AN INTRODUCTION TO RADIATION CHEMISTRY

Third Edition

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WATER AND INORGANIC AQUEOUS SYSTEMS

CONTENTS

WATER

The radiolysis of water and aqueous solutions is described in this and the following chapter, and the radiolysis of organic materials in Chapter 9. Apart from water itself, Chapters 7 and 8 deal primarily with solutions, where the predominant interest is the chemical change brought about in dissolved substances rather than any change in the water itself. However, water generally makes up the greater part of an aqueous system and acquires a correspondingly large fraction of the absorbed radiation energy. Thus, chemical changes to the solutes occur when these react with the products of water radiolysis, that is, with the radicals e_{aq}^-, H, OH, and HO_2 (or an ionic form of the radicals), and the molecular product H_2O_2 (Another molecular product of water radiolysis, H_2,

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normally takes very little part in the subsequent chemical action.) The main emphasis in this and the following chapter, therefore, is with the "indirect" effect of radiation on substances in solution. In contrast, the emphasis in Chapter 9 is on the radiolysis of pure materials, where the radiation affects the material directly rather than through an intermediary solvent. In other words, Chapter 9 deals with the "direct" effects of radiation on organic substances.

The division of topics between Chapters 7, 8, and 9 is convenient in practice because the radiolysis mechanisms fall into a similar pattern. Thus, Chapter 7 illustrates radiolytic oxidation–reduction reactions, Chapter 8 the reactions of organic radicals in aqueous solution, and Chapter 9 the reactions of excited and ionized organic molecules, and organic radicals, in organic media. All three chapters deal predominantly with liquid systems because the greater part of the published material deals with these, and they are the systems most readily studied by kinetic methods.

Similarities exist between the radiation chemistry of water and the radiolysis of other polar liquids, for example, liquid ammonia and the alcohols, because of the influence their polar character has on the solvation and reactions of the electron and other charged species produced upon irradiation. Solvation also occurs with less polar liquids and with gases but generally plays a smaller role in their radiolysis. As an example of the influence of polar character, geminate recombination of electrons with their parent positive ions is the normal reaction of ion pairs in nonpolar organic liquids, whereas the electron and ion become solvated and separated in water and other strongly polar liquids, with a significant effect upon the reactions taking place.

Early investigations on the radiolysis of water and aqueous solutions played a significant role in the development of radiation chemistry and are described briefly in Chapter 1, and by Hart (1), Allen (2), and Draganić and Draganić (3), and in the first edition of this book (4).

Water Vapor

The photochemistry of water vapor has been studied extensively at wavelengths ranging from 186 to below 120 nm (5). Primary processes are

$$H_2O \xrightarrow{h\nu} H + \cdot OH \tag{7.1}$$

and, at the shorter wavelengths and with a lower probability,

$$H_2O \xrightarrow{h\nu} H_2 + O \tag{7.2}$$

$$\xrightarrow{h\nu} H_2O^+ + e^- \tag{7.3}$$

The latter reaction, photoionization, is possible only at wavelengths below

TABLE 7.1   Threshold Energies for Processes in Water Vapor

Process	Minimum Energy Requirement			
	$kJ\,mol^{-1}$	$eV\,molecule^{-1}$	nm	Ref.
$H_2O \longrightarrow H_2O^*$ (lowest triplet)	405–435	4.2–4.5[a]	295–275	6
				7
$H_2O \longrightarrow H_2O^*$ (lowest singlet)	636	6.6	187[b]	8
				9
$H_2O \longrightarrow H_2(^1\Sigma_g^+) + O(^3P)$	485	5.02	246.8[b]	5
				10
$H_2O \longrightarrow H(^2S) + OH(X^2\Pi)$	494	5.12	242.0[b]	5
				10
$H_2O \longrightarrow H_2(^1\Sigma_g^+) + O(^1D)$	678	7.03	176.3[b]	5
				10
$H_2O \longrightarrow H_2(^1\Sigma_g^+) + O(^1S)$	908	9.39	132.0[b]	5
				10
$H_2O \longrightarrow H_2O^+(^2B_1) + e^-$	1220	12.61 ± 0.05[c]	98.3	11
				12
$H_2O \longrightarrow OH^+(^3\Sigma) + H + e^-$	1740	18.1 ± 0.1[c]	68.5	11
$H_2O \longrightarrow H^+ + OH + e^-$	1890	19.6 ± 0.25[c]	63.3	11
$H_2O \longrightarrow O + 2H + e^-$	2820	29.25 ± 0.3	42.4	11

[a]Energy of the triplet state above the ground state.
[b]From the absorption spectrum.
[c]Appearance potential of positive ion in mass spectrometer.

98.3 nm (threshold energies for processes of importance in the decomposition of water vapor are given in Table 7.1).

In closed systems the photolysis products, hydrogen and oxygen, build up to a small equilibrium concentration at which point the rate of formation is balanced by the rate at which the products are removed by back reactions. The presence of back reactions has been confirmed by flow experiments in which the products are analyzed after a very brief irradiation. These show much higher yields of products, corresponding to initial quantum yields for water decomposition rising from about 0.4 for 186 to 143 nm light to values greater than unity for light in the 143- to 125-nm region. Hydrogen peroxide is also observed as a product in the flow experiments. Reactions that have been proposed to account for the products include

$$H + OH + M \longrightarrow H_2O + M \tag{7.4}$$

$$2H + M \longrightarrow H_2 + M \tag{7.5}$$

$$2OH + M \longrightarrow H_2O_2 + M \tag{7.6}$$

$$H + OH \longrightarrow H_2 + O \tag{7.7}$$

$$2OH \longrightarrow H_2O + O \tag{7.8}$$

$$O + OH \longrightarrow O_2 + H \tag{7.9}$$

where M is a water molecule (or the wall of the container) and serves to remove excess energy from the products. Oxygen atoms formed by the dissociation of excited molecules and in other reactions (e.g., 7.7, 7.8, and 7.27) may also react with water molecules,

$$O + H_2O + M \longrightarrow H_2O_2 + M \tag{7.10}$$

$$O + H_2O \longrightarrow 2OH \tag{7.11}$$
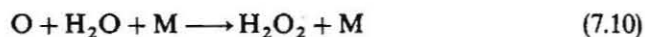
The relative importance of reactions such as 7.4 and 7.7, or 7.6 and 7.8, which involve the same pairs of reactive species, depends on the excited state of the reactants and the water vapor pressure, the termolecular reactions being favored by high vapor pressures and the bimolecular reactions by low vapor pressure and short-wavelength (i.e., higher energy) radiation. Energy-rich (i.e., "hot") hydrogen atoms formed when short-wavelength radiation is used may react directly with water to give molecular hydrogen (10, 13):

$$H^* + H_2O \longrightarrow H_2 + OH \tag{7.12}$$

Back reactions, for example,

$$OH + H_2 \longrightarrow H_2O + H \tag{7.13}$$

which break down the initial products, become significant as the concentration of products builds up and are responsible for the low steady-state concentrations of product observed.

The most abundant ions formed when water vapor is bombarded with electrons or α particles in the mass spectrometer are listed in Table 7.2 with their appearance potentials and the reactions that have been proposed to account for their formation; more detailed information on the mass spectroscopy of water vapor is given by Dixon (5). The same ions are produced by electron and α-particle irradiation but the ion abundances differ, the α particles producing rather less fragmentation than the electrons, which have a comparable velocity. The relative importance of the individual ions changes as the water vapor pressure is increased, the abundances of OH^+, H^+, and O^+ falling with increasing pressure and those of H_2O^+ and H_3O^+ increasing. The abundance of H_3O^+ increases in proportion to the square of the pressure, confirming that this ion is produced in an ion–molecule reaction (Eq. 7.20). It has been suggested that at high pressures H_3O^+ may also be formed via excited water (17).

$$H_2O^* + H_2O \longrightarrow H_3O^+ + OH + e^- \tag{7.25}$$

TABLE 7.2 Principal Ions Formed in Water Vapor in the Mass Spectrometer

Ion	Appearance Potential (V) (5,11)	Relative Intensity			Probable Formation Process (5, 11,16)	Eq. No.
		100-eV Electron (14)	50-eV Electron (15)	2.2-MeV α Particle (15)		
H^-	4.8	0.6			$H_2O + e^- \longrightarrow H^- + OH$	(7.14)
OH^-	4.7				$H^- + H_2O \longrightarrow OH^- + H_2$	(7.15)
	6.0				$H_2O + e^- \longrightarrow OH^- + H$	(7.16)
O^-	7.4	0.15			$H_2O + e^- \longrightarrow O^- + H_2$	(7.17)
					$\longrightarrow O^- + 2H$	(7.18)
H_2O^+	12.61	100	100	100	$H_2O + e^- \longrightarrow H_2O^+ + 2e^-$	(7.19)
H_3O^+	12.67		0.32[a]	0.54[a]	$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH$	(7.20)
OH^+	18.1	23	23.1	17.95	$H_2O + e^- \longrightarrow OH^+ + H + 2e^-$	(7.21)
H^+	19.6	5	4.3	1.11	$H_2O + e^- \longrightarrow H^+ + OH + 2e^-$	(7.22)
O^+	18.8	2	2.0	1.11	$H_2O + e^- \longrightarrow O^+ + H_2 + 2e^-$	(7.23)
	29.15				$\longrightarrow O^+ + 2H + 2e^-$	(7.24)

[a] Pressure dependent.

Negative ions are less abundant than positive ions in the mass spectrum of water vapor (18) and, because their formation involves incorporation of the incident electron in the products, require relatively low-energy electrons (5 to 15 eV); formation of negative ions may reach a maximum at certain electron energies that correspond to preferred energy states of the products of the reaction (i.e., the reaction may be a resonance process). The negative ion H_2O^- is not detected by mass spectrometry, and must therefore have a very brief existence. At low pressures, H^- is the most abundant negative ion and very little OH^- is formed, but at higher pressures the reverse is true and OH^- becomes the more abundant ion. This tendency is apparent when the negative ion abundances given in Table 7.2 are compared with the following relative abundances found by Muschlitz and Bailey (19) at 4.6 mm Hg pressure (a high pressure in the context of mass spectrometry), namely $H^-:O^-:OH^- = 1.2:23:31$. The changes are consistent with the suggestion that OH^- is formed, in part, by an ion–molecule reaction of H^- (Eq. 7.15). However, the total yield of negative ions is always much smaller than the total yield of positive ions. For example, Melton (18) has estimated that in water vapor at 6×10^{-6} mm Hg pressure bombarded with 100-eV electrons, less than 1% of the products result from the formation of negative ions, and the electron and hydrated electron remain the negative species of greatest interest. Larger negative ion abundances are found in the presence of oxygen and the formation of complex ions, or clusters, such as $O_2^-(H_2O)_m$, $O^-(H_2O)_m$, and $OH^-(H_2O)_n$ with values of n up to 5 has been reported (20).

Ion–molecule reactions observed in the mass spectrometer with water vapor are listed in Table 7.3. Reactions 7.20 and 7.27 are the most significant in the radiation chemistry of water vapor, with the former making the greater contribution; the higher pressures used in radiolysis favor reaction or collision quenching of excited H_2O^+ ions rather than fragmentation to give OH^+. Cluster formation between a positive or negative ion and neutral water molecules (i.e.,
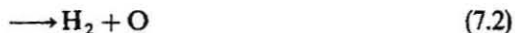
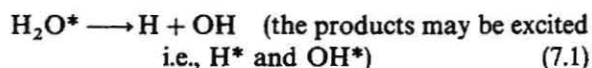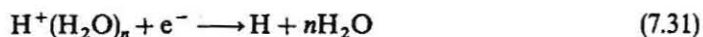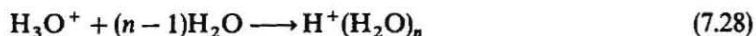TABLE 7.3   Ion–Molecule and Neutralization Reactions in Water Vapor (5)

Reaction	Eq. No.	Rate Constant[a] ($m^3\,mol^{-1}\,s^{-1}$)	$-\Delta H$ ($kJ\,mol^{-1}$)
$H^- + H_2O \longrightarrow OH^- + H_2$	(7.15)	$\sim 3 \times 10^9$	
$O^- + H_2O \longrightarrow OH^- + OH$	(7.26)		
$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH$	(7.20)	1×10^9	105–125
$OH^+ + H_2O \longrightarrow H_3O^+ + O$	(7.27)	1×10^9	240
$H_3O^+ + (n-1)H_2O \longrightarrow H^+(H_2O)_n$	(7.28)	($n = 1$ to 8, refs. 21, 22)	
$H_3O^+ + e^- \longrightarrow H_2O + H$	(7.29)	1.4×10^{11}	~ 610
$\longrightarrow 2H + OH$	(7.30)	1.4×10^{11}	~ 105
$H^+(H_2O)_n + e^- \longrightarrow H + nH_2O$	(7.31)		~ 190

[a]Rate constants for gas phase reactions are generally give in units of $cm^3\,molecule^{-1}\,s^{-1}$ for bimolecular reactions. To facilitate comparison with other rate constants given in this chapter, these units have been converted to $m^3\,mol^{-1}\,s^{-1}$ by multiplying rate constants given in units of $cm^3\,molecule^{-1}\,s^{-1}$ by 6.022×10^{17}.

solvation of the ion) has been observed (see, for example, 5, 20–22), confirming theoretical predictions by Magee and Funabashi (23) and earlier suggestions by Lind (24) that this might occur. Formation of clusters by successive addition of water molecules to an ion is significant because neutralization of the hydrated ion (e.g., Eq. 7.31) releases less energy than neutralization of the bare ion (e.g., Eq. 7.29 or 7.30) so that the products may differ in the two cases (25); reaction rates would also be expected to differ for the bare and solvated ions. Electrons may also become solvated in the vapor phase. Posey et al. (26), for example, describe the formation of hydrated electron clusters, $(H_2O)_n^-$, where n has values from 15 to 30. The negatively charged water clusters react with substances that are known to scavenge hydrated electrons in the liquid phase, for example, O_2 and CO_2, and in doing so form similar products, $O_2^-(H_2O)_{n-7}$ and $CO_2^-(H_2O)_{n-3}$, respectively. Electron hydration was observed in an ion source attached to a mass spectrometer, and will not necessarily occur to the same extent under radiolysis conditions.

The overall features of the radiation-induced decomposition of water vapor are similar to the photochemical decomposition, namely that breakdown occurs to give hydrogen and oxygen or hydrogen peroxide, which, because of back reactions, reach only small steady-state concentrations in pure water (5, 27). The equilibrium yields obtained depend in part on the experimental conditions (e.g., purity of the water used, nature and condition of the vessel walls, radiation type, and dose rate) and published results are not entirely consistent. However, representative results are those of Anderson and Best (reported in ref. 27) who found 10^{-2} mol% hydrogen and 3.8×10^{-3} mol% oxygen for proton irradiation at 1 atm pressure, 125 °C, and 8×10^4 Gy s^{-1}. The information available from photochemistry and mass spectrometry suggests that the following reactions will occur when water vapor is irradiated under the conditions normally employed, that is, pressures between 0.5 and 1.5 atm and temperatures below 150 °C:

$$H_2O \rightsquigarrow H_2O^+, e^- \tag{7.32}$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \tag{7.20}$$

$$H_3O^+ + (n-1)H_2O \longrightarrow H^+(H_2O)_n \tag{7.28}$$

$$H^+(H_2O)_n + e^- \longrightarrow H + nH_2O \tag{7.31}$$

$$H_2O^* \longrightarrow H + OH \quad \text{(the products may be excited} \\ \text{i.e., } H^* \text{ and } OH^*) \tag{7.1}$$

$$\longrightarrow H_2 + O \tag{7.2}$$

and possibly

$$H^* + H_2O \longrightarrow H_2 + OH \tag{7.12}$$

$$H_2O^* + H_2O \longrightarrow H_3O^+ + OH + e^- \tag{7.25}$$

Hydration of the proton will be reduced at lower pressures and higher temperatures, and reaction 7.31 may be replaced by 7.29 or 7.30 under these conditions. In any event, the reactions shown will be followed by others (e.g., 7.4 to 7.11) in which the radicals formed are converted to stable chemical products (H_2, O_2, H_2O_2, and H_2O). Back reactions such as reaction 7.13 and

$$H + H_2O_2 \longrightarrow H_2O + OH \tag{7.33}$$

assume importance as the concentration of molecular products builds up, and are responsible for the low steady-state concentrations of products observed under static (nonflow) conditions.

The W value for water vapor, $29.6 \pm 0.3\,eV$ per ion pair for electrons and γ radiation and $37.6\,eV$ per ion pair for α particles, is two to three times the ionization energy for water (12.61 eV) so that between 55 and 65% of the absorbed energy could be in the form of electronic or vibrational excitation of H_2O and H_2O^+. The decrease in the numbers of fragment ions with increasing pressure in the mass spectrometer suggests that excited ions produced by irradiation at even higher pressures will dissipate their energy without fragmentation. However, to account for radical yields measured in the presence of scavengers, a substantial part of the excitation energy transferred to neutral water molecules must result in dissociation.

The extent of water decomposition during vapor-phase irradiation can be estimated theoretically using the so-called optical approximation introduced by Platzman (28) in which the abundance of a particular ionized or excited state is assumed to be proportional to f/E, where f is the dipole oscillator strength for the transition from the ground state to the ionized or excited state and E is the energy of this state above the ground state. Applying this approach, Santar and Bednář (29, 30) estimated $g(-H_2O)$[1] to be in the range 0.71 to 0.81 $\mu mol\,J^{-1}$ for water vapor with g(ion pair) = 0.35 (see footnote 2) and g(excited states) = 0.36 to 0.47 $\mu mol\,J^{-1}$; the range in yields is the result in part of uncertainties regarding the effect of collisions of slow ($< 100\,eV$) electrons (see also, 31, 32). Platzman pointed out that molecules may be raised to superexcited states in which they have energies in excess of the ionization energy, and that these states may

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[1] The symbols g(ion), g(excited states), g(H), g(OH), etc., are used to represent the primary yields of the species in parentheses, that is, the earliest detectable yields, which are normally measured after reactions within spurs and tracks are complete but before the species has had an opportunity to react outside these zones. Thus, $g(-H_2O)$ refers to the total number of water molecules dissociated by irradiation even though some of the dissociation products may combine to reform water at a later stage; $G(-H_2O)$ gives the number of water molecules transformed into stable products, other than H_2O, when the radiolysis reactions are complete. $G(-H_2O)$ is normally smaller than $g(-H_2O)$ because some of the molecules dissociated are reformed, for example, by combination of H and OH. Several other symbols have been used for the primary yields, the most common being the use of subscripts with the symbol G, for example, G_{ion}, $G_{excited\ states}$, G_{OH}, etc. The latter were used in earlier editions of this book but use of the lower case g offers some advantages to typists and users of word-processing software. Final yields are always given in the form G(product).

[2] g(ion pair) = $10.36/W\ \mu mol\,J^{-1}$ when W is in units of eV per ion pair.

subsequently ionize or dissociate to give excited radicals (H* and OH* from water) capable of reactions such as 7.12 which are energetically not possible with ground-state radicals. Inclusion of superexcited states with a yield of about $0.1\,\mu\text{mol}\,\text{J}^{-1}$ raises the estimated $g(-\text{H}_2\text{O})$ to $0.81\pm0.1\,\mu\text{mol}\,\text{J}^{-1}$, which compares well with measured yields. Since the bond dissociation energy of water, $D(\text{HO}-\text{H})$, is 5.16 eV, a radiation-chemical yield of $0.81\,\mu\text{mol}\,\text{J}^{-1}$ corresponds to utilization of 35 to 45% of the absorbed energy in bond scission; the remainder is dissipated in the form of thermal energy or, to a very limited extent, light.

Experimental radiation-chemical yields for the primary species are determined by adding ion or radical scavengers to intercept the reactive intermediates. The yield of electrons, for example, can be estimated by irradiating water vapor containing nitrous oxide (33, 34), when $g(\text{e}^-)$ is found to be $0.31\pm0.04\,\mu\text{mol}\,\text{J}^{-1}$ on the basis of the scavenging reaction

$$\text{e}^- + \text{N}_2\text{O} \longrightarrow \text{N}_2\text{O}^- \longrightarrow \text{N}_2 + \text{O}^- \tag{7.34}$$
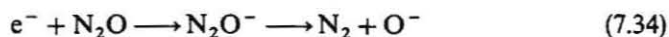
Saturated organic compounds such as alcohols and alkanes scavenge hydrogen atoms with the formation of molecular hydrogen, for example,

$$\text{H} + \text{CH}_3\text{OH} \longrightarrow \text{H}_2 + \cdot\text{CH}_2\text{OH} \tag{7.35}$$

so that the final yield of hydrogen is the sum of the primary or molecular yield of H_2 and the yield of hydrogen atoms, that is, $G(\text{H}_2)=g(\text{H}_2)+g(\text{H})$; hydroxyl radicals are also scavenged by the organic compounds but do not form H_2. Mixtures containing deuterium have also been used to estimate the yield of hydrogen atoms (35, 36) since

$$\text{H} + \text{D}_2 \longrightarrow \text{HD} + \text{D} \tag{7.36}$$

$$2\text{D} \longrightarrow \text{D}_2 \tag{7.37}$$

and $g(\text{H})=G(\text{HD})$; hydroxyl radicals are scavenged forming DOH, but not HD. However, hydrogen atom yields estimated using deuterium, $g(\text{H})=1.36\,\mu\text{mol}\,\text{J}^{-1}$ (36), are significantly higher than yields ($g(\text{H})=0.75\pm0.04\,\mu\text{mol}\,\text{J}^{-1}$) estimated using organic scavengers (5) or hydrogen halides (HCl and HBr also form H_2 with hydrogen atoms) (37). It appears, therefore, that HD can be formed in processes other than reaction 7.36, possibly by reaction of triplet excited water molecules with D_2, or when deuterium atoms combine in the presence of water (5, 37). Irradiation of D_2O itself gives essentially the same radical and molecular yields as irradiation of H_2O (5) (cf. Table 7.4).

Irradiation of water vapor in the presence of both an electron scavenger (N_2O or SF_6) and a hydrogen atom scavenger (an organic compound or hydrogen halide) gives the yield of hydrogen formed by molecular processes (e.g., reactions 7.2 and 7.12) and via excited molecules (Eq. 7.1), eliminating hydrogen formed as a result of ion neutralization (Eq. 7.31). Under these experimental conditions,

$G(H_2) = g(H_2) + g(H)_{exc} = 0.52 \pm 0.05\ \mu mol\ J^{-1}$. The yield of hydrogen formed by molecular processes (i.e., those that cannot be inhibited by adding a radical scavenger) can be estimated by measuring the yields of hydrogen in the presence of unsaturated organic compounds, or the yield of H_2 from solutions containing C_6D_6 (38), since under these conditions H and OH are scavenged but do not form H_2. Experiments of this kind give $g(H_2) = 0.05 \pm 0.01\ \mu mol\ J^{-1}$. The yield of hydroxyl radicals, $g(OH)$, is generally not measured, but is estimated from the stoichiometric relationship: $g(OH) = 2g(H_2) + g(H)$. Taken together, scavenger experiments with irradiated water vapor give

$$g(e^-) = 0.31 \pm 0.04 \qquad g(H_2) = 0.05 \pm 0.01 \qquad g(H) = 0.75 \pm 0.04$$
$$g(OH) = 0.85 \pm 0.06 \qquad g(-H_2O) = 0.85 \pm 0.06$$

The primary yields listed above apply particularly to electron and γ irradiation, but are expected to be relatively independent of LET because the low density of the vapor allows the active species to diffuse away from the region of the particle track before reaction. Boyd and Miller (39) found the same steady state and molecular yields from water vapor irradiated with low-LET γ radiation and very high-LET fission fragments, although in the presence of an organic scavenger, lower hydrogen atom yields were observed with the fission fragment irradiations. The lower yields were attributed to increased radical–radical reaction near the fission fragment tracks where the initial concentration of radicals is very high; radical–scavenger reactions predominate with the lower-LET radiation since these do not produce such high concentrations of radicals.

