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PRIMARY PRODUCTS OF THE RADIOLYSIS OF WATER AND THEIR REACTIVITY

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INTRODUCTION

It is well known that radiolytic transformations in dilute aqueous solutions result from reactions of the solutes with products of the radiolysis of water†. Until recently, research workers considered that these products were the H atom, the OH and HO_2 radicals, molecular hydrogen, and hydrogen peroxide. The latest stage in the development of the radiation chemistry of water and aqueous solutions has been marked by the discovery of yet another primary product of the radiolysis of water—the hydrated electron e^-_{aq}.

In recent years, considerable progress has also been made in the study of the kinetics of radiation reactions in aqueous solutions. The absolute values of the rate constants of many reactions involving intermediate products

† The radiolysis of water and aqueous solutions has been examined in detail by a number of authors [1-4].

of the radiolysis of water have now been determined. It is thus possible to compare their properties, and also (which is particularly important) their reactivities towards various dissolved substances‡.

1. THE FREE-RADICAL THEORY OF THE RADIOLYSIS OF WATER

In 1944 Weiss[5] put forward the hypothesis that the action of ionising radiation on water produces H and OH free radicals. Subsequently, this hypothesis was confirmed in many studies and was developed further.

The free radicals appear as a result of a number of physical and chemical processes, taking place after the passage of the ionising particle through the water. These processes can be characterised briefly by the following time parameters[6]. Transfer of the energy of the ionising radiation to the water takes place in 10^{-16}–10^{-18} s, with the production of excited water molecules, H_2O^* ions, and secondary electrons. The last of these have considerable energy, and ionise and excite more water molecules. Ultimately, with γ-radiation, X-rays, or electron irradiation, individual isolated groups of ionised and excited molecules ("spurs") are formed, where the primary stages of the chemical action of the ionising radiation develop. With heavy charged particles, these spurs lie close to one another, and immediately after their appearance they merge to form a continuous cylindrical column.

After about 10^{-13}–10^{-14} s, dissociation of the positive ion takes place:

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH. \qquad (1)$$

Reaction (1) in the gas phase has a rate constant[7] of 5×10^{11} litres mole^{-1} s^{-1}.

Opinions differ regarding the fate of the secondary electron. Most authors, following Lea[8], Gray[9], and Platzman[10-12], consider that the electron, before undergoing thermalisation, moves a considerable distance from its point of origin. At this distance, it is almost uninfluenced by the coulombic field of the mother ion (more accurately, the H_3O^+ ion), so that this electron becomes, as it were, free. It polarises the medium and as a result is "trapped" by the latter, i.e. it becomes hydrated, and in this form takes part in the radiolytic transformations of dissolved substances. The process of "self-capture" of the electron is complete in about 10^{-10}–10^{-11} s. It should be emphasised that the concepts of polarisation "self-capture" of the electron by the medium were first developed by Landau[13] and by Pekar[14] in the physics of solids, where such an electron is called a polaron. This theory was modified and applied to liquids by Davydov[15] and by Deigen[16]. It was extended by Platzman[10-12], with some limitations, to the radiation chemistry of water and aqueous solutions. The suggestion that an important part in the radiolytic transformations of dissolved substances is played by e^-_{aq} was first put forward by Stein[17,18] and by Weiss[19].

Another hypothesis has recently been developed by Magee[20] and by Sworski[21]. At the instant of formation of the H_3O^+ ion [reaction (1)], the dielectric relaxation of the water is not complete, so that this ion is not the ordinary solvated ion. In the opinion of these authors, the electron is attracted to this ion:

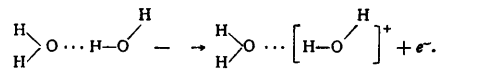
$$H_3O^+ + e^- \rightarrow H_3O. \qquad (2)$$

The H_3O particle may undergo thermal dissociation in two ways:

$$H_3O \rightarrow H + H_2O \qquad (3)$$

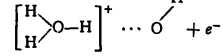
$$H_3O \rightarrow e^-_{aq} + H_3O^+. \qquad (4)$$

According to Sworski[21], the formation of OH and H_3O particles takes place as a result of the ionisation of one of two water molecules joined by a hydrogen bond:

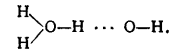


(5)

This is followed by transfer of a proton:



and neutralisation of the charges:



The main difference between these two hypotheses lies in the initial distribution of the e^-_{aq} and OH radicals. According to the first hypothesis, the hydrated electrons are distributed more diffusely than the OH radicals. According to the Magee–Sworski hypothesis, the two types of radicals have identical initial distributions§. It is difficult to give preference to either of these hypotheses. In order to settle this question, it is necessary to carry out accurate diffusion-kinetic calculations¶ of the initial dimensions of the spurs for the OH radicals and reducing-agent radicals, using up-to-date values for the rate constants of the reactions of H atoms, e^-_{aq}, and OH radicals.

Thus about 10^{-10}–10^{-11} s after passage of the ionising particle, the track contains OH radicals, e^-_{aq}, H_3O^+ ions, and excited water molecules. Their concentration is fairly high (~ 0.1–1.0 M), so that, with the track becoming broader as a result of diffusion, they react extremely rapidly with one another:

$$e^-_{aq} + OH \rightarrow OH^- \qquad (7)$$

$$e^-_{aq} + H_3O^+ \rightarrow H + H_2O \qquad (8)$$

$$e^-_{aq} + e^-_{aq} + H_2O \rightarrow H_2 + 2OH^- \qquad (9)$$

$$e^-_{aq} + H + H_2O \rightarrow H_2 + OH^- \qquad (10)$$

$$OH + OH \rightarrow H_2O_2 \qquad (11)$$

$$H + H \rightarrow H_2 \qquad (12)$$

$$H + OH \rightarrow H_2O \qquad (13)$$

$$H_3O^+ + OH^- \rightarrow 2H_2O. \qquad (14)$$

‡ Except where otherwise stated, the present review deals with radiolysis under the influence of X-rays, γ-radiation, and fast electrons.

§ Recently, Peers and Cottin[22] have studied the production of H_3O^+ ions on electron collision (energy of the electrons 11–20 eV) in water vapour. They find that these ions are formed chiefly from H_2O^+. Some of the ions, however, appear at a rate which is independent of the field intensity in the ion source. These workers conclude that the precursor of this fraction of the H_3O^+ is "excited water":

$$H_2O^* + H_2O \rightarrow H_3O^+ + (OH + e^-). \qquad (6)$$

It may therefore be assumed that in liquid water some of the hydrated electrons may be produced by the breakdown of H_2O^*.

¶ The problems of diffusion kinetics in the radiolysis of water have been examined in various reviews[23-26].

The above processes have high rate constants (5×10^9–10^{11} litres mole^{-1} s^{-1} [27-52]). Reactions (9)–(12) lead to formation of the so-called molecular products of the radiolysis of water (H_2 and H_2O_2), and reaction (8) leads to the production of H atoms. Kuppermann[53] made appropriate diffusion-kinetic calculations and found that the value of G_H, determined on the assumption that the H atoms are formed in the "spurs" by reaction (8), is close to the experimental value.

The reactions in the tracks take place in an interval 10^{-8}–10^{-10} s after passage of the ionising particle. When the time interval exceeds 10^{-8} s, the "spurs" have become so broad, and the concentration of particles in them has decreased to such an extent, that some of their reactions with dissolved substances in the bulk of the solution become significant.

2. THE HYDRATED ELECTRON

The formation of e^-_{aq} during the radiolysis of water has been proved many times. The proofs can be divided into the following categories.

1. Proof by the method of competing acceptors[54-102]. This method has revealed that the reducing radicals can exist in two forms.

2. Proof using the kinetic salt effect[27,55,103-111]. It is found for a number of reactions that the chief reducing species in the radiolysis of water has a charge of –1.

3. Proof by the pulse radiolysis method[31,42,112-117]. This method has revealed short-lived optical absorption with a maximum at 720 nm for H_2O [31,42,116,117] and 690 nm for D_2O [117] in irradiated liquid water†. This absorption does not appear in acid medium and disappears in the presence of electron acceptors.

4. Proof by electron spin resonance (e.s.r.)[126-127]. Trapped electrons have been identified by this method in alkaline[126-135] and neutral[136,137] vitreous frozen aqueous solutions subjected to the action of radiation at 77°K.

5. Proof by measurement of the electrical conductivity of irradiated water[138-140]. This method has shown, in particular, that the electrical conductivity of water "induced" by radiation disappears in a time interval which is approximately the same as that for the corresponding optical absorption.

Thanks to efforts in many laboratories, the properties of e^-_{aq} have been studied in considerable detail‡. The first point to be noted is that this species is a powerful reducing agent. It reacts with ions of the type M^{2+}, where M represents a metal, to give ions M^+ having an anomalous valency[162-164]. This has been demonstrated for Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, etc.

When the water does not contain e^-_{aq} acceptors, the hydrated electron, at low dose rates, reacts with water with the production of an H atom[31,42,44,115,154,165,166]:

$$e^-_{aq} + H_2O \rightleftarrows H + OH^-. \quad (15)$$

Reaction (15) is slow. According to the latest data[166], $k_{15} = 16$ litres mole^{-1} s^{-1}. The reaction is reversible, and the value of pK for the equilibrium is 9.6.[166] The conversion of the H atom into e^-_{aq} in alkaline medium was demonstrated by Matheson and Rabani[44], who measured the optical density of e^-_{aq} in neutral medium and in a solution of alkali (pH 13) saturated with hydrogen at pressures up to 100 atm, for equal radiation doses per pulse, and found that the optical density of e^-_{aq} is greater by a factor of about 2.2 in the second system than in the first. In alkaline solution reactions (15) (the reverse reaction) and (16) take place:

$$H_2 + OH \rightarrow H + H_2O. \quad (16)$$

Thus $G(e^-_{aq}) = Ge^-_{aq} + G_H + G_{OH} \simeq 2.2Ge^-_{aq}$.

