solutions in the presence of O_2	O_2 ($H+O_2\rightarrow HO_2$)	AET	$\sim$18	9	2 times	170
Oxidation of Fe^{2+} ions in acid medium (0.8 *N* H_2SO_4) in the presence of oxygen	(p_{O_2}=70—150 atm)	Fe^{2+} (0.001)	$\sim$23	11.5	$\sim$3 times	137
Reduction of $C(NO_2)_4$	C $(NO_2)_4$ ($4.2\cdot10^{-3}$)	ethyl alcohol 1–80%	5.85	5.85	1.6 times	136
Oxidation of ammonia in the presence of oxygen at pH = 11	O_2 (from air)	$NH_3\rightarrow NO_2^-$ (0.15)	1.3(6.8 equiv)	6.8	no reaction without O_2	129,245
Decolorisation of methylene blue (oxidation)	Fe $(NO_3)_3$ ($2.4\cdot10^{-4}$)	methylene blue (2.4×10^{-4})	3.9	7.8	$\sim$100*** times	242
Decolorisation of methylene blue (reduction)	methylene blue 2.2×10^{-4}	glucose, sodium benzoate, ethyl alcohol (0.5)	5.2	10.4	$\sim$10 times	242,247,248
Oxidation of the leuco-form of indigo in the presence of nitrate	$NaNO_3$ (1)	leuco-form (2×10^{-3})	5.0	10	10 times	74
Reduction of nitrate ion in the presence of glucose and glycerol	$NaNO_3$ (2)	glycerol, glucose (1×10^{-2})(1 M KOH)	6	12	2.6 times	75,86
Reduction of U^{6+} 5×10^{-3} M in acid medium	$UO_2^{2+}\rightarrow U^{4+}$	glycerol, glucose (0.5)	5	10	20 times	249
Formation of nitrite ion in the oxidation of ammonia and reduction of sodium nitrate	$NaNO_3$ (1)	NH_3 (0,15) (KOH—1)	6 3	10.5	2.3 times	245
Oxidation of the leuco-base of methylene blue at pH $\leqslant$ 2	$NaNO_3$ (1)	the leuco-base of methylene blue (2×10^{-3})	9	12	12 times	76
Oxidation of the leuco-base of malachite green in the presence of oxygen	O_2	the leuco-base (1.4×10^{-2})	4.7	9.4	almost no reaction without O_2	250
Reduction of methylene blue 22.9 *N* H_2SO_4	methylene blue (1.6×10^{-4})	ethyl alcohol (0.5)	3.4	3.4	no reaction	141,251
Oxidation of indigo-carmine in the presence of oxygen, 1 *N* H_2SO_4	O_2 (p_{O_2}=70 atm)	indigo-carmine (2×10^{-4})	12	12	1000*** times	168
Reduction of indigo-carmine to the leuco-base 1 *N* H_2SO_4	indigo-carmine (2×10^{-4})		1.7	3.4	17 times	168
Oxidation of dye at pH $\sim$ 4	sodium nitrate (1)	indigo-carmine (2×10^{-4})	2	4	200 times ***	168
Reduction of Fe^{3+}, pH = 3	Fe^{3+} (10^{-2})	glycerol (1), glucose (1)	10—12	10—12	20 times	252
Reduction of UO_2^{2+} and oxidation of U^{4+} in 0.8 *N* H_2SO_4	UO_2^{2+} ($5\cdot10^{-3}$)	UO^{2+} ($5\cdot10^{-3}$)	4	4	—	253

* Concentrations expressed in M.

** AET denotes *S*-(2-aminoethyl)-thiuronium dinitrate.

*** The value given represents the increase in the yield under conditions where the back reaction is suppressed.

hydrogen peroxide, unlike the H atoms formed directly on radiolytic breakdown of the water molecules. In the latter case no selectivity of action of the H atoms with respect to O_2 and H_2O_2 is observed. Allen concludes that the process involved in reaction (7) is the removal of an electron from the H_2 molecule, and not rupture of the H–H bond, so that the "H atom" is in fact H_2^+.

Experiments on the role of reaction (7) in the oxidation of phosphite[127] and iron(II) ions[155] and the reduction of nitrate[156] in solutions at pH 0.4 and 2–14 respectively show that saturation of the solutions with hydrogen and even increase in the H_2 pressure above the solution to 180 atm[155,156] has almost no influence on the conversion yield for these substances. Cottin, and also Shubin and Dolin, assuming that reaction (7) occurs at a high rate, concluded that atomic hydrogen, like OH, takes part in oxidation reactions. It is interesting that Dainton and Hardwick[157], in a kinetic study of the action of Fenton's reagent (a source of OH radicals) and Shubin and Dolin, in a radiation study of systems with Fe^{2+}, H_2O_2, O_2, and H_2 or CO, obtained almost identical relative rate characteristics for the fundamental reactions. Essentially identical initial assumptions were made. This might indicate that the kinetic characteristics of radicals obtained by different methods are identical. $G(-Fe^{2+})$ does not change with increase in the pressure of hydrogen above the system from 1 atm to 180 atm. Shubin and Dolin suggest that the fundamental reactions in the system are

$$OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \qquad (12)$$

$$\left.\begin{aligned} OH + H_2 &\rightarrow H + H_2O \text{ and } H + H^+ \rightarrow H_2^+ \\ Fe^{2+} + H_2^+ &\rightarrow Fe^{3+} + H_2 \end{aligned}\right\} \qquad (13)$$

The small change in the value of $G(-Fe^{2+})$ (5%) on going from degassed solutions to solutions saturated with H_2 indicates that the rates of processes (12) and (13) are of similar order of magnitude. This is also indicated by studies[129]

of the oxidation of Fe^{2+} in solutions of pH 0.2–3.0†, if allowance is made for the displacement of equilibrium (2a) to the right. The oxidation yield of salts of the Sn^{2+} and Ti^{3+} type depends little on the acidity of the solution and in these cases oxidation by H atoms (in the form of H_2^+, at least) may be less probable[118,119].