Radical yields from water vapor increase at temperatures above about 150 °C, $G(H_2)$ measured in the presence of organic scavengers increasing by about 0.2 to 0.35 $\mu mol\ J^{-1}$. The increase is approximately equal to $g(e^-)$, and it has been suggested that at the higher temperatures the neutralization reaction is 7.30 rather than 7.31, although not all the experimental evidence is consistent with this proposal (5):

$$H_3O^+ + e^- \longrightarrow 2H + OH \tag{7.30}$$
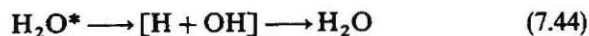
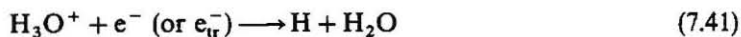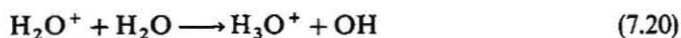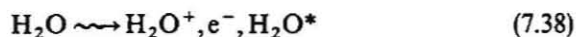$$H^+(H_2O)_n + e^- \longrightarrow H + nH_2O \tag{7.31}$$
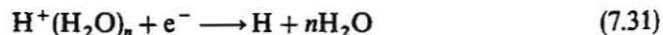
More extensive, or more detailed, discussions of the radiation chemistry of water vapor have been given by Dixon (5), Anderson (27), and Armstrong (40).

Ice

The initial action of radiation on ice is to produce ionized and excited water molecules as in water vapor, though the structure of the solid favors loss of energy from excited ions and molecules without dissociation, and caging and subsequent recombination of radicals. Thus, radiation-chemical yields are considerably

lower in ice (and in liquid water) than in water vapor; $G(-H_2O)$ falls from $0.43\,\mu\text{mol J}^{-1}$ in neutral water at $20\,°\text{C}$ to 0.35 in ice at $-10\,°\text{C}$, 0.10 at $-78\,°\text{C}$, and 0.05 at $-200\,°\text{C}$ (41, 42). The radiolysis yields can be accounted for on the basis of ionic reactions alone, leading to the conclusion that excitation energy is dissipated without producing any net chemical change. At the lower temperatures, $G(-H_2O)$ is appreciably less than $g(\text{ion pair})$ $(0.35\,\mu\text{mol J}^{-1})$, calculated taking the value of W for water vapor ($29.6\,\text{eV}$ per ion pair), indicating that extensive radical recombination is taking place. Probable steps in the radiolysis of pure ice include

$$H_2O \rightsquigarrow H_2O^+, e^-, H_2O^* \tag{7.38}$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \tag{7.20}$$

$$e^- \longrightarrow e_{tr}^- \tag{7.39}$$

$$e_{tr}^- + OH \longrightarrow OH^- \tag{7.40}$$

$$H_3O^+ + e^- \text{ (or } e_{tr}^-) \longrightarrow H + H_2O \tag{7.41}$$

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O \tag{7.42}$$

$$H_2O^* \longrightarrow H_2O \tag{7.43}$$

$$H_2O^* \longrightarrow [H + OH] \longrightarrow H_2O \tag{7.44}$$

$$H + OH \longrightarrow H_2O \tag{7.45}$$

$$2H \longrightarrow H_2 \tag{7.46}$$

$$2OH \longrightarrow H_2O_2 \tag{7.47}$$

where e_{tr}^- are trapped electrons, less completely solvated than the hydrated electron in liquid water. At very low temperatures, trapped electrons and other transient species are effectively immobilized where they are produced, though they may become mobile and react as shown above as the temperature is raised. Trapped electrons are also believed to react by a tunneling mechanism, which brings about relatively long-range electron transfer without diffusion of the reactants. The square brackets in Eq. 7.44 signify that the excited molecule dissociates to give two radicals that are prevented from moving apart by the neighboring molecules (i.e., are caged); the radicals eventually react together to reform water.

Radicals trapped in irradiated ice can be detected and identified by means of standard spectroscopic techniques including optical absorption and emission, and EPR spectroscopy; additional information can often be obtained by

following the changes produced as the frozen sample is warmed to room temperature (43–45a). For example irradiation of pure ice at $-269\,°C$ produces hydrogen atoms that are stable at this temperature and can be identified by their EPR spectrum (cf. Fig. 5.7). As the temperature is raised the hydrogen atoms begin to disappear and are completely gone at $-196\,°C$ (46). However, pure ice irradiated at $-196\,°C$ shows absorption characteristic of the hydroxyl radical (Fig. 5.7), which in turn disappears in the temperature range -170 to $-140\,°C$ (47) (an optical absorption peak at 280 nm disappears in the same temperature range). Hydrogen atoms are stable in acidified ice up to $-180\,°C$ but at higher temperatures disappear by a second-order process, probably combining to form molecular hydrogen; both hydrogen and hydrogen peroxide have been identified in melted irradiated ice.

Trapped electrons are not detected when acidified ice is irradiated, but are formed and can be observed with neutral and especially alkaline ice; upon irradiation alkaline ice becomes blue, with an absorption peak near 600 nm in the optical spectrum, similar to the absorption of the hydrated electron in water, though shifted toward the red region of the spectrum, and a single line near the free electron position in the EPR spectrum. Electrons may be held in shallower traps (i.e., with less orientation of the surrounding molecules) in ice than in liquid water, leading to optical absorption maxima in the near infrared. Both the absorption spectra and decay kinetics of electrons trapped in ice have been studied by pulse radiolysis using detectors whose sensitivity extends into the infrared (see, for example, 45a, 48). Similar studies have been carried out on trapped electrons in other frozen polar systems, most notably on the alcohol glasses (44, 45b). The investigations have shown that electrons are able to move from shallower to deeper traps in frozen matrices, with a corresponding blue shift in the optical absorption maximum, if energy is supplied by warming the sample or exposing it to ultraviolet light.

Radiation-induced chemical reactions can take place in frozen solutions (44). Ghormley and Stewart (41), for example, showed that hydrogen peroxide can be decomposed when ice containing dissolved hydrogen and hydrogen peroxide is irradiated at low temperatures. The amount of decomposition is increased when the irradiation is carried out at temperatures at which the hydroxyl radical is believed to be mobile (i.e., above about $-50\,°C$). Under these conditions both H and OH are able to diffuse through the solid and the mechanism is probably similar to the mechanism in the liquid phase, that is,

$$H + H_2O_2 \longrightarrow H_2O + OH \tag{7.33}$$

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \tag{7.48}$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \tag{7.49}$$

In some cases radiolysis reactions in ice can be followed by EPR measurements; for example, upon thermal activation of irradiated ice containing methanol the

following reaction occurs (44):

$$H + CH_3OH \longrightarrow H_2 + \cdot CH_2OH \qquad (7.50)$$
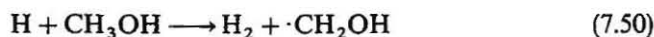
and the hydrogen atom doublet in the EPR spectrum is replaced by a triplet associated with the methanol radical.

Liquid Water

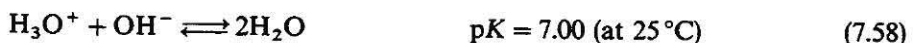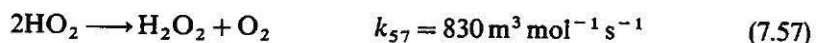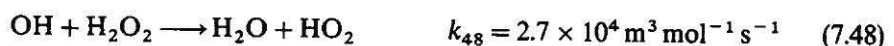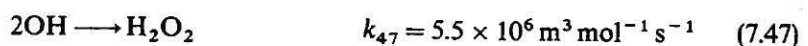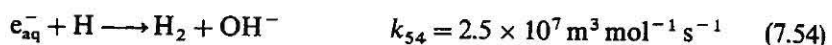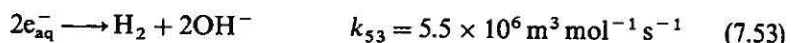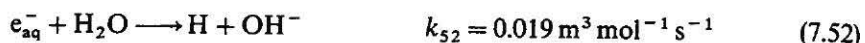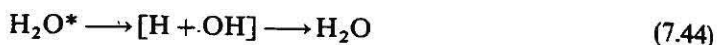The radiation chemistry of liquid water is similar to that of ice, differing from the radiolysis of water vapor in the following respects: (1) in the liquid all charged species with only thermal energy become hydrated[3] within approximately 10^{-11} s, (2) excitation energy is lost by collision processes more rapidly in liquids than in gases and in water this is facilitated by the highly hydrogen-bonded structure of the system, and (3) diffusion is slower in the liquid than in the gas phase so that species formed close together, particularly those formed with only thermal energy, will be constrained to remain close to one another for a longer period in the liquid phase. The latter leads to cage and LET effects in liquids that are largely absent in gas-phase radiolysis, and to the use in liquid-phase studies of the concepts of spurs and tracks to describe the nonhomogeneous distribution of the primary species.

Major reactions in the radiolysis of liquid water are

$$H_2O \rightsquigarrow H_2O^+, e^-, H_2O^* \qquad (7.38)$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \qquad (7.20)$$

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[3] Hydration resembles the clustering of water molecules about H_3O^+ observed in irradiated water vapor, though in liquid water all ions become hydrated, including the electron once it has slowed to thermal energy. The hydration (or solvation) process entails the orientation of water molecules about the charged species and therefore takes a finite time which is of the order of 10^{-11} s, the relaxation time for dipoles in water. The electron represents a special case and appears to become hydrated within about 10^{-12} s; it has been suggested that the electron may find an existing site within the water structure that meets its solvation needs, or that the intense electric field associated with the electron reduces the dielectric relaxation time by an order of magnitude. Various models have been proposed for the hydrated electron, e_{aq}^-, but for the present purposes it is sufficient to treat it as an electron associated with a group of orientated water molecules. Other hydrated ions can be considered as ions surrounded by shells of water molecules, one or two molecules thick, held more or less loosely by electrostatic attraction between the ion and solvent dipoles. Formation of the ion–dipole bonds releases energy of the order of $1 \, eV \, ion^{-1}$ (about $100 \, kJ \, mol^{-1}$), which may lead to significant differences in ΔH for reactions of the bare and hydrated ion (see, for example, reactions 7.29 and 7.31 in Table 7.3).

The hydrogen ion, H^+, can form a definite hydrate, H_3O^+, the oxonium ion. In aqueous solution (as opposed to the gas phase) and after sufficient time has elapsed for the ions to become solvated, the symbols H^+, H_3O^+, and H^+ (aq) all represent the hydrated hydrogen ion; both H^+ and H_3O^+ are used in this chapter. Although other ions will also be hydrated, this will be indicated specifically only when enthalpies, or other phase-specific data, are referred to.
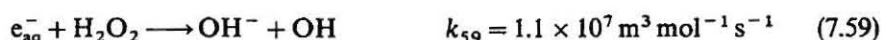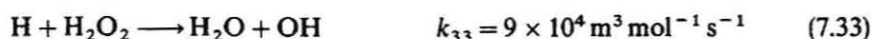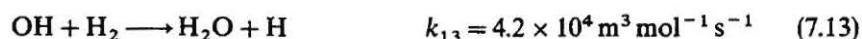
$$H_2O^* \longrightarrow H_2O \tag{7.43}$$

$$H_2O^* \longrightarrow [H + \cdot OH] \longrightarrow H_2O \tag{7.44}$$

$$e^- \longrightarrow e_{aq}^- \tag{7.51}$$

$$e_{aq}^- + H_2O \longrightarrow H + OH^- \qquad k_{52} = 0.019 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.52}$$

$$2e_{aq}^- \longrightarrow H_2 + 2OH^- \qquad k_{53} = 5.5 \times 10^6 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.53}$$

$$e_{aq}^- + H \longrightarrow H_2 + OH^- \qquad k_{54} = 2.5 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.54}$$

$$e_{aq}^- + OH \longrightarrow OH^- \qquad k_{55} = 3.0 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.55}$$

$$e_{aq}^- + H_3O^+ \longrightarrow H + H_2O \qquad k_{56} = 2.3 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.56}$$

$$2H \longrightarrow H_2 \qquad k_{46} = 7.8 \times 10^6 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.46}$$

$$H + OH \longrightarrow H_2O \qquad k_{45} = 7.0 \times 10^6 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.45}$$

$$2OH \longrightarrow H_2O_2 \qquad k_{47} = 5.5 \times 10^6 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.47}$$

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \qquad k_{48} = 2.7 \times 10^4 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.48}$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad k_{57} = 830 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.57}$$

$$H_3O^+ + OH^- \longrightarrow 2H_2O \qquad k_{42} = 1.43 \times 10^8 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.42}$$

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O \qquad pK = 7.00 \text{ (at } 25\,°C) \tag{7.58}$$

(Rate constants are from refs. 49 and 50; those shown for reactions 7.46, 7.47, 7.53, and 7.57 are values of k, not $2k$). A number of other radical reactions involving the primary radicals and radiolysis products are known, but those shown are the more important and with additional reactions described below are sufficient to allow for a reasonable discussion of the radiolysis of aqueous solutions.

Radiation-chemical yields for water, as for ice, can be explained without including a contribution from the dissociation of excited water molecules. In the sequence of reactions above, excited molecules are shown returning to the ground state without dissociation (Eq. 7.43) or dissociating to give a caged radical pair that subsequently react to reform water (Eq. 7.44). Fragmentation of excited H_2O^+ is also less probable in the liquid than the gas phase, and the predominant positive ion process is reaction of the parent ion to give hydroxyl radicals (Eq. 7.20). Virtually all electrons become hydrated and react with other radicals or, slowly, with water to give hydrogen atoms (Eq. 7.52). The major radical reactions form the radiolytic products hydrogen and hydrogen peroxide, or

reform water. Reaction 7.48, which produces perhydroxyl radicals (HO_2), occurs within the spurs or particle tracks where hydrogen peroxide formed by reaction 7.47 is available prior to spur or track expansion; perhydroxyl radicals are a relatively minor product with low-LET radiation.

Irradiation of pure water in a closed system by low-LET radiation leads to the establishment of a steady state in which low concentrations of hydrogen, oxygen, and hydrogen peroxide are present. The following reactions serve to maintain the concentrations of the molecular products at their low values:

$$OH + H_2 \longrightarrow H_2O + H \qquad\qquad k_{13} = 4.2 \times 10^4\,m^3\,mol^{-1}\,s^{-1} \qquad (7.13)$$

$$H + H_2O_2 \longrightarrow H_2O + OH \qquad\qquad k_{33} = 9 \times 10^4\,m^3\,mol^{-1}\,s^{-1} \qquad (7.33)$$

$$e_{aq}^- + H_2O_2 \longrightarrow OH^- + OH \qquad\qquad k_{59} = 1.1 \times 10^7\,m^3\,mol^{-1}\,s^{-1} \qquad (7.59)$$

The steady-state concentrations depend upon the LET of the radiation, increasing with increasing LET until with high-LET radiation, such as the recoil nuclei from the $^{10}B\,(n, \alpha)^7Li$ reaction, the water is decomposed continuously and a steady state is not reached.[4] Irradiation of pure water in a system that is not closed leads to buildup of a steady-state concentration of hydrogen peroxide in solution and the continual escape of hydrogen and oxygen from the system; in effect, the radiation decomposes the water into hydrogen and oxygen.

An approximate steady-state radical concentration can be estimated from the absorbed dose rate as described in Chapter 5, while competition kinetics can be applied to predict which of the competing radical reactions will predominate. Hydrated electrons, for example, are shown as reacting with water, hydrogen ion and hydrogen atoms, hydroxyl radicals, and other hydrated electrons. The relative importance of these five processes can be estimated from the values of k[reactant] for each reaction:

$$e_{aq}^- + H_2O : e_{aq}^- + H^+ : e_{aq}^- + H : e_{aq}^- + OH : e_{aq}^- + e_{aq}^-$$
$$= k_{52}[H_2O] : k_{56}[H^+] : k_{54}[H] : k_{55}[OH] : k_{53}[e_{aq}^-]$$

At pH 7 and dose rates of the order of 1 Gy s^{-1}, about 70% of the hydrated electrons react with H^+ and about 25% with water. Both reactions convert hydrated electrons to hydrogen atoms, which will react together and with hydroxyl radicals (Eqs. 7.46 and 7.45). The radicals may also react with hydrogen peroxide once it has reached a sufficient concentration. At lower pH, virtually all hydrated electrons are scavenged by hydrogen ion (Eq. 7.56), while in strongly basic solutions hydrated electrons react with water (Eq. 7.52) and, to a lesser extent with hydroxyl radicals (Eq. 7.55). The hydrated electron dosimeter

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[4] A bibliography covering studies on heavy particle radiolysis of liquids and aqueous solutions has been published by LaVerne et al. (51).
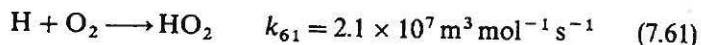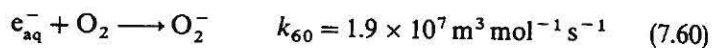
employs the latter conditions and consists of a strongly basic solution containing either hydrogen or ethanol to react with OH; the absorbed dose is estimated by measuring the strong optical absorption due to the hydrated electron and applying a correction for the disappearance of e_{aq}^- by reaction 7.53. The dosimeter containing hydrogen suffers no net change upon irradiation and can be reused, hydroxyl radicals being replaced by hydrogen atoms,
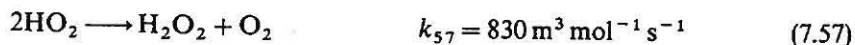
$$OH + H_2 \longrightarrow H_2O + H \qquad k_{13} = 4.2 \times 10^4 \, m^3 \, mol^{-1} \, s^{-1} \qquad (7.13)$$
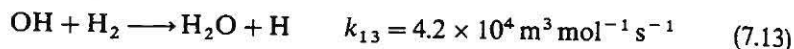
which reform molecular hydrogen (Eq. 7.46); "molecular" hydrogen peroxide presumably builds up to a small steady-state concentration limited by the back reactions 7.33 and 7.59.

Competition kinetics can also be applied to show that in air-saturated (about $0.25 \, mol \, m^{-3} \, O_2$) and oxygen-saturated (about $1.25 \, mol \, m^{-3} \, O_2$) water, virtually complete scavenging of hydrated electrons and hydrogen atoms by oxygen occurs at normal absorbed dose rates; the scavenging reactions are

$$e_{aq}^- + O_2 \longrightarrow O_2^- \qquad k_{60} = 1.9 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \qquad (7.60)$$

$$H + O_2 \longrightarrow HO_2 \qquad k_{61} = 2.1 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \qquad (7.61)$$

Both the superoxide ion (O_2^-) and its protonated form, the hydroperoxyl radical (HO_2), react together to give hydrogen peroxide and oxygen, or with OH to give oxygen alone:

$$O_2^- + HO_2 \longrightarrow H_2O_2 + O_2 + OH^- \qquad k_{62} = 9.7 \times 10^4 \, m^3 \, mol^{-1} \, s^{-1} \qquad (7.62)$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad k_{57} = 830 \, m^3 \, mol^{-1} \, s^{-1} \qquad (7.57)$$

$$O_2^- + OH \longrightarrow O_2 + OH^- \qquad k_{63} = 8 \times 10^6 \, m^3 \, mol^{-1} \, s^{-1} \qquad (7.63)$$

$$HO_2 + OH \longrightarrow O_2 + H_2O \qquad k_{64} = 6 \times 10^6 \, m^3 \, mol^{-1} \, s^{-1} \qquad (7.64)$$

In other than very basic solutions, the ion O_2^{2-} is protonated by water, which is stronger acid, giving hydrogen peroxide,

$$O_2^{2-} + 2H_2O \longrightarrow H_2O_2 + 2OH^- \qquad (7.65)$$

Hydrogen peroxide is the main radiolysis product from water in the presence of oxygen (52); $G(H_2O_2) = g(H_2O_2) + 0.5[g(e_{aq}^-) + g(H) - g(OH)]$.

Radical and Molecular Yields Radical and molecular yields in irradiated water are determined through the use of low concentrations of scavengers as described later in this chapter. Radical yields may also be determined by pulse radiolysis, though in practice this approach is limited to the hydrated electron since H and

OH show only weak absorption in the visible and ultraviolet regions of the spectrum. Picosecond pulse radiolysis has proved particularly valuable since it allows hydrated electron yields to be determined at an early stage of spur development. Scavenger experiments, on the other hand, measure the yields of radicals and molecular products that escape from the spurs. A selection of reported values determined using scavengers is given in Table 7.4; the values represent radiation-chemical yields about 10^{-7} s after the passage of an ionizing particle has deposited energy in the system, that is, after any reactions occurring within spurs and tracks are complete. The small quantities of perhydroxyl radical included in Table 7.4 are formed by a secondary reaction (Eq. 7.48) occurring in the spurs and particle tracks.

The radical products are e_{aq}^-, H, OH, and HO_2, and the molecular products are H_2 and H_2O_2. These are often subdivided into reducing radicals (e_{aq}^- and H) and oxidizing products (OH, HO_2, and H_2O_2) since the two groups tend to bring about reduction and oxidation of inorganic solutes, respectively; molecular hydrogen is relatively inert and normally plays little part in the subsequent reactions. Collectively, the radical and molecular products are sometimes referred to as primary radicals or products, though the term is relative since these "primary" species are derived from ionic and excited states formed at an earlier stage in the radiolysis.

To maintain a material balance, the radical and molecular yields must be related by

$$g(-H_2O) = 2g(H_2) + g(H) + g(e_{aq}^-) = 2g(H_2O_2) + g(OH) \qquad (7.66)$$

or, including HO_2, which is generally a minor product,

$$g(-H_2O) = 2g(H_2) + g(H) + g(e_{aq}^-) - g(HO_2)$$
$$= 2g(H_2O_2) + g(OH) + 2g(HO_2) \qquad (7.67)$$

In these equations $g(-H_2O)$ is the net yield of water molecules converted to primary products as determined by scavenger experiments. In liquid systems this is not necessarily the total number of water molecules broken down because some recombination may occur before the primary products escape from the spurs and tracks (in water vapor, where there are no comparable spurs or tracks, it is in principle possible to scavenge all radicals formed). To a first approximation, assuming that a collision between two radicals in the liquid phase has an equal probability of forming water as of forming H_2 or H_2O_2, the total yield of molecules dissociated is given by

$$g(-H_2O)_{total} = g(-H_2O) + g(H_2) + g(H_2O_2) \qquad (7.68)$$

For γ irradiation at a pH between 3 and 13, the values listed in Table 7.4 give $g(-H_2O)_{total}$ about $0.55\,\mu mol\,J^{-1}$ when $g(-H_2O)$ is $0.42\,\mu mol\,J^{-1}$. Picosecond

**TABLE 7.4 Radical and Molecular Product Yields (mol J^{-1}) in Irradiated Water and Water Vapor**

Radiation	pH	$g(-H_2O)$	$g(H_2)$	$g(H_2O_2)$	$g(e_{aq}^-)$	$g(H)$	$g(OH)$	$g(HO_2)$	Ref.
				Water Vapor					
Electron, γ radiation		0.85	0.05	0	$g(e^-) = 0.31$	0.75	0.85		See previous section
				Liquid Water					
γ and fast electron radiation	0.46[a]	0.461	0.041	0.081	0	0.378	0.301	0.0008[b]	3, 53
with 0.1–20-MeV energies	3–11	0.43	0.047	0.073	0.28	0.062	0.28	0.0027[c]	54
(D$_2$O solutions)[d]	1.3	0.448	0.033	0.068	$g(e_{aq}^- + D = 0.380)$		0.311		3
(D$_2$O solutions)[d]	4–13	0.427	0.037	0.068	0.307	0.045	0.294		3
^{3}H β particles (E_{av} 5.7 keV)	1	0.411	0.055	0.101	0	0.302	0.207		55
32 MeV He^{2+}	~7	0.312	0.099	0.104	0.075	0.044	0.094	0.005	56
12 MeV He^{2+}	~7	0.294	0.115	0.112	0.044	0.028	0.056	0.007	56
^{210}Po α particles (5.3 MeV)	0.46	0.375	0.163	0.150	0	0.062	0.052	0.011	57
^{10}B(n, α)^{7}Li recoil nuclei	0.46	0.368	0.171	0.161	0	0.026	0.047		58
Particle with infinitely high LET, extrapolated from results with accelerated ^{12}C and ^{14}N ions	0.46	~0.30	~0.15	~0.15	0	0	0		59

[a] 0.46 is the pH of 400 mol m^{-3} H$_2$SO$_4$.

[b] Ref. 60.

[c] Ref. 56.

[d] For D$_2$O, D should replace H where the latter appears in each of the column headings.

pulse radiolysis studies and theoretical calculations give comparable values for the number of water molecules initially dissociated.

