1.1 General

If the number of international meetings and symposia together with the frequency of review articles are to be taken as a valid criterion of activity and progress in any field of science, then radiation chemistry, in general, and of aqueous solutions in particular may be counted as one of the most active areas of research in physical science. This is clear from the number of review articles that appeared on radiation chemistry during the last twenty five years in 'Annual Review of Physical Chemistry'.

Radiation chemistry covers the study of the chemical changes produced in a system by the absorption of ionizing radiation. Short wavelength electromagnetic radiations, X-rays, high energy charged particles and \( \gamma \) radiations from radioactive nuclei are the examples of ionizing radiations.

Electromagnetic radiations in the ultraviolet and visible region of the spectrum, on the other hand, initiate chemical reactions, mainly via excited molecules. Such chemical reactions initiated by non-ionizing electromagnetic radiations form the subject matter of photochemistry.

Energy associated with ionizing particle or photon
is much greater than the energy of a non-ionizing photon. In a photochemical reaction one photon excites only one molecule which gives rise to products whereas in radiation chemistry one particle or photon can ionize or excite a large number of molecules which further react to give products. As a result the yields of the products in the former process are small and simpler as compared with those in the latter.

The first radiation induced chemical reaction was the decomposition of water in the presence of radioactive material reported by Giesel\(^1\) five years after the discovery of radium (1898). Debierne\(^2\) suggested three different factors leading to this reaction: (i) radiation emanation, (ii) the decay products of the radioactive material, and (iii) the action of the radiation itself. He conducted controlled experiments with a sealed ampoule of radium chloride as a source of radiation. He kept it in distilled water. The increase in pressure due to evolved gases was found to be proportional to time, therefore he concluded that the last factor was the most probable one.

Thus, the origin of radiation chemistry dates back to the beginning of this century. A study of the radiolysis of water assumes particular importance in view of the facts that (i) water is a major constituent of all living matter.
(ii) It is an ideal medium for many chemical and biological systems.

(iii) Water is the coolant widely used in nuclear reactors. Hence an understanding of the effects of radiation on water is very valuable to the development of nuclear technology.

In the early stages, the radiation sources available were of feeble intensity, being mostly sealed sources of radium. The studies were more often of a descriptive type. But the urgent need to know the precise behaviour of water in a strong radiation field during World War II and since then, efforts were directed to preparing powerful and suitably designed radiation sources and fast and precise detection techniques. As a result of this, significant development of the subject occurred during last three decades. Various advancements coupled with pulse radiolysis technique, a powerful tool for the deposition of sufficient energy within a few nano or even picoseconds, provided a base for a quantitative explanation of various phenomena. Pulse radiolysis enables the radiation chemist to separate the process of the formation of radiolysis products from their decay. The pulse radiolysis data help in establishing the rate constants and mechanisms of various decay processes, happening with the added solutes, both organic and inorganic, the creation of the reactants being completed.
For the interpretation of chemical behaviour of various systems under the influence of radiation it is quite essential to know about the elementary processes that take place during the interaction of radiation with matter and in particular with water.

1.2 Effects of energy transfer

\( \gamma \)-Irradiation produces excited and ionized atoms and molecules since the energy absorbed is transferred to electrons and dissipated along the path of these particles similar to the interaction of charged particles. When a \( \gamma \) photon interacts with a molecule the most common phenomenon is the ejection of a Compton electron and during the process of thermalization i.e. deceleration to energy corresponding to room temperature (\( \approx 0.025 \text{ eV} \)) the electron excites or ionizes many of the molecules lying along its path. For about every 30 eV of energy expended (by either primary or secondary electrons) one ion-pair is produced. As about only 15 eV are needed to ionize a molecule the remaining 15 eV are left over as the excitation energy of ion pairs. Thus in its deceleration to room temperature a 440 keV electron produces about 15,000 ion pairs and excited molecules.

The ionization effects have been discussed by Burton\(^3\). According to him the ionization process can be represented...
schematically as

\[ A \rightarrow A^+ + e^- \]  \hspace{1cm} \text {.. (1)}

The fate of the electron depends on the nature of the system. However, one important possibility is the recombination of the ion and the electron resulting in the formation of an excited particle.

\[ A^+ + e^- \rightarrow A^* \] \hspace{1cm} \text {.. (2)}

Alternatively the ions may lead to ion-molecule reactions. It is also possible that some of the excited molecules may be formed directly

\[ A \rightarrow A^* \] \hspace{1cm} \text {.. (3)}

The excited molecules may react according to one of the schemes shown below:

\[ A^* \quad \text{free radicals by bond rupture} \] \hspace{1cm} \text {.. (4a)}

\[ A^* \quad \text{new molecular species by rearrangement} \] \hspace{1cm} \text {.. (4b)}

Another possible reaction is

\[ M + e^- \rightarrow M^- \] \hspace{1cm} \text {.. (5)}

where \( M \) may be identical with \( A \) or may be any atom or molecule with sufficient electron affinity. The fate of \( M^- \), if it is formed, depends upon its own stability and various potential energy relationships within the whole system.
Excited states are produced when electrons in atoms and molecules are raised to higher energy levels. The overall result of the absorption of any type of radiation by matter is, thus, the formation of tracks of excited and ionized species. These species will, in general, be the same regardless of the type or energy of the radiation and hence all ionizing radiations will give rise to similar chemical effects. However, they lose energy in matter at different rates and consequently form tracks that may be densely or sparsely populated with the active species. The differences observed in the chemical effects of radiations in the quantities or relative yields of the chemical products formed arise from the different density of active species in the particle tracks. Electrons ejected by ionization may themselves be sufficiently energetic to produce further ionization and excitation. If the energy of these secondary electrons is relatively small, less than about 100 eV, their range in liquid or solid materials will be short and any secondary ionization may be produced will be only close to the original site of primary ionization, forming there a small cluster or spur of excited and ionized species. For fast particles such as the secondary electrons formed when energetic γ-rays are absorbed in water and organic liquids, Samuel and Magee calculated that the spurs occur at intervals of about $10^4 \text{Å}$ and that
they have an initial diameter of about 20 Å.