In an examination of the part played by reaction (7) in the radiolytic Fe^{2+} conversion, a suggestion of Hart and Lefort[103,159] is of interest. They state that, in contrast with gas phase behaviour, where reaction (7) takes place *via* H atoms, the oxidising action of H atoms (and not H_2^+ directly) in the liquid phase can be represented, owing to the presence of the hydration shells, by the scheme

$$Fe(H_2O^{2+})_n + H = H_2 + Fe^{2+}OH + (H_2O)_{n-1}. \quad (14)$$

As well as these examples on the oxidation of Fe^{2+}, other experimental features can be interpreted by taking into account the appreciable velocity of reaction (7) and the reducing properties of H atoms. Thus in acid solutions (pH $\geqslant$ 1) saturated with hydrogen, the conversion yield of Ce^{4+} and V^V is greater than that for solutions saturated with air[82,134]. However, the oxygen molecule in the solution is an active H-atom acceptor and may produce a sharp change in the processes of radiolytic conversion of dissolved substances (Table 1). This effect of dissolved oxygen should be particularly marked with solutions of substances at relatively low concentrations‡.

Generalisation of published data on the possible oxidising properties of H atoms or the conversion of OH radicals into H atoms according to reaction (7), or the similar reaction (15) studied by Dainton and Hardwick[157],

$$OH + CO = CO_2 + H_2 + 21.2\,\text{kcal mole}^{-1}\S. \quad (15)$$

indicates that there is insufficient experimental proof of these theories. All the proofs are based on the results of the kinetic study of complex systems from the initial and final products. The nature of the intermediate is not yet clear. It is possible that as a result of certain characteristics, *e.g.* ability to form "bulky" hydration sheaths, the iron ion may facilitate the transfer of the excitation from the H_2O molecules in solution to the molecules in the hydrate sheath. Some chemical reactions, including the capture of an electron from an iron(II) ion by an oxidising agent[131,161], may involve participation of the molecules of the hydration sheath.

C. The Part Played by HO_2 Radicals

At the 2nd Geneva Conference, Allen and Schwartz emphasised that one of the greatest recent achievements in radiation chemistry is the conclusion reached by Hart[162] and by Donaldson and Miller[163] that HO_2 can be regarded as a primary product of the decomposition of water molecules in the track of an ionising particle. This radical is formed in the case of γ-radiation with a yield of 0.02 and in the case of irradiation of solutions with α-particles from polonium with a yield of 0.25,[163] by a reaction involving three OH radicals

$$\begin{array}{l} OH + OH = H_2O_2 \\ H_2O_2 + OH = HO_2 + H_2O \\ \hline 3OH = HO_2 + H_2O \end{array} \quad (16)$$

The HO_2 radical apparently may also be formed in solutions containing molecular oxygen[96]:

$$H + O_2 = HO_2. \quad (17)$$

since the latter has a high electron affinity¶. Thus, in mechanistic studies of solutions saturated with oxygen, it is necessary to consider the possibility of reactions with HO_2. Direct methods of observing intermediate radical products (e.p.r. and luminescence analysis) have not yet enabled this radical to be identified in liquid media. In the solid phase, however, this radical has been detected[95,164]. The form of the spectrum of this radical is analogous to that of the spectrum observed in the salt NaO_2. The HO_2 radicals may reduce or oxidise dissolved substances, depending on the pH of the medium and the redox potential of the system. It has been estimated[108] that the sum of the electron affinity of HO_2 and its solvation energy is 106–136 kcal. Lefort[13] concludes that if the redox potential of the system is greater than 1.0 V, HO_2 may take part in a reduction reaction, so that its action does not differ from that of H atoms, for example, in acid solutions (0.8 *N* H_2SO_4) of Ce^{4+}. Cottin considers that in acid solutions HO_2 oxidises the intermediate product of the oxidation of phosphite to phosphate ion, whereas in neutral medium O_2^- and PO_3^{3-} (HO_2 dissociates[128] to O_2^- and H^+) do not react, due to electrostatic repulsion of the ions[127]. The possibility of dissociation of the HO_2 radical is indicated by observations by Kulkes-Pujo[98] and Dolin[102], on the formation of hydrogen peroxide in aqueous solutions at pH values from ~0 to ~14. These authors suggest that the decrease in the yield of hydrogen peroxide with increase in pH is due to conversion of the HO_2 radical to a more stable ionic form. The reducing power of the HO_2 radical increases with increase in pH[134,165,166]. The HO_2 radicals recombine to give hydrogen peroxide and molecular oxygen, and the hydrogen peroxide may act as an oxidising agent or reducing agent, depending on the pH of the medium and the reactivity of the substrate. Thus it is difficult to determine, from the nature of the final products, which reagent (HO_2 or H_2O_2) has reacted with different substances. In a number of cases, however, it has been shown that HO_2 apparently does not take part in oxidation reactions. Thus, in the oxidation of benzene[167] and the oxidation of indigo-carmine[168,169], it has been established that HO_2 does not play a direct part in the oxidation processes. Of particular interest is the study of the role of this radical in the oxidation of iron(II) ions. According to Krenz and Dewhurst's scheme, HO_2 should have three equivalents of oxidising power and should thus increase the

† Rothschild and Allen[158] believe that the oxidation of iron(II) ions by H_2^+ ion takes place at a pH of 0.4–2.

‡ It may be concluded that molecular hydrogen plays a part in determining the conversion yield of a given substance only by comparison with the results of vacuum experiments (or with solutions saturated with inert gases).

§ From data given by Elbe[160].