Values reported in Table 7.4 are for concentrations of scavenger less than about $1 \, mol \, m^{-3}$ (more precisely, values of k[scavenger] less than about $10^7 \, s^{-1}$), room temperature, and moderate absorbed dose rates. Higher concentrations of scavenger (actually k [scavenger]) and higher temperatures give rather higher yields of the primary radicals and rather lower molecular product yields. Very high absorbed dose rates (above $10^7 \, Gy \, s^{-1}$) and high-LET radiation, on the other hand, give lower radical and higher molecular yields. The variations in radical and molecular yields are attributed to the effect of the changing conditions on the extent of radical scavenging and interradical reactions within spurs and particle tracks. Higher scavenger concentrations, for example, are visualized as scavenging radicals that at lower concentration react within the spurs and tracks to give molecular products or reform water (54). Interference with the latter reaction leads to somewhat higher $G(-H_2O)$ at high scavenger concentrations, illustrated in Table 7.4 by the effect of low pH upon the radiolysis yields. High LET favors reaction between radicals in the columnar particle tracks, and high dose rates similarly favor interradical reactions in the system as a whole. An increase in the proportion of interradical reaction increases the proportion of molecular products (H_2, H_2O_2, and H_2O) at the expense of the scavengeable radical products (e_{aq}^-, H, and OH). The rather higher radical and lower molecular yields observed at temperatures above ambient have been attributed to more rapid diffusion of radicals from the spurs at the higher temperatures.

Hydrogen and hydrogen peroxide, the molecular products, are believed to be formed largely by the interradical reactions shown above. Small amounts of hydrogen may be formed by dissociation of excited water molecules (Eq. 7.2) or the ion–molecule reaction

$$H^- + H_2O \longrightarrow OH^- + H_2 \tag{7.15}$$
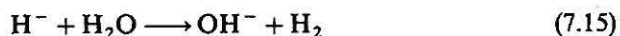
though the hydride ion becomes less abundant in the mass spectrometer as the water vapor pressure is increased. Hydrogen peroxide may be formed in part by oxygen atoms produced by dissociation of excited water (Eq. 7.2) or the ion–molecule reaction
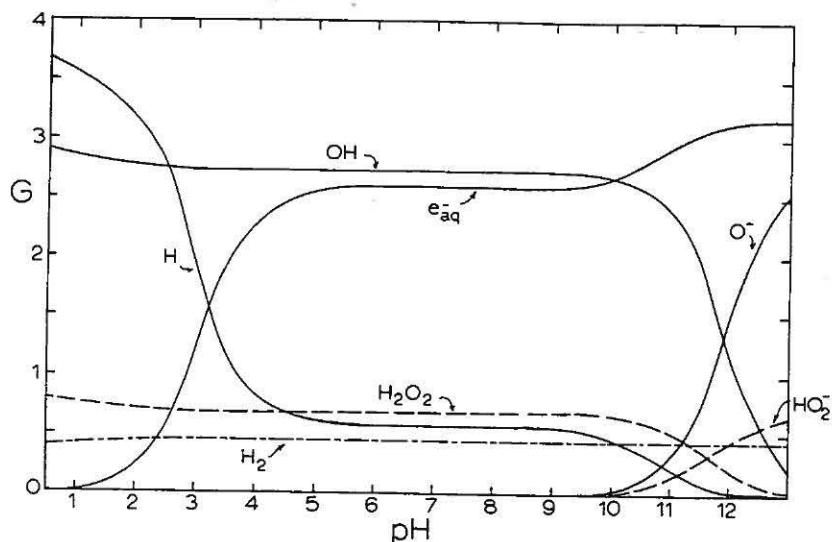
$$OH^+ + H_2O \longrightarrow H_3O^+ + O \tag{7.27}$$

followed by

$$O + H_2O \longrightarrow H_2O_2 \tag{7.10}$$
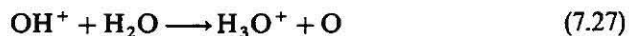
However, scavenging experiments with cyclopentene, which forms ethene and 2-propenal (acrolein) with oxygen atoms, have shown only small yields ($G = 8 \times 10^{-4}$ to $0.002 \, \mu mol \, J^{-1}$) of a species believed to be the oxygen atom in γ-irradiated water (61).

*Effect of pH*   Radiation-chemical yields of the primary products are pH

Figure 7.1 Effect of pH on the primary products of water irradiation. Yields are for γ or fast-electron radiation with energies of the order of 0.1 to 20 MeV, and assume that OH and H_2O_2 achieve acid-base equilibrium. The yields of H and e_{aq}^- are the amounts of these species that would react with $1\, mol\, m^{-3}$ scavenger (S) if $k(e_{aq}^- + S) = 2 \times 10^7\, m^3\, mol^{-1}\, s^{-1}$ and $k(H + S) = 10^4\, m^3\, mol^{-1}\, s^{-1}$.

dependent (Fig. 7.1). At low pH the hydrated electron is rapidly scavenged by hydrogen ion (Eq. 7.56) and converted to a hydrogen atom. Yields of "reducing" radical shown in Table 7.4 are therefore reported as H at pH below 1. High concentrations of hydrogen ion are able to scavenge hydrated electrons within spurs and tracks interfering to some extent with the back reactions forming water; consequently, overall radical and molecular product yields at low pH are rather higher than in neutral and basic solutions (Table 7.4).

The perhydroxyl radical, which is a minor product when pure water is irradiated but may be formed in relatively large amounts when air or oxygen is present, dissociates at pH above 4 to give the superoxide ion, O_2^-, which is also an oxidizing radical,
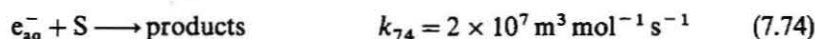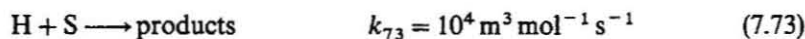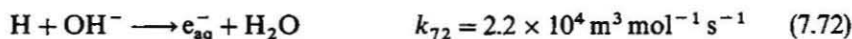
$$HO_2 \rightleftharpoons H^+ + O_2^- \qquad pK_a = 4.8 \qquad (7.69)$$
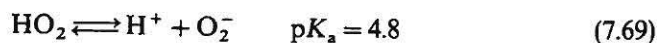
In basic solution (pH > 11) the hydroxyl radical and hydrogen peroxide dissociate to give the oxide ion and a peroxide ion, respectively,

$$OH \rightleftharpoons H^+ + O^- \qquad pK_a = 11.9 \qquad (7.70)$$

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad pK_a = 11.6 \qquad (7.71)$$
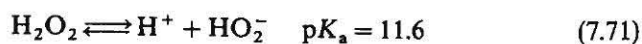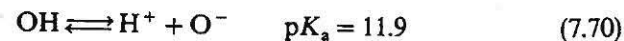
The effect of these acid–base equilibria on the primary yields from water is

illustrated in Fig. 7.1, which shows the nature and yields of the primary species that would be expected to react with a dilute ($1\,mol\,m^{-3}$)solution of scavenger at various pH in the range 0.5 to 13. In preparing the figure it was assumed that acid–base equilibria for OH and H_2O_2 would be established before reaction with the solute, but that the proportions of H and e_{aq}^- reacting with the solute would be governed by competition between the various possible reactions, that is, between reaction 7.56 and the following:

$$H + OH^- \longrightarrow e_{aq}^- + H_2O \qquad k_{72} = 2.2 \times 10^4\,m^3\,mol^{-1}\,s^{-1} \qquad (7.72)$$

$$H + S \longrightarrow products \qquad k_{73} = 10^4\,m^3\,mol^{-1}\,s^{-1} \qquad (7.73)$$

$$e_{aq}^- + S \longrightarrow products \qquad k_{74} = 2 \times 10^7\,m^3\,mol^{-1}\,s^{-1} \qquad (7.74)$$

The rate constants for reactions 7.73 and 7.74 are assumed values based on typical reactions of hydrogen atoms and hydrated electrons. This procedure was adopted because hydrated electron reactions often have extremely high rate constants, while hydroxyl radicals react more slowly (though still very rapidly), so that there is a greater possibility of establishing an acid–base equilibrium before reaction occurs with OH than with the hydrated electron. Figure 7.1 does not include the possibility that in strongly acid solution H will form H_2^+.

Track Structure and Related Phenomena   Water occupies a central position in radiation chemistry both as an example of a simple highly polar liquid and because of its related role as a solvent in chemical and biological systems. The wealth of theoretical and experimental information available makes water a useful model to illustrate the concepts of track structure and the sequence of events that follow energy deposition by a charged particle (see, for example, 62, 63).

Passage of a charged particle through a liquid results in the transfer of discrete "packets" of energy to molecules of the liquid. The packets are not all of equal size and it is convenient to divide them into arbitrary groups based on the amount of energy transferred. Following the suggestions of Burton (64) and Magee (62, 65) and their colleagues, the groups (Fig. 2.24) and the quantity of energy transferred per interaction are described as δ rays or branch tracks ($> 5000\,eV$), short tracks (500 to 5000 eV), blobs (100 to 500 eV), and spurs (6 to 100 eV). The spurs and blobs are pictured as more or less spherical collections of ground-state and excited molecules and ions, and the short tracks as columnar zones containing a high proportion of ionized and excited molecules along the track of a fast electron. In most cases the term spur is used to cover both spurs as defined above and the larger blobs.

In liquid water W is probably between 25 and 30 eV per ion pair, and spurs, blobs, and short tracks correspond to the formation of about 1–4, 2–20, and 20–200 ion pairs, respectively. Electrons become hydrated and the positive ions react to form radicals while within the volume of the track or spur. Interradical

reaction to give the "molecular" products listed in Table 7.4 follows and is most favored where the radical concentration is highest, that is, within blobs and short tracks rather than in spurs, provided the groups of radicals are separated from neighboring groups. In the case of low-LET radiation and δ rays, the groups of radicals are widely separated from one another along the track of the ionizing particle, and they behave independently. With high-LET radiation the groups will be formed closer together and may coalesce to give a cylindrical "track," densely populated with radicals, along the path of the parent particle. Interradical reaction will be particularly favored in the columnar track zones produced by high-LET radiation, but in all cases the spurs and tracks will eventually expand by diffusion and release any remaining radicals into the bulk of the medium, where their reaction with both radicals and solutes is governed by homogeneous reaction kinetics.

Mozumder and Magee (62, 65) have estimated the fraction of the total absorbed energy deposited in short tracks, blobs, and spurs for various types of radiation, finding for low-LET ^{60}Co γ radiation and moderately high-LET tritium β radiation, for example:

Energy Deposited in	^{60}Co γ Radiation	^{3}H β Radiation
Short tracks	25%	74.4%
Blobs	11%	7.6%
Spurs	64%	18.0%

The values illustrate a general tendency toward increased energy deposition in short tracks as the LET of the radiation is increased. Mozumder and Magee (65, 66) have also estimated the distribution of spur sizes for fast electrons and γ rays stopped in water, finding that 56% of the absorbed energy is deposited in spurs with one or two radical pairs, 20.6% in spurs with three to six radical pairs, and the remainder in aggregates with more than six radical pairs.

Radical and molecular yields reported in Table 7.4 were, with the exception of hydrogen ion, measured using relatively low concentrations of scavengers that would not be expected to interfere with reactions taking place within spurs or tracks.[5] Experiments with high concentrations of scavengers give higher primary yields because some of the radicals that normally combine within the spurs and tracks are scavenged. The higher yields are consistent with other evidence relating to early events in the radiolysis mechanism. Picosecond pulse radiolysis of aqueous systems, for example, gives hydrated electron yields of the order of 0.42 to 0.50 m^3 μmol J^{-1} at very short times (3×10^{-11} s) after the pulse (67–69), while an initial $g(e_{aq}^-)$ of 0.50 μmol J^{-1} has been estimated on the basis of diffusion kinetic calculations (70). Electron yields greater than the gas-phase yields of 0.35 μmol J^{-1} point to the existence of ionization processes in the liquid that are

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[5] At pH 0.46, some scavenging of hydrated electrons within the spurs and tracks is believed to occur and to be responsible for the rather higher radical and hydrogen peroxide yields observed at this pH.

absent, or are less effective, in water vapor. It is possible that some of the excited states that dissociate to radical products in the vapor give rise to ionization in liquid water,

$$H_2O^* \longrightarrow e_{aq}^- + OH + H_3O^+ \tag{7.75}$$
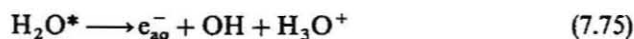
since Boyle and his colleagues (71) find that in liquid water the threshold energy for the formation of hydrated electrons by photoionization is about half the ionization energy (12.6 eV) in water vapor. However, no unequivocal evidence of a contribution by excited states to the radiation chemistry of water has been published, although there is speculation that excited states may sometimes contribute to the radiolysis of concentrated solutions (72, 30).

The quantum yield for the photochemical dissociation of pure water is low (e.g., 0.02 for H_2 using 184.9 nm light) but increases considerably in the presence of organic scavengers (reported quantum yields for H_2 include 0.33 at 184.9 nm, 0.7 at 147 nm, and 1.03 at 123.6 nm in the presence of organic solutes e.g., 5 mol m^{-3} methanol; refs. 73–75) due to

$$H_2O + h\nu \rightleftharpoons [H + OH] \xrightarrow{\text{organic solute}} H_2 + \text{other products} \tag{7.76}$$
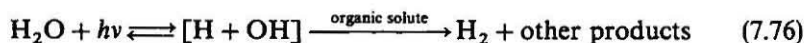
The radicals in brackets represents a geminate radical pair confined, briefly, in a cage of solvent molecules. While the low quantum yield with pure water is consistent with the radiolysis results, the higher quantum yields in the presence of organic scavenger are not, since they imply a much larger increase in radical yield with scavenger concentration than is normally observed in radiolysis experiments. The photochemical and radiolysis results would be compatible if the excited state that dissociates in the photochemical experiments normally returns to the ground state without dissociation under radiolysis conditions. This might occur if, for example, dissociation takes place from a triplet excited state whose lifetime is shortened by the presence of paramagnetic ions and radicals in the spurs and tracks.

The formation of H_3O^+ in reaction 7.20 renders the spur more acid than the surrounding medium. Evidence of this has been obtained by irradiating solutions of 1,1-diethoxyethane (diethylacetal) buffered to pH 7 and showing that hydrolysis occurs although it normally requires a pH much lower than 7 (76); the authors estimate that the pH within the spur must be about 1.4 to account for the observed hydrolysis:

$$CH_3CH(OC_2H_5)_2 + H_2O \xrightarrow{H^+} CH_3CHO + 2C_2H_5OH \tag{7.77}$$

A second experiment indicative of an acid spur is the obsevation of absorption attributed to Cl_2^- when concentrated ($> 10^3$ mol m^{-3}), neutral solutions of inorganic chloride are irradiated; the formation of Cl_2^- normally requires an acid

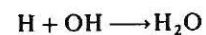**TABLE 7.5 Approximate Time Scale for the Radiolysis of Liquid Water**

	pt	Events	Reactions	Species Present
Physical stage (Interaction of the primary radiation with the water; energy transferred is in the form of electronic motion.)	18	Electron with energy in the megaelectron volt range transverses a distance of the order of a molecular diameter.		H_2O^+
	17	α-particle with energy in the megaelectron volt range transverses a molecule.		e^-
	16	Loss of energy by secondary electrons.	$H_2O \rightsquigarrow H_2O^+ + e^-$	$^1H_2O^*$
	15	Time between successive ionizations produced by a megaelectronvolt energy electron.	$H_2O \rightsquigarrow {}^1H_2O^*, {}^3H_2O^*$	$^3H_2O^*$
		Time for "vertical" excitation to an electronic excited state.		(Localized in spurs or tracks)
	14	Ion–molecule reactions.	$H_2O^+ + H_2O \longrightarrow$ $[H_3O^+ + OH]$ $g(OH) \sim 0.5\,\mu mol\,J^{-1}$	$[H_3O^+ + OH]$ In solvent cage
		Period of molecular vibration. Part of the electronic energy transformed into vibrational energy.		
		Dissociation of molecules excited to repulsive states.	$^1H_2O^* \longrightarrow [H + OH]$ $\longrightarrow [H_2 + O]$	$[H + OH]$ $[H_2 + O]$ In solvent cage
Physicochemical stage (Part of the transferred energy degraded to vibrational and rotational motion; energy transfer, dissociation, ion–molecule reactions	13	Secondary electrons reduced to thermal energy (about 0.025 eV).		
		Some electrons captured by positive ions; others become hydrated.	$H_3O^+ + e^- \longrightarrow H_2O + H$ $e^- \longrightarrow e_{aq}^-$	H e^-, e_{aq}^-
		Geminate recombination of trapped radicals. Internal conversion from higher to lowest electronically excited state.	$[H + OH] \longrightarrow H_2O$	
	12	Radical moves one molecular diameter by diffusion.	initial $G(e_{aq}^-) \sim 0.5\,\mu mol\,J^{-1}$	
		Spur temperature reaches a maximum estimated to be 50 °C above ambient for a spur of 3-nm radius and 50-eV excess energy (ref. 87).		

Chemical stage
(Radical–radical reactions in spur and track zones followed by diffusion of the radicals and molecular products into the bulk of the liquid. Reaction of solute with radicals and molecular products which are essentially homogeneously distributed in the liquid after about 10^{-7} s).

11 Relaxation time for the dipole orientation water; ions become solvated

$H_3O^+ \longrightarrow H^+(aq)$

H, OH, e_{aq}^-
H^+ (aq), $^3H_2O(?)$
In spurs and tracks

10 Minimum time for diffusion controlled reactions in the bulk of the liquid.
9 Temperature of expanded spur about 1 °C above ambient.
8 Radiative lifetime of singlet excited states. Formation of molecular products complete in γ-ray spur.
7 Formation of molecular products complete in α-particle track. Spur expansion complete.

$H + OH \longrightarrow H_2O$
$2H \longrightarrow H_2$
$2OH \longrightarrow H_2O_2$
$e_{aq}^- + OH \longrightarrow OH^-$ etc.
Formation water and molecular products in spurs and tracks

H, OH, e_{aq}^-,
H^+ (aq), H_2, H_2O_2
$^3H_2O^*(?)$
Diffusing from spurs and tracks
Yields as shown in Table 7.4

6 Reaction radicals with $10 \, mol \, m^{-3}$ solute essentially complete if $k(R\cdot + S) = 10^5 \, m^3 \, mol^{-1} \, s^{-1}$
4 Time for radical to diffuse the interspur distance in track of megaelectronvolt energy electron.
Reaction of radicals with $10 \, mol \, m^{-3}$ solute essentially complete if $k(R\cdot + S) = 10^3 \, m^3 \, mol^{-1} \, s^{-1}$

3 Approximate radiative lifetime of triplet excited state.
0 Chemical reaction complete.

H_2, H_2O_2, and products of radical reactions with solute

medium (77). An alternative explanation of the formation of Cl_2^- is that the high concentrations of chloride ion are scavenging H_2O^+ (sometimes described as a "positive hole") in the spurs,

$$H_2O^+ + Cl^- \longrightarrow H_2O + Cl \tag{7.78}$$

$$Cl + Cl^- \longrightarrow Cl_2^- \tag{7.79}$$
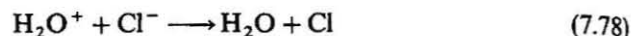
Adopting this approach, Hamill and his colleagues (78) estimated the yield of H_2O^+ to be $0.39 \, \mu mol \, J^{-1}$ based the experimental results of Anbar and Thomas (77, 118), and obtained similar results with high concentrations of other positive ion scavengers. The positive ion yields are comparable to the early hydrated electron yields detected by picosecond pulse radiolysis.

In some cases it is possible to follow the changes taking place in irradiated water and aqueous solutions directly. The hydrated electron, for example, absorbs light over a broad range of wavelengths centered at 715 nm and has been observed as early at 3×10^{-11} s after an electron pulse and 4×10^{-12} s after a light pulse by the techniques of picosecond pulse radiolysis and picosecond spectroscopy, respectively. The decay of the hydrated electron in irradiated solutions is readily followed at times greater than about 10^{-8} s by conventional pulse radiolysis. Although the absorption maximum of the hydroxyl radical is in the ultraviolet and is weaker than that of e_{aq}^-, the presence and decay of OH has been investigated by pulse radiolysis by utilizing high absorbed-dose rates. When the products of radical or scavenger reactions absorb light, these too may be studied directly using the same techniques, so that a large number of rate constants are available for reactions that occur in irradiated aqueous systems. Reaction rates and pathways are also often inferred from the effect produced by adding a scavenger for one or more of the primary radical intermediates. By combining data obtained in these and other ways, it is possible to draw up a time scale for the events that follow absorption of radiation energy, as in Table 7.5 (see also 62, 63, 79, 80). Times given in the table are those after passage of an ionizing particle through the system and are expressed using a logarithmic scale in which $pt = -\log t$, so that 10^{-16} s becomes pt 16 and 10^{-5} s becomes pt 5. The time scale refers specifically to liquid water but a very similar scale will apply to other liquids and to water vapor (40). The table is divided into three stages—physical, physicochemical, and chemical—as suggested by Platzman (81) and Kuppermann (60), corresponding with the initial dissipation of energy in the system, the establishment of thermal equilibrium, and the establishment of chemical equilibrium, respectively. The distribution of reactive species is heterogeneous during the physical and physicochemical stages (they are concentrated in spurs, blobs, etc.), but radicals that have not yet reacted, and molecular products, become homogeneously distributed throughout the system as the chemical stage progresses.

The events taking place following the deposition of energy in water by an ionizing particle can be modeled by computer programs that take into account

such data as electron hydration pathways, diffusion, and the rate constants of the reactions taking place. Variables that can be entered into the program might be the absorbed dose rate, the LET or energy of the ionizing particles, and solute concentrations. Some published examples cover the very early events from various viewpoints (e.g., 82–85), others the chemical reactions that accompany and follow spur expansion (86, 87), while others combine both regions (88). Programs frequently use the Monte Carlo method in which results of a large number of calculations, each following the history of one molecule whose actions are randomly synthesized according to pre-established probabilities, are combined to model the behavior of a large group of molecules over the selected time span.

AQUEOUS SOLUTIONS

In this section the properties and reactions of the primary radical and molecular products formed in water upon irradiation are described, together with a rather arbitrary selection of inorganic and organic systems that illustrate the main features of the radiolysis of aqueous solutions. Very often the radiolysis products will themselves react with the primary radicals, particularly if irradiation is prolonged, but this experimental complication has largely been ignored. Radiation-chemical yields are generally given in this chapter for low-LET radiation such as ^{60}Co γ radiation or fast electrons. The same chemical products are formed by higher-LET radiation, but generally with some change in yield due to the effect of LET upon the radical and molecular product yields from water.

When dilute aqueous solutions are irradiated practically all the energy absorbed is deposited in water molecules and the observed chemical changes are brought about *indirectly* by the molecular and, particularly, the radical products of water radiolysis. *Direct* action due to energy deposited directly in the solute is generally not important in dilute solutions (i.e., at solute concentrations below about $100\,mol\,m^{-3}$). At higher solute concentrations direct action may be significant, and there is evidence that high concentrations of solutes may react directly with the initial products of energy deposition, the unsolvated (or dry) electron and H_2O^+ (or positive hole); reaction with excited water molecules may also be possible, but is less well substantiated.

Estimates of steady-state concentrations of primary radicals produced by continuous irradiation (Chapter 5) show that these will be low except at very high absorbed dose rates, and that reactions between the primary radicals and solutes will almost always predominate over interradical reactions provided the radical–solute reactions are thermodynamically allowed. Consequently interradical reactions in dilute solutions are generally between pairs of relatively unreactive radicals, often organic radicals or peroxy radicals such as HO_2.

The chemical changes produced reflect the nature of the solute. The examples given include ferrous ion, a readily oxidized ion, and ceric ion, which is strongly oxidizing. With these solutes the effects observed are oxidation and reduction,

respectively. A variety of systems containing organic solutes are described in Chapter 8. Radiolysis of the aqueous organic systems generates organic radicals, generally by reaction at a specific site in the molecule. The organic radicals react to give stable products by addition and disproportionation reactions or, in the presence of oxygen, oxidation products formed through peroxy radicals.

The Reducing Radicals (e_{aq}^- and H)

Until about 1960, the reducing species in irradiated water was assumed to be the hydrogen atom produced by the dissociation of excited water molecules formed directly or by ion recombination. However, evidence was accumulating that rate constants for reactions of the reducing species varied with the pH of the system, and that the reducing spcies formed in neutral solutions reacted at a different rate to hydrogen atoms formed by

$$OH + H_2 \longrightarrow H_2O + H \qquad (7.13)$$

or produced externally in a discharge and introduced into the solution (89–92).