1.3 Absorption of radiation in water

One of the most critically studied systems in radiation chemistry of aqueous solutions is water itself. At sufficiently higher photon energies all the three processes (photoelectric effect, Compton scattering and pair-production) of energy transfer, take place simultaneously in water. However, it should be noted that every incident photon is not necessarily involved in one of these processes. The probability that a photon will interact at all by any process during its passage is given by the Lambert's law of absorption

\[ I = I_0 e^{-\mu x} \]  \hspace{1cm} (6)

where \( I_0 \) is the intensity of the incident radiation, \( I \) is the intensity of the radiation transmitted through a layer of thickness \( x \) of the absorber and \( \mu \) is total linear absorption coefficient, whereas \( \mu_{\text{total}} \) is given by

\[ \mu_{\text{total}} = \mu_{\text{Ph}} + \mu_{\text{Co}} + \mu_{\text{PP}} \]  \hspace{1cm} (7)

where \( \mu_{\text{Ph}}, \mu_{\text{Co}} \) and \( \mu_{\text{PP}} \) are the absorption coefficients for photoelectric effect, the Compton effect and the pair production respectively. The three different modes of energy transfer in water for different energies of the incident
photons are shown in Fig. 1.1. The Compton effect as can be seen from the Fig. 1.1 is the dominant process during the energy deposition in water by $\gamma$-rays from $^{60}$Co, the energy of the photons being 1.17 and 1.33 MeV. (Fig. 1.3a)

Thus, the agency which affects water during its $\gamma$-radiolysis is mostly the fast moving electrons produced by Compton effect. The fast moving electrons lose their energy gradually as they pass through water by the Coulombic interaction with the electrons of the water molecules. Depending on how close the ionizing particle passes and the velocity of its motion the electron in the shell of the water molecule, takes up a larger or smaller amount of energy and momentum. The consequence of this energy and momentum transfer
Fig. 1.3b - Atomic absorption coefficients for water: the total absorption coefficient (1), the photoelectric coefficient (2), the total Compton coefficient (3), and the pair production coefficient (4).
is the change in the position and motion of the electrons which may lead to excitation or ionization of water molecule depending upon energy acquired by the electron of the water molecule.

1.3.1 Time scale of events occurring in the water radiolysis

The overall process of producing chemical changes starting with the projection of high energy radiation in water or aqueous solution and terminating with the reestablishment of chemical equilibrium is usually divided into three stages: the physical stage, the physico-chemical stage and the chemical stage.

In the physical stage the energy is transferred to the water molecule during the time period of $10^{-16}$ s or less. The incident radiation produces directly or indirectly the ionization of water:

$$\text{H}_2\text{O} \rightarrow e^- + \text{H}_2\text{O}^+$$  \hspace{1cm} \text{(8)}

as well as excitation

$$\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^*$$  \hspace{1cm} \text{(9)}

The physico-chemical stage consists of processes which lead to the establishment of thermal equilibrium in the system. It occurs in the time scale of the order of $10^{-11}$ s or less. Electrons ejected in the ionization process become thermalized.
and hydrated.

\[ e^- \rightarrow e^\text{thermalized} \rightarrow e^\text{aq} \quad \ldots \ (10) \]

During the same time \( \text{H}_2\text{O}^+ \) ions undergo a proton transfer reaction with neighbouring water molecules

\[ \text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH} \quad \ldots \ (11) \]

It is obvious that the point of formation and the initial spatial distribution of \( \text{H}_3\text{O}^+ \) and \( \text{OH} \) are essentially the same but different from those for \( e^\text{aq}^- \).

The dissociation of the excited water molecules leads to the formation of the hydrogen atom and hydroxyl radical as the main products,

\[ \text{H}_2\text{O}^+ \rightarrow \text{H} + \text{OH} \quad \ldots \ (12) \]

It seems, however, that the contribution of excited water molecules to the formation of primary free radical products in water radiolysis is of less importance in comparison with that of the ions produced.

The chemical stage consists of diffusion away from the point of origin and chemical reaction of primary species (\( e^\text{aq}^- \), \( \text{H} \), \( \text{OH} \), \( \text{H}_3\text{O}^+ \)). This diffusion leads to the establishment of a chemical equilibrium. It begins in the spurs about \( 10^{-11} \) s after the passage of the radiation and in about \( 10^{-10} \) s in the bulk of the solution (see Table 1.1).
<table>
<thead>
<tr>
<th>Stage</th>
<th>Event</th>
<th>Duration Time/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>I Nuclear excitation</td>
<td>$\gamma$-traverses a nucleus</td>
<td>$10^{-23}$</td>
</tr>
<tr>
<td></td>
<td>Nucleon traverses a nucleus</td>
<td>$10^{-22}$, $10^{-21}$</td>
</tr>
<tr>
<td>II Atomic excitation</td>
<td>$\gamma$-traverses an atom/molecule</td>
<td>$10^{-12}$</td>
</tr>
<tr>
<td></td>
<td>Fast electron traverses a water molecule</td>
<td>$10^{-17}$, $10^{-12}$</td>
</tr>
<tr>
<td></td>
<td>Slow electron (thermal) traverses a molecule</td>
<td>$10^{-16}$</td>
</tr>
<tr>
<td>III Physico-chemical</td>
<td>Atomic vibration period</td>
<td>$10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>Excited atom loses vibrational energy</td>
<td>$10^{-13}$</td>
</tr>
<tr>
<td></td>
<td>Radical jump period</td>
<td>$10^{-12}$</td>
</tr>
<tr>
<td></td>
<td>Water dipole relaxation (formation of hydrated electron)</td>
<td>$10^{-11}$</td>
</tr>
<tr>
<td>IV Chemical reactions</td>
<td>Bimolecular reactions</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td></td>
<td>$e_{aq} + \text{solute} \rightarrow \text{Products}$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>Radical + Radical (H+H, OH+OH, H+OH) $\rightarrow$ Products</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>Fluorescence singlet state</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>Radical + solute (redox reactions) $\rightarrow$ Products</td>
<td>$10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>Triplet-state, phosphorescence</td>
<td>$10^{-3}$</td>
</tr>
</tbody>
</table>
1.3.2 **Spurs, blobs and tracks**