¶ According to calculated data[108], the electron affinity of O_2 is 15.8 kcal mole^{-1} (calculated for compounds of the KO_2 type) and the sum of the solvation energy and electron affinity for molecular oxygen is 85.8 kcal mole^{-1}.

oxidation yield of iron in solution in the presence of oxygen by a factor of 4 compared with the case when oxygen is absent[121]†.

$$\begin{aligned} Fe^{2+} + OH + H^+ &\rightarrow Fe^{3+} + H_2O \\ H + O_2 &\rightarrow HO_2 \\ Fe^{2+} + HO_2 &\rightarrow Fe^{3+} + HO_2^- \\ HO_2^- + H^+ &\rightarrow H_2O_2 \\ Fe^{2+} + H_2O_2 &\rightarrow Fe^{3+} + OH^- + OH \\ H^+ + OH^- &\rightarrow H_2O \\ \hline 4Fe^{2+} + OH + HO_2 + 4H^+ &= 4Fe^{3+} + 3H_2O \end{aligned} \quad (18)$$

In the oxidation of iron(II) ions (Fricke's dosimeter solution) in the presence of oxygen, however, $G(Fe^{3+})$ is ~1.9 times greater than *in vacuo*. Proskurnin[131] suggested the following reaction scheme

$$\begin{aligned} Fe^{2+} + OH + H^+ &\rightarrow Fe^{3+} + H_2O \\ H + O_2 &\rightarrow HO_2 \\ 2HO_2 &\rightarrow H_2O_2 + O_2 \\ 2Fe^{2+} + H_2O_2 + 2H^+ &\rightarrow 2Fe^{3+} + 2H_2O. \end{aligned} \quad (19)$$

In Zansokhova and Orekhova's experiments with solutions of Fe^{2+} and O_2 of different concentrations, it was shown that at p_{O_2} = 75 atm, $G(Fe^{3+})$ reaches a value of ~24 equiv. and remains constant with further increase in p_{O_2} to 150 atm, that is, it corresponds to the complete utilisation of the radical products from 12 radiolysed water molecules. The decomposition of *S*-(2-aminoethyl)--thiuronium dinitrate in the presence of oxygen under the influence of γ-rays from ^{60}Co takes place with a conversion yield corresponding to the use of ~8.6 pairs of H and OH radicals at acceptor concentrations of 2×10^{-3}–5×10^{-3} M ‡.[170]

Thus, some workers suggest that the oxidising power of HO_2 radicals is realised only indirectly *via* hydrogen peroxide formed by radical recombination.

Summarising our discussion of the characteristics of the intermediate radical products controlling radiolytic reactions, we must note the following points. Since there are no direct experiments confirming the existence of H, OH, and HO_2 radicals in the liquid phase in the exact form in which they have been represented here, and since the hydration of radicals is a problem in physical chemistry which has been only slightly studied, all conclusions regarding their chemical characteristics should be regarded as hypothetical. In our opinion, the further development of radiation chemistry will depend on how well the intermediate products are studied by a combination of kinetic methods and such methods as ultra-violet, infra-red, and radiowave spectroscopy, measurement of the magnetic properties of the intermediate products, and electrochemical measurements. Kinetic studies, which by themselves give information on the disappearance of the original radiolysis products and the accumulation of the final products, cannot give unambiguous results on the intermediate stages of the process.

By generalising data for different systems, efforts are being made to reduce all kinetic characteristics of the conversion of substances in the liquid phase to the characteristics of several (perhaps even one) well-studied reactions in the gaseous phase. It is assumed that a given reaction is characterised by the same parameters in both the liquid and gas phases. Undoubtedly, with greater precision, by reducing the parameters of all radiolytic processes to one "standard", it may be possible to convert the relative rate constants to absolute values, after studies have been made of the characteristics of this "standard" reaction in the liquid phase, for example the reaction $H + D_2 = HD + D$, chosen by Riesz and Hart[171].

3. IONISED AND EXCITED WATER MOLECULES IN RADIOCHEMICAL REACTIONS OF DISSOLVED SUBSTANCES

A. Routes for the Redistribution of the Energy Absorbed by a Solution

If it is assumed that the average value of the energy of formation of one pair of ions for γ- and X-rays is 32.5 eV and the ionisation potential of the water molecule is 12.59 eV,[172] then only ~40% of the absorbed energy is used in the ionisation step. Approximately 50% of the absorbed energy is used in the excitation step. From ultra-violet spectroscopy it is known that water vapour absorbs light in the wavelength ranges 1785–1550 Å and 1392–1000 Å with absorption maxima at ~1650 Å and 1350 Å, corresponding to excitation of the bonding and non-bonding electrons[173,174]. Moreover, according to data obtained by the electron collision method, there is a further excitation level of the water molecule, corresponding to an excitation energy of 5.6 eV.[42]

A definite quantity of energy is removed by electrons whose energy is less than the first excitation potential of water for electron collision. The fraction removed by these electrons has been estimated by Platzman[60] to be approximately 15% of the absorbed energy and by others[59,175] to be ~10%.

To excite water vapour (bonding electron) in optical studies requires ~7.5 eV. If allowance is made for the fact that rupture of the H–OH bond requires ~5.2 eV,[42] it may be concluded that in both cases (excitation of the molecules to the 7.5 eV and 5.6 eV levels with corresponding redistribution of energy) the water molecule may dissociate to H and OH, so that for each ionisation step there are approximately two excitation steps.

If the radical products are to react with the dissolved substances, it is necessary, firstly, that the latter have a sufficiently high chemical activity, and secondly, that they are present in the solution in concentrations which at least exceed the concentration of radicals in the track of the ionising particle. The concentration of H and OH radicals ensuring conversion of the dissolved substances depends on the dose power of the radiation (the number of particles in unit time) and on the density of the ionisation (the number of ions per unit length of track of the ionising particle). For aqueous solutions of Ce^{III} and Fe^{III} it has been shown that the conversion yields of these substances change under the action of accelerated electrons and high dose powers reaching 10^{24} eV ml^{-1} sec^{-1}. This is due to overlap of the

† Here no allowance is made for the oxidation of Fe^{2+} by atomic hydrogen. The oxidising properties of H atoms have been confirmed by experiments in which the atomic hydrogen was prepared by methods other than radiation methods[149,150] (Editor).

‡ Anderson and Joseph[170] suggest that the conversion of the original substance takes place by a chain mechanism, which does not, however, explain the attainment of "limiting" values of the conversion yields for the substances.

tracks and an increase in the role of radical recombination[176-178]. The ionisation density and the recombination yield for the radicals increase[48] with decrease in the path length of different types of ionising particle with the same energy.