In acid medium, e^-_{aq} is effectively converted into the H atom [reaction (8)]. The rate constant for this reaction is 2×10^{10} litres mole^{-1} s^{-1}.[27-31,42]. This transformation also takes place in the reactions of e^-_{aq} with ions which are proton donors (e.g. $H_2PO_4^-$, HPO_4^{2-}, etc.)[89,154,165].

The reactions of the hydrated electron can be divided into three groups[160]. The first group corresponds to simple addition, e.g.

$$e^-_{aq} + O_2 \rightarrow O_2^- \quad (17)$$

$$e^-_{aq} + C_{10}H_8 \rightarrow C_{10}H_8^-. \quad (18)$$

The second group corresponds to simple reduction, of the type

$$e^-_{aq} + Cu^{2+} \rightarrow Cu^+. \quad (19)$$

The third group corresponds to dissociative addition:

$$e^-_{aq} + ClCH_2COOH \rightarrow [ClCH_2COOH]^- \rightarrow Cl^- + CH_2COOH. \quad (20)$$

The pulse radiolysis method has identified many-short-lived species which are products of the reactions of e^-_{aq} with dissolved substances. The characteristics of the optical spectra of these species are given in Table 1.

The rate constants for the reactions of e^-_{aq} with about 400 compounds have now been determined, chiefly by the pulse radiolysis method. Scheme 1, prepared from published data[27-32,42,44,50,92,106,114,117-153,165,166,171,176-180,183-205] characterises the reactivity of e^-_{aq} with respect to various substances§. Most of these constants have been found from the rate of disappearance of the optical absorption of e^-_{aq} in the presence of the given compound.

On the basis of published data, some general conclusions may be reached regarding the reactivity of this reducing species.

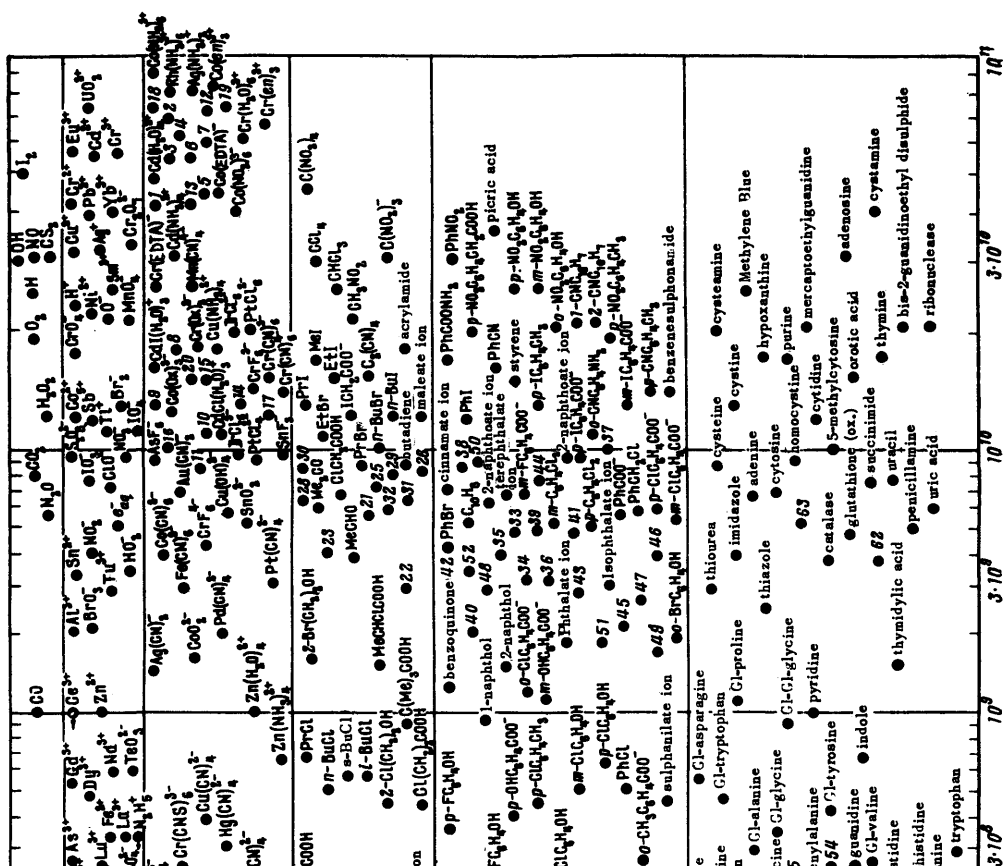
1. The hydrated electron is highly reactive towards molecules which have unpaired electrons, e.g. H, OH, and NO.

2. In the reactions of e^-_{aq} with cations, the rate constants are generally greater the greater the charge and dimensions of the cation.

† An identical absorption band has been observed in the flash photolysis of aqueous solutions of various inorganic ions (Cl^-, Br^-, I^-, CNS^-, $Fe(CN)_6^{4-}$, and OH^-) and organic compounds (phenol, alanine, etc.)[118-123]. In these examples, e^-_{aq} is produced by excitation of the solute by light. Similar phenomena are observed with solutions in ethanol[124,125].

‡ The properties of e^-_{aq} have been examined in a book by Pikaev[4] and in various reviews[141-161].

§ A large number of absolute values of the rate constants for the reactions of e^-_{aq} are given in Pikaev's book[4] and in various reviews[141-143,152,204,205].

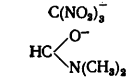
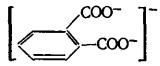
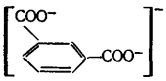
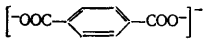
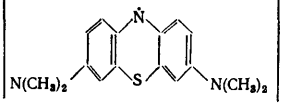


Scheme 1. Rate constants for the reactions of e^-_{aq} in aqueous solution at room temperature:
1) $[CoCl_2en_2]^+$; 2) *cis*-$[Co(CNS)_2en_2]^+$; 3) *trans*-$[Co(CNS)_2en_2]^+$; 4) $[Co(H_2O)(NH_3)_5]^{3+}$; 5) $[Co(H_2O_2(NH_3)_4]^{3+}$; 6) $[CoCl(NH_3)_5]^{2+}$; 7) $[Co(NH_3)_6$ (teraphthalate)$]^{+*}$; 8) $[CoCl(CN)_5]^{3-}$; 9) $[Co_2N_3(CN)_4]^{3-}$; 10) $[Co(OH)(CN)_5]^{3-}$; 11) $[Co(NO_2)(CN)_5]^{3-}$; 12) $[CrCl_2en_2]^+$; 13) $[Cr(CNS)_2en_2]^+$; 14) *cis*-$[CrOx_2(H_2O)_2]^-$; 15) *trans*-$[CrOx_2(H_2O)_2]^-$; 16) PbO_2^-; 17) $[PdCl_4]^{2-}$; 18) $[Os(NH_3)_6]^{3+}$; 19) $[Ru(NH_3)_6]^{3+}$; 20) $[Ir(NH_3)_6]^{3+}$; 21) bromopropionate ion; 22) β-bromopropionate ion; 23) $ClCH_2COO^-$; 24) β-phenylpropionate ion; 25) β-iodopropionate ion; 26) CCl_3COO^-; 27) nitrilotriacetate ion; 28) $BrCH_2COO^-$; 29) fumarate ion; 30) methacrylate ion; 31) pyruvate ion; 32) CF_3Cl; 33) *o*-iodobenzoate ion; 34) *o*-hydroxybenzoate ion; 35) *p*-fluorobenzoate ion; 36) *o*-fluorobenzoate ion; 37) *p*-cyanobenzoate ion; 38) *o*-hydroxybenzonitrile; 39) *m*-hydroxybenzonitrile; 40) *p*-hydroxybenzonitrile; 41) *o*-dichlorobenzene; 42) *p*-bromophenol; 43) *o*-bromophenol; 44) *p*-bromobenzoate ion; 45) *p*-aminobenzoate ion; 46) benzenesulphonate ion; 47) *m*-toluate ion; 48) *p*-toluate ion; 49) toluene-*p*-sulphonate ion; 50) α-trichlorotoluene; 51) α-trichlorotoluene; 52) trimesate ion; 53) leucylglycine; 54) leucyl-leucine; 56) phenylalanine; 57) sarcosine; 58) serine; 59) thiobarbiturate ion; 60) tyrosine; 61) acetylglycine; 62) acemosine-5-phosphate**; 63) adenylic acid; 64) alanylalanine; 65) alanylglycine; 66) alanyl-leucine; 67) *d*-sorbitol; 68) *d*-xylose; Me= CH_3; Et = C_2H_5; Pr = C_3H_7; Bu = C_4H_9; Ph = C_6H_5; Gl = glycyl; Hd = histidyl; Lc = leucyl; en = ethylenediamine; EDTA = ethylenediaminetetra-acetate ion; Ox = oxalate; ⟵ = upper limiting value of constant; ⟵• = lower limiting value of constant.

Notes. (1) In those instances where the published values of the constants were given for various pH-values, the Scheme gives the value at pH 6÷8. (2) The rate constants for the reactions of e^-_{aq} with H_2O and D_2O are 16 and 200 litres mole^{-1} s^{-1} respectively.