Energy deposition by passage of high energy radiation through water results in the formation of spurs, blobs and short tracks. These are the groups of the molecules within the liquid containing the initial products of energy deposition, namely ionized and excited molecules and electrons, in proportion to the energy deposited, the spurs representing an energy loss of about 6 to 100 eV, blobs about 100 to 500 eV and short tracks about 500 eV to 5 keV. The concentration of reactive species increases in the sequence spur, blob, short track and determines the proportion in which these species escape into the bulk of the liquid or react with one another (i.e. the relative proportion of radical and molecular products). The fraction of the total energy deposited in spurs, blobs and short tracks has been estimated for various types of radiation by Muzumdar and Magee\(^5\)\(^-\)\(^7\), who find that for \(^{60}\)Co \(\gamma\)-rays 64% of the absorbed energy is deposited in isolated spurs, 11% in blobs and 25% in short tracks. The spurs and blobs are pictured as more or less spherical collections of molecules and the short tracks as columnar zones containing a high proportion of ionized and excited molecules along the track of a fast secondary electron.

Spurs, blobs and short tracks produced by the absorption of
low linear energy transfer (LET) radiation are widely separated from one another along the tracks of the ionizing radiations, but those produced by high LET radiations will be close together and may coalesce to give a cylindrical track.\(^6\)\(^8\)

1.4 Radical and Molecular Products of Water Radiolysis

A number of very rapid processes take place before the spurs and tracks expand and dissipate by the normal process of diffusion. The net effect of these processes is to produce a relatively high concentration of radicals in the spurs and particle tracks soon after they are formed. The radical concentrations fall as the spurs and the tracks expand, but in the early stages the conditions favour the radical-radical reactions which result partly in the reformation of water molecules and partly in the formation of other molecular products, like hydrogen peroxide and molecular hydrogen

\[
\begin{align*}
H + H & \longrightarrow H_2 \quad \cdots \quad (13) \\
\text{OH} + \text{OH} & \longrightarrow \text{H}_2\text{O}_2 \quad \cdots \quad (14) \\
H + \text{OH} & \longrightarrow \text{H}_2\text{O}^* \longrightarrow \text{H}_2\text{O} \quad \cdots \quad (15)
\end{align*}
\]

Radicals that do not react, while the spurs and tracks are expanding escape into the bulk of the solution and represent the radical products.

The expression for radiation induced decomposition
of water

\[ \text{H}_2\text{O} \rightarrow e_{\text{aq}}^-, \text{H}, \text{OH}, \text{HO}_2, \text{H}_2\text{O}_2^+, \text{H}_2, \text{H}_2\text{O}_2 \quad (16) \]

represents the state in the irradiated water about \(10^{-9} \text{s}\) after the passage of high energy radiation, when the reactions in spurs, blobs and short tracks are practically terminated. These products are found in irradiated water irrespective of type and energy of radiation. The most recent values of their amounts per 100 eV of energy absorbed (i.e. the primary product yields) are given in Table 1.2\(^a\).

**Table 1.2** : Radical and molecular yields (\(G\) values) in irradiated water by \(\text{Co-}\gamma\)-rays in the pH range 4-9 \(^a\)

<table>
<thead>
<tr>
<th>Species</th>
<th>Yield (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_2\text{O})</td>
<td>4.3</td>
</tr>
<tr>
<td>(\text{H}_2)</td>
<td>0.45</td>
</tr>
<tr>
<td>(\text{H}_2\text{O}_2)</td>
<td>0.75</td>
</tr>
<tr>
<td>(e_{\text{aq}}^-)</td>
<td>2.8</td>
</tr>
<tr>
<td>(\text{H})</td>
<td>0.6</td>
</tr>
<tr>
<td>(\text{OH})</td>
<td>2.8</td>
</tr>
<tr>
<td>(\text{CHO}_2)</td>
<td>0.03</td>
</tr>
</tbody>
</table>
1.4.1 **Hydrated electron (e\textsubscript{aq})**

Until 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 the rate constants for reactions of the reducing species varied with the pH of the system, and that the reducing species formed in neutral solutions reacted at a different rate compared to hydrogen atoms formed by

\[
\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} \quad \text{(17)}
\]

or produced externally in a discharge and introduced into the solution\textsuperscript{9-14}. Relative reaction rate determinations made in the presence of chemically inert salts\textsuperscript{15,16} showed that the reducing species in neutral solutions behaved as if 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 reaction between ions of opposite charge decrease, and there is relatively little effect if one of the reactants is uncharged.

Czapski and Schwarz\textsuperscript{16} studied the effect of ionic strength upon following ratios of the rate constants
$k(R^* + O_2)/k(R^* + H_2O_2); \quad k(R^* + H^+)/k(R^* + H_2O_2)$

$k(R^* + NO_2)/k(R^* + H_2O_2)$ among which the first was found unaffected, the second decreased, and the third increased by increasing ionic strength. This observation was consistent with a negative charge on the radical $R^*$. Further analysis of their results showed that the charge corresponded to a single negative charge. The conclusion drawn from these, and many other experiments was that the major reducing species in neutral and basic solution is the hydrated electron and that in acid solutions this is rapidly converted to the hydrogen atom.

At the present time the hydrated electron is probably the most extensively studied of any radical species and its physical properties have been summarized in the Table 1.3.