Studies of relative reaction rates measured in the presence of chemically inert salts showed that the reducing species in neutral solutions behaved as though it had a unit negative charge. The method depends on the fact that rate constants for reactions between ions of similar charge increase with increasing ionic strength, while rate constants for reactions between ions of opposite charge decrease, and there is relatively little effect if one of the reactants is uncharged. Czapski and Schwarz (93) studied the effect of ionic strength upon the following rate constant ratios for the reducing species R: $k(R + O_2)/k(R + H_2O_2)$, $k(R + H^+)/k(R + H_2O_2)$, and $k(R + NO_2^-)/k(R + H_2O_2)$. They found that the first ratio was unaffected, the second decreased, and the third increased by increasing the ionic strength, which is consistent with R being a negatively charged species. Further analysis of the results showed the charge to be a single negative charge. Collinson and Dainton and their colleagues (94) studied the effect of ionic strength on the reactions of the reducing species with Ag^+ and propenamide (acrylamide), concluding that at pH 4 the species had a unit negative charge but that at pH 2 it was uncharged. Similar experiments intended to establish the charge, if any, on the oxidizing radical produced by irradiation of water showed this to be uncharged (95), supporting the view that the oxidizing species is the OH radical.

The nature of the reducing species was resolved by Hart and Boag (96) who irradiated deaerated water using a high-intensity electron pulse and observed a broad transient absorption band at about 700 nm which was similar to the known absorption of the solvated electron in liquid ammonia. The intensity of the transient absorption was reduced by low concentrations of electron scavengers such as oxygen, carbon dioxide, and nitrous oxide, and was weak, if present at all, in acid solutions. The conclusion drawn from these and many other experiments was that the major reducing species in neutral and basic solutions is
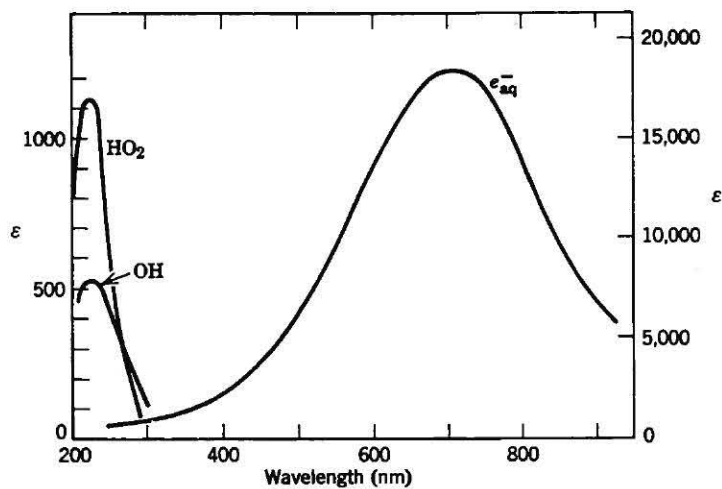
Figure 7.2 Absorption spectra of e_{aq}^- (ref. 103), OH(ref. 105), and HO_2 (ref. 106). The vertical axes give the extinction coefficient ($L\,mol^{-1}\,cm^{-1}$); the left scale refers to OH and HO_2 and the right to e_{aq}^-.

the hydrated electron and that in acid solutions this is rapidly converted to the hydrogen atom. Further work has fully confirmed these conclusions, and at the present time the hydrated electron is probably the most extensively studied of any radical species (see, for example, 97–103).

Molecular hydrogen, though a reducing species and a product of water radiolysis, plays a minor role in the radiolysis of aqueous solutions and is not included in this discussion of the reducing intermediates. Reasons for the limited role of molecular hydrogen are its low solubility in water, so that most of it escapes from solution, and the high H—H bond dissociation energy, which leads to rather low rate constants for the reactions of H_2. The reaction of most direct interest.

$$OH + H_2 \longrightarrow H_2O + H \qquad k_{13} = 4.2 \times 10^4 \, m^3 \, mol^{-1} \, s^{-1} \qquad (7.13)$$
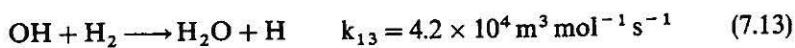
cannot normally compete with other hydroxyl radical reactions unless the pressure of hydrogen is increased above atmospheric (a solution saturated with H_2 at atmospheric pressure contains about $0.8 \, mol \, m^{-3} \, H_2$). However, this reaction is significant if pure water is irradiated in a closed system since it contributes to the back reactions keeping the net decomposition low, or if aqueous systems are irradiated under high pressures of hydrogen (104).

Hydrated Electron   The absorption spectrum of the hydrated electron is shown in Fig. 7.2 and some of its properties are listed in Table 7.6 (cf. 107). For many purposes it is sufficient to regard the hydrated electron as an electron trapped by a small group of water molecules that have become orientated as a consequence of

TABLE 7.6 Properties of the Hydrated Electron[a]

Radius of charge distribution	0.25 to 0.3 nm
Diffusion constant	$4.90 \times 10^{-9} m^2 s^{-1}$
Absorption maximum	
Wavelength	715 nm
Energy equivalent	1.73 eV ($167 kJ mol^{-1}$)
Extinction coefficient	$1.85 \times 10^3 m^2 mol^{-1}$
Enthalpy of hydration (ΔH)	$-159 kJ mol^{-1}$
Entropy of hydration (ΔS)	$-8.0 J mol^{-1}$
$E^0 (e_{aq}^- + H^+ \longrightarrow \frac{1}{2}H_2)$	2.9 V
Half-life	
In neutral water (pH 7.0)	$2.1 \times 10^{-4} s$
In basic solution[b]	$6.6 \times 10^{-4} s$

[a] Data are for 25 °C and are from tables prepared by Thomas (101) and Hart and Anbar (103).
[b] Assuming that all hydrated electrons react with water (Eq. 7.52).

the electron's presence, though more detailed models are available (103, 108–110). Orientation of the water molecules that constitute the trap takes about 10^{-12} s once a free thermal (or "dry") electron is introduced into the system. Hydrated electrons are believed to be formed as transient intermediates when alkali metals dissolve in water (99, 111) and at the cathode when dilute aqueous solutions of salts are electrolyzed (99). They are also produced by the photolysis of a variety of inorganic ions and organic compounds in polar solvents such as water (99, 100, 112–114), for example,

$$I^-(aq) + h\nu \rightleftharpoons [I + e_{aq}^-] \tag{7.80}$$
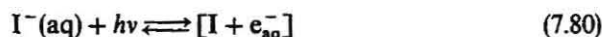
The products are formed within a solvent cage and normally recombine, but may be scavenged by electron or radical scavengers; the quantum yield for reaction 7.80 in the presence of a scavenger is 0.29 at 25 °C with 253.7-nm light (112).

The standard redox potential (E^0) provides a measure of the strength of the hydrated electron as a reducing agent and is derived using the following cycle (115):

$$e_{aq}^- + H_2O \longrightarrow H(aq) + OH^-(aq) \quad \Delta G^0 = +35.2 kJ mol^{-1} \tag{7.81}$$

$$H(aq) \longrightarrow H(g) \quad \Delta G^0 = -19.3 kJ mol^{-1} \tag{7.82}$$

$$H(g) \longrightarrow \frac{1}{2}H_2(g) \quad \Delta G^0 = -203 kJ mol^{-1} \tag{7.83}$$

$$H_3O^+(aq) + OH^-(aq) \longrightarrow H_2O \quad \Delta G^0 = -89.1 kJ mol^{-1} \tag{7.84}$$

$$e_{aq}^- + H_3O^+(aq) \longrightarrow \frac{1}{2}H_2(g) \quad \Delta G^0 = -276 kJ mol^{-1} \tag{7.85}$$
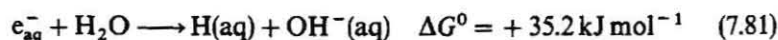
For reaction 7.81, ΔG^0 is calculated from the equilibrium constant by substituting in $\Delta G^0 = -RT \ln K$ and taking $K = k_{forward}/k_{back} = 0.016/(2.3 \times 10^4)$, while

ΔG^0 for reaction 7.82 is assumed to be the same as the free energy of hydration of the helium atom, that is, $-19.3\,kJ\,mol^{-1}$; the remaining free energies are established values (116). The quantity E^0 for reaction 7.85 is found by substituting in $\Delta G^0 = -nFE^0$ where the number of moles of electrons (n) transferred between the species is one and F is the Faraday ($96.49\,kJ\,equiv^{-1}\,V^{-1}$), giving $E^0 = 2.86\,V$. This is also the standard redox potential for the half-reaction

$$e_{aq}^- \rightleftharpoons nH_2O + e^- \tag{7.86}$$

since E^0 for the second half-reaction making up reaction 7.85,

$$H_3O^+ + e^- \rightleftharpoons \tfrac{1}{2}H_2(g) \tag{7.87}$$
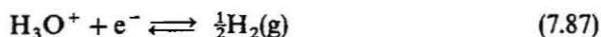
is, by definition, zero. The corresponding value for the hydrogen atom $(E^0 = 2.31\,V)$ is found by adding Eqs. 7.82 and 7.83.

Rate constants for typical reactions of the hydrated electron are collected in Table A3.5 (Appendix 3; see also ref. 107) and compared with the corresponding reactions of the hydrogen atom . To facilitate comparison of the rate constants shown in this and the succeeding tables in Appendix 3, rate constants are given in units of $10^4\,m^3\,mol^{-1}\,s^{-1}$, that is, the actual values are divided by 10^4 to give numbers that can be compared more easily. Many of the hydrated electron reactions listed have low activation energies (between 10 and $20\,kJ\,mol^{-1}$ (107)) so that most, if not all, of the collisions between the reactants lead to reaction, and the rate of reaction is governed by the rate at which the reactants diffuse together; such "diffusion-controlled" reactions have rate constants of the order of $10^7\,m^3\,mol^{-1}\,s^{-1}$ (i.e., ~ 1000 on the scale used in the tables). The expected rate of a diffusion-controlled reaction can be calculated (117) using

$$k_{AB} = \frac{4\pi r_{AB} D_{AB} N_A}{1000} \left[\frac{Z_A Z_B e^2 / r_{AB} \varepsilon kT}{\exp(Z_A Z_B e^2 / r_{AB} \varepsilon kT) - 1} \right] \tag{7.88}$$

where r_{AB} (m) is the sum of the radii of the reacting species A and B, $D_{AB}\,(m^2\,s^{-1})$ is the sum of their diffusion coefficients, N_A is the Avogadro constant, Z_A and Z_B are the charge on A and B respectively, e(esu) is the charge on the electron, k (erg molecule$^{-1}\,K^{-1}$) is the Boltzman constant, and ε is the dielectric constant of the solution. If either A or B is uncharged, the expression reduces to

$$k_{AB} = \frac{4\pi r_{AB} D_{AB} N_A}{1000}\,m^3\,mol^{-1}\,s^{-1} \tag{7.89}$$

which is the encounter rate of A and B; the additional terms in Eq. 7.88 allow for electrostatic forces if both A and B are charged. Some hydrated electron reactions are faster than calculated for diffusion-controlled processes and it has been suggested that in these instances the electron migrates by a tunneling mechanism, moving from trap to solute without displacing the intervening molecules (103).

Tunneling can also explain the mobility of the hydrated electron, which is much higher than expected for a singly charged ion with a radius of 0.3 nm.

Hydrated electron reactions are single-electron transfer processes represented by

$$e_{aq}^- + S^n \longrightarrow S^{n-1} \tag{7.90}$$

where n is the charge $(+, 0, \text{ or } -)$ on the solute. Thus, cations possessing an oxidation potential (Table A3.4) less than that of the hydrated electron are reduced; for example,

$$e_{aq}^- + Cu^{2+} \longrightarrow Cu^+ \tag{7.91}$$

The hydronium ion, H_3O^+, represents an especially important scavenger for hydrated electrons which, in acid solutions, are converted to hydrogen atoms,

$$e_{aq}^- + H_3O^+ \longrightarrow H + H_2O \qquad k_{56} = 2.3 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.56}$$
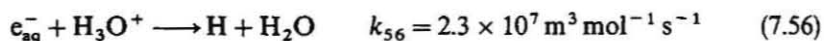
The intermediate in this reaction, H_3O, is usually assumed to have too short a lifetime to react directly with solutes, but is sometimes postulated as an independent species (e.g., 118, 119). Other proton donors can convert hydrated electrons to hydrogen atoms in neutral solution; for example, Ye and Schuler (120) have suggested the use of $10^3 \, mol \, m^{-3} \, H_2PO_4^-$ for this purpose in pulse radiolysis studies in the pH region from 5 to 7.

Reaction of the hydrated electron with water itself,

$$e_{aq}^- + H_2O \longrightarrow H + OH^- \qquad k_{52} = 0.019 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.52}$$
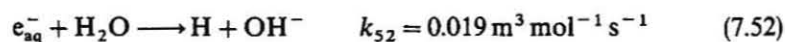
sets an upper limit to the lifetime of the hydrated electron in water, the half-life being given by $r_{1/2} = 0.693/(k_{52}[H_2O]) = 6.6 \times 10^{-4} \, s$, since the reaction is pseudo-first order. The rate constant for reaction 7.52 was determined by following the decay of the hydrated electron absorption by pulse radiolysis of slightly basic solutions (pH 8.3 to 9) containing exceptionally low concentrations ($< 5 \times 10^{-6} \, mol \, m^{-3}$) of impurities (121). The solutions were given low absorbed doses of 0.01 to 0.02 Gy to produce concentrations of e_{aq}^- of about $5 \times 10^{-6} \, mol \, m^{-3}$. Under these conditions, reaction 7.52 is the only reaction of e_{aq}^- that need be considered. In neutral solutions the low concentration of hydrogen ions present is sufficient to scavenge a significant fraction of the hydrated electrons, the half-life of e_{aq}^- being reduced to $2.1 \times 10^{-4} \, s$ at pH 7.

Negative ions formed by reaction of the hydrated electron with neutral species are Bronsted–Lowry bases and generally dissociate, giving a stable negative ion, or react with water with the formation of a radical and OH^-. Examples of the former are
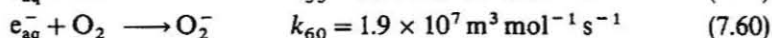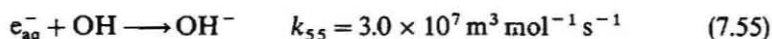
$$e_{aq}^- + H_2O_2 \longrightarrow OH^- + OH \tag{7.59}$$

$$e_{aq}^- + H_2S \longrightarrow HS^- + H \tag{7.92}$$

$$\longrightarrow S^- + H_2 \tag{7.93}$$

and examples of the latter are

$$e_{aq}^- + N_2O \longrightarrow N_2O^- \xrightarrow{H_2O} N_2 + OH^- + OH \tag{7.94}$$

$$e_{aq}^- + CO \longrightarrow CO^- \xrightarrow{H_2O} OH^- + H\dot{C}O \tag{7.95}$$
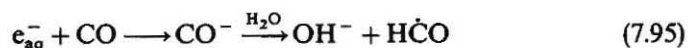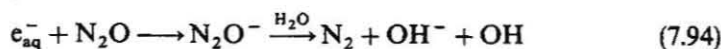
Inorganic radicals generally react at diffusion-controlled rates and yield stable negative ions, for example,

$$e_{aq}^- + OH \longrightarrow OH^- \qquad k_{55} = 3.0 \times 10^7\, m^3\, mol^{-1}\, s^{-1} \tag{7.55}$$
$$e_{aq}^- + O_2 \longrightarrow O_2^- \qquad k_{60} = 1.9 \times 10^7\, m^3\, mol^{-1}\, s^{-1} \tag{7.60}$$

though organic radicals are rather less reactive.

Reactions of the hydrated electron with organic compounds have been reviewed by Anbar and Hart (102, 103) and by Neta and Harriman (122) and have been shown to be those expected of a nucleophilic reagent. Attack on alkene double bonds, for example, is enhanced by adjacent electron-withdrawing substituents (cf. Table A3.5). Neighboring substituents also affect the reactivity of other multiple bonds ($C\equiv C$, $C=O$, $N=O$) in aliphatic compounds toward the hydrated electron. Singly bonded compounds containing only C, H, O, N, or F are unreactive (solvated electrons have relatively long lifetimes in liquid alcohols and amines), but compounds containing halogen (other than fluorine), disulfide ($-S-S-$), or thiol ($-SH$, but not $-S^-$) groups react rapidly. Aliphatic halogen compounds (RX where X = Cl, Br, or I) are quantitatively dehalogenated by reaction with e_{aq}^-,

$$e_{aq}^- + RX \longrightarrow RX^- \longrightarrow R + X \tag{7.96}$$
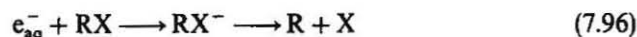
the rate of reaction increasing in the series Cl < Br < I. Nitro compounds are also highly reactive and the rates of reaction with the polychloro- and polynitrometh-anes appear to be higher than calculated, assuming the reaction to be diffusion controlled, suggesting that a tunneling mechanism may be operating. Among the aromatic compounds, benzene, phenol, and aniline react relatively slowly with hydrated electrons but benzoic acid and the halogen and nitro-substituted benzenes react at rates that are, or are close to, diffusion controlled.

The extinction coefficient of the hydrated electron was established using the reaction with tetranitromethane,

$$e_{aq}^- + C(NO_2)_4 \longrightarrow C(NO_2)_3^- + NO_2 \tag{7.97}$$
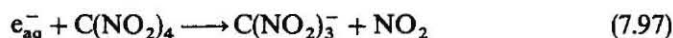
to give a stable anion (nitroform) whose extinction coefficient was known. The experiment involved simultaneous observation of the decrease in the hydrated electron absorption at 578 nm and the increase in the anion absorption at 366 nm, where the anion has a molar extinction coefficient of $1020 \, m^2 \, mol^{-1}$, and led to a value of $\varepsilon_{578} = 1060 \, m^2 \, mol^{-1}$ for the hydrated electron (123); the extinction coefficients at other wavelengths were calculated knowing the absorption spectrum of e_{aq}^-.

Hydrogen Atom   The properties and reactions of the hydrogen atom have not been documented as extensively as those of the hydrated electron, primarily because the hydrogen atom does not absorb in a readily accessible region of the spectrum (in the gas phase, ground-state hydrogen atoms do not absorb at wavelengths longer than 122 nm). However, a substantial number of rate constants for hydrogen atom reactions have been determined indirectly by pulse radiolysis and competition experiments (Table A3.5) and the behaviour of hydrogen atoms in aqueous systems is well understood. Hydrogen atoms can also be produced by passing hydrogen through an electrodeless high-frequency electric discharge, and this method has been used to study hydrogen atom reactions in several systems of interest to radiation chemists (e.g., 89–92).

The hydrogen atom ($E^0 = 2.3$ V) is a slightly less powerful reducing agent than the hydrated electron ($E^0 = 2.9$ V), but reduces cations with an oxidation potential lower than its own in a similar manner to the latter, for example,

$$H + Cu^{2+} \longrightarrow H^+ + Cu^+ \tag{7.98}$$
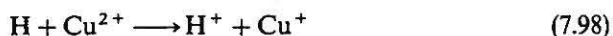
With saturated organic compounds, hydrogen atoms usually abstract hydrogen to give molecular hydrogen and an organic radical,

$$H + CH_3OH \longrightarrow H_2 + \cdot CH_2OH \tag{7.99}$$
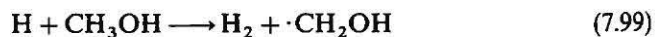
while addition reactions occur with unsaturated and aromatic compounds,

$$H + CH_3C \equiv N \longrightarrow CH_3CH = \dot{N} \quad (\text{or } CH_3\dot{C} = NH) \tag{7.100}$$

$$H + C_6H_6 \longrightarrow \cdot C_6H_7 \tag{7.101}$$
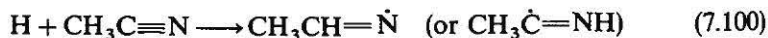
and, at or near diffusion-controlled rates, with species having unpaired electrons,

$$H + OH \longrightarrow H_2O \qquad k_{45} = 7.0 \times 10^6 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.45}$$

$$H + O_2 \longrightarrow HO_2 \qquad k_{61} = 2.1 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.61}$$
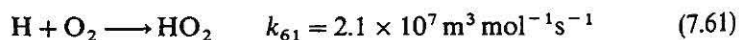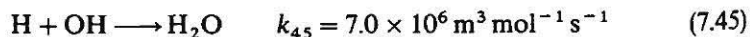
In strongly basic solutions (pH > 10) the hydrogen atom may react with OH^- to form a hydrated electron,

$$H + OH^- \longrightarrow e_{aq}^- + H_2O \qquad k_{72} = 2.2 \times 10^4 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.72}$$
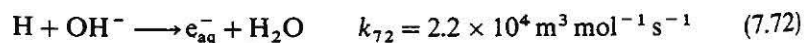
The reaction has a fairly high rate constant and will often compete with hydrogen atom–solute reactions. Reaction of hydrogen atoms with hydrogen ion can occur in strongly acid solutions to give H_2^+,

$$H + H^+ \longrightarrow H_2^+ \qquad k_{101} = 2.6 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.102}$$
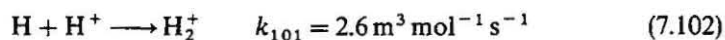
though the reaction has a relatively low rate constant and is usually not significant.

Hydrogen atoms and hydrated electrons differ in their reaction with many organic compounds, the hydrogen atom generally abstracting hydrogen to give molecular hydrogen, as in reaction 7.99, while the hydrated electron reacts to give other products. Advantage can be taken of this difference between the two reducing radicals to measure $g(H)$ at neutral pH by irradiating solutions containing both an electron scavenger (e.g., acetone, ferricyanide, or bicarbonate) and an organic compound that gives H_2 with H atoms (e.g., formate ion, methanol, and 2-propanol), when $G(H_2) = g(H_2) + g(H)$.

The Oxidizing Species (OH, HO$_2$, and Their Anions; H$_2$O$_2$)

The hydroxyl radical, OH, is the main oxidizing radical formed when aqueous solutions are irradiated. With high-LET radiation, considerable interradical reaction occurs in the particle track, producing H_2O, H_2, and H_2O_2, and reaction of OH with the latter creates a small yield of perhydroxyl radicals, HO_2, before the track disperses:

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \qquad k_{48} = 2.7 \times 10^4 \, m^3 \, mol^{-1} \, s^{-1} \quad (7.48)$$
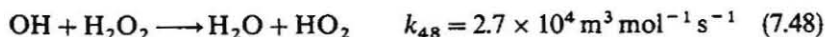
Larger yields of HO_2 are formed in aerated solutions by reaction of e_{aq}^- and H with oxygen

$$e_{aq}^- + O_2 \longrightarrow O_2^- \qquad k_{60} = 1.9 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.60}$$

$$H + O_2 \longrightarrow HO_2 \qquad k_{61} = 2.1 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.61}$$
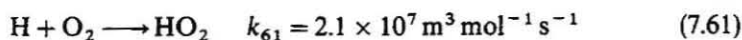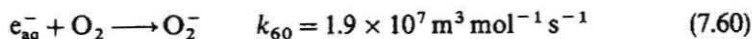
Both the hydroxyl and the perhydroxyl radical are weak acids and in solution enter into an equilibrium with their anions, O^- (the oxide ion) and O_2^- (the superoxide or perhydroxide ion), the relative proportions of acid and anion at equilibrium depending upon the pH of the solution. Properties of the hydroxyl and perhydroxyl radicals are outlined in Table 7.7 (see also, 106, 124–126).
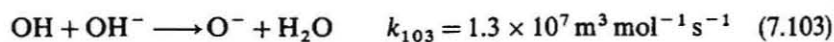
The Hydroxyl Radical   The pK_a of the hydroxyl radical is rather high and the undissociated, acid form predominates at pH up to about 12 (Fig. 7.1). The radical is also reactive so that reaction with a solute may precede establishment of the acid–base equilibrium and, in many cases, it is more convenient to regard hydroxyl ions and solute as competing for hydroxyl radicals in strongly basic

TABLE 7.7   Properties of the Hydroxyl and Perhydroxyl Radicals

Hydroxyl Radical[a]	
Diffusion constant	$2.3 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$
Absorption maximum	
OH	$230\,\mathrm{nm},\ \varepsilon_{230} = 53\,\mathrm{m^2\,mol^{-1}}$
	$\varepsilon_{260} = 37\,\mathrm{m^2\,mol^{-1}}$
O^-	$240\,\mathrm{nm},\ \varepsilon_{240} = 24\,\mathrm{m^2\,mol^{-1}}$
Enthalpy of hydration (ΔH)	$-370\,\mathrm{kJ\,mol^{-1}}$
$E^0\ (OH + H^+ + e^- \rightleftharpoons H_2O)$	2.7 V (acid solution)
$E^0\ (OH + e^- \rightleftharpoons OH^-)$	1.8 V (basic solution)
$pK_a\ (OH \rightleftharpoons O^- + H^+)$	11.9 ± 0.2

Perhydroxyl Radical[b]	
Diffusion constant, O_2^-	$1.5 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$
Absorption maximum	
HO_2	$225\,\mathrm{nm},\ \varepsilon_{225} = 140 \pm 8\,\mathrm{m^2\,mol^{-1}}$
O_2^-	$245\,\mathrm{nm},\ \varepsilon_{245} = 235 \pm 12\,\mathrm{m^2\,mol^{-1}}$
Enthalpy of formation, ΔH_f^0	
HO_2	$138 \pm 4\,\mathrm{kJ\,mol^{-1}}$
O_2^-	$80\,\mathrm{kJ\,mol^{-1}}$
Enthalpy of hydration, O_2^-	$395\,\mathrm{kJ\,mol^{-1}}$
$E^0\ (O_2 + e^- \rightleftharpoons O_2^-)$, pH 7	-0.33 V
$pK_a\ (HO_2 \rightleftharpoons O_2^- + H^+)$	4.8 ± 0.1
$pK_a\ (H_2O_2^+ \rightleftharpoons HO_2 + H^+)$	1.0 to 1.2

[a]Ref. 125.
[b]Refs. 106, 124, 126.

solution than to treat the OH as a weak acid; the hydroxyl ion–hydroxyl radical reaction is

$$OH + OH^- \longrightarrow O^- + H_2O \qquad k_{103} = 1.3 \times 10^7\,\mathrm{m^3\,mol^{-1}\,s^{-1}} \qquad (7.103)$$

Rate constants for hydroxyl radical reactions are given in Table A3.6 (see also 107). The hydroxyl radical has a rather weak absorption and the rate constants are normally measured by pulse radiolysis by following the formation of a product if this has a sufficiently high extinction coefficient, or by a competition method; the latter technique is described briefly in Chapter 5.