* Possibly $[Co(teraphthalate)(NH_3)_5]^+$ (Ed. of Translation).
** This entry may be a misprint in the Russian, and the compound referred to may be adenosine-5'-phosphate (Ed.of Translation).

TABLE 1. Characteristics of the optical spectra of the species produced in the reactions of e^-_{aq} with dissolved substances.

Substance	Reaction product	λ_{max}, nm	ϵ at λ_{max}, litres mole^{-1}	Ref.
O_2	O_2^-	240—250	$9.8\cdot10^3$ at 253.7 nm	12,167,168
I_2	I_2^-	370—390	—	165
CO_2	CO_2^-	250	$2.4\cdot10^3$	169
Ag^+	Ag^0	313	$2.3\cdot10^4$	106,170,171
Tl^+	Tl^0	~400	—	172
Mn^{2+}	Mn^+	300	—	106,162
Co^{2+}	Co^+	300	—	106,162
Ni^{2+}	Ni^+	300	$2.1\cdot10^3$ at 313 nm	106,173
Zn^{2+}	Zn^+	300	$5.2\cdot10^3$ at 313 nm	106,162
Cd^{2+}	Cd^+	300	$7.5\cdot10^3$ at 313 nm	106,162
Pb^{2+}	Pb^+	300	—	162
Eu^{3+}	Eu^{2+}	320, 250	—	174
CrO_4^{3-}	Cr(V)	365	—	106
$PtCl_4^{2-}$	Pt(I)	450, 300	—	106
$S_2O_8^{2-}$	SO_4^-	444	—	175
CH_3I	I^-	220	—	176
$(CH_3)_2CO$	$(CH_3)_2COH$*	absorption in the range 200—300 nm	—	177
CH_3NO_2	$CH_3NO_2^-$	270	$2.8\cdot10^3$	178
$C(NO_2)_4$	$C(NO_2)_3^-$	350	$1.48\cdot10^4$	92,179
		380	—	180
$C_6H_5COO^-$	$[C_6H_5COO^-]^-$	444, 322	—	181
Phthalate		310	—	177
Isophthalate		430, 330	—	177
Terephthalate		520, 360	—	177
Benzophenone	$(C_6H_5)_2CO^-$	610	—	182
Methylene Blue		420	$1.04\cdot10^4$	183

* Produced with the intermediate formation of $(CH_3)_2CO^-$.

TABLE 2.

Property of e^-_{aq} *	Numerical value	Ref.
Charge	—1	27,55,103—111
λ_{max} in H_2O (25 °C)	720 nm	31,42,116,117
λ_{max} in D_2O (25 °C)	690 nm	117
$\epsilon^{H_2O}_{720}$	15 800 litres mole^{-1} cm^{-1}	179
E^0	$\leqslant$2.58 V	166,206—208
Hydration energy	1.75—1.87 eV	166,207,208
Free energy of formation ΔG^0_f	—37.5 kcal mole^{-1}	207
Entropy of hydration ΔS^0_{hydr}	—1.9 cal mole^{-1} deg^{-1}	207
Entropy in 1 M ideal soln. S^0	3.1 cal mole^{-1} deg^{-1}	207
Diffusion coeff.	$4.7\cdot10^{-5}$ cm^2 s^{-1}	139
Mean radius of distribution of charge	2.5—3.4 A	207,209,210
k ($e^-_{aq} + H_2O$)	16 litres mole^{-1} s^{-1}	166
$\tau_{1/2}$	$\geqslant7.8\cdot10^{-4}$ s	166
pK ($e^-_{aq} + H_2O \rightleftarrows H + OH^-$)	9.6	166
$G_{e^-_{aq}}$ (pH 7.0)	2.6 (±10%)	179
$G_{e^-_{aq}}$ (pH 13.0)	3.6—3.8	55,91,117

* In this and subsequent tables, ϵ, E^0, and $\tau_{1/2}$ denote respectively the molecular extinction coefficient, standard redox potential, and half-life.

3. The reactivity of e^-_{aq} with respect to anions decreases with increase in the charge on the anion. The hydrated electron reacts slowly with the anions of elements in higher oxidation states, and with anions whose central atom has no vacant orbital accessible to the electron.

4. The reactivity of complex compounds towards e^-_{aq} is parallel to their reactivity in outer-sphere redox processes. Here, however, the hydrated electron is a much more powerful reductant than most ordinary chemical reducing agents.

5. The hydrated electron reacts with organic substances as the strongest nucleophilic reagent, and it generally reacts at the positive centre of the molecule.

The chief properties of the hydrated electron are summarised in Table 2.

The question of the magnitude of $G_{e^-_{aq}}$ has been the subject of lively discussion for a number of years. For a neutral medium, various authors[55,60,72—75,77,81,82,89—91,97,101,107,110,211—236] have given values for the yield of e^-_{aq} of 2.2–2.9. These contradictory values are evidently due to the fact that the yields were not determined under comparable conditions. This might have led to differences in the values of $G_{e^-_{aq}}$ as a result of the suppression of reaction (7) in the spurs to different extents[217,237], or to differences in the contribution made by "excited water" to the reaction with the acceptor[54,55,107,108,218], depending on the concentration of the latter and its reactivity. Moreover, it is not excluded that oxygen atoms, which, as postulated by Allen[238], may be produced as a primary product of the radiolysis of water, may react with some substances and be inactive towards others¶. It has recently been found by the pulse radiolysis method that in neutral medium $G_{e^-_{aq}} = 2.6$ (accuracy ±10%)[179]. In these examples the yield was found directly from the measured values of $\epsilon G_{e^-_{aq}}$ and ϵ.

Published data[55,107,108,221,224,233,234,240—250] on the magnitude of $G_{e^-_{aq}}$ in alkaline medium are also contradictory. Most authors consider, however, that the yield of e^-_{aq} is greater in alkaline than in neutral medium. This is confirmed by direct measurement of $G_{e^-_{aq}}$ at various pH-values, using the pulse radiolysis method[117,251]. There may be several reasons for the increase in $G_{e^-_{aq}}$ in alkaline medium. Firstly, the H atom (if it is formed as a primary product of the radiolysis of water) is converted in alkaline solution into e^-_{aq}. This process alone, however, can increase $G_{e^-_{aq}}$ to only 3.2–3.4. Secondly, it is possible that hydrated electrons are produced by the reaction of OH^- ions with excited water molecules or radical pairs (H + OH) in the cell[54,55]:

$$OH^- + H_2O^* \rightarrow e^-_{aq} + OH + H_2O \quad (21)$$

$$OH^- + (H + OH) \rightarrow e^-_{aq} + OH + H_2O. \quad (22)$$

Thirdly, $G_{e^-_{aq}}$ may increase as a result of the partial suppression of reaction (7) in the spurs by OH^- ions[224]. Fourthly, it is not excluded that $G_{e^-_{aq}}$ under these conditions may increase partly as a result of the excitation of

¶ The problem of the value of $G_{e^-_{aq}}$ in various media has been discussed in detail by Haïssinsky[239].

OH^- ions by radiation, followed by breakdown of the $(OH^-)^*$ formed:

$$(OH^-)^* \rightarrow OH + e^-_{aq}. \quad (23)$$

In the theory of the self-capture of an electron by a polar medium, use is often made of a model in which the solvent is regarded as a continuous dielectric medium, characterised by macroscopic properties (static and optical dielectric constants, D_{st} and D_{opt}). The additional electron interacts with the polarisation field of the medium. The equation for the energy of bonding of the electron to the medium contains the term $1/D_{opt} - 1/D_{st}$. Since D_{opt} is generally close to unity, capture of the electron by the medium requires that $D_{st} \gg 1$. Calculations based on this model can be made in two ways—(1) by using the electronic-adiabatic theory, and (2) by using the self-consistent field theory—in the first of which it is assumed that the mean velocity of an electron which is weakly bound to the medium is low compared with the velocity of the valency and inner electrons of the solvent molecules. This method has been used by Weiss [61,252], who finds that the mean radius of e^-_{aq} is about 5 Å. A sphere with this radius can contain ~ 10 water molecules. The second theory considers the influence of the mean charge distribution of the additional electron on the electrons of the medium. Jortner [210] considers that this theory is more applicable than the first theory to this problem. The chief results of his calculations are as follows: (1) the radius R_0 of the cavity containing the electron is much smaller for water than for ammonia (it is possible that for water $R_0 = 0$); (2) the mean radius of the distribution of the charge of the electron in the energy ground state is 2.5–3.0 Å; and (3) the optical absorption maximum of e^-_{aq} is due to a $1s \rightarrow 2p$ transition. Since according to the Franck–Condon principle the water molecules retain their orientation during the transition, the excited $2p$-state is not an equilibrium state, and λ_{max} for e^-_{aq} corresponds almost exactly to the hydration energy of this radiolysis product (720 nm = 1.72 eV).

A number of experimental data, however, provide evidence in support of the so-called "cavity" theory [185,253-259], which has often been used to explain the characteristic features of the optical absorption spectra of halide ions in solution [253-258]. According to this theory, the halide ion (in our case e^-_{aq}) is present in a spherical "cavity" (i.e. in a certain volume accessible to the ion in solution), whose radius depends on the nature of the ion and the solvent. The absorption maximum is determined chiefly by the energy required to remove the ion from the cavity into the bulk of the solvent. Contraction of the cavity leads to displacement of λ_{max} towards shorter wavelengths. Decrease in the dimensions of the cavity takes place with fall in temperature and with the addition, to the solution, of anions which bind firmly the protons of water molecules. The optical absorption maximum of e^-_{aq} for concentrated electrolyte solutions is displaced towards shorter wavelengths compared with pure water [185]. Decrease in temperature also displaces λ_{max} for this species towards shorter wavelengths [160]; this effect is observed not only for water, but also for alcohols [260]. Similar relationships are observed in the radiolysis of vitreous aqueous solutions at 77°K. [137,261]

Natori and Watanabe [262] have recently developed a structural theory for e^-_{aq}. On the assumption that the electron is trapped in a quasi-tetrahedron of the icelike structure of water and interacts with the nearest four oxygen atoms and eight hydrogen atoms, they calculated the energy of the optical transition at the absorption maximum and the oscillator strength as 0.8 and 0.26 eV respectively (compared with experimental values of 1.72 and 0.6–0.7 eV).