Analysis of data on the effect of the dissolved substance concentration on its conversion yield shows that with strongly-ionised radiation the initial conversion yield for the substances increases with increase in the concentration of reagent in the range of "intermediate" concentrations ($\sim 10^{-4}$–10^{-1} M) and reaches limiting values G_{ion} (ionised) corresponding to the utilisation of the radical products from the ionised water molecules. It has been shown, in a study of the influence of ionisation density on the conversion yield for a number of dissolved substances[13,179] in the concentration range 10^{-6}–10^{-2} M, that for electromagnetic forms of radiation (γ- and X-rays) $G(-H_2O)$ is of the order of 4.5. The number of radiolysed water molecules drawn into the reaction depends on the pH of the solution, as Schwarz and coworkers have shown on the basis of their own work[52,53] and that of Schuler and Allen. In neutral medium $G(-H_2O) = 3.62$ and in acid (0.8 N H_2SO_4) ~ 4.5, which Schwarz attributes to a change in the mechanism of electron capture in the track of the ionising particles§.

We have compared the results of various studies of the dependence of the conversion yields of substances on their concentration (Table 1). We assumed that the dissolved substances are only acceptors for one or other of the radicals, irrespective of the way in which the authors of the studies regarded the conversion mechanism of a given substance. The data given in Table 1 lead to the following important conclusions.

1. With increasing concentration, the conversion yield of the dissolved substances at first increases and then, in a definite concentration range (10^{-4}–10^{-1} M) reaches "limiting" values [the first "step" on the curve giving the dependence of $G(-Ac)$ on the acceptor concentration], irrespective of the nature of the dissolved substance. In most cases the conversion yield of the substances in this concentration range varies from 3 to 5 equiv. per 100 eV, that is, it corresponds to the utilisation of the conversion products from the ionised water molecules (in Table 1 the values of the yields are given per 100 eV).

2. It may be supposed that the limiting conversion yield of a dissolved substance will be reached earlier the more reactive the substance. The lack of data on the concentration dependences of the yields makes it impossible to observe this directly, except in 2–3 cases. Subsequently, by collecting analogous concentration dependences of $G(-Ac)$, we may be able, by extrapolating them to the curve for the most active acceptor of H and OH radicals, to estimate in this purely chemical way the concentration of H and OH radicals avoiding recombination in the track.

3. The presence in the solution, in addition to the acceptor, of a second substance which is also a radical acceptor, for example molecular oxygen, has a considerable influence on the conversion yield for the first acceptor. The influence of the second acceptor may be competitive or sensitising, depending on the type of acceptor (see Table 2 for the sensitising effect). To obtain information on the conversion mechanism for a given acceptor then, it is necessary to make allowance for the nature of the gas saturating the solution. Unfortunately, until recently, research workers often did not attach particular importance to the presence of O_2 in the solution.

From published data it can also be concluded that in some cases, particularly in concentrated solutions and in solutions of certain substances, the conversion yield for the reagents exceeds the utilisation of the radical products from the ionised water molecules. With radical acceptor concentrations from 1 M upwards, the conversion yield of the substances sometimes also reaches limiting values of 8–9 equiv. per 100 eV. Until recently, some workers attributed this increase in the yield of radiolytic decomposition to an increase in the part played by the direct action of radiation on the dissolved substance[206,207,227,228]. A number of non-Russian scientists also attributed this phenomenon to "direct action", but they signified by this term the transfer of excitation energy from the water molecule of dissolved substance, *i.e.* they were considering the utilisation of the energy of excited water molecules. Strictly speaking, the term "direct action of radiation" should signify the effect of the interaction between the ionising particle and the molecule, accompanied by excitation or ionisation of this molecule. This is equally true of the molecule of the solvent and the molecule of the dissolved substance. The effect of direct action is directly proportional to the electronic fraction of the substances and allowance must therefore be made for it in concentrated solutions. In the estimation of this effect, the solutions are often frozen, since in this case the rate of diffusion of the radicals decreases and the part played by the direct action is reduced to a minimum. It is also assumed that the distribution of the primary products of the radiolysis of water is independent of the state of aggregation of the system (solid or liquid). Available data appear to confirm the first assumption. For example, Duane and Scheuer and Bonet-Maury observed a decrease in the yield of gaseous products from ice irradiated with α-rays, compared with that for the liquid phase. According to Haissinsky and Lefort's data[124], the oxidation yield of arsenite on irradiation of its frozen solutions (10^{-2}–10^{-1} M, -196°) by α- and X-rays is from one-thirtieth to one-half of the yield in the liquid phase. An analogous phenomenon is also observed in the irradiation of frozen nitrate solutions by γ-rays[142,230,231].

Even in frozen solutions, however, we cannot neglect the diffusion of intermediate products and the possibility of radical reactions, which have been shown to depend on the temperature of the frozen system. Lefort found that almost no H_2O_2 is detectable between -196° and -120° on irradiation of ice with X-rays. Increase in the temperature to -4° increases $G(H_2O_2)$ slightly, and it increases sharply on melting (0°).[232] In the work cited, the conversion yield for the substances was determined after the solutions had been thawed, so that during thawing, diffusion and recombination of the radical products is possible. A fundamental error has thus been introduced in the "estimation" of the effect of direct action. Moreover, it has been shown by a number of methods (radio- and optical spectroscopy) used directly under low-temperature conditions that in frozen aqueous solutions the H and OH and possibly HO_2 radicals

§ It may be expected, contrary to Schuler and Allen's suggestion[180], that the electric fields of the ions should also influence the process of electron capture, since the introduction of ions (particularly polyvalent ions) into the solution creates a high local intensity and thus changes the trajectory of the emitted electron.

formed can move freely at temperatures of -196° (H) and -160° to -120° (OH and HO_2)¶ and react with one another and with dissolved substances[90]†.

It has been found that the larger radicals formed from the dissolved substances disappear rapidly at a higher temperature (-70° to -90°).[104,142,231] It should be noted that the method of freezing the solutions, even with analysis of the conversion products (under conditions where the temperature at which the irradiation was carried out is maintained), is suitable for "estimating" the effect of the direct action of irradiation only if the structure of the solutions remains unchanged on freezing.