With inorganic solutes the hydroxyl radical generally behaves as an oxidizing agent in keeping with its high oxidation potential, giving the hydroxyl ion by a reaction that is more complex (and slower) than simple electron transfer,
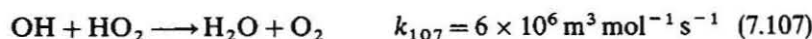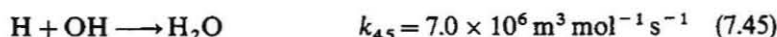
$$OH + S^n \longrightarrow OH^- + S^{n+1} \qquad (7.104)$$
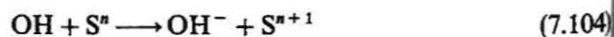
The solute may be an ion (either positive or negative) or a neutral species, for

example,

$$OH + Fe^{2+} \longrightarrow OH^- + Fe^{3+} \tag{7.105}$$

$$OH + CO_3^{2-} \longrightarrow OH^- + CO_3^- \tag{7.106}$$
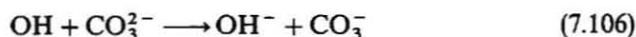
Rapid addition reactions occur with radicals (but not with oxygen unless the OH is ionized to the oxide ion), for example,

$$H + OH \longrightarrow H_2O \qquad k_{45} = 7.0 \times 10^6\, m^3\, mol^{-1}\, s^{-1} \quad (7.45)$$

$$OH + HO_2 \longrightarrow H_2O + O_2 \qquad k_{107} = 6 \times 10^6\, m^3\, mol^{-1}\, s^{-1} \quad (7.107)$$

Hydrogen tri- or sesquioxide, H_2O_3, is an intermediate in some (but not all) OH–HO$_2$ collisions and has a significant, pH-dependent half-life of the order of seconds at pH 1 (106, 124).

Organic compounds containing aromatic systems or carbon–carbon multiple bonds undergo addition reactions with OH in a similar manner to the addition of H to these compounds, for example,

$$OH + CH_2{=}CH_2 \longrightarrow HOCH_2CH_2{\cdot} \tag{7.108}$$

$$OH + C_6H_6 \longrightarrow {\cdot}C_6H_6OH \tag{7.109}$$

while hydrogen abstraction is the usual reaction with saturated organic compounds, including those containing carbonyl groups,

$$OH + CH_3COCH_3 \longrightarrow H_2O + {\cdot}CH_2COCH_3 \tag{7.110}$$
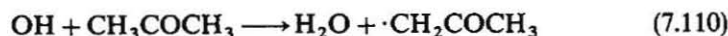
Weaker C–H bonds are attacked in preference to stronger bonds; for example, with 2-propanol 95% of the reaction occurs at the secondary (α) carbon atom,

$$OH + CH_3CH(OH)CH_3 \longrightarrow H_2O + CH_3\dot{C}(OH)CH_3 \tag{7.111}$$
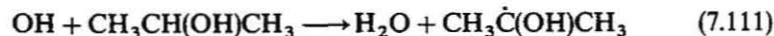
compared with only 37% from the α-carbon (C-1) of 1-butanol, where the C–H bonds are more nearly equal in bond dissociation energy. However, OH is less selective than H in abstraction reactions because formation of the H–OH bond is $57\,kJ\,mol^{-1}$ more exothermic than formation of the H–H bond. Inductive effects influence the site and rate of hydroxyl radical attack since the radical is a strongly electrophilic reagent, reacting preferentially at sites of high electron density. This is illustrated by the higher rate of reaction with carboxylate anions than with the undissociated acids, and the increase in rate of reaction in the series of alcohols methanol, ethanol, 1-propanol, and 1-butanol as larger alkyl groups replace one of the methyl hydrogen atoms in CH_3OH (Table A3.6).

Relatively few rate constants are available for the oxide ion, O^-, which must

be studied in strongly basic solution because of the high pK of the hydroxyl radical. Rate constants that have been measured show that O^- is a little less active in hydrogen abstraction reactions and very much less active in addition to unsaturated and aromatic compounds than OH; O^- is a nucleophile, whereas OH is an electrophile. The oxide ion is also less effective than OH in oxidizing inorganic anions (E^0 is lower in basic solutions, Table A3.4), but reacts readily with oxygen to form the ozonide ion, O_3^-, whereas OH is unreactive toward oxygen:

$$O^- + O_2 \rightleftharpoons O_3^- \tag{7.112}$$

Hydroxyl radicals can be produced without the use of ionizing radiation by the photolysis of hydrogen peroxide,

$$H_2O_2 + h\nu \longrightarrow 2OH \tag{7.113}$$
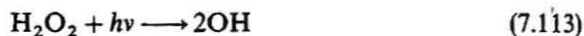
(253.7 nm light gives a primary quantum yield of 0.5 (127)), and by reaction of certain transition metal ions (e.g., Fe^{2+} and Ti^{3+}) with hydrogen peroxide (e.g., 128, 129),

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + OH^- + OH \tag{7.114}$$

However, the latter reaction is probably more complicated than the equation implies and may form a complex of radical and metal ion rather than free OH.

Perhydroxyl Radical The perhydroxyl radical (HO_2) and its anion, the superoxide ion (O_2^-), play a minor role in the radiolysis of oxygen-free solutions but become important when oxygenated systems are irradiated because oxygen is an efficient scavenger of e_{aq}^- and H (Eqs. 7.60 and 7.61). The superoxide ion is also of considerable importance in living systems, where it can be formed by enzymatic processes that do not involve ionizing radiation (e.g., 126, 130). The pK_a of HO_2 (4.8) is such that HO_2 is the predominant form below about pH 4.5, while O_2^- predominates above about pH 5; the two forms rapidly equilibrate in solution so that pH is an important consideration when studying the kinetics of HO_2/O_2^- reactions (126). A protonated form, $H_2O_2^+$, is stable in strongly acid solutions. Properties of the perhydroxyl radical are listed in Table 7.7 and Tables A3.4 (electrode potentials) and A3.7 (rate constants), and have been reviewed by Bielski and his colleagues (106, 126) and Czapski (124). Both HO_2 and O_2^- absorb sufficiently strongly in the ultraviolet to be observed directly in pulse radiolysis investigations.

Radiation-chemical studies on HO_2/O_2^- can be carried out by irradiating aqueous solutions containing both oxygen and formate ion; the oxygen converts e_{aq}^- and H to HO_2 or O_2^-, depending upon the pH, while formate ion scavenges

OH to give CO_2^-, which subsequently reacts with oxygen to give O_2^-,

$$OH + HCO_2^- \longrightarrow H_2O + CO_2^- \qquad k_{115} = 3.2 \times 10^6 \, m^3 \, mol^{-1} \, s^{-1} \quad (7.115)$$

$$CO_2^- + O_2 \longrightarrow CO_2 + O_2^- \qquad k_{116} = 2.4 \times 10^6 \, m^3 \, mol^{-1} \, s^{-1} \quad (7.116)$$
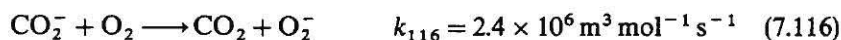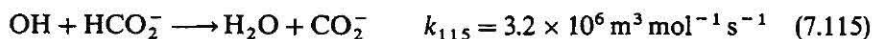
In this system, which is independent of pH, all primary radicals are rapidly and quantitatively converted to HO_2/O_2^- (126).

Perhydroxyl radicals act as oxidizing or reducing agents depending on the solute. Ferrous ion, which is readily oxidized, is converted to ferric ion be reaction with HO_2,

$$HO_2 + Fe^{2+} \longrightarrow Fe^{3+} + HO_2^- \quad (+H^+ \longrightarrow H_2O_2) \qquad (7.117)$$
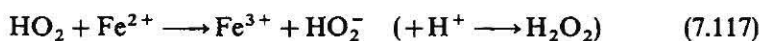
while ceric ion, which is a strong oxidizing agent, is reduced to cerous ion,

$$HO_2 + Ce^{4+} \longrightarrow Ce^{3+} + O_2 + H^+ \qquad (7.118)$$
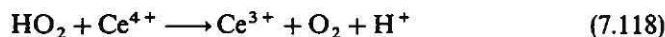
Electrode potentials for the perhydroxyl radical in acid and basic solution (Table A3.4) suggest that HO_2 is a much stronger oxidizing agent than O_2^-, while the anion is the slightly stronger reducing agent. Both forms of the radical are inert toward organic compounds unless these contain a relatively weakly bonded hydrogen atom (e.g., ascorbic acid, cysteine, and hydroquinone) when hydrogen abstraction can occur, for example, with cysteine (RSH),

$$HO_2 + RSH \longrightarrow H_2O_2 + RS\cdot \qquad (7.119)$$

Electron transfer to tetranitromethane to give a product with an intense optical absorption, $C(NO_2)_3^-$, has been used as a method for the detection of O_2^- (note that the same product is formed when e_{aq}^- reacts with tetranitromethane),

$$O_2^- + C(NO_2)_4 \longrightarrow O_2 + C(NO_2)_3^- + NO_2 \qquad (7.120)$$

In the absence of other reaction, perhydroxyl radicals react together to form hydrogen peroxide and oxygen,

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad k_{57} = 830 \, m^3 \, mol^{-1} \, s^{-1} \qquad (7.57)$$

or

$$O_2^- + HO_2 \longrightarrow H_2O_2 + O_2 + OH^- \quad k_{62} = 9.7 \times 10^4 \, m^3 \, mol^{-1} \, s^{-1} \quad (7.62)$$
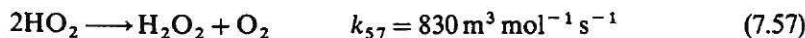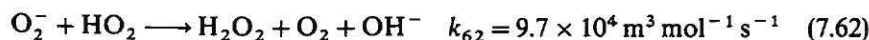
although reaction between two O_2^- radicals appears to be negligible (126). Reactions analogous to Eqs. 7.57 and 7.62 also occur with organic peroxy radicals ($RO_2\cdot$), giving organic peroxides and hydroperoxides, for example,

$$RO_2\cdot + HO_2 \longrightarrow RO_2H + O_2 \qquad (7.121)$$
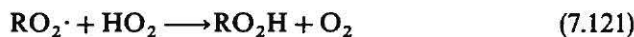
Perhydroxyl radicals can be produced photochemically by photolysis of hydrogen peroxide solutions under conditions that allow the hydroxyl radicals formed to react with H_2O_2 (131), and chemically by reaction of ions such as Ce^{4+} and Ti^{4+} with excess hydrogen peroxide (124, 132),

$$H_2O_2 + Ce^{4+} \longrightarrow Ce^{3+} + HO_2 + H^+ \tag{7.122}$$
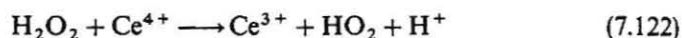
Salts of the radical such as potassium superoxide, KO_2, are stable solids.

Hydrogen Peroxide   Hydrogen peroxide, like the perhydroxyl radical, can act as an oxidizing agent (Eq. 7.114) or a reducing agent (Eq. 7.122), depending upon the material present, and as a weak acid which dissociates in strongly basic solution,

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \qquad pK = 11.6 \tag{7.123}$$
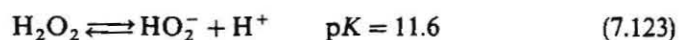
and can form salts such as potassium peroxide, K_2O_2. Hydrogen peroxide is inert toward most organic compounds but may react with some organic radicals, for example,

$$H_2O_2 + \cdot CO_2H \longrightarrow CO_2 + H_2O + OH \tag{7.124}$$
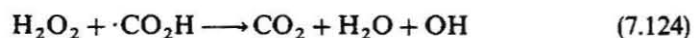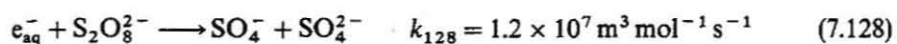
Generation of Secondary Radicals

The range of pulse and steady-state radiolysis experiments can be extended if the primary radical products are rapidly scavenged by solutes that generate secondary radicals. For example, the properties and reactions of the CO_2^- radical can be investigated by scavenging e_{aq}^- with CO_2 or by reaction of OH and H with formic acid or formate ion:

$$e_{aq}^- + CO_2 \longrightarrow CO_2^- \qquad\qquad k_{125} = 7.7 \times 10^6\,m^3\,mol^{-1}\,s^{-1} \tag{7.125}$$

$$OH + HCO_2^- \longrightarrow H_2O + CO_2^- \qquad k_{115} = 3.2 \times 10^6\,m^3\,mol^{-1}\,s^{-1} \tag{7.115}$$

$$H + HCO_2^- \longrightarrow H_2 + CO_2^- \qquad k_{126} = 2.1 \times 10^5\,m^3\,mol^{-1}\,s^{-1} \tag{7.126}$$
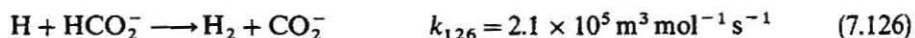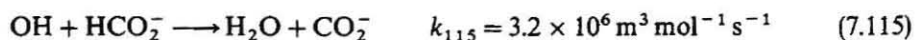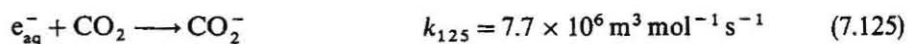
The CO_2^- radical, which becomes protonated in strongly acid solution to form $\cdot CO_2H$, is a strong reducing agent and formate ion is frequently used to convert the oxidizing OH radical to a reducing radical. Oxygen is reduced by CO_2^- to O_2^- (Eq. 7.116).
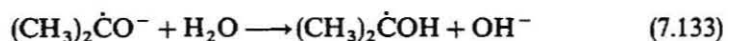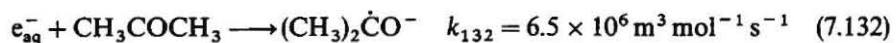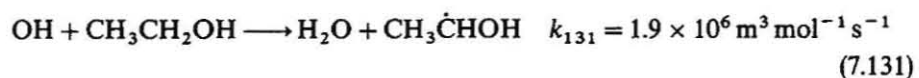
A large number of other inorganic radicals can be produced in a similar manner including, for example, the azide radical (N_3), the sulfate radical (SO_4^-), and the dichloride radical ion (Cl_2^-), which can be generated, respectively, by

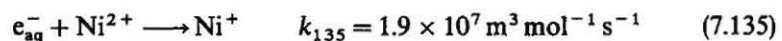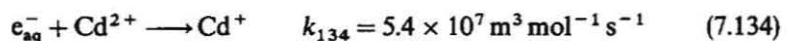$$OH + N_3 \longrightarrow OH^- + N_3 \qquad k_{127} = 1.2 \times 10^7\,m^3\,mol^{-1}\,s^{-1} \tag{7.127}$$

$$e_{aq}^- + S_2O_8^{2-} \longrightarrow SO_4^- + SO_4^{2-} \quad k_{128} = 1.2 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.128}$$

$$OH + Cl^- \longrightarrow ClOH^- \qquad k_{129} = 4.3 \times 10^6 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.129}$$

$$ClOH^- \xrightarrow{\text{H}^+, \text{Cl}^-} Cl_2^- + H_2O \tag{7.130}$$
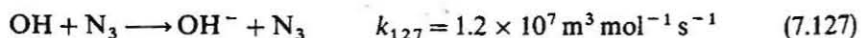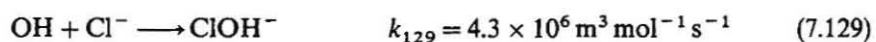
Rate constants for reactions of the above radicals and also CO_3^-, O_3, NH_2, NO_2, NO_3, PO_3^{2-}, PO_4^{2-}, SO_2^-, SO_3^-, SO_5^-, SeO_3^-, $(SCN)_2^-$, Br_2^-, I_2^-, ClO_2, and BrO_2 have been compiled by Neta et al. (133). In some cases it is advantageous to replace OH by one of the other inorganic radicals because the latter are more selective oxidizing agents than OH and are less likely to abstract hydrogen from organic materials present.

Organic radicals can be formed using organic solutes, the most extensively studied being α-hydroxyalkyl radicals produced by reaction of OH with alcohols or by addition of e_{aq}^- to carbonyl compounds (134); for example,

$$OH + CH_3CH_2OH \longrightarrow H_2O + CH_3\dot{C}HOH \quad k_{131} = 1.9 \times 10^6 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.131}$$

$$e_{aq}^- + CH_3COCH_3 \longrightarrow (CH_3)_2\dot{C}O^- \quad k_{132} = 6.5 \times 10^6 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.132}$$

$$(CH_3)_2\dot{C}O^- + H_2O \longrightarrow (CH_3)_2\dot{C}OH + OH^- \tag{7.133}$$

Generation of Metal Ions in Unusual Valency States

Reaction of metal ions and complexes with radicals generated by radiolysis may be used to produce metal ions in unusual valency states which, in some cases, are not accessible by other methods. For example, reactions between the hydrated electron and the divalent ions of cadmium, cobalt, nickel, and zinc generate the monovalent ions Cd^+, Co^+, Ni^+, and Zn^+, respectively; for example,

$$e_{aq}^- + Cd^{2+} \longrightarrow Cd^+ \qquad k_{134} = 5.4 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.134}$$

$$e_{aq}^- + Ni^{2+} \longrightarrow Ni^+ \qquad k_{135} = 1.9 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.135}$$

Rate constants for reactions of these, and other, metal ions in unusual oxidation states have been tabulated by Buxton and Sellers (135).
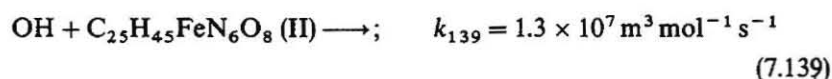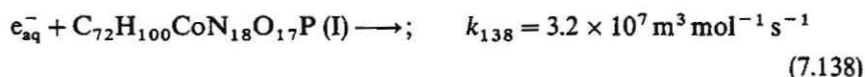
Reactions between radicals and transition-metal complexes have been extensively investigated (see, for example, 136, 122) because of their relation to catalysis and biochemical processes. Both reduction and oxidation are observed; for example, the pentacyanocobaltate(II) ion is reduced by the hydrated electron,

$$e_{aq}^- + Co(CN)_6^{3-} \longrightarrow Co(CN)_6^{4-} \qquad k_{136} = 1.3 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.136}$$
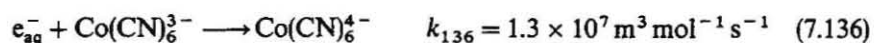
while the ferrocyanide ion is oxidized by the hydroxyl radical,

$$OH + Fe(CN)_6^{4-} \longrightarrow OH^- + Fe(CN)_6^{3-} \qquad k_{137} = 1.1 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1}$$
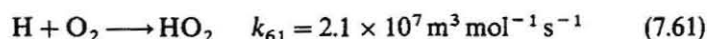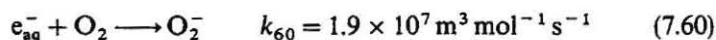$$(7.137)$$
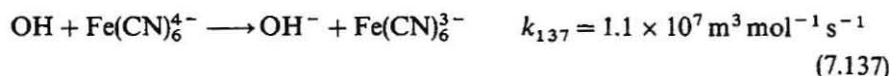
Similar reactions occur with large molecules of biological origin that contain bound transition-metal atoms, for example, with coenzyme B_{12} (I) and ferrioxamine B (II),

$$e_{aq}^- + C_{72}H_{100}CoN_{18}O_{17}P \; (I) \longrightarrow; \qquad k_{138} = 3.2 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1}$$
$$(7.138)$$

$$OH + C_{25}H_{45}FeN_6O_8 \; (II) \longrightarrow; \qquad k_{139} = 1.3 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1}$$
$$(7.139)$$

Gaseous Solutes

Aqueous systems are generally irradiated in the presence of air or of another gas used to displace air from the solution. In solutions saturated with air or oxygen, which contain about 0.25 and 1.3 $mol \, m^{-3}$ O_2, respectively, at 25 °C and atmospheric pressure, hydrated electrons and hydrogen atoms are rapidly scavenged by oxygen to give HO_2 below pH 4, and O_2^- at neutral and higher pH,

$$e_{aq}^- + O_2 \longrightarrow O_2^- \qquad k_{60} = 1.9 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \qquad (7.60)$$

$$H + O_2 \longrightarrow HO_2 \qquad k_{61} = 2.1 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \qquad (7.61)$$

Solutes that react with the reducing radicals with high rate constants may intervene and reduce the extent of reaction with oxygen. At low pH, for example, hydrogen ion can compete with oxygen for hydrated electrons,

$$e_{aq}^- + H_3O^+ \longrightarrow H + H_2O \qquad k_{56} = 2.3 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \qquad (7.56)$$
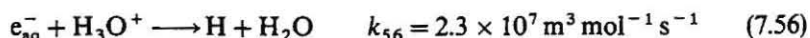
The ratio of $(e_{aq}^- + O_2)/(e_{aq}^- + H_3O^+)$ is equal to $k_{60}[O_2]/k_{56}[H_3O^+]$. For air-saturated solutions the ratio is unity at pH 3.7, though electron scavenging by hydrogen ion will have little effect upon the final outcome if the hydrogen atoms subsequently react with oxygen.
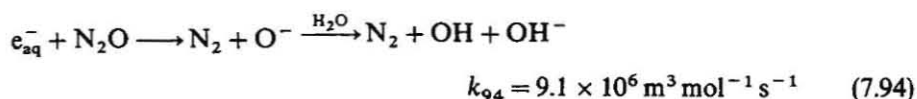
    Since oxygen can also react rapidly with organic radicals, irradiations carried out in the presence of air or oxygen often lead to quite different products to those performed under oxygen-free conditions. Oxygen can be removed from aerated solutions by repeated freeze–pump–thaw cycles or, generally more conveniently, by passing a stream of inert gas through the solution for at least several minutes. Argon, helium, and nitrogen are frequently used for this purpose.