3. THE HYDROGEN ATOM

In 1954 Livingston and his coworkers [263,264], using the e.s.r. method, detected the formation of H atoms in the radiolysis of aqueous solutions of the acids $HClO_4$, H_2SO_4, and H_3PO_4 at 77°K. Later the production of H atoms in frozen aqueous solutions of acids was observed by many workers [265-277]. The spectrum of atomic hydrogen consists of a doublet with a splitting of 500 oersteds and a g-factor close to that of the free electron. The spectrum of the D atom for a solution of an acid in D_2O consists of a triplet with a separation between the components of ~ 78 oersteds. The yield of H atoms depends on the nature of the anion and the concentration of the acid, and also on the state (crystalline or vitreous) in which the frozen solution is irradiated.

Atomic hydrogen is not detected in pure ice irradiated at 77°K. Its spectrum has been recorded at 4.2°K. [273-276] The initial yield of H atoms amounts in this instance to 0.5–0.9 [273,274]. Rexroad and Gordy [275] consider that the H atoms in ice irradiated at 4.2°K are produced as a result of the capture of electrons ejected from water molecules by H_3O^+ ions present in the matrix. The probability of such capture is obviously increased considerably in acid solutions. This probably explains the increase in the yield of H atoms in frozen solutions of inorganic acids, to 2.0–2.2 in perchloric acid solution at 77°K. [270,277]

The e.s.r. spectrum of H atoms has also been observed in solutions of alkalis and various inorganic salts, irradiated at 77°K. [126,127,129,137,272] In this instance, however, the yield of H is low; it is higher in crystalline alkaline ice than in the vitreous material [129].

At present there is no direct proof of the formation of H atoms in the radiolysis of liquid aqueous solutions. There is only indirect evidence for the production of this species. It has been shown [62-65] that the kinetic characteristics of the reducing species in the radiolysis of acid solutions are identical to those of atomic hydrogen prepared by non-radiative methods.

The part played by H atoms is most significant in the radiolysis of acid solutions. This is due to the fact that, since k_8 is high, e^-_{aq} is converted into H even in dilute acid solutions.

In neutral medium the greater part of the reducing radicals consist of hydrated electrons. The yield of H atoms is 0.5–0.6. This value has been found for G_H by many workers [82,83,86,88,90,97,100,213,278].

When neutral solutions do not contain acceptors of hydrated electrons, the latter, at low dose rates, are transformed by reaction (15) into H atoms, which can evidently take part in corresponding processes. This phenomenon is observed, for example, in neutral solutions of methanol. In this system $G(H_2)$ is almost equal [213] to the sum $G_{H_2} + G_H + Ge^-_{aq}$.

According to Baxendale [279] the reactions of H atoms can be divided into three main groups. The first group corresponds to simple reduction, e.g.

$$H + Cu^{2+} \rightarrow H^+ + Cu^+. \quad (24)$$

The second group comprises the addition of H to unsaturated bonds, e.g.

$$C_6H_6 + H \rightarrow C_6H_7. \quad (25)$$

The third group involves the detachment of H with the formation of H_2. Reactions of this group are extremely characteristic of saturated organic compounds, e.g.

$$CH_3OH + H \rightarrow CH_2OH + H_2. \quad (26)$$

The H atom is characterised by strong reducing properties. Its reactivity is indicated in Table 3, which includes data obtained using pulse radiation. The H atom is generally a weaker reducing agent than e^-_{aq}. This is true for the reactions with NO_3^-, NO_2^-, H_2O_2, N_2O, Ag^+, Cu^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, etc.[56,62,64,66,94,95,146,212,278,285-390] The reactivities of H and e^-_{aq} towards O_2 and OH are almost identical. These reactions involve simple addition of H and e^-_{aq}. The H atom is more reactive than e^-_{aq} towards certain organic compounds, e.g. alcohols. The redox potential of H is 2.1 V.[208]

The rate constants for the reactions of H atoms in aqueous solution are greater (by not more than one order of magnitude) than the constants for the analogous gas-phase reactions. This is in accordance with the theory of chemical kinetics[301].

Hydrogen atoms and e^-_{aq} often give the same reaction products. There is one characteristic property of H atoms, however, by means of which they can be distinguished on the basis of an analysis of the final products. Unlike e^-_{aq}, they exhibit a dehydrogenating action in reactions with saturated organic compounds.

The yield of H atoms is 3.65[1] in acid medium (pH < 2) and 0.5–0.6 in neutral medium[238]. In alkaline medium this species is effectively transformed into e^-_{aq} [reverse reaction (15)].

In 1950 Weiss[302] postulated the formation of H_2^+ radical-ions in acid medium:

$$H + H^+ \rightarrow H_2^+. \quad (27)$$

Later various characteristic features of the radiolysis of acid solutions were also attributed to the production of this radical-ion[71,72]. As shown subsequently, however, the rate constant for reaction (27) is comparatively low, 10^2–2.6×10^3 litres mole^{-1} s^{-1}.[37,296] It has been shown[303] that $G(Fe^{3+})$ in aqueous Fe^{2+} solutions is independent of the acid concentration, indicating that H_2^+ plays little part, even in strongly acid solutions According to certain authors[62,303,304], the oxidation of Fe^{2+} by atomic hydrogen involves the intermediate formation of hydride complexes:

$$Fe^{2+} + H \rightleftarrows FeH^{2+} \quad (28)$$

$$FeH^{2+} + H^+ \rightarrow Fe^{3+} + H_2. \quad (29)$$

The H_2^+ radical-ion apparently does not oxidise methanol in sulphuric-acid solutions[305].

There are two hypotheses regarding the mechanism of formation of H atoms as a primary product of the radiolysis of water. According to the first, these particles are produced by reaction (8), taking place in the spurs[53,79,80,306]. The second hypothesis[76-78,307-309] suggests that H atoms are produced from highly excited water molecules. According to Anbar and Meyerstein[308] substances which are efficient excitation-quenching agents (in particular ions of variable valency) can apparently react directly with the possible precursors—H_2O^* molecules—of the H atoms. These authors regard[309] the second hypothesis as confirmed by the results of a study of H/D isotope effects in the radiolysis of water. They find[309] that the isotope effect in the formation of H atoms is much greater in acid medium than in neutral medium. At present, however, there are no direct experimental data in support of either hypothesis.

TABLE 3. Rate constants for the reactions of H atoms with dissolved substances at 20–25°C.

Solute	k, litres mole^{-1} s^{-1}	Ref.	Solute	k, litres mole^{-1} s^{-1}	Ref.
Fe^{2+}	$2 \cdot 10^7$	35	HO_2	$2 \cdot 10^{10}$	147
Fe^{3+}	$9 \cdot 10^7$	37	H_2O_2	$(0.9–1.6) \cdot 10^8$	34, 36, 37
Ag^+	$1.15 \cdot 10^{10}$	171	e^-_{aq}	$2.5 \cdot 10^{10}$	28, 44
H	$1.0–1.5 \cdot 10^{10}$	34–46	MnO_4^-	$2.36 \cdot 10^{10}$	283
O_2	$0.53–2.6 \cdot 10^{10}$	33, 34, 37, 45, 280	CH_3OH	$1.6 \cdot 10^6$	171
OH	$0.7–4.5 \cdot 10^{10}$	33, 34, 45, 51	CH_2OH	10^{10}	283
Br_2	$\sim 10^{10}$	281	$C(NO_2)_4$	$(0.55–2.6) \cdot 10^9$	92, 179
OH^-	$(1.8–2.3) \cdot 10^7$	44, 282	$H_2^+ (+H_2^+)^*$	$<5 \cdot 10^6$	284

* Rate constant for the recombination of H_2^+ radical-ions.

4. THE OH RADICAL

The formation of OH radicals by the action of radiation on water has been observed repeatedly. Dainton and Collinson[310], in a study of the radiation polymerisation of acrylonitrile in water, observed in the infrared absorption spectrum of the polymer a broad band due to OH groups. A large number of products of the reactions of OH radicals with dissolved substances have now been identified by the pulse radiolysis method. A list of these products and some characteristics of their optical spectra are given in Table 4.

Recently, Hart, Matheson, et al.[51], using the pulse radiolysis method, have recorded the optical absorption spectrum of the OH radical in irradiated liquid water. It is found that λ_{max} for this radical lies at $\leqslant$ 230 nm.

One of the most important pieces of evidence for the formation of OH radicals in the radiolysis of water is provided by data obtained from the e.s.r. spectra of irradiated ice. The e.s.r. spectrum of OH radicals radicals in ice irradiated at 77°K was first observed by Matheson and Smaller[265,267]. The e.s.r. spectrum due to OH radicals (in H_2O) and OD radicals (in D_2O) has since been observed by many workers[126,127,137,271-277,328-338]. The e.s.r. spectrum of the OH radical consists of a doublet with a separation of ~ 40 oersteds between the components and a g-factor of 2.01, and that of the OD radical consists of a triplet with a separation of ~ 6 oersteds between the components.