The increase in the conversion yields of dissolved substances in concentrated solutions should, in our opinion, be attributed to the part played by excited molecules, in addition to the radical products formed from ionised water molecules.

As already mentioned, an average of two excitation steps take place for every ionisation step. Obviously, when suitable conditions obtain, there may be a directed transfer of excitation energy from the solvent molecules to the dissolved substances, increasing the efficiency of the action of the radiation on the dissolved substances.

The excitation energy absorbed by the water molecules can be transferred to the dissolved substances in various ways: (1) by direct collision between an excited water molecule and a molecule of dissolved substance; (2) by direct transfer of a quantum of energy (emission and absorption); (3) by resonance transfer; etc.

The first method of energy transfer is possible since the excited water molecules formed on radiolysis are present in a higher excited state and may, in a time of the order of 10^{-13} sec and without altering their multiplicity, move to a lower excited state. The molecules exist for a considerable time in the lower triplet excited state[59] (for some substances the lifetime may reach 1 sec). In this time these molecules, by diffusing and colliding with molecules of dissolved substance, may transfer the excitation energy to the dissolved substances and thus bring about their conversion. Some workers[206,208] atribute the increase in the conversion yield for substances in concentrated solutions to the collision between excited solvent molecules and molecules of dissolved substances. The resonance transfer of excitation energy from one solvent molecule to another requires a time of the order of 10^{-13} sec.[78] Resonance transfer of energy (related to the transfer of electronic excitation energy) may take place over a distance of up to 50 Å.

These methods of transferring the excitation energy from the solvent molecules to the molecules of the dissolved substances are not, in the final analysis, related to the dissociation of the molecule to H and OH radicals and hence cannot, in our opinion, explain why additives, in solutions of certain substances which are radical acceptors, influence their conversion yields. Nevertheless, certain additives have a marked influence on the conversion yields of substances which are radical acceptors, increasing or decreasing the yield by a considerable factor, sometimes amounting to several orders of magnitude (Table 2). The surprising feature of the sensitising action of additives is that it is shown in solutions containing the additives in concentrations of $\sim 10^{-4}$ M. Change in the viscosity or temperature of the solution in this case does not influence the magnitude of the limiting yield of a given radical acceptor.

In our opinion, these effects are satisfactorily explained by Voevodskii's suggestion[236] that the transfer of excitation energy in aqueous solutions can take place along systems of hydrogen bonds or by a relay mechanism of active particle transfer.

The time required for the energy transfer is obviously determined by the stability of the excited water molecule (to H–OH bond rupture) and should apparently be of the order of $\sim 10^{-13}$ sec. An interesting feature of Voevodskii's mechanism of directed transfer of energy along a "chain" at the ends of which there are conjugated acceptors (in the terms of Proskurnin's conjugated acceptor theory) is that the H and OH radicals formed from a single excited water molecule appear at two different points in the volume of the solution. Due to the high probability of formation, by the water molecules, of different combinations of hydrogen bonds, there are a large number of chains which might transfer the excitation energy; the one chosen is that at whose ends are situated an H-radical acceptor and an OH-radical acceptor (conjugated acceptors). Thus one of the conjugated acceptors may, at a considerable distance from the other ‡, facilitate the reaction between the conjugated aqueous radical and its acceptor. It thus becomes clear why a low concentration of one of the conjugated acceptors is so effective in the process of conversion of the other and why subsequent increase in the concentration of the first acceptor in the solution does not change the conversion yield for the second.

It may be assumed, following Proskurnin[131], that in the solutions there is directed transfer of excitation energy from a water molecule in the depth of the solution to a water molecule in the hydration sheath of a given radical acceptor. At the same time it is assumed that the directed transfer of energy takes place as a result of the fact that the electronic levels of the water molecules are displaced under the influence of the forces of interaction and decrease in the direction towards the molecules of dissolved substances. According to this mechanism, the excited water molecule formed in the hydration sheath dissociates under the influence of the forces of the hydrolysed ion-acceptor to H and OH radicals which then react with it.

In the transference of energy of the excited water molecules by the radical method, it is necessary to take into account the Frank–Rabinowitch cell effect[237]; the H and OH radicals in this cell exist for approximately 10^{-13} sec[238] (time of one vibration). Thus if the recombination of H and OH radicals is to be suppressed, the radical acceptor must

¶ Matheson and Smaller[90] erroneously attribute the observed spectra to combined atomic hydrogen (magnitude of the hyperfine splitting ~30 G) and the OH radical. The spectrum of free atomic hydrogen (splitting between doublet lines ~ 500 G[37]) in pure ice disappears below -196°[36]. Comparison of various data[91–95,233–235] indicates that the spectrum observed[90] is probably due to the presence of OH and HO_2 radicals.

† By gradually increasing the temperature of the specimen[95], Siegel *et al.* were able to detect the successive disappearance of the doublet lines (g = 2.008 ± 0.002) due to the presence of the OH radical at 100°K and the single broad line (g = 2.08) of a radical identified as HO_2 at 145°K.

‡ The distance is obviously determined by the probability of formation of a system of hydrogen bonds *via* water molecules at a given concentration of radical acceptors in the chain: H-radical acceptor..... OH-radical acceptor, that is, the chain along which the energy transfer can take place.

be present in the solution in high concentration[238].

According to Firestone's data[239] the yield of H and OH radicals in water vapour is 11.7 per 100 eV of absorbed energy. In the gas phase the Frank–Rabinowitch cell effect is excluded and the recombination of H and OH is less probable, so that $G(H,OH)$ corresponds to the limiting value of the decomposition yield for the water molecules $G(-H_2O) \sim \sim 12$.

B. Proskurnin's Concept of Conjugate Radiochemical Reactions

According to Proskurnin *et al.*[86], conditions for the suppression of the recombination of H and OH in the liquid phase are produced when two conjugated H- and OH-radical acceptors are introduced simultaneously into the solution§; the concentration of one of the acceptors may differ from that of the other by 2–4 orders of magnitude. It is assumed that the conjugated acceptors act as follows. In their presence it becomes possible for the H and OH radicals formed as a result of the "breakdown" of the excited water molecules to overcome the cell effect and react with dissolved substances. Experiments on a number of systems of conjugated acceptors have shown that with change in the concentration of one of the conjugated acceptors (the concentration of the other should obviously be not less than the concentration of radical in the track), given values of the conversion yields of substances are reached at lower concentrations of the first acceptor than under conditions where the conjugated acceptors were not introduced[75].