Hydroxyl radicals are converted to hydrogen atoms in solutions saturated with hydrogen at atmospheric pressure (about $0.78 \, mol \, m^{-3} \, H_2$ at 25 °C),

$$OH + H_2 \longrightarrow H_2O + H \qquad k_{13} = 4.2 \times 10^4 \, m^3 \, mol^{-1} \, s^{-1} \qquad (7.13)$$
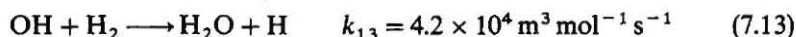
but substantially higher hydrogen pressures are necessary if this reaction is to compete with other hydroxyl radical reactions in the systems described in this chapter.

Aqueous solutions are very often purged with nitrous oxide so that hydrated electrons are converted to hydroxyl radicals by the sequence of reactions represented by

$$e_{aq}^- + N_2O \longrightarrow N_2 + O^- \xrightarrow{H_2O} N_2 + OH + OH^-$$

$$k_{94} = 9.1 \times 10^6 \, m^3 \, mol^{-1} \, s^{-1} \qquad (7.94)$$

The rate constant and solubility for nitrous oxide in water (a saturated solution contains about $25 \, mol \, m^{-3} \, N_2O$ at 1 atm, 25 °C) are sufficiently high that this reaction can compete sccessfully with other e_{aq}^- reactions, provided the other reactants are present at concentrations of about $1 \, mol \, m^{-3}$ or less (i.e., if $k[reactant]$ is less than about $10^7 \, s^{-1}$). The initial product of the reaction is the N_2O^- ion, which is generally considered to have too short a lifetime to react directly with low concentrations of solute, but a subsequent transient species is O^-, which may react with some solutes before protonation occurs to give OH (137).

Carbon dioxide, which is often adventitiously present in air-saturated solutions, reacts rapidly with hydrated electrons but only slowly with hydroxyl radicals; reaction with e_{aq}^- gives CO_2^-, which is an intermediate in the radiolysis of formate solutions and which can react with oxygen to give O_2^- (Eq. 7.116).

Ferrous Sulfate (Fricke Dosimeter)

The radiation-induced oxidation of ferrous sulfate solutions is one of the most thoroughly studied reactions in radiation chemistry and is the basis for the widely used Fricke dosimeter (see Chap. 3; ref. 138). Since the mechanism is well established, the reaction is also used to derive information about the primary radical and molecular yields in irradiated water.

The oxidation is invariably studied in acid solution to avoid precipitation of basic iron compounds, the most frequently used solvent being $400 \, mol \, m^{-3}$ (0.4 M) sulfuric acid (pH 0.46). Solutions may be saturated with air or oxygen or purged with an inert gas to remove oxygen, though yields of ferric ion are appreciably lower when oxygen is absent; $^{60}Co \, \gamma$ irradiation, for example, gives $G(Fe^{3+})$ values of 1.61 and $0.85 \, \mu mol \, J^{-1}$, respectively, in the presence and absence of oxygen. Oxygen is consumed during the course of the irradiation, but the yield of ferric ion is not affected significantly by the changing oxygen
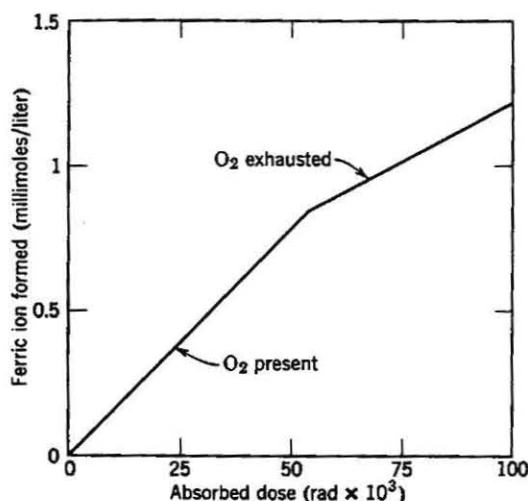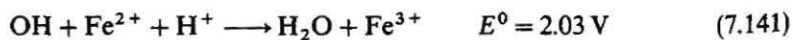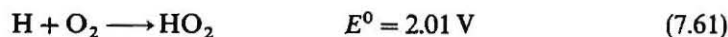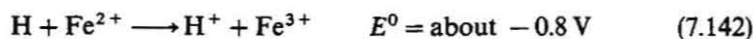
Figure 7.3   Radiation-induced oxidation of air-saturated ferrous sulfate solutions (^{60}Co γ radiation).

concentration until the oxygen is virtually exhausted, when the yield quickly falls to the value characteristic of oxygen-free solutions (Fig. 7.3). The consumption of oxygen is rarely measured precisely, but assuming an initial concentration of about $0.25 \, \text{mol m}^{-3} \, O_2$ in an air-saturated solution, the break in the plot shown in Fig. 7.3 at about 550 Gy corresponds to $G(-O_2) = 0.38 \, \mu\text{mol J}^{-1}$ for ^{60}Co radiation. Curves of the same general shape as Fig. 7.3 are typical of many other radiation-induced reactions in aqueous solution where the yield of product is dependent upon the presence of oxygen. The break in such curves is often quite sharp, showing that oxygen is an effective radical scavenger down to very low concentrations.

Reactions that are likely to contribute to the radiolysis of ferrous sulfate solutions can be found in the tables given in Appendix 3. For example, assuming that the primary radicals (e_{aq}^-, H, and OH) present in relatively low concentration will react preferentially with the stable solutes (Fe^{2+}, H^+, HSO_4^-, SO_4^{2-}, O_2) present in much higher concentration, the following possible reactions can be derived by combining pairs of half reactions from Table A3.4:

$$e_{aq}^- + Fe^{2+} \longrightarrow Fe^+ \qquad E^0 = \text{about } -0.3 \, \text{V} \quad (7.140)$$

$$e_{aq}^- + H^+ \longrightarrow H \qquad E^0 = 0.46 \, \text{V} \qquad (7.56)$$

$$e_{aq}^- + O_2 \longrightarrow O_2^- \qquad E^0 = 2.21 \, \text{V} \qquad (7.60)$$

$$OH + Fe^{2+} + H^+ \longrightarrow H_2O + Fe^{3+} \qquad E^0 = 2.03 \, \text{V} \qquad (7.141)$$

$$H + Fe^{2+} \longrightarrow H^+ + Fe^{3+} \qquad E^0 = \text{about } -0.8\,V \qquad (7.142)$$

$$H + O_2 \longrightarrow HO_2 \qquad E^0 = 2.01\,V \qquad (7.61)$$

Under the standard conditions applicable to the data given in Table A3.4 (25 °C, unit activity of reactants and products) reactions having positive values of E^0 are thermodynamically possible, since this corresponds to a negative free energy change. In radiolysis experiments the reactions will not be taking place under standard conditions where each species is at unit activity, but the potentials that apply under the experimental conditions can be estimated by substituting the experimental activities in the Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \qquad (7.143)$$
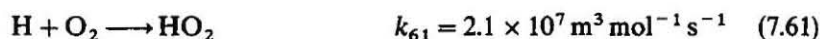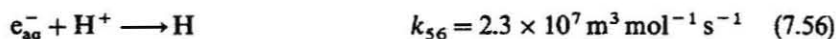
for the reaction $aA + bB \longrightarrow cC + dD$ where a is the activity of the species specified, R the ideal gas constant, T the absolute temperature, n the number of electrons transferred from the species oxidized to the species reduced in the equation as written, and F the Faraday; for practical purposes, the activity of a species present in dilute solution is the same as its concentration. The Nernst equation shows that the reaction will have a positive value of E (i.e., will be spontaneous) if E^0 is positive and the concentrations of the reactants are higher than the concentrations of the products, or if the magnitude of a negative E^0 is smaller than the positive effect due to high reactant and low product concentrations. In practice, positive E^0 values greater than about 0.5 V are strong presumptive evidence that the reaction will be spontaneous under normal radiolysis conditions.

Although tables of electrode potentials can be used to determine which reactions are thermodynamically possible, they do not give any information about the rates of these reactions; whether, for instance, a particular reaction will be fast enough to contribute significantly, or which of several competing reactions will predominate. This information is obtained from tables of rate constants such as those given in Appendix 3. The reactions listed above include three in which the hydrated electron takes part, each of which is, or may be, spontaneous based on the E^0 values shown. The rates of the three reactions with Fe^{2+}, H^+, and O_2 are 1.6×10^5 (k_{140}), 2.3×10^7 (k_{56}), and 1.9×10^7 (k_{60}) $m^3\,mol^{-1}\,s^{-1}$, respectively, while the concentrations of the three solutes in the standard dosimeter solution are 1, 350, and $\sim 0.25\,mol\,m^{-3}$, respectively. The relative contributions of the three reactions to the Fricke dosimeter are given by

$$e_{aq}^- + Fe^{2+} : e_{aq}^- + H^+ : e_{aq}^- + O_2 = k_{140}[Fe^{2+}] : k_{56}[H^+] : k_{60}[O_2]$$

$$= 1 : 50{,}000 : 30$$

In other words, about 99.9% of the hydrated electrons that escape from the spurs

and tracks will react with H^+, so that this is the only reaction of e_{aq}^- that need be considered. Proceeding in the same manner for OH and H shows that reactions 7.105 and 7.61, which are both spontaneous and rapid, account for the behavior of hydroxyl radicals and hydrogen atoms respectively in the Fricke dosimeter. With the selection of HO_2 and H_2O_2 reactions on the same basis, the following mechanism can be developed for the oxidation of ferrous ion in the standard Fricke dosimeter solution:

$$e_{aq}^- + H^+ \longrightarrow H \qquad\qquad k_{56} = 2.3 \times 10^7\,m^3\,mol^{-1}\,s^{-1} \quad (7.56)$$

$$H + O_2 \longrightarrow HO_2 \qquad\qquad k_{61} = 2.1 \times 10^7\,m^3\,mol^{-1}\,s^{-1} \quad (7.61)$$

$$OH + Fe^{2+} \longrightarrow OH^- + Fe^{3+} \qquad k_{105} = 2.3 \times 10^5\,m^3\,mol^{-1}\,s^{-1} \quad (7.105)$$

$$HO_2 + Fe^{2+} \longrightarrow HO_2^- + Fe^{3+} \qquad k_{117} = 1.2 \times 10^3\,m^3\,mol^{-1}\,s^{-1} \quad (7.117)$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \qquad\qquad\qquad\qquad (7.144)$$

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + OH^- + OH \quad k_{114} = 0.05\,m^3\,mol^{-1}\,s^{-1} \qquad (7.114)$$
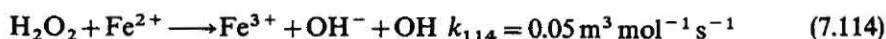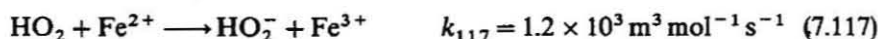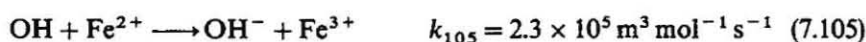
The yield of ferric ion is related to the primary radical and molecular yields by

$$G(Fe^{3+}) = 2g(H_2O_2) + 3[g(e_{aq}^-) + g(H) + g(HO_2)] + g(OH) \qquad (7.145)$$

since each molecule of hydrogen peroxide oxidizes two ferrous ions by reactions 7.114 and then 7.105, while the reducing radicals each oxidize three ferrous ions by sequential reactions involving HO_2, H_2O_2, and OH, respectively.

At normal dose rates the radical concentrations are low compared with the solute concentrations and the reactions can be treated as pseudo-first order, so that the half-life and time for the reaction to reach 99% completion for each step are given by $\ln 2/(k[S])(= 0.693/k[S])$ and $\ln 100/(k[S])(= 4.605/k[S])$, respectively. Substitution of k_{105} and $[Fe^{2+}] = 1$ mol m^{-3} in the second of these expressions shows that reaction 7.105 will be 99% complete within about 2×10^{-5} s (20 µs). Reactions 7.56 and 7.61 will also be complete within this time span, but the oxidation of ferrous ion by HO_2 is slower and requires 6 to 7×10^{-3} s (6 to 7 ms) for completion. Reaction of hydrogen peroxide (both the molecular product yield and that formed by reaction 7.144) with ferrous ion (Eq. 7.114) is even slower and requires about 90 s for 99% reaction with 1 mol m^{-3} Fe^{2+}.

As a result of the differences in reaction rate, $G(Fe^{3+})$ is time dependent if the radiation is delivered as a pulse that is short compared with the lifetimes of the reactions making up the radiolysis mechanism. For 1 mol m^{-3} Fe^{2+}, for example, the following stages will be observed following short (nanosecond or micro-second) radiation pulses:

Stage 1 (at 20 μs)

$$G(Fe^{3+}) = g(OH) \qquad (G = 0.30) \qquad (7.146)$$

Stage 2 (at 10 ms)

$$G(Fe^{3+}) = g(e_{aq}^-) + g(H) + g(OH) + g(HO_2) \qquad (G = 0.68) \qquad (7.147)$$

Stage 3 (at times > 100 s)

$$G(Fe^{3+}) = 2g(H_2O_2) + 3[g(e_{aq}^-) + g(H) + g(HO_2)] + g(OH) \qquad (G = 1.61)$$
$$(7.145)$$

$$G(-O_2) = g(e_{aq}^-) + g(H) \qquad (G = 0.38) \qquad (7.148)$$

The values is parentheses are radiation-chemical yields ($\mu mol\,J^{-1}$) for fast electron and γ radiation obtained by substituting primary yields from Table 7.4 in the expressions given for $G(Fe^{3+})$; $g(HO_2)$ was assumed to be 0.0027, but the other primary yields are those given for pH 0.46.

Keene (139) observed the three stages in ferrous ion oxidation and also found that the absorption spectrum of the product changes with time from that of uncomplexed Fe^{3+} (stage 1) to that of a mixture containing a hydroxyl complex of Fe^{3+} formed by reaction 7.117 (stage 2) and, finally, to the spectrum of a sulfate complex of Fe^{3+} ($FeSO_4^+$) which is stable in $400\,mol\,m^{-3}\,H_2SO_4$ (stage 3). The intermediate complexes formed in the oxidation of ferrous ion have been described in some detail by Jayson et al. (140) but, for simplicity, they are omitted from the equations given in this section. Also in the interests of clarity, ferrous and ferric ions are represented as Fe^{2+} and Fe^{3+} rather than as complexes with water and anions, for example, $Fe^{2+}(H_2O)_5HSO_4^-$, that would more properly represent the ions in sulfuric acid solution. In other words, the equations used give the correct stoichiometric relationships but do not give the detailed mechanism of the reactions. Dainton and his colleagues (141) pointed out that reaction 7.114 can be neglected if the ferric ion formed is measured immediately following a short irradiation of dilute ($< 0.01\,mol\,m^{-3}$) ferrous ion solution, since at these concentrations the half-life of the reaction is of the order of 20 min or longer; under these conditions $G(Fe^{3+})$ is given by Eq. 7.147. The normal yield of ferric ion is obtained if the irradiated solution is allowed to stand for several hours.

Values of $G(Fe^{3+})$ are affected by factors that alter the primary yields, for example, pH (Fig. 7.1), LET (Table 7.4), absorbed dose rate at extremely high dose rates, and the concentration of acid and ferrous ion. Increasing LET (e.g., by using α particles instead of γ radiation) has the effect of reducing the radical yields but increasing the molecular product yields from water (Table 7.4). Substitution of typical yields in Eq. 7.145 shows that this leads to a decrease in $G(Fe^{3+})$ with increasing LET (see also Table 3.7). The anticipated effect of LET upon $G(Fe^{3+})$ has been estimated by Magee and Chatterjee using theoretical models for

electron and heavy-particle tracks (63, 142); the estimated values agree well with experimental yields reported by other workers. LaVerne and Schuler (143) have observed an additional effect with heavy-particle radiation which results in a small increase in $G(Fe^{3+})$ with increasing particle atomic number (Z).

At the very high dose rates attainable with electron accelerators, $G(Fe^{3+})$ is reduced by the occurrence of interradical reactions such as
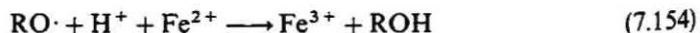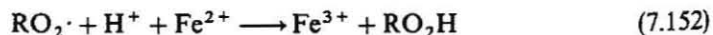
$$2HO_2 \longrightarrow H_2O_2 + O_2 \tag{7.57}$$

which compete with the radical–solute reactions (e.g., 7.117) that predominate at lower dose rates. The effect of higher dose rates can be compensated to some extent by using higher concentrations of ferrous ion and oxygen; the "super Fricke" dosimeter containing $10 \, mol \, m^{-3} \, Fe^{2+}$ in $400 \, mol \, m^{-3} \, H_2SO_4$ saturated with oxygen is usable to dose rates of the order of $10^8 \, Gy \, s^{-1}$ (144). Lower than normal concentrations of acid and ferrous ion increase the possibility that other reactions will compete with those listed above, in addition to the effect that changing pH will have upon the primary yields. Low ferrous ion concentrations also increase the possibility of competition between Fe^{2+} and Fe^{3+} for radicals as the concentration of Fe^{3+} grows, for example, between reaction 7.117 and

$$HO_2 + Fe^{3+} \longrightarrow Fe^{2+} + O_2 + H^+ \tag{7.149}$$
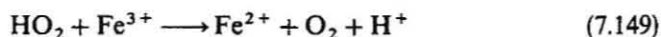
However, in spite of the latter possibility, the response of the standard 1-$mol \, m^{-3} \, Fe^{2+}$ dosimeter solution is linear with absorbed dose to at least 400 Gy, which corresponds to conversion of 65% of the ferrous ion originally present to ferric ion.

Organic impurities (RH) can increase the yield of ferric ion in aerated solutions (138, 145) by the sequence of reactions

$$OH + RH \longrightarrow R\cdot + H_2O \tag{7.150}$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \tag{7.151}$$

$$RO_2\cdot + H^+ + Fe^{2+} \longrightarrow Fe^{3+} + RO_2H \tag{7.152}$$

$$RO_2H + Fe^{2+} \longrightarrow Fe^{3+} + RO\cdot + OH^- \tag{7.153}$$

$$RO\cdot + H^+ + Fe^{2+} \longrightarrow Fe^{3+} + ROH \tag{7.154}$$

In this sequence each hydroxyl radical brings about oxidation of three ferrous ions instead of one as in the normal series of reactions, and the yield of ferric ion is spuriously high. Deliberate addition of organic compounds sometimes leads to even higher yields of ferric ion than predicted on the basis of the above sequence. For example, $G(Fe^{3+})$ values up to $7.8 \, \mu mol \, J^{-1}$ in the presence of ethanol (145) and about $25 \, \mu mol \, J^{-1}$ in solutions containing formic acid (146) have been

reported. In these instances a chain reaction must be responsible for the high yields and reaction 7.154 is probably replaced by

$$RO\cdot + RH \longrightarrow R\cdot + ROH \tag{7.155}$$

to give a chain reaction whose propagation steps (reactions 7.151 to 7.153 and 7.155) produce ferric ion and an alcohol,

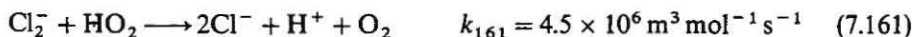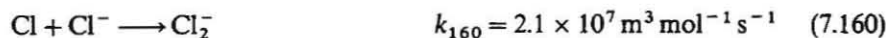$$2Fe^{2+} + RH + O_2 + H^+ \longrightarrow 2Fe^{3+} + ROH + OH^- \tag{7.156}$$
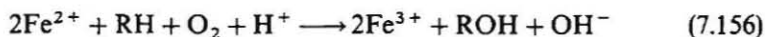
Addition of small quantities of sodium chloride (e.g., 1 mol m^{-3}) reduces the effect of organic impurities by converting hydroxyl radicals to chlorine atoms in a reaction whose overall stoichiometry is represented by

$$OH + Cl^- + H^+ \longrightarrow Cl + H_2O \tag{7.157}$$
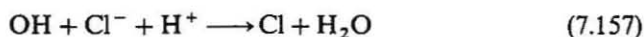
The chlorine atom may react with either ferrous ion or the organic compound,

$$Cl + Fe^{2+} \longrightarrow Cl^- + Fe^{3+} \tag{7.158}$$

$$Cl + RH \longrightarrow R\cdot + Cl^- + H^+ \tag{7.159}$$
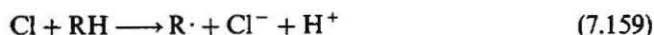
but, in fact, reacts predominantly with Fe^{2+} with the net result that each OH leads to the oxidation of only one ferrous ion, regardless of the presence of the organic material. At very high dose rates the presence of chloride reduces the yield of ferric ion because a proportion of the chlorine atoms react with chloride ion to give Cl_2^-, which subsequently reacts with HO_2 and does not oxidize ferrous ion (147),

$$Cl + Cl^- \longrightarrow Cl_2^- \qquad k_{160} = 2.1 \times 10^7\,m^3\,mol^{-1}\,s^{-1} \tag{7.160}$$

$$Cl_2^- + HO_2 \longrightarrow 2Cl^- + H^+ + O_2 \qquad k_{161} = 4.5 \times 10^6\,m^3\,mol^{-1}\,s^{-1} \tag{7.161}$$

Reaction 7.161 is only significant when the radical concentration is high (i.e., at high dose rates) since ferrous ion can compete successfully for the radicals at low radical concentrations.

In the absence of oxygen, reaction 7.61 is replaced by

$$H + H^+ + Fe^{2+} \longrightarrow H_2 + Fe^{3+} \tag{7.162}$$
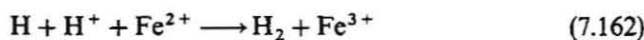
in which the hydrogen atom takes the unusual role of an oxidizing agent, and the yield of ferric ion becomes

$$G(Fe^{3+}) = 2g(H_2O_2) + g(e_{aq}^-) + g(H) + g(OH) + 3g(HO_2) \tag{7.163}$$

$$G(H_2) = g(H_2) + g(e_{aq}^-) + g(H) \tag{7.164}$$

Substituting primary yields from Table 7.4 for γ radiation and pH 0.46 with $g(HO_2) = 0.026$, these expressions give $G(Fe^{3+}) = 0.85$ and $G(HO_2) = 0.42 \, \mu mol \, J^{-1}$ for fast electron and γ radiation, which agree with experimentally determined values. Although the stoichiometry of reaction 7.162 is well established, the mechanism is less certain. Alternative mechanisms that have been proposed include the association of H and H^+ to form H_2^+, which might readily accept an electron from Fe^{2+} to form H_2 (148) although the association reaction itself is rather slow (Table A3.5), abstraction by the hydrogen atom of hydrogen from a polarized water molecule in the solvation shell of the ferrous ion (149, 150),

$$H + Fe^{2+}H_2O \longrightarrow Fe^{3+}OH^- + H_2 \qquad (7.165)$$
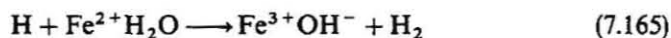
and the formation of an intermediate hydride complex, FeH^{2+} (151–153),

$$H + Fe^{2+} \longrightarrow FeH^{2+} \xrightarrow{H^+} Fe^{3+} + H_2 \qquad (7.166)$$
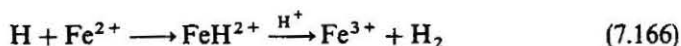
The part played by sulfuric acid and its anions is generally ignored when the ferrous sulfate system is described, although with the standard dosimeter solution (400 mol m^{-3} H_2SO_4) about 40% of the hydroxyl radicals react with HSO_4^-,

$$OH + HSO_4^- \longrightarrow OH^- + HSO_4 \qquad k_{167} = 700 \, m^3 \, mol^{-1} \, s^{-1} \quad (7.167)$$

This does not affect $G(Fe^{3+})$ since HSO_4 is stoichiometrically equivalent to OH, oxidizing one ferrous ion to a ferric ion

$$HSO_4 + Fe^{2+} \longrightarrow HSO_4^- + Fe^{3+} \qquad (7.168)$$
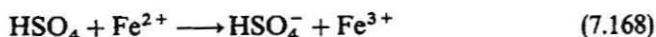
or dimerizing to a product that, like H_2O_2, oxidizes two ferrous ions. Even in solutions as dilute as 400 mol m^{-3} H_2SO_4, a small yield ($G = 0.019$) of HSO_4 is formed by the direct action of the radiation on HSO_4^- (154),

$$HSO_4^- \rightsquigarrow HSO_4 + e^- \qquad (7.169)$$
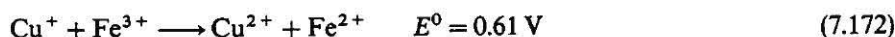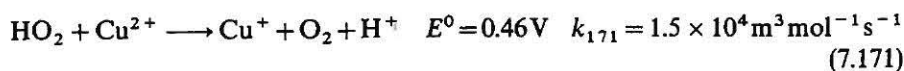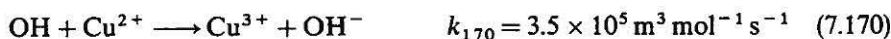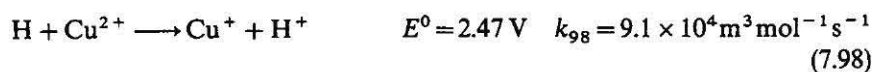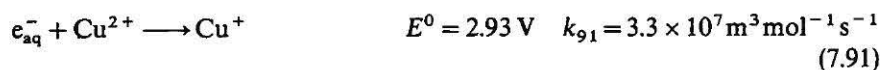
Perchloric acid can be substituted for sulfuric acid without changing the yield of ferric ion, but according to Schwarz (155) hydrochloric acid cannot be used because back reactions occur between H and the ferric complexes $FeCl_2^+$ and $FeCl^{2+}$.