1.4.2 Chemical behaviour

The hydrated electron, $e_{\text{aq}}^-$, is a reducing species with an unusually high electron donor capacity as its characteristic chemical behaviour. The reactions are usually single electron transfer processes which can be represented as

\[
AB + e_{\text{aq}}^- \rightarrow AB^-
\]

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow A + B^- & \quad \cdots (18a) \\
S & \rightarrow ABH + OH^- & \quad \cdots (18b) \\
\text{AB}^- & \rightarrow AB + S^- & \quad \cdots (18c) \\
\end{align*}
\]

\[
\text{AB}^2- \rightarrow AB + \text{AB}^2- & \quad \cdots (18d)
\]


Table 1.3: Physical properties of hydrated electron 
\( (e_{aq}^-) \) at 25 °C 8a

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extinction coefficient at maximum absorption (715 nm)</td>
<td>( 1.85 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} )</td>
</tr>
<tr>
<td>Half width</td>
<td>0.93 eV</td>
</tr>
<tr>
<td>Oscillator strength</td>
<td>0.71</td>
</tr>
<tr>
<td>ESR g factor</td>
<td>2.0002</td>
</tr>
<tr>
<td>ESR line width</td>
<td>0.5 gauss</td>
</tr>
<tr>
<td>Charge</td>
<td></td>
</tr>
<tr>
<td>Radius of charge distribution</td>
<td></td>
</tr>
<tr>
<td>Primary yield of ( (e_{aq}^-) ) at pH 7</td>
<td></td>
</tr>
<tr>
<td>( \text{pK} \left[ (e_{aq}^-) + H_2O \leftrightarrow H + OH^- \right] )</td>
<td>9.7</td>
</tr>
<tr>
<td>( k (e_{aq}^- + H_2O) )</td>
<td></td>
</tr>
<tr>
<td>Half life in neutral water (pH 7)</td>
<td></td>
</tr>
<tr>
<td>In basic solution</td>
<td></td>
</tr>
<tr>
<td>Diffusion constant</td>
<td></td>
</tr>
<tr>
<td>Equivalent conductivity</td>
<td></td>
</tr>
<tr>
<td>Mobility</td>
<td></td>
</tr>
<tr>
<td>( F_{\text{hydration}} )</td>
<td></td>
</tr>
<tr>
<td>( S_{\text{hydration}} )</td>
<td></td>
</tr>
<tr>
<td>( H_{\text{hydration}} )</td>
<td></td>
</tr>
<tr>
<td>( E^0(e_{aq}^- + H^+ \leftrightarrow 1/2 H_2) )</td>
<td>( -2.77 ) V</td>
</tr>
</tbody>
</table>
In all the above cases the primary product of the electron transfer reaction acquires an additional electron before undergoing any subsequent chemical change and in many cases the primary product is thermodynamically unstable. It, therefore, undergoes further reactions such as protonation, disproportionation or dissociation. Some representative examples are

**Protonation**

\[ H + e^-_{aq} \longrightarrow H^+ \]  \hspace{1cm} (19)
\[ H^+ + H_2O \longrightarrow H_2 + OH^- \]  \hspace{1cm} (20)

**Protonation followed by dissociation**

\[ N_2O + e^-_{aq} \longrightarrow N_2O^- \]  \hspace{1cm} (21)
\[ N_2O + H_2O \longrightarrow N_2OH + OH^- \]  \hspace{1cm} (22)
\[ N_2OH \longrightarrow N_2 + OH \]  \hspace{1cm} (23)

**Disproportionation**

\[ I_2 + e^-_{aq} \longrightarrow I_2^- \]  \hspace{1cm} (24)
\[ I_2^- + I_2^- \longrightarrow I_3^- + I^- \]  \hspace{1cm} (25)

**Association**

\[ Ag^+ + e^-_{aq} \longrightarrow Ag \]  \hspace{1cm} (26)
\[ Ag + Ag^+ \longrightarrow Ag_2^+ \]  \hspace{1cm} (27)

**Dissociation**

\[ H_3O^+ + e^-_{aq} \longrightarrow H_3O^+ \longrightarrow H + \text{water} \]  \hspace{1cm} (28)
1.4.3 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 wavelength 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 and the behaviour of hydrogen atoms in aqueous systems is well understood. The hydrogen atom is a slightly less powerful ($E^0 = -2.31$ V) reducing agent than the hydrated electron ($E^0 = -2.77$ V), but reduces cations with lower oxidation potentials, e.g.

$$H + Cu^{2+} \rightarrow H^+ + Cu^+ \quad \text{(29)}$$

Addition reactions occur with species containing unpaired electrons

$$H + CH \rightarrow H_2O \quad \text{(15)}$$
$$H + O_2 \rightarrow HO_2 \quad \text{(30)}$$

and with unsaturated and aromatic organic compounds

$$H + CH_2-C≡N \rightarrow CH_2-CH=NH \quad \text{(31)}$$

$$H + \begin{array}{c}
\text{O} \\
\text{H}
\end{array} \rightarrow \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \quad \text{(32)}$$
The usual reaction with saturated organic compounds is hydrogen abstraction to give molecular hydrogen and an organic radical,

$$H + CH_3OH \rightarrow H_2 + \cdot CH_2OH \quad \cdots (33)$$

In strongly basic solutions (pH > 10), the hydrogen atom may react with $OH^-$ to form a hydrated electron

$$H + OH^- \rightarrow e^-_{aq} + H_2O \quad \cdots (34)$$

The reaction has a fairly high rate constant and will often compete with hydrogen atom-solute reactions. Reaction of hydrogen atoms with hydrogen ions can occur in strongly acid solutions to give $H_2^+$

$$H + H^+ \rightarrow H_2^+ \quad \cdots (35)$$

but this reaction has a relatively low rate constant and is generally not significant.

One of the main differences between the hydrogen atom and the hydrated electron, apart from the reaction rates, is that the former often abstracts hydrogen from organic solutes giving molecular hydrogen while the latter reacts to give other products. Advantage is taken of this difference to measure $G_H$ in neutral solutions by irradiating solutions containing an electron scavenger (acetone, bicarbonate ..) and an organic compound that will give $H_2$ with H atoms (formate, methanol), when $G_{H_2} + G_H = G(H_2)$.
1.4.4 Molecular hydrogen

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 species. This is so both because of the solubility of hydrogen in water is low, so that most of it escapes from the solution and because the rate constants for molecular hydrogen reactions are rather low. The reaction of most direct interest

\[ \text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O} \]  \quad (17)

cannot normally compete with other hydroxyl radical reactions unless pressure of hydrogen is increased above atmospheric (a solution saturated with H\textsubscript{2} at atmospheric pressure contains about 7.8 x 10\textsuperscript{-4} M H\textsubscript{2}).