The chief source of OH radicals is H_2O^+ ions (reaction 1). Weiss[252] suggested that H_2O^+ (or, in his terminology, the positive polaron) in liquid water has a lifetime which is sufficient to enable it to take part directly in the radiolytic transformation of various substances. Later, Weiss and Moorthy[339,340] have reported that they were able to record the e.s.r. signal of this ion in a study of the radiolysis of frozen solutions of various acids. Hummel and Allen[341] found, however, that the ionic strength does not influence the rate of the reaction between the oxidising

TABLE 4. Characteristics of the optical spectra of short-lived species which are products of the reactions of OH and O^- radicals with dissolved substances.

Solute	Reaction product	λ_{max}, nm	ϵ at λ_{max}, litres mole^{-1} cm^{-1}	Ref.
O_2 (alkaline medium)	O_3^-	430	$1.9\cdot10^3$	52, 167, 168, 311—313
	NO_2	400	—	314
NO_2^-	CNS	500	$7.1\cdot10^3$	49, 52, 168, 313—316
CNS^-	Cl_2^-	340	$1.25\cdot10^4$	317
Cl^-	Br_2^-	360	$9.6\cdot10^3$	189, 281, 318, 319
Br^-	I_2^-	370—390	—	47, 117, 314, 315
I^-	AsO_2	335	—	314, 315
AsO_2^-	CO_3^-	600	$(1.9—2.9)\cdot10^3$	169, 311, 315, 320
CO_3^{2-}	SiO_3^-	625	—	314, 315
SiO_3^{2-}	SeO_3^-	435	$1.34\cdot10^3$	314, 315
SeO_3^{2-}	TeO_3^-	350	$3.5\cdot10^3$	314, 315
TeO_3^{2-}	$S_2O_3^-$	375	$1.72\cdot10^3$	314, 315
$S_2O_3^{2-}$	HSO_3^{2-}	730	—	314
SO_3^{2-}	HSO_4 (or SO_4^-)	450	$\sim10^3$	321, 322
SO_4^{2-}	Ag^{2+}	270	—	171
Ag^+	Cu^{III}	300 (pH 7) or 265(pH 2)	$1.1\cdot10^3$ for Cu^{3+} and $5.7\cdot10^3$ for $CuOH^{2+}$	106, 323
Cu^{2+}	Mn^{III}	~450	$8.3\cdot10^2$	170
Mn^{2+}	Tl^{2+}	260	—	182
Tl^+	Fe^{IV}	345	$6\cdot10^3$	324
Fe^{3+}	CH_3CHOH	266, 257, 247	$(2.3—2.4)\cdot10^3$ at 296.7 nm	30, 325
C_2H_5OH	$(CH_3)_2COH$	absorption in the range 200—300 nm	—	177
$(CH_3)_2CHOH$				
$HCOO^-$ or CO_2	CO_2^- (COOH)	250	$2.4\cdot10^3$	169
$(NH_2)_2C=S$	$NH_2\diagdown C=S$ / NH	400	—	194
	or $NH_2\diagdown C—S$ // NH			
C_6H_6	C_6H_5OH	313	$3.5\cdot10^3$	326, 327
C_6H_5Cl	OHC_6H_5Cl	324	—	326
C_6H_5Br	OHC_6H_5Br	326	—	326
C_6H_5OH	OHC_6H_5OH	320	—	326
$C_6H_5CH_3$	$OHC_6H_5CH_3$	317	—	326
C_6H_5COOH	OHC_6H_5COOH	350	—	327
$C_6H_5COO^-$ (alkaline medium)	(O^-) $C_6H_5COO^-$	328	—	181

species in the radiolysis of water and bromide ion. Hochanadel[298] found that in the pH range 2–7 the oxidising species in the radiolysis and the OH radical obtained photochemically have the same reactivity towards hydrogen and hydrogen peroxide. From this it follows that the species being considered is not charged. Moreover, the e.s.r. signal observed by Weiss and Moorthy[339,340] has later been shown[137,277] to be due most probably to the OH radical. Nevertheless, it is not excluded that H_2O^+ ions may take part in radiolytic transformations in strongly acidic or highly concentrated solutions, when the reactions of the substances with this species may take place at a greater rate than reaction (1).

The OH radical is a strong one-electron oxidant. On reaction with a solute it oxidises one equivalent of the latter. It can sometimes act as a reducing agent, e.g. in the radiolysis of potassium permanganate solutions[342].

The most characteristic reactions of OH radicals can be divided into three groups. The first group corresponds to ordinary oxidation, e.g.

$$Ce^{3+} + OH \rightarrow Ce^{4+} + OH^-. \qquad (30)$$

The second group comprises the addition of OH to unsaturated bonds. The third group involves the abstraction of H with the formation of H_2O.

In alkaline medium the OH radical dissociates[343]:

$$OH \rightleftarrows O^- + H^+. \qquad (31)$$

The value of pK for this dissociation[39] is 11.9 ± 0.2. Like the OH radical, the O^- radical-ion absorbs in the wavelength range below 300 nm.[39] The ozonide ion O_3^- has been observed during the pulse radiolysis of alkaline solutions of oxygen[167,311] (see Table 4). This ion may be formed by the reaction

$$O^- + O_2 \rightarrow O_3^- \qquad (32)$$

which provides evidence for the existence of O^- in alkaline medium. The dissociation of the OH radical according to Eqn. (31) is also confirmed by measurements of the e.s.r. spectra of irradiated frozen alkaline solutions[126–135,344].

The O^- radical-ion is a weaker oxidising agent than the OH radical. In alkaline medium the yields of a number of oxidation processes—$G(AsO_4^{3-})$ for the oxidation of arsenite[345,346], $G(CO_2)$ for the radiolysis of oxalic acid solutions[347–351], $G(I_2)$ for the radiolysis[221] and photolysis[296] of KI solutions in the presence of N_2O, etc. —show a decrease. On the other hand, there is an increase in the yields for reductions, when the product undergoes reconversion into the starting material as a result of reaction with OH. For example, $G(NO_2^-)$ for $NaNO_3$ solutions increases sharply in alkaline medium[91]. Sometimes it is even necessary to assume that the O^- radical-ion has a reducing action[221,296].

Scheme 2, which indicates the reactivities of OH and O^- radicals, uses data[30–34,36,38,39,44,47,49,51,52,117,147,167–170,177,179,181,182,189,194,200,202,311–327,352–354] obtained in studies in which the reaction rate constants for these radicals were determined by means of pulsed radiation. In addition, a large number of relative rate constants for the reactions of OH and O^- have been determined by the method of competing acceptors[38,205,238,293,341,355–369].

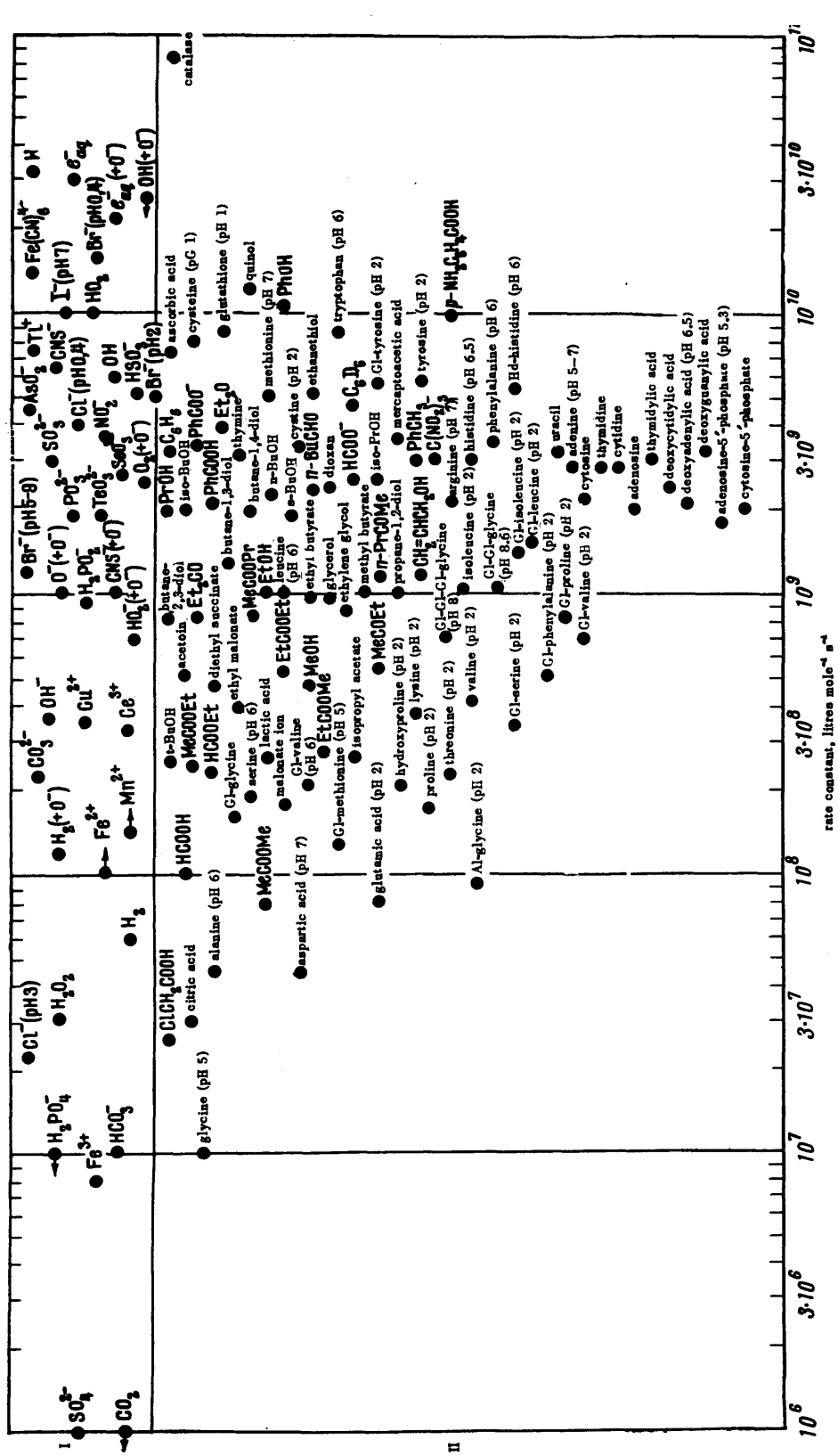
An important feature of the kinetics of reactions involving OH radicals is that the rate constants for reactions of type (13) have much larger values in aqueous solution than in the gaseous phase. Thus $k_{OH + H_2}$ for the gaseous phase is[370,371] about 10^4 litres mole^{-1} s^{-1}; for aqueous solutions, this constant has the value[38] $(4–6)\times10^7$ litres mole^{-1} s^{-1}. There are as yet, however, insufficient experimental data for a rigorous explanation of this effect.