Systems containing ferrous ion are difficult to investigate at neutral pH because the final product is a precipitate of iron(III) compounds. However, Stuglik and Zagórski (156) have shown that the nucleation process is sufficiently slow that there is a window of several milliseconds during which the products of the reaction between Fe^{2+} and OH can be observed by pulse radiolysis. The first product observed is $Fe(OH)_{aq}^{2+}$ and the authors determined that this is formed by a hydrogen abstraction mechanism rather than by outer sphere charge transfer.

Ferrous Sulfate–Cupric Sulfate

A number of modified ferrous sulfate systems have been suggested for use as chemical dosimeters or investigated to establish radiolysis mechanisms and yields (138). One of the earliest studied and best known is a mixture of ferrous and cupric sulfates dissolved in dilute sulfuric acid which was proposed as a dosimeter by Hart (157); the solution used for this purpose contains $1 \, mol \, m^{-3} \, FeSO_4$, $10 \, mol \, m^{-3} \, CuSO_4$, $5 \, mol \, m^{-3} \, H_2SO_4$, and is air saturated. As a dosimeter the solution has the advantage over the standard Fricke dosimeter that the yield of ferric ion does not depend on the presence of oxygen, so that the range of the dosimeter is much greater (10^3 to 10^5 or $10^6 \, Gy$).

Examination of the tables of electrode potentials and rate constants in Appendix 3 suggests that the following reactions of cupric ion may contribute to the radiolysis mechanism:

$$e_{aq}^- + Cu^{2+} \longrightarrow Cu^+ \qquad E^0 = 2.93 \, V \quad k_{91} = 3.3 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.91}$$

$$H + Cu^{2+} \longrightarrow Cu^+ + H^+ \qquad E^0 = 2.47 \, V \quad k_{98} = 9.1 \times 10^4 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.98}$$

$$OH + Cu^{2+} \longrightarrow Cu^{3+} + OH^- \qquad k_{170} = 3.5 \times 10^5 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.170}$$

$$HO_2 + Cu^{2+} \longrightarrow Cu^+ + O_2 + H^+ \quad E^0 = 0.46 \, V \quad k_{171} = 1.5 \times 10^4 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.171}$$

$$Cu^+ + Fe^{3+} \longrightarrow Cu^{2+} + Fe^{2+} \qquad E^0 = 0.61 \, V \tag{7.172}$$

Cuprous ion may also react with HO_2 and H_2O_2 although these reactions are likely to be slower than the electron-transfer reaction 7.172, which will also be favored by the increasing concentration of ferric ion as the irradiation progresses. Cupric ion is present in relatively high concentration and scavenges over 75% of the hydrated electrons and about 5% of the hydrogen atoms in competition with the hydrogen ion (Eq. 7.56) and oxygen (Eq. 7.61) scavenging reactions, respectively. Virtually all HO_2 radicals formed by the latter reactions react with cupric ion (Eq. 7.171) so that effectively each hydrated electron or hydrogen atom formed eventually reduces one cupric ion to a cuprous ion. About 10% of the hydroxyl radicals formed oxidize ferrous ion to ferric (Eq. 7.105) while about 90% react via reaction 7.170. However, experiment shows that the Cu^{3+} produced oxidizes Cu^+ to Cu^{2+} or Fe^{2+} to Fe^{3+}, so that effectively each OH oxidizes one Fe^{2+} to Fe^{3+}. Hydrogen peroxide oxidizes two ferrous ions to ferric ion as in the Fricke dosimeter, while cuprous ions each reduce one ferric ion to a ferrous ion, so that the overall yield of ferric ion is given by a relatively simple expression,

$$G(Fe^{3+}) = 2g(H_2O_2) - g(e_{aq}^-) - g(H) + g(OH) - g(HO_2) \tag{7.173}$$

Oxygen enters into the sequence of reactions but is not consumed since each HO_2, formed with the consumption of one molecule of oxygen, releases a molecule of oxygen when it reacts with cupric ion. At high absorbed dose rates $G(Fe^{3+})$ increases because the higher radical concentration favors dismutation of HO_2 to give H_2O_2 (Eq. 7.57) rather than reaction with cupric ion (Eq. 171) (158).
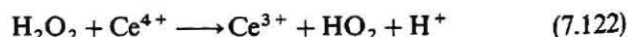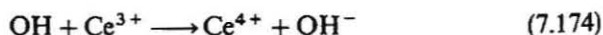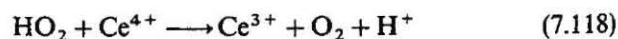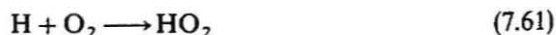
In the absence of oxygen all hydrogen atoms react directly with Cu^{2+},

$$H + Cu^{2+} \longrightarrow H^+ + Cu^+ \tag{7.98}$$
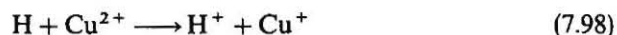
but the yield of ferric ion is unchanged since stoichiometrically it is immaterial whether H or HO_2 reduces Cu^{2+}. However, oxygen formed when deaerated solutions are irradiated can be used to measure the primary yield of perhydroxyl radicals, since under these conditions $G(O_2) = g(HO_2)$.

Ceric Sulfate

Solutions of ceric sulfate in sulfuric acid are also used in dosimetry and, like the ferrous sulfate system, played an important part in the development of an understanding of the radiation chemistry of water and aqueous solutions. In the ceric sulfate dosimeter, solutions containing 10^{-2} to $400 \, mol \, m^{-3} \, Ce^{4+}$ in air-saturated $400 \, mol \, m^{-3} \, H_2SO_4$ are reduced to Ce^{3+} by a process that does not consume oxygen and that is only slightly affected by the oxygen concentration (159). Several of the rate constants necessary to evaluate the extent of competition between the various possible reactions in the system have not yet been measured, although the main features of the radiolysis mechanism are well established. Ceric ion is a strong oxidizing agent, though weaker than the hydroxyl radical, and oxidizes all the species with which it reacts except OH, leading to the following mechanism:
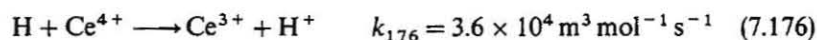
$$e_{aq}^- + H^+ \longrightarrow H \tag{5.56}$$

$$H + O_2 \longrightarrow HO_2 \tag{7.61}$$

$$HO_2 + Ce^{4+} \longrightarrow Ce^{3+} + O_2 + H^+ \tag{7.118}$$

$$OH + Ce^{3+} \longrightarrow Ce^{4+} + OH^- \tag{7.174}$$

$$H_2O_2 + Ce^{4+} \longrightarrow Ce^{3+} + HO_2 + H^+ \tag{7.122}$$

which gives

$$G(Ce^{3+}) = 2g(H_2O_2) + g(e_{aq}^-) + g(H) - g(OH) + g(HO_2) \tag{7.175}$$

This relationship, which has been confirmed by experiment, predicts an increase in $G(Ce^{3+})$ with increasing LET, as observed (Table 3.8). In the absence of

oxygen, reactions 7.61 and 7.118 are replaced by

$$H + Ce^{4+} \longrightarrow Ce^{3+} + H^+ \qquad k_{176} = 3.6 \times 10^4 \, m^3 \, mol^{-1} \, s^{-1} \quad (7.176)$$

which does not affect the stoichiometry, or Eq. 7.175, since both H and HO_2 reduce one ceric ion. When no oxygen is present initially,

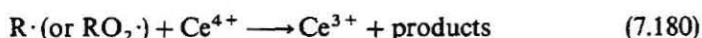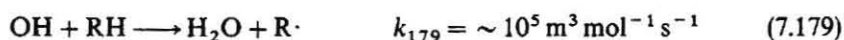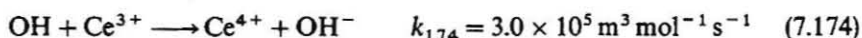$$G(O_2) = g(H_2O_2) + g(HO_2) \tag{7.177}$$

The mechanism given above has been simplified by describing the cerium ions as simple ions rather than ions complexed with H_2O, HSO_4^-, and SO_4^{2-}, and by ignoring any direct reduction of Ce^{4+} by e_{aq}^-, although this is to be expected at high ceric concentrations. The possibility of interaction between the primary radicals and H_2SO_4 and its anions has also be disregarded. However, these omissions should not affect the stoichiometry of the reaction. Back reactions, for example,

$$HO_2 + Ce^{3+} \longrightarrow HO_2^- + Ce^{4+} \tag{7.178}$$

become more probable as the irradiation progresses and the concentration of cerous ion increases, and $G(Ce^{3+})$ falls at high absorbed dose.

The ceric sulfate dosimeter is particularly sensitive to traces of organic impurities, which increase $G(Ce^{3+})$, but, unlike the Fricke dosimeter case, the effect of impurities cannot be counteracted by adding small amounts of sodium chloride. Addition of at least $3 \, mol \, m^{-3}$ cerous ion does, however, reduce the effect of organic contaminants (159). The evidence appears to be consistent with competition between cerous ion and the organic material (RH) for OH,

$$OH + Ce^{3+} \longrightarrow Ce^{4+} + OH^- \qquad k_{174} = 3.0 \times 10^5 \, m^3 \, mol^{-1} \, s^{-1} \quad (7.174)$$

$$OH + RH \longrightarrow H_2O + R \cdot \qquad k_{179} = \sim 10^5 \, m^3 \, mol^{-1} \, s^{-1} \quad (7.179)$$

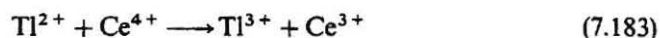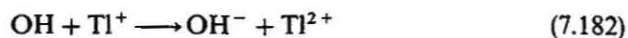$$R \cdot (or \, RO_2 \cdot) + Ce^{4+} \longrightarrow Ce^{3+} + products \tag{7.180}$$

with the organic radicals, which will be weaker oxidizing agents than OH, bringing about reduction of ceric ion either directly or by way of a peroxy radical $(RO_2 \cdot)$ as in the case of H, and generating an increase in $G(Ce^{3+})$. In the early stages of the irradiation the concentration of cerous ion may be quite low and competition between reactions 7.174 and 7.179 may favor reaction 7.179; however, it appears that addition of cerous ion before irradiation can bias the competition in favor of reaction 7.174, so that small amounts of organic material produce a negligible effect. Sodium chloride is presumably ineffective because the chlorine atom is a weaker oxidizing agent than ceric ion and will not oxidize cerous ion to ceric.

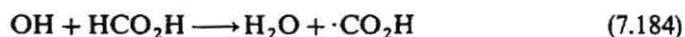Deliberate addition of thallous ion or formic acid (159, 160) prior to

irradiation does replace OH by species that are weaker oxidizing agents than ceric ion, which under these conditions oxidizes all the water radical and molecular products except H_2, so that

$$G(Ce^{3+}) = 2g(H_2O_2) + g(e_{aq}^-) + g(H) + g(OH) + g(HO_2) \qquad (7.181)$$

The scavenging and subsequent oxidation reactions are

$$OH + Tl^+ \longrightarrow OH^- + Tl^{2+} \qquad (7.182)$$

$$Tl^{2+} + Ce^{4+} \longrightarrow Tl^{3+} + Ce^{3+} \qquad (7.183)$$

and

$$OH + HCO_2H \longrightarrow H_2O + \cdot CO_2H \qquad (7.184)$$

$$\cdot CO_2H + Ce^{4+} \longrightarrow Ce^{3+} + CO_2 + H^+ \qquad (7.185)$$

Determination of Molecular and Radical Yields

Molecular and radical yields can be determined from the extent of radiation-induced changes produced in aqueous systems if the detailed radiolysis mechanism is known. In acid solutions the systems described above based on the oxidation of ferrous ion and the reduction of ceric ion can be utilized, using, for example, the following radiation-chemical yields for ^{60}Co γ radiation and solutions in $400 \, mol \, m^{-3} \, H_2SO_4$:

$$G(Fe^{3+})_{+O_2}, 1.61 \qquad G(H_2)_{Fe^{2+}, -O_2}, 0.420 \qquad G(Ce^{3+}), 0.244$$

$$G(Fe^{3+})_{-O_2}, 0.85 \qquad G(O_2)_{Fe^{2+}, Cu^{2+}}, 0.0027 \qquad G(Ce^{3+})_{Tl^+}, 0.845$$

$$G(Fe^{3+})_{Cu^{2+}}, 0.081$$

where the subscripts identify the system and any special conditions. The radiation-chemical yields (G) are related to the primary yields by the expressions derived in the previous pages and collected in Table 7.8. Individual molecular and radical yields are derived algebraically, for example;

$$g(e_{aq}^-) + g(H) = 0.5[G(Fe^{3+})_{+O_2} - G(Fe^{3+})_{-O_2}] = 0.378$$

$$g(H_2) = G(H_2)_{Fe^{2+}, -O_2} - (g(e_{aq}^-) + g(H)) \quad = 0.042$$

$$g(OH) = 0.5[G(Ce^{3+})_{Tl^+} - G(Ce^{3+})] \qquad = 0.301$$

$$g(H_2O_2) = 0.25[G(Fe^{3+})_{Cu^{2+}} + G(Ce^{3+})] \quad = 0.081$$

$$g(HO_2) = G(O_2)_{Fe^{2+}, Cu^{2+}} \qquad\qquad = 0.0027$$

The experimental data can obviously be combined in other ways to derive the

primary yields, while the number of measurements necessary can be reduced by including the material balance equations given at the head of Table 7.8. With low-LET radiation, $g(HO_2)$ is small and is often ignored, leading to simpler relationships, for instance,

$$G(Fe^{3+})_{+O_2} = 2g(H_2O_2) + 3[g(e_{aq}^-) + g(H)] + g(OH) \qquad (7.186)$$

$$G(Fe^{3+})_{-O_2} = 2g(H_2O_2) + g(e_{aq}^-) + g(H) + g(OH) \qquad (7.187)$$

$$G(Ce^{3+}) = 2g(H_2O_2) + g(e_{aq}^-) + g(H) - g(OH) \qquad (7.188)$$

and

$$g(e_{aq}^-) + g(H) = 0.5[G(Fe^{3+})_{+O_2} - G(Fe^{3+})_{-O_2}]$$

$$g(OH) = 0.5[G(Fe^{3+})_{-O_2} - G(Ce^{3+})]$$

$g(H_2O_2)$ can be found by substituting the radical yields in one of the equations 7.186 to 7.188, and $g(H_2)$ by substituting in the material balance equation (Table 7.8). The quantities $g(e_{aq}^-)$ and $g(H)$ cannot be determined separately using the strongly acid ferrous and ceric sulfate systems, although they are readily distinguished in neutral and basic solutions by choice of suitable scavengers (cf. Table 7.8 and refs. 2, 3). In choosing a scavenger it is not essential that each primary radical react completely with a single solute. However, rate constants must be available for any competing reactions so that corrections can be applied, and it is essential that the radiolysis mechanism be thoroughly understood. In practice, results from a wide variety of systems are considered when attempting to arrive at definitive values of the primary yields (e.g., Table 7.4) so that experimental and interpretative errors are minimized.

Scavenger concentrations used in estimating primary yields are generally of the order of $1 \, mol \, m^{-3}$, since they need to be high enough to scavenge all reactive species and yet not so high that significant scavenging occurs within the spurs and tracks. The optimum range of concentration will depend on the rate constants for the solute–radical reactions and will vary from solute to solute; Buxton (53, 54) has suggested that interspur scavenging becomes significant when $k(\text{radical} + \text{solute})$ [solute] is greater than $10^7 \, s^{-1}$. Such scavenging is unavoidable at low pH and is the reason for the higher radical yields observed with strongly acid solutions (at pH 0.46, $k(e_{aq}^- + H^+)[H^+] = 8.0 \times 10^9 \, s^{-1}$). Similar increases in radical yields are to be expected in the presence of relatively high concentrations of hydroxyl radical scavengers (cf. 161).

Dichromate Systems

Several acid aqueous systems containing dichromate have been developed as chemical dosimeters for the range of absorbed dose and dose rates (0.2 to 40 kGy, at dose rates from 1 to $600 \, Gy \, s^{-1}$) of interest in radiation processing (e.g., 162–164). Typically, the dosimeter solutions contain 0.1 to $2.5 \, mol \, m^{-3}$

TABLE 7.8 Systems for Measuring Molecular and Radical Yields in Aqueous Solutions

System	pH Range	Yield Equation[a]
Material balance equations		$\begin{cases} 2g(H_2) + g(e_{aq}^-) + g(H) = 2g(H_2O_2) + g(OH) + 3g(HO_2) \\ g(-H_2O) = 2g(H_2) + g(e_{aq}^-) + g(H) - g(HO_2) = 2g(H_2O_2) \\ \qquad + g(OH) + 2g(HO_2) \end{cases}$
Boiling water	Acid to basic	$G(H_2) = 2G(O_2) = g(H_2)$
Bromide (0.001 to 10 mol m^{-3})	Acid or neutral	
Oxygen-free		$G(H_2) = g(H_2)$
+ Oxygen		$G(H_2O_2) = g(H_2O_2) + 0.5[g(e_{aq}^-) + g(H) - g(OH) + g(HO_2)]$
Carbon monoxide (0.15 to 0.65 mol m^{-3})	Acid to basic	$\begin{cases} G(H_2) = g(H_2) \\ G(CO_2) = g(OH) \\ G(H_2O_2) = g(H_2O_2) + 0.5[e_{aq}^- + g(H) + g(OH) + g(HO_2)] \end{cases}$
+ Oxygen (0.15 to 0.35 mol m^{-3})		
Ceric sulfate (0.01 to 10 mol m^{-3})	Acid	
With or without oxygen		$G(Ce^{3+}) = 2g(H_2O_2) + g(e_{aq}^-) + g(H) - g(OH) + g(HO_2)$
Oxygen-free		$G(O_2) = g(H_2O_2) + g(HO_2)$
Ceric sulfate + thallous sulfate	Acid	$G(Ce^{3+}) = 2g(H_2O_2) + g(e_{aq}^-) + g(H) + g(OH) + g(HO_2)$
or formic acid + oxygen		
Deuterium, oxygen-free	Neutral	$G(HD) = g(H)$
Ferrous sulfate (1 mol m^{-3}) + oxygen	Acid	$\begin{cases} G(Fe^{3+}) = 2g(H_2O_2) + 3[g(e_{aq}^-) + g(H) + g(HO_2)] + g(OH) \\ G(H_2) = g(H_2) \end{cases}$
Ferrous sulfate (0.01 mol m^{-3}) with or without	Acid	$G(Fe^{3+}) = g(e_{aq}^-) + g(H) + g(OH) + g(HO_2)$
oxygen; rapid analysis		
Ferrous sulfate (1 mol m^{-3}), oxygen-free	Acid	$\begin{cases} G(Fe^{3+}) = 2g(H_2O_2) + g(e_{aq}^-) + g(H) + g(OH) + 3g(HO_2) \\ G(H_2) = g(H_2) + g(e_{aq}^-) + g(H) \end{cases}$

Ferrous sulfate ($1\,\text{mol m}^{-3}$) + cupric sulfate ($10\,\text{mol m}^{-3}$)   Acid

  With or without oxygen $G(\text{Fe}^{3+}) = 2g(\text{H}_2\text{O}_2) - g(\text{e}_{\text{aq}}^-) - g(\text{H}) + g(\text{OH}) - g(\text{HO}_2)$

  Oxygen-free $G(\text{O}_2) = g(\text{HO}_2)$

Ferrocyanide ($5\,\text{mol m}^{-3}$) + oxygen[b]   Acid or basic $G(\text{Fe(CN)}_6^{3-})_{\mu s} = g(\text{OH})$

Water + hydrogen, oxygen-free[b]   Neutral or basic $G(\text{e}_{\text{aq}}^-)_{\mu s} = g(\text{e}_{\text{aq}}^-)[\,+ g(\text{H}) + g(\text{OH})$, if strongly basic]

Water + ethanol ($10\,\text{mol m}^{-3}$), oxygen-free[b]   Neutral or basic $G(\text{e}_{\text{aq}}^-)_{\mu s} = g(\text{e}_{\text{aq}}^-)[\,+ g(\text{H})$, if strongly basic]

Acrylamide ($0.1\,\text{mol m}^{-3}$), oxygen-free   Acid to basic $G(\text{H}_2\text{O}_2) = g(\text{H}_2\text{O}_2)$

Formic acid or formate ($1\,\text{mol m}^{-3}$), or oxalic acid   Acid to basic

  or oxalate ($50\,\text{mol m}^{-3}$) + oxygen

$$\left\{ \begin{array}{l} G(\text{H}_2) = g(\text{H}_2) \\ G(\text{H}_2\text{O}_2) = g(\text{H}_2\text{O}_2) + 0.5[g(\text{e}_{\text{aq}}^-) + g(\text{H}) + g(\text{OH}) + g(\text{H}_2\text{O}_2)] \\ G(-\text{O}_2) = 0.5[g(\text{e}_{\text{aq}}^-) + g(\text{H}) + g(\text{OH}) - g(\text{HO}_2)] \\ G(\text{CO}_2)_{\text{formic}} = g(\text{OH}) \\ G(\text{CO}_2)_{\text{oxalic}} = 2g(\text{OH}) \\ G(-\text{oxalic acid}) = g(\text{OH}) \end{array} \right.$$

Formic acid ($1\,\text{mol m}^{-3}$), oxygen-free   Acid $G(\text{H}_2) = g(\text{H}_2) + g(\text{e}_{\text{aq}}^-) + g(\text{H})$

2-Propanol ($25\,\text{mol m}^{-3}$) + H_2O_2 ($1\,\text{mol m}^{-3}$), oxygen-free   Neutral $G(\text{H}_2) = g(\text{H}_2) + g(\text{H})$

2-Propanol ($25\,\text{mol m}^{-3}$) + N_2O (0.01 to $0.1\,\text{mol m}^{-3}$),   Neutral $\left\{ \begin{array}{l} G(\text{H}_2) = g(\text{H}_2) + g(\text{H}) \\ G(\text{N}_2) = g(\text{e}_{\text{aq}}^-) \end{array} \right.$

  oxygen-free

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[a] The equations refer to initial yields, since accumulations of radiolysis products may alter the stoichiometry.
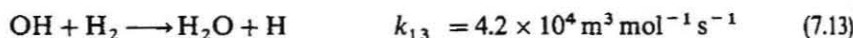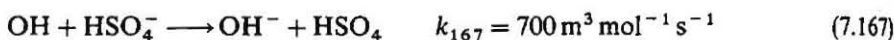
[b] Product yield measured by pulse radiolysis at microsecond times after the pulse; hydrated electron yields corrected for any decay prior to the measurement.

$Cr_2O_7^{2-}$ (either silver dichromate or a mixture of silver and potassium dichromates) in 100 mol m^{-3} $HClO_4$ solution. Loss of dichromate upon irradiation is followed spectrophotometrically at either 440 nm ($\varepsilon = 46 \text{ m}^2 \text{ mol}^{-1}$) or 350 nm ($\varepsilon = 312.2 \text{ m}^2 \text{ mol}^{-1}$); $G(-Cr_2O_7^{2-}) = 0.039 \,\mu\text{mol J}^{-1}$ (164).