1.4.5 Hydroxyl radical (OH)

It is the main oxidizing radical formed when aqueous solutions are irradiated. It is a powerful oxidizing agent \((E^0 = +2.8 \text{ V} \text{ for the pair OH-OH}^- \text{ at C}_{H^+} = 1.0 \text{ M})\) oxidizes all inorganic ions \((\text{Fe}^{2+}, \text{Co}^{2+}, \text{Ce}^{3+})\) which have a higher valence state. Various chemical reactions effected by the radical are

\[ \text{OH} + \text{R}^{n+} \rightarrow \text{R}(n+1)^+ + \text{OH}^- \]  \quad (36)

the solute may be neutral, positive or negative ion as in
The rapid addition reactions occur with free radicals:

\[
\begin{align*}
\text{OH} + \text{Fe}^{2+} & \rightarrow \text{OH}^- + \text{Fe}^{3+} \\
\text{OH} + \text{I}^- & \rightarrow \text{OH}^- + \text{I} \\
\text{OH} + \text{CO}_3^{2-} & \rightarrow \text{OH}^- + \text{CO}_3^-
\end{align*}
\]

.. (37)  .. (38)  .. (39)

Organic compounds containing aromatic systems with carbon-carbon multiple bonds undergo addition reactions with OH radical

\[
\begin{align*}
\text{OH} + \text{H} & \rightarrow \text{H}_2\text{O} \\
\text{OH} + \text{HO}_2 & \rightarrow \text{H}_2\text{O}_3 \\
& \rightarrow \text{H}_2\text{O} + \text{O}_2
\end{align*}
\]

.. (15)  .. (40a)  .. (40b)

While hydrogen abstraction is the usual reaction with saturated organic compounds including those containing carbonyl groups.

\[
\begin{align*}
\text{OH} + \text{CH}_2 = \text{CH}_2 & \rightarrow \text{HO} - \text{CH}_2 - \cdot \text{CH}_2 \\\n\text{OH} + \text{CH}_3 - \cdot \text{CO} - \text{CH}_3 & \rightarrow \text{H}_2\text{O} + \cdot \text{CH}_2 - \cdot \text{CO} - \text{CH}_3 \\
\text{OH} + \text{CH}_3 - \cdot \text{CH}_2 - \text{OH} & \rightarrow \text{H}_2\text{O} + \cdot \text{CH}_3 - \cdot \text{CHOH}
\end{align*}
\]

.. (41)  .. (43)  .. (44)

1.4.6 Conversion of OH into O⁻ in alkaline media

The dissociation of the hydroxyl radical in alkaline media has been considered frequently. It is represented in
terms of formal ionization as

\[ \text{OH} \rightleftharpoons \text{H}^+ + \text{O}^- \]  \hspace{1cm} (45)

for which \( p_{\text{OH}} = 11.9 \) is given. But it seems more convenient to consider the conversion of the hydroxyl radical into \( \text{O}^- \) simply in terms of the reaction

\[ \text{OH} + \text{OH}^- \rightarrow \text{O}^- + \text{H}_2\text{O} \]  \hspace{1cm} (46)

Change in the rate constant of reaction of the hydroxyl radical with ferrocyanide, with change in pH was first observed by Habani and Matheson\(^{17}\). The oxidation rate decreases with increasing pH which implies alteration of the nature of the OH radical. Like the hydroxyl radical, the \( \text{O}^- \) ion radical is an oxidizing species but some differences in their behaviour may be quite important.

(i) The radical ion \( \text{O}^- \) reacts rapidly with oxygen, whereas the hydroxyl radical is inert or reacts very slowly.

(ii) The radical ion \( \text{O}^- \) reacts more rapidly with \( \text{H}_2 \) and \( \text{H}_2\text{O}_2 \) than does the OH radical.

(iii) The recombination of \( \text{O}^- \) is considerably slower than that of OH.

(iv) In electron transfer reactions, the difference in behaviour is great, \( \text{O}^- \) reacts much more slowly than does OH , \( \text{CNS}^- , \text{CO}_3^{2-} \) and \( \text{Fe(CN)}_6^{2-} \) are less effectively oxidized—
(10^{-10^3} \text{ times}) \text{ by } O^{-}.

(v) In hydrogen abstraction reactions, O^{-} and OH seem to be about equally efficient.

1.4.7 Primary hydrogen peroxide

The recombination reaction of hydroxy radicals is the probable source of primary hydrogen peroxide

\[
\text{OH} + \text{OH} \longrightarrow \text{H}_2\text{O}_2
\]  

(14)

Decomposition of H_2O_2 occurs by the usual chemical reactions with the substances present in the irradiated solutions or due to the reactions of e_{aq}^{-} and H atoms produced in the radiolysis. H_2O_2 is known to act both as an oxidizing and a reducing agent depending on the nature of the solute.\textsuperscript{18,19} For example,

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{OH} + \text{OH}^{-}
\]  

(47)

\[
\text{H}_2\text{O}_2 + \text{Ce}^{4+} \longrightarrow \text{Ce}^{3+} + \text{HO}_2 + \text{H}^{+}
\]  

(48)

It is inert towards most of the organic compounds but may react with some organic radicals such as •COOH.

\[
\text{H}_2\text{O}_2 + \text{•COOH} \longrightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{OH}
\]  

(49)

1.5 Radiation chemical yields of primary products of water radiolysis

Number of free radicals C_{R} (where R is H, OH or e_{aq}^{-}) or molecules, C_{M} (where M is H_2 or H_2O_2) produced by absorbing 100 eV of energy per gram present during the chemical stage of
water radiolysis is termed as radiation chemical yield. The most often used method of determining it is as follows: A solute which reacts with the primary species whose yields are to be determined is added to water before irradiation. The chemical changes of the solute are measured during and after irradiation, and then the radiation chemical yield is calculated from the amount of these changes. For these calculations it is necessary to assume a sequence or mechanism of reactions which must be thermodynamically possible and probable. The most probable reaction scheme enables one to relate the amount of observed changes to the amount of primary species studied, that is, to their radiation chemical yields. More than one reaction scheme may be possible all of which are compatible with one and the same set of C values obtained by measurement. Therefore to confirm the radiation yield of the species under consideration it is necessary to study a number of systems.