It is necessary to note that the introduction of the conjugated acceptors should first of all apparently also facilitate the removal, into the reaction, of radical products from the ionised water molecules as a result of the favourable conditions for the suppression of the reverse process — reactions (4) and (5). In this case the depence of G(acceptor) on the acceptor concentration should also show characteristic "levels" of constant yields due to utilisation of the radical products from the ionised water molecules; this has been studied for the case of the glycerol–nitrate, nitrate–glycerol, and glycerol (or glucose)–methylene blue systems[75,86,241-246].

According to this theory, substances which have different individual chemical properties are identical as far as their radiolytic behaviour as acceptors of H and OH radicals is concerned. As a result, the limiting conversion yield for a dissolved substance cannot (if this is not a chain process) exceed the total conversion yield of the radiolysed water molecules, that is, 12¶.[74,131,137,168,242] This theory can be proved, however, only from the results of an analysis of the products of the conversion of the oxidising component and the products of the conversion of the reducing component.

The results of experiments carried out in the presence of conjugated acceptors are given in Table 2, which also gives data on the conversion of certain substances in the presence of a number of organic and inorganic compounds[66,82,170,202]. The authors of these papers explain their results on the basis of various other mechanisms differing from the conjugated acceptor mechanism†.

In our opinion, the processes in the various systems can be readily incorporated in a general scheme of conjugated radiolytic reactions without any further particular assumptions. The correctness of this suggestion will be discussed in more detail for the case of the Tl^+–NO_3^-–Ce^{4+} system studied by Sworski[228], who established that in sulphuric acid ($[Ce^{4+}] = 4 \times 10^{-4}$ M) in the presence of the thallium ion (Tl^+) as OH-radical acceptor ($[Tl^+] = 10^{-5}$–10^{-2} M), $G(Ce^{3+})$ increases by a factor of 2.5. The introduction of nitrate into the solution in sufficiently high concentration (up to 0.5 M) increases $G(Ce^{3+})$ by 3 equivalents, both in the presence and in the absence of Tl^+ ($G(Ce^{3+})$ equals 11 and 5 respectively). The nitrite ions formed from NO_3^- reduce Ce^{4+} to Ce^{3+}. The curves giving the dependence of $G(Ce^{3+})$ on the NO_3^- concentration are symbathic [change in the same sence], and Sworski concludes that the reduction of the nitrate is independent of the radiolytic conversion of the Ce^{4+} and Tl^+ ions. The mechanism of radiolysis of the NO_3^- ion involves the transfer to the nitrate ion of the excitation energy from water molecules on collision, and also from the superthermal electrons[254]. The possibility that radical products from the excited water molecules take part in the reduction of the nitrate was not considered by Sworski, although the concentration of the radical acceptor (NO_3^-) is fairly high. Sworski states that the formation of intermediate products of reduction and oxidation of the nitrate as a result of its reaction with H and OH radicals, and the participation of these intermediate products in the reduction of Ce^{4+} and oxidation of Tl^+, would lead finally to the same result as the action of H and OH on Ce^{4+} and Tl^+, that is, to a result for which allowance is already made by the action of the ionised water molecules. This conclusion is incorrect in this respect, that if the nitrate ion is not capable of oxidising Tl^+, and thallium of oxidising nitrite, because the Tl^{2+}/Tl^+ potential is lower than the NO_3^-/NO_2^- potential, then neither can the intermediate products of the oxidation bring this about.

The effect of the direct action of radiation on the nitrate ion under these conditions (up to 0.5 M $NaNO_3$), in accordance with the electronic fraction of the nitrate, does not exceed 2% (in 0.5 M) of the total absorbed energy and, as can be seen from the curve giving the dependence of $G(Ce^{3+})$ on $[NO_3^-]$, the most effective concentration range is that up to 0.2 N; subsequently, the shape of the curve is typical of that showing saturation. As far as the role of superthermal electrons in the reduction of nitrate ion is concerned, their

§ Another method of utilising the radicals produced from excited water molecules, which normally recombine with one another as a result of the cell effect, is by increasing the temperature of the irradiated mixture. Barelko and coworkers showed that with increase in the temperature of an irradiated benzene–water mixture, the initial rate of the yield of phenol formation increases (that is, there is an increase in the probability of removal of radicals from the cell into the reaction)[240]. In the temperature dependence, as in the case of the concentration dependence[75], G (conversion of radical acceptor) should not be greater than the utilisation of 12 radiolysed water molecules.

¶ Clark and Coe studied the action of conjugated acceptors as early as 1937. They suggested that additives (benzene, acetic acid, etc.) by removing the energy of the activated water molecules, facilitate, for example, the reduction of Ce^{4+}[202].

† For example, the OH radical oxidises an organic substance according to the reaction RH + OH → H_2O + R. The radical R, by reacting with another dissolved substance S, increases the conversion yield for the latter according to the scheme: $\left.\begin{matrix} S + R \\ S + H \end{matrix}\right\}$ → reduction product.[148]

fraction corresponds to the utilisation of about 10–15% of the total quantity of absorbed energy. This shows that the superthermal electrons cannot play a very important part in the reduction of the nitrate.

In our opinion, the system studied by Sworski can be regarded as an example of the action of conjugated acceptors of H atoms (Ce^{4+}) and OH radicals (Tl^{+}) as a result of which a further quantity of H atoms are drawn from the excited water molecules into the reduction reaction of Ce^{4+} due to suppression of the recombination reaction $H + OH = H_2O$. This is indicated by the sharp increase in $G(Ce^{3+})$ when very small quantities of Tl^{+} (from 10^{-5} M) are added. $G(Ce^{3+})$ remains constant with change in the thallium ion concentration from 10^{-5} M to 10^{-2} M (compare, for example, the nitrate–glycerol system [74,110], where change in the concentration of the latter in the range 5×10^{-4} M to 0.1 M has no influence on $G(NO_2^-)$. With the introduction of the second H-atom acceptor, the nitrate ion, in concentrations greater than $[Ce^{4+}]$, the conversion yield of the latter increases due to the nitrite ions formed. In 0.5 M nitrate solution, the value reached by $G(Ce^{3+})$ coincides with data on the yield of nitrite¶ in the presence of glycerol [74,110] corresponding to the combination of 10.5–11 H atoms from the ionised and excited water molecules.