Six electrons are necessary to reduce $Cr_2O_7^{2-}$ [Cr(VI)] to two Cr^{3+} ions, and

$$G(-Cr_2O_7^{2-}) = \tfrac{1}{6}[2g(H_2O_2) + g(H) - g(OH)] \tag{7.189}$$

indicating that the mechanism is similar to that shown for the reduction of ceric ion to cerous ion. In this case also, the rate constant for reaction between the reduced species (Cr^{3+}) and OH is relatively low and other OH scavengers can compete successfully for OH. In the dichromate systems these include sulfuric acid and molecular hydrogen (162):

$$OH + HSO_4^- \longrightarrow OH^- + HSO_4 \qquad k_{167} = 700 \text{ m}^3 \text{ mol}^{-1}\text{s}^{-1} \tag{7.167}$$

$$OH + H_2 \longrightarrow H_2O + H \qquad k_{13} = 4.2 \times 10^4 \text{ m}^3 \text{ mol}^{-1}\text{s}^{-1} \tag{7.13}$$

The perturbing effect of sulfuric acid is avoided by using perchloric acid to control pH, and the influence of molecular hydrogen and traces of other OH scavengers is avoided by adding silver ion so that OH is rapidly replaced by the less reactive and more specific intermediate Ag(I).
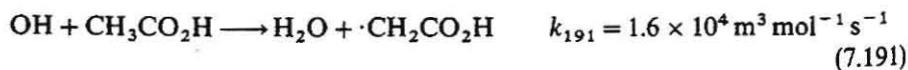
$$OH + Ag^+ \longrightarrow AgOH^+ \qquad k_{190} = 1.4 \times 10^7 \text{ m}^3 \text{ mol}^{-1}\text{s}^{-1} \tag{7.190}$$
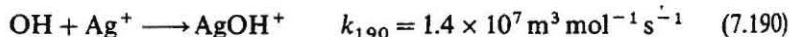
In the absence of silver ion, $G(-Cr_2O_7^{2-})$ increases with dose rate over the range 20 to 500 Gy s^{-1} due to the buildup of OH to sufficient levels for the reaction

$$2OH \longrightarrow H_2O_2 \qquad k_{47} = 5.5 \times 10^6 \text{ m}^3 \text{ mol}^{-1}\text{s}^{-1} \tag{7.47}$$
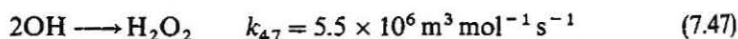
to become important (162).

Organic solutes, for example, 100 mol m^{-3} acetic acid (164, 165), may be added deliberately to increase $G(-Cr_2O_7^{2-})$ by replacing OH by an organic radical that is oxidized by dichromate ion:

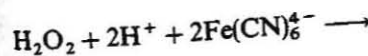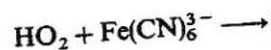$$OH + CH_3CO_2H \longrightarrow H_2O + \cdot CH_2CO_2H \qquad k_{191} = 1.6 \times 10^4 \text{ m}^3 \text{ mol}^{-1}\text{s}^{-1} \tag{7.191}$$
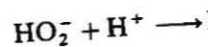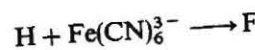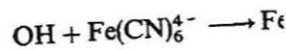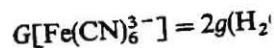
Ferrocyanide–Ferricyanide System

The ferrous sulfate system played an important role in the development of the radiation chemistry of aqueous solutions but is limited to acid conditions. To extend the experimental range to higher pH, a variety of other inorganic redox systems have been investigated. One of the earliest of these was the ferrocyanide–ferricyanide system in which ferrous and ferric ions are stabilized by formation of

a complex ion with cyanide; the con
acid to strongly basic solution.

On the basis of the standard elect
the following steps are thermodyn
ferrocyanide, $Fe(CN)_6^{4-}$, and ferric
cases rate constant measurements
that they are rapid reactions.

$$OH + Fe(CN)_6^{4-} \longrightarrow Fe$$

$$e_{aq}^- + Fe(CN)_6^{3-} \longrightarrow F$$

$$H + Fe(CN)_6^{3-} \longrightarrow F$$

$$HO_2 + Fe(CN)_6^{4-} \longrightarrow F$$

$$HO_2^- + H^+ \longrightarrow$$

$$HO_2 + Fe(CN)_6^{3-} \longrightarrow$$

$$H_2O_2 + 2H^+ + 2Fe(CN)_6^{4-} \longrightarrow$$

The E^0 values are for acid or neu
sign in basic solutions; in strong
with ferrocyanide with a rate cor
than 1% of the rate at which (
solutions containing concentrat
saturated with air of oxygen
ferrocyanide is oxidized by OH
three and two equivalents of fe

$$G[Fe(CN)_6^{3-}] = 2g(H_2$$
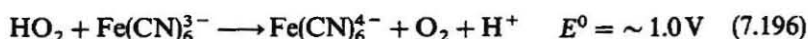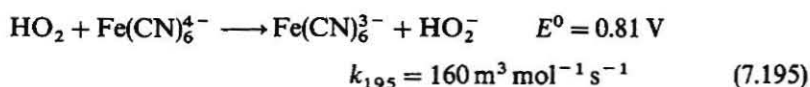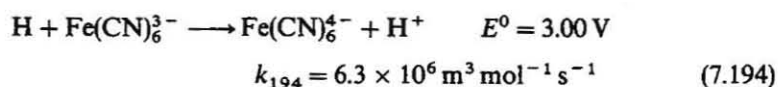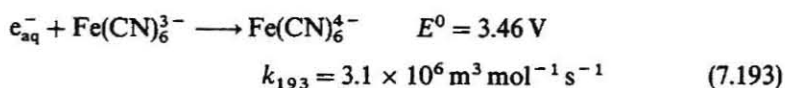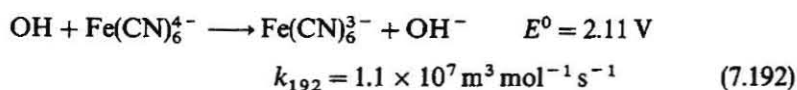
The reactions with HO_2 a
observed within a few micros
about oxidation and

$G[$

a complex ion with cyanide; the complex ions are stable over the pH range from acid to strongly basic solution.

On the basis of the standard electrode potentials for the reactions (Table A3.4), the following steps are thermodynamically feasible when solutions containing ferrocyanide, $Fe(CN)_6^{4-}$, and ferricyanide, $Fe(CN)_6^{3-}$, are irradiated; in several cases rate constant measurements have confirmed that the reactions occur, and that they are rapid reactions.

$$OH + Fe(CN)_6^{4-} \longrightarrow Fe(CN)_6^{3-} + OH^- \qquad E^0 = 2.11\,V$$
$$k_{192} = 1.1 \times 10^7\,m^3\,mol^{-1}\,s^{-1} \qquad (7.192)$$

$$e_{aq}^- + Fe(CN)_6^{3-} \longrightarrow Fe(CN)_6^{4-} \qquad E^0 = 3.46\,V$$
$$k_{193} = 3.1 \times 10^6\,m^3\,mol^{-1}\,s^{-1} \qquad (7.193)$$

$$H + Fe(CN)_6^{3-} \longrightarrow Fe(CN)_6^{4-} + H^+ \qquad E^0 = 3.00\,V$$
$$k_{194} = 6.3 \times 10^6\,m^3\,mol^{-1}\,s^{-1} \qquad (7.194)$$

$$HO_2 + Fe(CN)_6^{4-} \longrightarrow Fe(CN)_6^{3-} + HO_2^- \qquad E^0 = 0.81\,V$$
$$k_{195} = 160\,m^3\,mol^{-1}\,s^{-1} \qquad (7.195)$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \qquad (7.144)$$

$$HO_2 + Fe(CN)_6^{3-} \longrightarrow Fe(CN)_6^{4-} + O_2 + H^+ \qquad E^0 = \sim 1.0\,V \quad (7.196)$$

$$H_2O_2 + 2H^+ + 2Fe(CN)_6^{4-} \longrightarrow 2Fe(CN)_6^{3-} + 2H_2O \qquad E^0 = 1.09\,V \quad (7.197)$$

The E^0 values are for acid or neutral solutions and change in magnitude and even sign in basic solutions; in strongly basic solution OH ionizes to O^-, which reacts with ferrocyanide with a rate constant less than $7 \times 10^4\,m^3\,mol^{-1}\,s^{-1}$, that is, less than 1% of the rate at which OH reacts with ferrocyanide. In neutral or acid solutions containing concentrations of the order of $10\,mol\,m^{-3}$ ferrocyanide and saturated with air of oxygen, e_{aq}^- and H are scavenged by oxygen, and ferrocyanide is oxidized by OH, HO_2, and H_2O_2, the HO_2 and H_2O_2 oxidizing three and two equivalents of ferrocyanide, respectively. Then,

$$G[Fe(CN)_6^{3-}] = 2g(H_2O_2) + 3[g(e_{aq}^-) + g(H) + g(HO_2)] + g(OH) \qquad (7.198)$$

The reactions with HO_2 and H_2O_2 are relatively slow and if the system is observed within a few microseconds of a brief radiation pulse, only OH brings about oxidation and
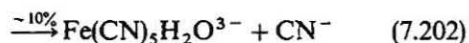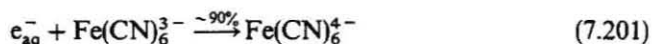
$$G[Fe(CN)_6^{3-}]_{\mu s} = g(OH) \qquad (7.199)$$

This is the basis for the use of ferrocyanide solutions as dosimeters in pulse radiolysis. The yield of ferricyanide can be approximately doubled by saturating the solution with nitrous oxide to convert e_{aq}^- to OH, when

$$G[Fe(CN)_6^{3-}]_{N_2O, \mu s} \simeq g(e_{aq}^-) + g(OH) \tag{7.200}$$

In the N_2O-saturated solutions, hydrogen atoms are scavenged by both ferrocyanide and the radiation-produced ferricyanide so that Eq. 7.200 may not be strictly true; the extent of any back reaction will depend on the ferrocyanide concentration and the absorbed dose.

The radiolysis of ferrocyanide and ferricyanide solutions is appreciably more complex than the radiolysis of ferrous and ferric solutions both because of the greater pH range covered and because additional reactions become possible as the complexity of the solute is increased (166). Reaction of hydrated electrons with ferricyanide for example, gives not only ferrocyanide (Eq. 7.193) but also about 10% of a pentacyano complex formed by loss of a CN^- ion,

$$e_{aq}^- + Fe(CN)_6^{3-} \xrightarrow{\sim 90\%} Fe(CN)_6^{4-} \tag{7.201}$$

$$\xrightarrow{\sim 10\%} Fe(CN)_5H_2O^{3-} + CN^- \tag{7.202}$$

Radical and molecular yields determined using oxygen-free ferrocyanide and ferricyanide systems are therefore rather less certain than those estimated using the simpler ferrous and ceric sulfate systems, though the complex ions cover a range of pH that is not accessible using the simple ions.

Aqueous solutions of many other transition-metal complexes (e.g., Ag, Cd, Co, Cr, Cu, Pt, Rh, Ru, and the actinides) have been irradiated (see, for example, refs. 107, 167, and the references cited therein), both for their intrinsic interest and for the light they shed on the mechanisms of biological processes.

Halide and Pseudohalide Ions

The halide ions (X^-) are inert toward e_{aq}^- and H but undergo rapid electron-transfer-type reactions with OH to give products (Cl_2^-, Br_2^-, and I_2^-), which incorporate a second halide ion and are stoichiometrically equivalent to $X + X^-$:

$$OH + X^- \xrightarrow{X^-} X_2^- + OH^- \tag{7.203}$$
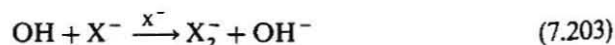
With chloride and bromide the reaction is more rapid in the presence of hydrogen ion, but with iodide it is independent of pH. Pulse radiolysis has shown that the reaction with chloride takes place through the following steps

(168):

$$OH + Cl^- \longrightarrow ClOH^- \qquad k_{129} = 4.3 \times 10^6\,m^3\,mol^{-1}\,s^{-1} \quad (7.129)$$

$$ClOH^- + H^+ \longrightarrow Cl + H_2O \qquad k_{204} = 2.1 \times 10^7\,m^3\,mol^{-1}\,s^{-1} \quad (7.204)$$

$$Cl + Cl^- \longrightarrow Cl_2^- \qquad k_{160} = 2.1 \times 10^7\,m^3\,mol^{-1}\,s^{-1} \quad (7.160)$$
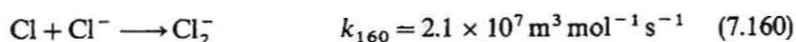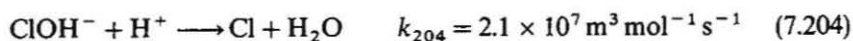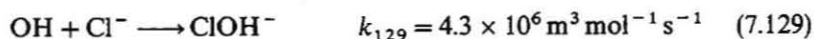
each of which is reversible. The authors estimate that in the Fricke dosimeter solution containing $1\,mol\,m^{-3}\,Cl^-$ all OH, including those formed by reaction of H_2O_2 with Fe^{2+} (Eq. 7.114), enter into reactions 7.129 and 7.204 to form Cl, and that 81% of the chlorine atoms so formed react directly with ferrous ion (Eq. 7.158) while 19% form Cl_2^-, which also oxidizes ferrous ion,

$$Cl_2^- + Fe^{2+} \longrightarrow 2Cl^- + Fe^{3+} \qquad (7.205)$$

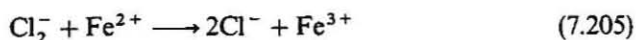The Cl_2^- ion absorbs strongly at 340 nm ($\varepsilon_{340} = 880\,m^2\,mol^{-1}$) and is readily detected when acidified chloride solutions are pulse irradiated. The characteristic absorption is also detected, though less strongly, immediately following pulse irradiation of more concentrated $> 10^3\,mol\,m^{-3}$) neutral chloride solutions where the higher pH precludes formation of Cl_2^- via reaction 7.204, and it has been suggested that this demonstrates the presence of H_3O^+ in the spurs where the rapid formation of Cl_2^- is presumed to take place (77,118). Hamill and his coworkers (78,169) have offered an alternative explanation, suggesting that formation of Cl_2^- in concentrated neutral chloride solutions is not the result of OH scavenging in an acid spur, but rather the result of H_2O^+ (i.e., positive hole) scavenging by Cl^-,

$$H_2O^+ + Cl^- \longrightarrow H_2O + Cl \qquad (7.206)$$
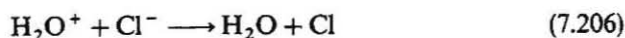
which competes with

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \qquad (7.20)$$
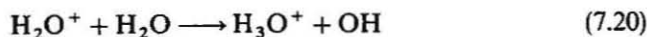
The competition is described by the empirical expression

$$P = \frac{G(Cl_2^-)}{G^0} = \frac{\sigma_1[Cl^-]}{\sigma_1[Cl^-] + \sigma_2} \qquad (7.207)$$

where P is the probability of electron transfer from Cl^- to H_2O^+, $G(Cl_2^-)$ the observed yield, and G^0 the yield of H_2O^+ available to react with Cl^-; $\sigma_1[Cl^-]$ and σ_2 are the relative probabilities that H_2O^+ will react with Cl^- or undergo an alternative first-order or pseudo-first-order reaction (i.e., reaction 7.20); rate constants are not used because the processes described take place within an extremely short time of energy deposition, far too rapidly for any

diffusion-related processes to occur. Applied to the data of Anbar and Thomas (77, 118), this expression gives $\sigma_1/\sigma_2 = 0.38$ and $G^0 = 0.39 \,\mu\text{mol J}^{-1}$; the latter may be compared with radiation-chemical yields of about $0.5 \,\mu\text{mol J}^{-1}$ for the earliest yields of e_{aq}^- detected by picosecond pulse radiolysis. This approach has given consistent results when applied by Hamill to positive ion (i.e., hole) trapping by anions other than Cl^-, including anions such as acetate and oxalate which do not react rapidly with e_{aq}^-, H, or OH and which must, therefore, be reacting with some other reactive species.

Dimerization of the species produced by reaction of OH with halide ions produces the corresponding halogen (X_2), or an ion derived from it (X_3^-),

$$2X_2^- \longrightarrow X_2 + 2X^- \quad (\text{or } X_3^- + X^-) \tag{7.208}$$
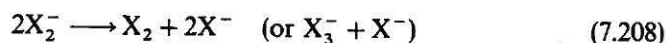
However, only low steady-state concentrations of halogen are produced when halide solutions are irradiated, and it is clear that back reactions with e_{aq}^- and H are occurring to reform halide ion, for example,

$$e_{aq}^- + X_2 \longrightarrow X_2^- \tag{7.209}$$

$$e_{aq}^- + X_2^- \longrightarrow 2X^- \tag{7.210}$$

$$H + X_2 \longrightarrow H^+ + X^- + X \tag{7.211}$$
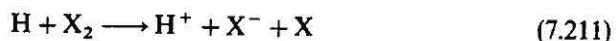
The rate constants for these reactions are high and, with reaction 7.203, they serve to protect the molecular hydrogen formed upon irradiation from radical attack. Thus, $g(H_2)$ can be determined by measuring the yield of hydrogen when dilute (10^{-3} to $10 \,\text{mol m}^{-3}$) solutions of Br^- or I^- in deaerated acid, or neutral, solution are irradiated; under these conditions $G(H_2) = g(H_2)$.

In the presence of air or oxygen, e_{aq}^- and H form HO_2 which reacts

$$2HO_2 \longrightarrow H_2O_2 + O_2 \tag{7.57}$$

or

$$HO_2 + Br_2 \longrightarrow H^+ + Br^- + Br + O_2 \tag{7.212}$$
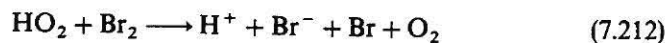
so that when dilute aerated bromide solutions are irradiated

$$G(H_2O_2) = g(H_2O_2) + 0.5[g(e_{aq}^-) + g(H) - g(OH) + g(HO_2)] \tag{7.213}$$

Solutions of hydrogen peroxide, containing higher concentrations than are normally produced by irradiation, are broken down by a chain reaction in the presence of bromide; the chain-propagating steps are reaction 7.212 and

$$Br + H_2O_2 \longrightarrow HO_2 + H^+ + Br^- \tag{7.214}$$
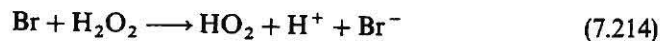
The thiocyanate ion behaves like the halide ions in giving a dimeric

radical–ion upon reaction with OH,

$$CNS^- + OH \longrightarrow CNS + OH^- \tag{7.215}$$

$$CNS + CNS^- \longrightarrow (CNS)_2^- \qquad k_{216} = 1.1 \times 10^7 \, m^3 \, mol^{-1} \, s^{-1} \tag{7.216}$$
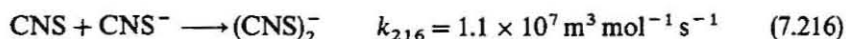
The dimer absorbs strongly at 472 nm ($\varepsilon_{472} = 758 \pm 6 \, m^3 \, mol^{-1}$; 161) and use is made of this fact in pulse radiolysis experiments for dosimetry, and also to determine hydroxyl radical rate constants by the competition kinetic method (125). As with the chloride ion, the reaction involves the intermediate formation of a hydroxyl radical adduct, $(CNSOH)^-$, which has been observed by pulse radiolysis (170). The dimer disappears by a second-order reaction that may be

$$2(CNS)_2^- \longrightarrow 2CNS^- + (CNS)_2 \tag{7.217}$$

although the complete radiolysis mechanism has not been established. Final products from the radiolysis of relatively concentrated thiocyanate solutions ($> 100 \, mol \, m^{-3}$) include CN^-, SO_4^{2-}, and sulfur in aerated solution, and CN^-, H_2S, and sulfur in the absence of oxygen; cyanide and sulfur are formed by direct action of radiation on the solute at higher thiocyanate concentrations (171).

The cyanide ion also reacts with OH to give an adduct, although in this instance the adduct reacts with water and rearranges to give the formamide radical, $\cdot CONH_2$, which is also formed by reaction of OH with formamide, $HCONH_2$ (172):
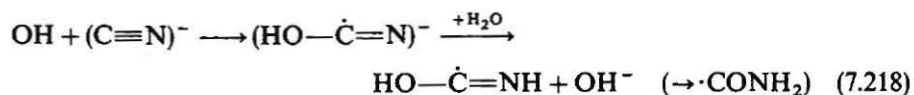
$$OH + (C\equiv N)^- \longrightarrow (HO-\dot{C}=N)^- \xrightarrow{+H_2O}$$
$$HO-\dot{C}=NH + OH^- \quad (\rightarrow \cdot CONH_2) \tag{7.218}$$

Formamide and cyanate, which are major products, can be formed by disproportionation of the formamide radicals,

$$2 \cdot CONH_2 \longrightarrow HCONH_2 + HCNO \tag{7.219}$$
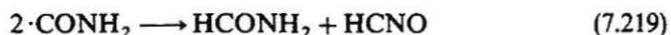
Other products include the amino acids glycine and alanine (173).

Dimeric radical–ions similar to Cl_2^- and $(SCN)_2^-$ are also formed when hydroxyl radicals react with HS^- and thiols.

Other Solutes

Table 7.9, which is very far from complete, lists data for a number of other inorganic compounds that have been irradiated in aqueous solution. Only major products are given and for more detailed information the reader is referred to the references and to the current literature; the radiation-chemical yields listed

TABLE 7.9   Radiolysis of Aqueous Solutions

Solute	Conditions	Products and Yieds (μmol J^{-1})	Ref.
NH_3	$+ O_2$	Formation NO_2^- via $NH_3 + OH \rightarrow NH_2 + H_2O$; NH_4^+ unreactive.	174
N_2H_4	O_2-free	(pH 6); NH_3, 0.30; N_2, 0.28	175
	$+ O_2$	(pH < 8); H_2, N_2, H_2O_2	176
H_2S	O_2-free	$G(S) = 0.5[g(H) + g(OH)]$; $G(H_2) = g(H_2) + g(H)$	177 178
	$+ O_2$	Sulfur formed by a short chain reaction; $G(S)$ 0.8 to 2.4 under conditions used; SO_4^{2-} formed in lower yield.	
H_2O_2		Decomposed to $O_2 + H_2O$ by chain reaction; $G(O_2) \propto [H_2O_2]^{0.5}$ (dose rate)$^{-0.5}$.	179
CO	O_2-free	(pH ~ 0.7); H_2, 0.10; H_2O_2, 0; CO_2, 0.27; HCHO, 0.05; HCO_2H, 0.04; OHCCHO, 0.03. In basic solutions HCO_2^- is formed by a short-chain reaction, G ~ 4.6.	180
	$+ O_2$	(pH 6.9); H_2, 0.053; H_2O_2, 0.340; CO_2, 0.225; $-CO$, 0.224; $-O_2$, 0.260.	181
CO_2		Primary products formic acid and aldehydes, with oxalic acid and ethanediol as secondary products; yields depend on pH and total dose.	182
Arsenite (H_3AsO_3)	$+ O_2$	(pH 1.4); arsenate (H_3AsO_4), 0.33; H_2O_2, 0.44; As(III) oxidized by OH and HO_2.	183
BH_4^-	O_2-free	$G(H_2) = 0.70$ (immediate) $+ 0.65$ (released during several hours). $OH + BH_4^- \rightarrow OH^- + BH_4$ (OH is converted to a reducing species).	184
NO_2^-	O_2-free	NO_2^- oxidized to NO_3^- by H_2O_2; H, OH, and e_{aq}^- react with NO_2^- but reaction products reform NO_2^-.	185
NO_3^-	O_2-free	H_2O_2, 0.077; NO_2^-, 0.03. NO_2^- and O_2 formed by direct action at high ($> 10^3$ mol m^{-3}) concentrations.	186 187
Dihydrogen phosphate ion ($H_2PO_4^-$)		Acts as a proton donor to convert e_{aq}^- to H in the pH range 5–7.	120
Phosphite (H_3PO_3)	$+ O_2$	Phosphate formed by short-chain reaction with yields up to about 3 μmol J^{-1}.	188
Borates, OH^-, CO_3^{2-}, ClO_4^-, PO_4^{3-}, SO_4^{2-}		Little permanent change when irradiated as dilute solutions.	

generally refer to low-LET radiation, that is, electron or γ radiation or high-energy x rays. Relatively little work has been carried out using nonaqueous inorganic solvents, and only slightly more using such organic solvents as alcohols and amines, although the properties of solvated electrons in nonaqueous solvents have been investigated quite extensively.

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