While selecting the system (solute) it is necessary that the solute should fulfil several conditions. The ideal solute should have the following characteristics:
(i) It should not change chemically over a wide range of pH.
(ii) It should have a high solubility in water.
(iii) Its reaction with the primary species under study should be known.
(iv) It should be possible to measure simply and precisely the product of this reaction.

(v) The product of the reaction should not be susceptible to chemical changes under the working conditions.

Finding a suitable solute is then obviously a difficult task. Different solutes have different analytical difficulties. For example, solubilities of $H_2$, $O_2$, $N_2O$ are limited hence these cannot employed at higher concentrations.

1.5.1 Influence of various factors on $G_R$ and $G_M$

It is important to note that the radiolytic products are produced in very fast processes therefore the number of factors affecting their yields is limited.

LET and dose rate affect the spatial distribution of primary species. The larger the amount of energy deposited in a given volume and at a given instant of time, that is, higher the LET or the dose rate, the closer is the approach of ionized and excited water molecules and thereby also of the species originating from them. This implies higher probability of occurrence of certain reactions which are not manifested at low LET and dose rates.

1.5.2 Reactivity

Reactivity of the substance used as the scavenger is
another important factor in deriving the values of primary yields from experimental measurements. The reactivity is defined as a product of rate constant of the scavenger with the species of interest and the scavenger concentration \( \{ k_R + s \times [S] \} \), scavenger concentration is expressed in terms of moles per litre and \( k_R + s \) in terms of \( M^{-1}s^{-1} \), therefore units for reactivity are reciprocal seconds. Then the reactivity is sufficiently high, the solute-radical reaction may compete with radical-radical recombination reaction and thereby affecting on the values of \( G_R \) and \( G_M \).

1.5.3 Scavenger concentration

If a solute \( S \) reacts with short-lived species \( R \) which is a primary product of radiolysis, to give the product \( P \) according to the reaction

\[ R + S \rightarrow P \] .. (50)

then the increase of the concentration of \( S \) may be conveniently followed by the increase of \( G(P) \). This increasing process should continue until all the species \( R \) escaping recombination \( (R + R \rightarrow M) \) are scavenged. From this argument one can easily understand why the scavenger concentration in solution studies is important \( 20-23 \) if \( G(P) \) is to be used in calculating \( G_R \). Some of the earlier contradictory conclusions regarding primary yields were due to the fact that the measurements of
the stable products were carried out over a narrow concentration range.

At very low concentrations, the scavenger cannot react with all radicals because their other reactions with molecular products or impurities are also effective, at moderately low concentrations it removes all $R$ species in the bulk of the solution. Then increase in $G(P)$ begins to occur on account of $G_M$. Sworski was the first to show a decrease in $G_{H_2O_2}$ due to increase in concentration of halide ions$^{24,25}$. Schwarz$^{26}$ was the first to report that the increase in the concentration of scavenger for short-lived reducing species leads to a decrease in $G_{H_2}$. There are many other evidences$^{27-41}$ supporting this type of the dependence of $G_M$ on scavenger concentration. It has also been shown$^{42,43}$ that many discrepancies in $G_M$ values obtained by different authors would be removed if the reactivities are taken into account.

Some of the empirical procedures which minimize uncertainties involved in the calculations are:

1. Plotting the $G(P)$ values as a function of the scavenger concentration. The plateau value is taken as a maximum value for $G(P)$. A disadvantage of such a procedure is that the plateau may appear in the region of low reactivity and give a low value for the 'correct' product yield. The reason for
this is the loss of primary radicals in a competition between the solute and some impurities, or radiolytic products which is otherwise absent.

(ii) Determination of the $G(P)$ for different scavenger concentrations corresponding to the reactivity values lying within the range of chemical stage on time scale. This concentration range avoids the possibility of competition between solute and impurities for radicals. Reciprocals of $G(P)$ are then plotted versus reciprocal of concentration. A straight line is obtained with an intercept on the Y axis, which corresponds to the reciprocal of the maximum $G(P)$ due to reactions of radicals in bulk; hence presenting maximum value for the radical in bulk.

1.5.4 *Effect of pH*

At pH 3-13 no change in $G_R$ and $G_M$ values occurs. An increase in the acidity ($pH < 3$) undoubtedly leads to a slight increase in $G_R$ values as well as small increase in $\text{CH}_2\text{O}_2$; while $\text{CH}_2$ under these conditions remains constant or slightly decreases. From the analysis of published work given by Heissinsky it can be seen that answers may considerably differ from one other, depending on the system from which they are derived. Thus for neutral pH, $G_{\text{OH}}$ values vary between 2.1 and 2.7, and those of $G_H + G_{\text{aq}}^-$ vary between
2.7 and 3.1; similar discrepancies are also encountered in alkaline media, where $G_R$ values are often larger by as much as 30% than those for the neutral medium. Hayon\textsuperscript{42} tried to explain the disagreement between the results obtained with different systems by the fact that the effect of reactivity was disregarded in some cases and moreover he ascribed the increase in $G_R$ at the end of pH range to the increased reactivity due to the occurrence of the reactions

\begin{align*}
e^-_{aq} + H_3O^+ &\longrightarrow H + H_2O & \text{(28)} \\
OH + OH^- &\longrightarrow O^- + H_2O & \text{(46)}
\end{align*}

respectively.

Czapski\textsuperscript{45} concluded that in many cases where the $G$ values of radicals seemed to depend on pH or scavenger concentration, the effect was in reality an artifact resulting from disregard of the effect of back reactions.