This theory of the mechanism of action of conjugated acceptors may be confirmed only on the basis of an analysis of the products of the conversion of both the oxidising and the reducing components of the radiolysis of water. There are at present a number of reports of the attainment of limiting conversion yields of 12 for water molecules. Thus Zansokhova and Orekhov have shown that under certain conditions (high O_2 pressure above the solution), H atoms take part in the formation of products (HO_2 or H_2O_2) which are capable of oxidising Fe^{2+} ions, so that in the radiolytic reactions ~24 equivalents of oxidising power are realised, that is 12 pairs of H and OH radicals [137]. An analogous picture has also been observed for the oxidation of indigo-carmine [168].

The limiting conversion yield, that is, with the participation of 12 radiolysed water molecules, can also be reached in the radiolysis of solutions of substances which are vigorous acceptors of both radicals (H and OH), such as $ON(SO_3)_2^{2-}$ [246,255] or α,α-diphenyl-β-picrylhydrazyl-p,p'-disulphonic acid [256].

C. The Participation of Two Types of Excited Water Molecule in the Reactions

In some cases it has also been possible, without the presence of conjugated acceptors, to observe a limiting conversion yield for an ordinary acceptor of one of the radicals equal to the utilisation, for example, of H atoms from 12 radiolysed water molecules. Thus in the case of the irradiation of molar nitrate solutions with γ-rays from ^{60}Co at low dose powers, the yield of nitrite reaches 12 equivalents per 100 eV, whereas at ordinary dose powers $G(NO_2^-)$ = 8–9 equivalents per 100 eV. [142] It may be assumed that the lifetime of the excited water molecules (~4) taking part additionally in the reaction at low dose powers is sufficient for the purpose under these conditions. In the range of high dose powers, these molecules are probably deactivated by collision with one another. It may be concluded that in aqueous solutions two types of excited water molecule are formed, differing apparently in the level and form of their excitation (dissociating or not dissociating in the liquid phase to H and OH radicals). One type of excited water molecule reacts in the general case in highly-concentrated solutions of radical acceptors on in dilute solutions at high temperatures [75,243,244]. A characteristic feature of this type of excited water molecule is that the radicals formed at the moment of its dissociation may move apart to a considerable distance from one another and react with solute. For the second type of excited water molecule to be drawn into the reaction, the solution must contain conjugated radical acceptors or substances which are simultaneously acceptors of H atoms and OH radicals [246,255,256]. However, in concentrated solutions of nitrate, which is an acceptor of one of the radicals (H atoms), as already mentioned, it is possible, in irradiation with γ-rays of low§ intensity [142], to attain yields which also correspond to the utilisation of approximately 12 H atoms from ionised and excited water molecules.

Data have been published indicating that the excited water molecules formed during radiolysis exist in an upper excitation level for times of the order of 10^{-13}–10^{-14} sec and then move to a lower excitation level without altering their multiplicity. The lifetime of an excited water molecule in the lower triplet excitation level is of the order of 10^{-8} sec. The comparatively long lifetime of these molecules evidently facilitates their reaction with dissolved substances.

It is also possible that a slight additional interaction, for example, a magnetic interaction, between the triplet-excited water molecule and the dissolved substance (nitrate ion) becomes sufficient for reaction to take place in concentrated solutions and with irradiation with γ-rays of low intensity. It may therefore be assumed that excited water molecules of the second type are in a triplet state. The total number of excited water molecules reacting is thus 8.

Confirmation that the excited water molecules take part in the reactions by a radical mechanism is provided by experiments on the measurement of the yield of the "molecular products" of the decomposition of water with change in the concentration of an acceptor of one or other of the radicals; in particular, the yield of H_2 with change in the concentration of nitrate ion.

As already mentioned, in the case of irradiation of aqueous solutions with γ-rays from ^{60}Co, the formation yield of the products of the radical reactions in the presence of a competing acceptor is proportional to the acceptor concentration to the power $\frac{1}{3}$. The nature of this dependence is not yet clear. The generally-accepted qualitative interpretation given by Sworski [66] is that when the concentration of radical acceptor in solution is sufficiently high (Sworski studied Br^- solutions saturated with oxygen), the acceptor, by capturing the radicals (OH) in the region of high ionisation density, decreases their recombination yield. Sworski concludes that the rate of the reaction of the bromide ion with OH radicals should be related to the average distance separating the bromide ion from the region of high ionisation density.

‡ At the most effective glycerol concentration (5×10^{-4} M to 0.1 M) and $[NO_3^-]$ = 0.5–1 M.

§ In very concentrated solutions of NO_3^- ions, heated to ~70°–90° and irradiated at ordinary (moderate) power doses, $G_{NO_2^-}$ also reaches ~12 equiv. per 100 eV.

It may be assumed, on the basis of general theories of reaction kinetics in the volume of the track, that in this case the rate of molecular product formation depends on the rate of the competing processes; the product of the rate constants of the main competing reactions and the corresponding reagent concentrations evidently appears in the general expression for the reaction rate, to the power 3, and the conditions for the competing reactions are averaged Thus the rate of the reaction R + R depends on the concentration of one of the competing reagents to the power $\frac{1}{3}$. In the general form

$$G_{R-R} = A + B\,[Ac]^{1/3}, \qquad (a)$$

where B obviously characterises the probability of the reaction of the acceptor (Ac) with the radical product R, and A is the accumulation yield of the product of recombination of the radicals under conditions where the acceptor does not influence the formation of molecular products in the track.