The yields of OH radicals are greater in acid and alkaline media than in neutral medium. Since the processes of

TABLE 5.

Property of OH radicals	Numerical value	Ref.
λ_{max} H_2O (25 °C)	230 nm	51
$\epsilon_{260}^{H_2O}$	370 litres mole^{-1} cm^{-1}	51
E^0 (pH 0)	—2.1 V	372
E^0 (pH 14)	—1.25 V	372
Hydration energy	0.26 eV	372
Diffusion coeff.	$\geqslant2.3\cdot10^{-5}$ cm^2 s^{-1}	202
pK $(OH+OH^-\rightleftarrows O^-+H_2O)$	11.9	39
G_{OH} (pH 0)	2.95	1
G_{OH} (pH 7)	2.6 (±10%) *	
G_{O^-} (pH 13)	3.0—3.1	54, 55, 79

* Mean value from results given in a large number of papers.



Scheme 2. Rate constants for the reactions of OH and O$^-$ radicals in aqueous solution at room temperature. The constants for O$^-$ are denoted (+O$^-$); Al = alanyl; the other symbols are the same as those used in Scheme 1.

OH and e^-_{aq} formation are interrelated, the reasons for the increase in G_{OH} in alkaline medium are for the most part the same as those for the increase in Ge^-_{aq}.

The chief properties of OH radicals in water are summarised in Table 5.

5. THE HO_2 RADICAL

A study of the radiolysis of the Fe^{2+}–Cu^{2+} system by Hart in 1956 showed[373-375] that the perhydroxyl radical HO_2 is formed as a primary product. It is produced in the spurs as a result of reaction between H_2O_2 and OH. The yield of HO_2 for $^{60}Co\gamma$-radiation is extremely low (~ 0.02)[373]. For heavy particles, however, G_{HO_2} is much greater. For ^{210}Po α-particles, $G_{HO_2} = 0.23$.

The HO_2 radical is formed very efficiently in solutions containing oxygen, by reaction between O_2 and H or e^-_{aq}. Since k_{H+O_2} and $ke^-_{aq}+O_2$ have extremely high values, it may be concluded that the HO_2 radical plays an important part in these solutions.

Formation of the perhydroxyl radical has been demonstrated by many methods. Schmidt[377,378] observed an increase in electrical conductivity due to the presence of O_2^-—a product of the dissociation of HO_2—in irradiated water containing oxygen. The pulse radiolysis method has been used[167,177,311,313] to record the optical absorption spectra of HO_2 and O_2^- radicals. The absorption maximum of the HO_2 radical lies at 230 nm, and that of the O_2^- radical-ion at 240 nm. Proof of the formation of HO_2 radicals was also obtained in a study of the e.s.r. spectra of irradiated frozen water and various aqueous solutions[126,127,328,329,333].

The HO_2 radical is amphoteric. In neutral and alkaline media it dissociates according to the equation

$$HO_2 \rightleftarrows H^+ + O_2^-. \qquad (33)$$

The pK value for this dissociation is 4.4–4.5.[167,179,379] According to Bielski and Allen[380], the perhydroxyl radical is present in strongly acidic medium in the form $H_2O_2^+$:

$$HO_2 + H^+ \leftrightarrows H_2O_2^+ \qquad (34)$$

the pK value for this equilibrium being 1.0 ± 0.4.[380]

The perhydroxyl radical may act as either an oxidising agent or a reducing agent, depending on the conditions and the nature of the dissolved substance. Under ordinary conditions, the oxidising power of HO_2 [208] is close to that of Ce^{4+}. In oxidations HO_2 is converted into H_2O_2, and in reductions it is converted into H_3O^+ and O_2.

The reactions of HO_2 with the OH radical require special mention. Until recently it was assumed that this reaction takes place as follows:

$$HO_2 + OH \rightarrow H_2O + O_2. \qquad (35)$$

Kinetic proof has been obtained[379], however, of the formation of H_2O_3 by the combination of HO_2 and OH. The yield of H_2O_3 at pH 2–3 is 1.7. The pK value for the dissociation

$$H_2O_3 \rightleftarrows H^+ + HO_3^- \qquad (36)$$

is 9–10. The disappearance of H_2O_3 depends on the acidity of the medium. Its half-life is ~ 2 s in 0.02 M acid, and less than 0.1 s in 1 M and 10^{-4} M acid. This substance does not react with Ce^{4+}, tetranitromethane, or KI in neutral solution, but it oxidises Fe^{2+}. The formation and the stabilisation of compounds of the type H_2O_3 are observed[381] in various free-radical reactions on cooled surfaces.

TABLE 6. Rate constants for the reactions of perhydroxyl radicals in aqueous solution at 20–25°C.

Reaction	Medium	k, litres mole^{-1} s^{-1}	Ref.
HO_2+Fe^{3+}	0.5 M H_2SO_4	$7.3\cdot10^5$	382
HO_2+Cu^{2+}	pH 2.3	$1.5\cdot10^7$ *	383
$HO_2+MnO_4^-$	pH 3	$8\cdot10^6$	280
$HO_2+Br_2^-$	pH 2	$(1.6—6.4)\cdot10^9$	281, 318, 319
$HO_2+Br_3^-$	pH 2	10^8	319
HO_2+Br_3	pH 2	$1.5\cdot10^8$; $<4\cdot10^8$	281, 319
HO_2+CNS^-	pH 1	$1.6\cdot10^9$	316
$HO_2+C(NO_2)_4$	acidic	$<1.9\cdot10^4$	179
$O_2^-+C(NO_2)_4$	pH 5.6—6.2	$(1.9—2.0)\cdot10^9$	179, 92
HO_2+HO_2	pH$\leqslant$3	$(1.9—2.7)\cdot10^{6}$**	167, 379, 380, 383—385
$O_2^-+O_2^-$	pH$\geqslant$5	$(1.35—1.7)\cdot10^{7}$**	167, 377, 380, 384
$H_2O_2^+ + H_2O_2^+$	pH$<$1 0	$5\cdot10^5$	378

* Determined by the pulse radiolysis method.
** Includes the value of constants obtained without using ionising radiation.

TABLE 7. Properties of perhydroxyl radicals in water.

Property	Numerical value	Ref.
λ_{max} for HO_2 in H_2O (25°C)	230 nm	167
$\varepsilon^{HO_2}_{230}$	$1.15\cdot10^3$ litres mole^{-1} cm^{-1}	167
λ_{max} for O_2^- in H_2O (25°C)	240 nm	167
$\varepsilon^{O_2^-}_{240}$	$1,06\cdot10^3$ litres mole^{-1} cm^{-1}	167
$E°(HO_2, H^+/H_2O_2)$ (oxidant)	—1.7 V	385
$E°(H^+, O_2/HO_2)$ (reductant)	+0.3 V	385
pK ($HO_2 \rightleftarrows H^+ + O_2^-$)	4.4—4.5	167, 172, 379
pK ($H_2O_2^+ \rightleftarrows H^+ + HO_2$)	1.0	380

Table 6 gives absolute reaction rate constants for HO_2, O_2^-, and $H_2O_2^+$ radicals in aqueous solution, determined by various authors. The chief properties of perhydroxyl radicals in water are summarised in Table 7.

6. THE OXYGEN ATOM

The possible formation of atomic oxygen as a primary product of radiolysis has been postulated by a number of workers[238,385]. Allen[238] gives some indirect evidence for the production of O atoms in the decomposition of neutral water under the influence of radiation. He argues that, if it is assumed that H atoms are produced in yield 0.55 in neutral medium, $G(-H_2O)$ becomes 4.3. In this case, however, the oxidising products do not balance. To preserve the balance, it is necessary to assume the formation of another oxidising radiolysis product, which, from results for radiolytic transformations in a number of systems, should not react with hydrogen or ethanol, but is reactive towards hydrogen peroxide. Since in neutral medium $G_{OH} = 2.2$ and $G_{H_2O_2} = 0.7$, the yield of this product should be 0.7 equiv. eV^{-1}. If this product is atomic

oxygen, $G_O = 0.35$. Allen uses this hypothesis to explain various features of the radiolysis of a number of systems—H_2O_2–O_2 [57], NO [226], formate solutions [386], and H_2O_2 in H_2O. [18,387]

Allen [238] suggests the OH^+ ion as a possible source of atomic oxygen. Mass-spectroscopic data [388] in fact show that H_2O^+ and OH^+ ions (ratio 100 : 23.2 [289]) are formed in largest quantities in water vapour as a result of electron collisions (energy of electrons 100 eV). Baxendale and Gilbert [390] consider that OH^+ ions react in the gaseous phase with H_2O to give OH radicals:

$$OH^+ + H_2O \rightarrow H_2O^+ + OH \qquad (37)$$

but it has recently been shown experimentally [391] that this reaction produces H_3O^+ ions:

$$OH^+ + H_2O \rightarrow H_3O^+ + O. \qquad (38)$$

According to the data of Thynne and Harrison [391], in the gaseous phase $k_{38} = 2.9 \times 10^{11}$ litres mole^{-1} s^{-1}.