1.5.5 **Effect of linear energy transfer**

The linear rate of loss of energy by an ionizing particle traversing a material medium is termed as linear energy transfer (LET). Its units are keV $\cdot M^{-1}$. The increase of LET leads to the increase in the density of primary events per unit space and unit time. This should favour reactions of recombinations of primary species. The value of $G_M$ is
expected to increase, while $G_R$ should decrease. If the product $P$ comes mainly from the solute reactions with free radicals ($H$, $OH$ and $e_{aq}^-$), then $G(P)$ should decrease. This can be seen in Fig. 1.55 which represents the dependence of $G(Fe^{3+})$ on radiation LET$^4$. The yields of ferric ion formed in the aerated ferrous sulphate ($10^{-3}$ M) solution in sulphuric acid ($0.4$ M), vary slightly when irradiated with photons or charged particles of various energies. Measurements in the region of LET of about $1$ keV $\mu m^{-1}$ refer to soft x-rays. Most of the other measurements were carried out in solutions subjected to charged particles (protons, neutrons and heliums) of different energies produced by the cyclotron. The highest LET value in this diagram of $220$ keV $\mu m^{-1}$ refers to the radiation of an internal source - the fragments of the nuclear reaction $^{10}$B(n,$\alpha$)$^7$Li.

In passing from high energy photons to charged particles that is by increasing LET and favouring the recombination reactions, $G(Fe^{3+})$ decreases as the yields of primary free radicals decrease. It is true that the yield of $H_2O_2$ is increasing at the same time, but as is seen in equation

$$G(Fe^{3+}) = 3(G_{e_{aq}} + G_H) + G_{OH} + 2G_{H_2O_2} \quad \ldots (51)$$
Fig 1.5.5—Dependence of ferric ion yields, in aerated $1 \times 10^{-3}$ M ferrous sulphate solution in 0.4 M sulphuric acid, on LET.
its contribution to the total oxidation yield under the above conditions is less important than that of free radicals.

The effects of reactivity of various substances on the yields of \( \text{H}_2 \) were studied in irradiations with \( ^{60}\text{Co} \gamma \)-rays as well as with 18.9 MeV neutrons, mixed pile radiation, or fission fragments. The results reported show that in the case of high LET radiations the effect of reactivity is important.

1.5.6 Effect of dose rate

In the radiolysis of water, higher dose rates (\( > 10^9 \) rad/sec) favour inter-radical reactions, the concentrations being higher in the tracks. These reactions, therefore, lead to an increase in molecular products as observed in high LET radiations due to the deposition of energy along short tracks, rather than in the spurs. The effect of dose rate has been studied in different aqueous systems. The \( \text{Fe}^{2+}/\text{Fe}^{3+} \) system has been studied in detail in this regard too because of its importance in dosimetry. It has been found that \( G(\text{Fe}^{3+}) \) decreases with increasing dose rate the effect being more pronounced after about \( 10^8 \) rad/s.

1.5.7 Effect of temperature

...
scattering of the primary species is expected, hence an increase in radical yields and a decrease in molecular yields. This effect was also verified with Fe$^{2+}$/Fe$^{3+}$ system in 0.4 M sulphuric acid. Effects due to raising the temperature on the yields of primary species assuming reaction schemes given in other papers show that the results are as expected, namely a rise of $G_H$ and a fall of $G_N$. The temperature coefficient determined are within 0.06 to 0.20% that is why usual variations of room temperature do not have an appreciable effect on the measured yields of primary products.

1.5.8 Effect of pressure

The effect of pressure on the yields of different primary radiolytic products of water has been recently investigated and it has been shown that there is no change in their yields upto 7 kbar of pressure. Hentschel et al. studied the pressure effect in different systems upto 6.4 kbar, a discussion of a typical system is narrated here.

In the radiolysis of ferrous sulphate solution in the presence of sulphuric acid, the yields of Fe$^{3+}$, O$_2$ and H$_2$ were measured. The increase in pressure from 0 to 6.4 kbar resulted in an increase in $G(H_2)$ from 0.44 to 0.8 with a simultaneous decrease in $G(Fe^{3+})$ and $G(-O_2)$ from 15.6 and—
3.66 to 14.68 and 3.24 respectively. Further the analysis of experimental data showed that the sums of the measured yields are independent of the pressure

\[
\begin{align*}
\text{G}(\text{H}_2) + \text{G}(\text{O}_2) &= 4.1 \\ 
\text{G}(\text{Fe}^{3+}) + 2\text{G}(\text{H}_2) &= 16.4
\end{align*}
\]

The authors further established by kinetic study that the first expression is equal to \(\text{G}_\text{H} + \text{G}_\text{H}_2\) and the second is equal to \(4(\text{G}_\text{H} + \text{G}_\text{H}_2)\). This indicates that there is no effect of pressure on the yields of primary reducing species, hydrogen atom and molecular hydrogen.

1.6 Radiolysis kinetics

In the study of radiation chemistry of aqueous solutions a knowledge of the rate constants for the reactions of the radical and molecular products with the solutes is of utmost importance. A very efficient method of determining absolute rate constants consists of pulse technique\(^{67-72}\) whereas the classical method of determining relative rate constants of the radical or molecular products with different solutes is known as competition kinetics\(^{73-76}\). Essentials of both the methods are discussed here.

1.6.1 Pulse radiolysis

In this method a large amount of energy in the form
of ionizing radiation is deposited in the system in a very short time interval, of the order of $10^{-9}$ to $10^{-12}$ s. This amount of energy produces enough concentration of the transients to be measured. Physical properties of the transient like optical, conductivity, ESR spectrum etc. are of use in measuring its concentration from time to time. Optical absorption method needs selection of a suitable wavelength at which other reactants or products do not interfere. A typical oscilloscopic pattern shown in Fig. 1.4 explains the decay of the transient as given by the increase in the intensity of the transmitted light with time.

![Oscilloscope Pattern](image)

**Fig.1.6.1** - Typical oscilloscope pattern showing decay of transient with time.

Trace 1 is the base line representing 0% transmission. Trace 2 represents transmission through medium without transient. And trace 3 presents the transmission through the
medium when transient (pulsed electrons in above example) is present in the medium. Log $I_0/I_t$ gives optical density at time $t$ which is proportional to the concentration of the transient at time $t$. Thus knowing the relative concentrations of the transient from time to time kinetics of the decay processes of the transient in the pure matrix as well as in the presence of some other reactants can be studied.