As Mahlman's observations on the $NO_3^- - Br^- - H_2O$ system [257] have shown, the relationship (a) may remain linear, that is the value of B does not change over a wide concentration range, if the concentration of dissolved substance is replaced in the expression by its activity. The value of A corresponding to the yield of molecular products under conditions where [Ac] = 0 has been shown to depend on the composition, acidity, and temperature of the solution [66,67]. Further study of this type of dependence, in which a mutual relationship between the chemical (activity, pH, and temperature of the solution) and physical (the specific properties of the radiation and the energy of the ionising particles) factors is found, together with a physical picture of the interaction between ionising radiation and matter (described by the previously-proposed models, which do not make allowance for the chemistry of the radiolytic processes and suffer from this fundamental shortcoming) should make it possible to gain an insight into the nature of the reactions in the track and radiolytic processes in general.

In connection with the reactions by radical products formed not only from the ionised water molecules but also from the excited ones, it is interesting to consider experiments in which the relationship $G_{R-R} \propto [Ac]^{\frac{1}{3}}$ was studied over a wide range of concentrations of radical acceptor (nitrate ion). With increase in the concentration of radical acceptor in the solution, as we have seen, conditions are produced for the withdrawal, into the reaction, of radical products first from the ionised and then from the excited water molecules. Since the distributions of the radical products for these cases are different, the conditions of competition between the processes H + Ac and H + H change with increase in the acceptor concentration. This also explains the inflection on the curve for the above relationship [69¶], where the slope of the straight sections in this case should correspond to the introduction of H atoms formed from the ionised (at $[NO_3^-] < 1$ M) and excited (at $[NO_3^-] > > 1$ M) water molecules. The fact that the section of the curve in the range of high nitrate ion concentrations is linear indicates that the conditions for the radical–radical and radical–acceptor reactions do not change, although the electronic fraction of the acceptor changes by approximately 2–1.5 orders of magnitude; in other words, the mechanism of nitrate reduction is retained in solutions of concentrations of 1–15.9 M.

The fairly detailed data given here on the radiolysis of the nitrate–water system, which is one of the most widely studied, indicate that the method involving the G_{R-R} *vs.* $[Ac]^{\frac{1}{3}}$ relation may be useful in a particular case in the examination of the distribution in the tracks of different forms of excited water molecule.

This review shows that the interpretations given by a number of authors to explain radiolytic processes do not yet explain unambiguously the accumulated experimental data on different radiolytic processes.

Radiation chemists in recent years have begun to acknowledge the decisive part played by the reactions of the primary radical products of the radiolysis of water with the dissolved substances. At the same time the urgency of the problem of the molecular decomposition of water has disappeared.

One of the fundamental problems in radiation chemistry is the part played by excited states in the processes of radiation conversion and methods for the transfer of absorbed energy between molecules in solution.

¶ Agreement is observed, within the limits of experimental error, between the experimental data on the yield of hydrogen obtained by Sowden [69] for the case of mixed $n + \gamma$ radiation and data for γ- and X-irradiation [70,243] of neutral and alkaline nitrate solutions at 80° and 20° with change in the dose power of the radiation over a range of about 8 orders of magnitude. This apparently indicates that the reaction taking place is the recombination of H atoms, and not the recombination of other products which then yield H atoms (for example H_2O^- in alkaline medium).

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APPLICATION OF SIMILARITY THEORY TO CHEMICAL PROCESSES

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CONTENTS

I. Similarity criteria in chemical processes 297
II. Approximate simulation 300
1. Simulation of processes occurring in the kinetic range 301
2. Simulation of processes occurring in the diffusion range 302
3. Simulation of processes occurring in the diffussion–kinetic range 302
III. Scale equations 303
IV. Some particular cases of the practical use of similarity theory 305

I. SIMILARITY CRITERIA IN CHEMICAL PROCESSES

Design of reaction vessels for chemical processes requires in general the simultaneous examination of the following set of differential equations, for an infinitesimal element of the vessel: (1) equation for mass balance; (2) equation for the energy balance; (3) fundamental equation of hydrodynamics or equation of motion; (4) rate equation for the reaction; and (5) equations defining the conditions for single-valuedness. Since even in the absence of chemical reactions it is impossible to solve this set of equations for the general case, similarity theory is widely used for such problems.

The application of similarity theory to chemical processes requires the simultaneous consideration of all the differential equations enumerated above supplemented by terms taking into account the presence of point sources of energy and mass, which considerably complicate this problem. The complexity lies in the fact that in general it is impossible to observe simultaneously the hydrodynamic, thermal, diffusion, and purely chemical similarity of processes accomplished in apparatus differing in size. It is characteristic of chemical processes that one system cannot be simulated by another, as would be the case with physical processes.

Thus although in the case of hydrodynamic similarity we can maintain the Reynolds number Re constant in the model and in the prototype by changing the system, we cannot do this in the case of chemical similarity since a chemical reaction of a given group of compounds cannot in general be reproduced in compounds of a different group.

As a result of this and other difficulties, similarity theory is comparatively rarely used at present for the simulation of chemical processes. It is quite widely used, however, in the generalisation of experimental results for a great variety of such processes[1].

Transformations of the set of differential equations have yielded the following criteria of chemical similarity:[2-5]

Damköhler's Group I

$$Da_I = \frac{Ul}{cw}, \qquad (1)$$

where U is the reaction velocity in kmole m^{-3} h^{-1}, l a linear dimension in the direction of flow in metres, w the linear rate of flow in metre h^{-1}, and c the concentration of the reactant in kmole m^{-3}.

Since l/w measures the time of flow through the reaction vessel, the ratio c/U will measure the duration of the reaction at constant velocity. Consequently Da_I can be defined as the ratio of the residence time of the flow in the reaction vessel to the duration of the reaction occurring at a constant rate until the reactant is completely exhausted. This dimensionless group can, of course, be treated also as the ratio of the reaction velocity to the rate of flow, both expressed in the same units†, as the ratio of the concentration of substance which has reacted to the concentration introduced by the flow, or finally as the ratio of the actual

† The group $W = w_x/U_k$, deduced by Matz, [6] in which the reaction velocity U_k is expressed in flow-rate units, or for a first-order reaction, as a rate constant; it follows from the definition of Da_I that the Matz number is identical with it.