It is of course difficult to suppose that the relative proportions of H_2O^+ and OH^+ should be the same in the gaseous phase and in the liquid, but it may be assumed that the OH^+ ion is also produced by the action of radiation on liquid water. It may evidently then be a precursor of atomic oxygen. It is probable that in neutral medium OH^+ dissociates with the formation of O and H_3O^+ [reaction (38)]. In this connection it is interesting to note that the proposed ratio G_{OH}/G_O is close to the ratio of the quantities of H_2O^+ and OH^+ in the gaseous phase. It should be emphasised that the production of O by this mechanism should be accompanied by the formation of the same quantity of H:

$$H_2O \rightsquigarrow OH^+ + H + e^-. \qquad (39)$$

In acid medium, because of the presence of H_3O^+ ions, different routes for the disappearance of OH^+ are possible.

Another source of O atoms may be the recombination of OH radicals [392]:

$$OH + OH \rightarrow H_2O + O. \qquad (40)$$

Experiments [393,394] on the radiolysis of acidic and neutral water at high absorbed dose rates—i.e. under conditions where the recombination of radicals is highly probable—show, however, a significant increase in $G(H_2O_2)$ compared with low dose rates. It is thus unlikely that atomic oxygen is formed by the recombination of OH radicals.

There are at present no quantitative data on the properties of atomic oxygen in aqueous solutions. Taube [395], in a study of the reactions of excited O atoms (in the ^1D-state), showed that these atoms react readily with water to form hydrogen peroxide. In the ground state O atoms do not react with water. Katakis and Allen [396], studying the radiolysis of concentrated perchloric acid solutions, have observed not an increase but a decrease in $G_{H_2O_2}$ with increase in the $HClO_4$ concentration. In these solutions the direct action of radiation on perchloric acid produces excited perchlorate ions, which decompose to ClO_3^- and O. From the observed dependence of the yield of H_2O_2 on $[HClO_4]$, these workers conclude that the O atoms produced are in the ground state. Formation of O atoms is possible in the radiolysis of concentrated solutions of various other oxygen-containing anions (NO_3^-, $KMnO_4$, etc.).

7. EXCITED WATER

As already noted, the passage of ionising radiation through water leads to ionisation and excitation of H_2O molecules. The fate of the "excited water" and the part it plays have not yet been elucidated, however.

Excited water molecules may be formed [397] in two ways—(1) by capture of the ejected electron by the H_2O^+ ion (Samuel–Magee hypothesis), and (2) by collision of slow electrons with water molecules—and Magee [398] considers that water molecules in the singlet and triplet states may be produced in a spur, in the ratio 1 : 3, as a result of the first process.

Platzman [399] suggests that, in the gaseous phase, irradiation produces both ionised and excited molecules in equal yields. In the condensed phase "superexcited" molecules (their energy exceeding the ionisation potential) use up the excess of energy, not only for ionisation but also for other processes. For example, breakdown of the molecule into two radical fragments is possible. In Allen's opinion [1], however, excitation of H_2O to an upper electronic level in liquid water may lead to ionisation. According to Voevodskii [400,401] the excitation in liquid water may be transferred through hydrogen bonds and be localised at impurities, leading to the formation of H, OH, H_2, and H_2O_2. If the excitation of water does not lead to ionisation, the H and OH radicals formed by the breakdown of H_2O^* will be produced close to one another and will possibly, as a result of the "cage effect" [402], recombine for the most part, to re-form water. It is of course not excluded that a certain proportion of the H atoms, because of their very small dimensions, will escape from the "cages" into the bulk of the liquid, through the cavities in the quasi-crystalline water lattice. If, however, excitation of the water leads to ionisation (see footnote on p. 603), the H (or e^-) and the OH formed from the H_2O^* produced as a result of the capture of the ejected electron by H_2O^+ will be in the same small spur as the H_3O^+ and OH (from the H_2O^+), as is assumed by Matheson [403]. This also facilitates the H + OH reaction. These considerations lead to the conclusion that, in dilute solutions of ordinary substances, the part played by excited molecules is small. The radiolysis of concentrated solutions is quite different. As first postulated by Proskurnin [404–407], at high concentrations a solute can penetrate into the "cage", as a result of which its reaction with radicals becomes possible. Later, Bakh and his coworkers [408], Pikaev [409], Kabakchi [410,411], Sowden [412,413], and Katakis and Allen [396] attributed various features of the radiolysis of concentrated solutions to reactions in which H_2O^* takes part. Dainton and his coworkers [54,55] put forward similar explanations for the increase in the yields of radical products of the radiolysis of water in acid and alkaline media, and also in relatively concentrated N_2O solutions. Shubin and Dolin [414,415] observed a considerable increase in yields in a number of systems when these were saturated with inert gases under very high pressures. It was suggested that in these experiments ordering of the water structure takes place. This creates favourable possibilities for the transmission of excitation along a chain of hydrogen bonds. In the opinion of these authors, the excitation here appears in the form of exciton-like formations (electron–positive-hole pairs).

Recently, the idea that "excited water" takes part in radiation reactions has been introduced into the interpretation of certain features of the radiolysis of dilute aqueous

solutions of a number of substances. Hayon[78] considers that, in the radiolysis of neutral solutions, certain substances (e.g. O_2) may react directly with H_2O^*. Shinohara and his coworkers[416,417], in a study of the radiolysis of neutral or weakly acidic HgX_2–NaN_3 and HgX_2–$NaNO_2$ solutions, conclude that under the most favourable conditions about five excited water molecules per 100 eV absorbed energy may take part in radiolytic transformations. Anbar and Meyerstein[307,308,418], in an investigation of the influence of ions of the type Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+} on the magnitude of G(HD) in irradiated solutions of 2-deuteriopropan-2-ol and methanol (0.01–0.1 M), have been forced to postulate the possibility of reactions between H_2O^* and these ions and alcohols. Shagisultanova et al.[419] attribute the hydrolytic decomposition of oxalato-complexes of Co^{III} in aqueous solution under the influence of ^{60}Co γ-radiation to the penetration of excited water molecules into the coordination sphere of these compounds. Getoff[420] assumes that the carboxylation of amines in aqueous solution is due partly to reactions involving H_2O^*. Kabakchi et al.[421,422] attribute the characteristic features of the radiolysis of the H_2O_2–O_2–H_2 system to the reactions of the dissolved substances with exciton-like formations.

There is at present no direct experimental proof of the formation of excited water molecules. Niira[423] has predicted theoretically that water has a triplet excited state, and Kuppermann[424], in a study of the scattering of electrons with energies of 25–100 eV in the gaseous phase, has detected an excited state of H_2O with an energy 4.2 ± 0.2 eV higher than the energy of the ground electronic state. Sitharamarao and Duncan[425], in an examination of the emission of light from water during γ-irradiation, conclude that H_2O^* and OH^* are formed in appreciable yield during the radiolysis of water. More recently, however, a similar investigation by Czapski and Katakis[426], carried out at a higher experimental level, has shown that the radiation yield of light emission is negligible ($\leq 10^{-5}$).

In the liquid phase an excited molecule in the triplet state has a lifetime of 10^{-4} s or more[427]. The possibility that this also applies to water cannot be excluded. It is evident that, as a result, these H_2O^* molecules may also take part in radiation reactions in comparatively dilute solutions. Chemically, however, H_2O^* molecules are generally equivalent to (H + OH), so that they should "develop" only with certain solutes[54,55]. This effect can be observed particularly clearly when the solution contains "conjugated acceptors"[404–407,428–431], i.e. when, as it were, both an acceptor for H atoms and an acceptor for OH radicals are present. At the same time it is necessary that a given acceptor be an effective excitation "quencher".

There are no experimental or theoretical data on the possibility of the existence of excitons in liquid water. According to Protopopov[432,433], free and local excitons may exist in aromatic liquids and solutions. In addition to the local exciton, the liquid also contains a state of local ordering, which is termed an orienton. The lifetime of these formations is short ($\leq 10^{-9}$ s), however. Davydov[434] considers that in some instances excitons of the Wannier–Mott type (an electron–positive-hole pair) may be produced in the liquid phase. Jortner[435] has recently carried out quantum-mechanical calculations and demonstrated the possibility of the existence of excitons in media of the liquefied inert gas type. For water, it is apparently necessary to make allowance for its high polarity. It follows from theory that the bond energy of the exciton decreases in proportion to the square of the dielectric constant of the medium[436]. Moreover, with marked polarisation, the bound electron and positive hole can in principle form a polaron pair[437]. Finally, it must be emphasised that water is characterised by a high reactivity towards H_2O^+ ions. It can therefore probably be concluded that, although water has a crystal structure with short-range order, excitons in it, if they are produced, have an extremely short lifetime, and in dilute aqueous solutions they break down (possibly to OH and e^-_{aq}) without being able to spread. These discussions are of course qualitative, and it would be extremely desirable for the appropriate quantum-mechanical calculations to be carried out.

In connection with the foregoing, considerable interest attaches to work[438–440] using the pulse radiolysis method, which has established the formation of triplet-excited molecules of naphthalene and other aromatic substances during irradiation of their solutions in benzene and cyclohexane. In aqueous solutions, however, the yields are negligible[439].

Thus excitation of water can be observed only under strictly specific conditions. In dilute aqueous solutions of ordinary substances, the part played by this process is small.

8. THE MOLECULAR PRODUCTS H_2 AND H_2O_2

Hydrogen and hydrogen peroxide are the primary molecular products of the radiolysis of water. Many workers[268,272,273,286–301,356,361,408,412,413,441–455] have shown that the yields of H_2 or H_2O_2 decrease with increase in the concentration of dissolved substances which are acceptors of H atoms (e^-_{aq}) or OH radicals respectively. The following relationship is observed

$$G_{R_2} = G^0_{R_2} - A[S]^{1/2}$$

where G_{R_2} is the yield of H_2 or H_2O_2 at a given concentration of the acceptor S, $G^0_{R_2}$ the yield of molecular product at zero concentration of the acceptor, [S] the molar concentration of the acceptor, and A a parameter defining the probability of interaction between the acceptor and the corresponding radical.

Byakov and his coworkers[456,457] have carried out a theoretical treatment of the dependence of G_{R_2} on [S] on the basis of a simplified diffusion–radical model for the radiolysis of water. They have shown that this dependence is given by the equation

$$G_{R_2} = G^0_{R_2} - G^0_{R_2}\left(\frac{k_{R+S}}{k_{R+R}}\frac{v_0}{n_0}\right)^{1/2}[S]^{1/2}$$

where n_0 is the initial number of radicals in the spur, v_0 is the initial volume of the spur, and k_{R+S} and k_{R+R} are the rate constants for the corresponding reactions. Byakov and Bugaenko[458] use this equation and the experimental dependence of G_{R_2} on [S] to calculate a large number of relative rate constants for radiation reactions. The calculated values are close to the experimental values. The agreement between the constants provides evidence in support of the hypothesis that at least the greater part of the H_2 and H_2O_2 is formed as a result of the recombination of radicals in the spurs [reactions (9–12)].

Weiss and Hayon[59], Hayon[459], and Rabani and Stein[212] postulated that a large proportion of the molecular hydrogen is formed as a result of the recombination of e^-_{aq} in

the spurs or at a short distance from the latter. Proof for the possibility of formation of H_2 from e^-_{aq} was obtained by Dorfman and Taub[30], who measured the yields of HD and D_2 in alkaline and acidic solutions of C_2H_5OD in D_2O. Production of H_2 occurs also[28,29] by the reaction of e^-_{aq} with H at sites of high radical concentration. The mechanisms of these two interesting reactions are still unknown, however. The recombination of e^-_{aq} possibly passes through a stage involving the formation of $(e^-_{aq})_2$. The production of such "bipolarons" was postulated in one of the theories of metal-ammonia solutions[460]. Anbar and Meyerstein[461,462] have studied the isotopic effect in the formation of hydrogen by the recombination of e^-_{aq}, and found that this effect is much greater than would be expected on the basis of the hypothesis that the H_2 is produced by the diffusion-controlled process $e^-_{aq} + e^-_{aq}$. They therefore conclude that the recombination of e^-_{aq} involves the formation of $(e^-_{aq})_2$, and that decomposition of the latter (into $H_2 + 2OH^-$) with rupture of the H–O bond takes place much more readily than the corresponding decomposition with rupture of the D–O bond. In the second reaction, the H^- ion is probably produced as an intermediate product.

There are other theories regarding the ways in which the molecular products of the radiolysis of water are produced. Many authors[245,388,459,461-465] suggest that H_2 and H_2O_2 may be produced by the decomposition of "excited water". Stein and his coworkers[387,463] have studied the radiolysis of H_2O_8 in $H_2{}^{18}O$. According to their data, one fraction of the H_2O_2 precursors is readily captured by acceptors of OH radicals, whereas the other fraction does not exhibit this property. These authors conclude that the yield of H_2O_2 corresponding to the second type of precursor (possibly H_2O^*) is about 0.4. Similar results[245] have been obtained in a study of the dependence of $G_{H_2O_2}$ on the concentration of $[Fe(CN)_6]^{3-}$. Here the yield of H_2O_2 corresponding to H_2O^* amounts to 0.3. It should be emphasised, however, that these values of the H_2O_2 yield, which are independent of the concentration of acceptors of OH radicals, are apparently too high. Czapski[466] has represented the results of published work[245,388,463] graphically by plotting $G_{H_2O_2}$ against $[S]^{1/3}$, and obtained an almost linear relationship. Some of these authors have subsequently[467] agreed with this conclusion. Anbar and Meyerstein[388,463,461,462] find that the isotopic effect in the formation of H_2 as a result of the radiolysis of water is much smaller than that for the recombination of e^-_{aq} obtained photochemically. On this basis they conclude that, in the irradiation of water, a large proportion of the H_2 is produced, not by the reaction $e^-_{aq} + e^-_{aq}$ in the spurs, but as a result of various other processes (e.g. the decomposition of "excited water"). It is undoubtedly extremely desirable to confirm this very interesting observation for a number of other materials, and to establish the fraction of H_2 and H_2O_2 produced from "excited water".

In Platzman's opinion[468], a certain proportion of the H_2 is formed by the reaction of underexcited electrons (of energy ≤ 6.5 eV) with water, with the intermediate formation of H^- ions. The calculations show that the yield of H_2 as a result of this reaction may reach 0.2 ± 0.1.

Molecular hydrogen generally does not react with dissolved substances. When the solution contains large quantities of H_2, however, or when no other acceptors of hydroxyl radicals are present, the hydrogen reacts with OH radicals, converting them into H atoms in acidic and neutral media, and into e^-_{aq} in alkaline medium.

Hydrogen peroxide may exhibit reducing properties or oxidising properties, depending on the nature of the dissolved substance and the pH of the medium†. Hydrogen peroxide undergoes electrolytic dissociation:

$$H_2O_2 \rightleftarrows HO^-_2 + H^+ \qquad (41)$$

the pK value for this reaction being 11.75.

9. MAXIMUM YIELD IN THE DECOMPOSITION OF WATER

The magnitude of $G(-H_2O)$ is determined by the ionisation of the water, without allowance for the reactions $H + OH$ and $e^-_{aq} + OH$ in the spurs. If we assume that in neutral water H is produced in addition to e^-_{aq}, we reach the conclusion that $G(-H_2O)$ depends little on pH. The values found for this yield are 4.55, 4.3, and 4.6–4.8 in acidic, neutral, and alkaline media respectively. It is difficult to make accurate allowance for the contribution of the reactions $H + OH$ and $e^-_{aq} + OH$, taking place in the spurs. According to Hochanadel[397], the yield for the decomposition of water $G'(-H_2O)$ with allowance for these reactions amounts to ~ 6. Diffusion-kinetic calculations carried out by Byakov et al.[457] show, however, that this yield may reach ~8. Various data provide evidence in support of this last value. Proskurnin and his coworkers[407,428,429] found that $G(NO_2^-)$ in concentrated (1 M and above) alkaline solutions of $NaNO_3$ saturated with nitrogen is 4.0–4.5 ions per 100 eV. If it is assumed that two reducing particles are used up in the formation of one nitrite ion, $G(-H_2O) \simeq 8-9$. Baxendale and Gilbert[390] studied the radiolysis of mixtures of the vapours of H_2O and methanol, ethanol, ether, or cyclohexane, and concluded that $G'(-H_2O) = 8.0 \pm 0.7$. According to Anderson et al.[470,471] in the gaseous phase in the presence of cyclohexane or ammonia $G(-H_2O)$ has the values 7.0 (over the range 125–250°C) and 10.6 (above 300°C).

Firestone[472] studied the formation of HD in mixtures of gaseous D_2 and water vapour containing tritium, and found that $G(HD) = 11.7 \pm 0.6$. If it is assumed that the HD is produced as a result of the reaction $H + D_2$, it is obvious that $G(HD) = G(-H_2O)$. Baxendale and Gilbert[390], discussing these results, have suggested that, in the D_2–H_2O system, isotopic exchange by deuterium involves both ionised and excited water molecules. If this is so, the difference between the yields for the decomposition of water, observed in these experiments, gives the yield of excited molecules. This difference is ~4. The same value for the H_2O^* yield can be obtained by examining the results of work by Proskurnin and his coworkers[407,428,429]. These authors found that $G(NO_2^-)$ in concentrated alkaline solutions of $NaNO_3$ increases to ~6 ions per 100 eV when a "conjugated acceptor"—glycerol or glucose—is added. Finally, it has been shown[414,415] that under certain conditions the yield for the decomposition of water may reach ~14.

Thus definite data have now been obtained, indicating that the maximum yield for the decomposition of water amounts to 12–14 molecules per 100 eV. The maximum yield due to ionisation is 6–8 molecules per 100 eV. It is evident that in dilute solutions these yields can be achieved only in exceptional instances, if at all.

† The properties of hydrogen peroxide have been described in detail in a monograph[469].

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VIBRATIONAL AND ELECTRONIC SPECTRA OF AROMATIC SIX-MEMBERED AZACYCLIC COMPOUNDS

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