1.6.2 Competition kinetics

It consists in adding two solutes, which react in competition with the species studied, to the solution to be irradiated. Consider the competition of solutes $S_1$ and $S_2$ in solution for radical $R$:

$$ R + S_1 \rightarrow P_{S_1} \quad \ldots (54) $$

$$ R + S_2 \rightarrow P_{S_2} \quad \ldots (55) $$

where $P_{S_1}$ and $P_{S_2}$ are the corresponding products. The fraction of the radicals reacting with solute $S_1$ is given by the expression

$$ \frac{k_{S_1} S_1}{k_{S_1} S_1 + k_{S_2} S_2} \quad \ldots (56) $$

where $k_{S_1}$ and $k_{S_2}$ are the rate constants for the reactions with $S_1$ and $S_2$ respectively. $Q_R$ is the radiochemical yield
of the radical. Then

\[ G(P_{S_1}) = G_R \frac{k_{S_1} S_1}{k_{S_1} S_1 + k_{S_2} S_2} \]  \hspace{1cm} (57)

where \( G(P_{S_1}) \) is the radiochemical yield of the product of the reaction. Further

\[ \frac{1}{G(P_{S_1})} = \frac{1}{G_R} + \frac{1}{G_R} \cdot \frac{k_{S_2} S_2}{k_{S_1} S_1} \]  \hspace{1cm} (58)

Then if we plot \( \frac{1}{G(P_{S_1})} \) versus \( S_2 / S_1 \) for various compositions of \( S_2 / S_1 \) the intercept on Y axis gives radiochemical yield of the radical whereas from the slope relative rates of the reactions can be evaluated. If rate constant for either of the reactions is known the rate constant for the other reaction can be calculated.

Rate constants for the reactions involving \( e^{-}aq, H^{+} \)

and \( OH \) are quoted in Tables 1.4 and 1.5.

1.7 Scope of the present work

Steady state and pulse radiolysis of oxyanions in aqueous solution show that the reducing radicals of water radiolysis react with the solute forming transients which are usually highly oxidizing in nature. These transients could be utilised to oxidize a reducing agent if present in the solution. For example, Anbar and Mets \( ^{77} \) have shown that the
Table 1A: Rate constants for reactions of hydrated electron (e$_{aq}^-$) and hydrogen atom (H)

<table>
<thead>
<tr>
<th>Reactant</th>
<th>e$_{aq}^-$</th>
<th>Ref.</th>
<th>H</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>e$_{aq}^-$</td>
<td>540</td>
<td>76a</td>
<td>2500</td>
<td>76c</td>
</tr>
<tr>
<td>H</td>
<td>2500</td>
<td>76a</td>
<td>1300</td>
<td>76c</td>
</tr>
<tr>
<td>OH</td>
<td>3000</td>
<td>76a</td>
<td>3200</td>
<td>76c</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>1200</td>
<td>76a</td>
<td>9</td>
<td>76c</td>
</tr>
<tr>
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<td>76a</td>
<td>-</td>
<td>76c</td>
</tr>
<tr>
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<td>76a</td>
<td>-</td>
<td>76c</td>
</tr>
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<td>770</td>
<td>76a</td>
<td>-</td>
<td>76c</td>
</tr>
<tr>
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<td>76a</td>
<td>-</td>
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</tr>
<tr>
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<td>76b</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
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<td>76b</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C$_2$O$_4^{2-}$</td>
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<td>76b</td>
<td>-</td>
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Table 1a:

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Rate constant/10^7 M^{-1}s^{-1}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>eaq</td>
<td>3000</td>
<td>8a</td>
</tr>
<tr>
<td>H</td>
<td>2000</td>
<td>8a</td>
</tr>
<tr>
<td>OH</td>
<td>530</td>
<td>8a</td>
</tr>
<tr>
<td>H_2</td>
<td>4.9</td>
<td>8a</td>
</tr>
<tr>
<td>H_2O_2</td>
<td>2.7</td>
<td>8a</td>
</tr>
<tr>
<td>Br^-</td>
<td>110</td>
<td>8a</td>
</tr>
<tr>
<td>I^-</td>
<td>1550</td>
<td>8a</td>
</tr>
<tr>
<td>NO_3^-</td>
<td>620</td>
<td>8a</td>
</tr>
</tbody>
</table>

Br(IV) transient, formed in the radiolysis of the solution containing bromate and iodide ions, oxidizes iodide ions to iodine.

With this view in mind we have studied $\gamma$-induced redox reactions, effected through transients such as Br(IV), which are thermodynamically possible but either do not proceed or proceed very slowly in the absence of radiation at room temperature. Our work on $(n,\gamma)$ reactions in aqueous solutions
of the mixtures of $\text{IO}_3^-$/$\text{BrO}_3^-$ under conditions of $\text{ClO}_3^-$ = 0.2 M and $\text{CBrO}_3^-$ varied over the range 0.0025 M to 0.02 M showed that almost all of $^{128}\text{I}$ formed remains in the form of iodate when the solutions were irradiated with neutrons from a photo-neutron source ($\gamma$-dose $\approx 4$ kGy) while only about 18% of $^{128}\text{I}$ formed was found in the form of iodate, the rest being in the lower oxidation state when the same mixtures were irradiated with pure neutrons in the absence of $\gamma$.

Further from standard reduction potential data, namely, $E^0 = 1.44$ V for the reaction

$$\text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons 3\text{H}_2\text{O} + \text{Br}^- \quad (59)$$

and $E^0 = 1.086$ V for the reaction

$$\text{IO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons 3\text{H}_2\text{O} + \text{I}^- \quad (60)$$

one can see that the reaction

$$\text{BrO}_3^- + \text{I}^- \rightleftharpoons \text{IO}_3^- + \text{Br}^- \quad (61)$$

is thermodynamically possible with $E^0 = 0.355$ V. This suggests the possibility of oxidation of iodide to iodate by bromate in a mixture iodide/bromate in aqueous solution. However, the reaction does not proceed at room temperature. Therefore it was felt interesting to investigate the $\gamma$-radiolysis of redox mixtures such as $\text{I}^-$/3$\text{BrO}_3^-$. The work presented in this thesis covers the study of following systems
besides the radiolysis of pure bromate and oxalate ions: iodide/bromate, iodine/bromate, oxalate/bromate, oxalate/iodate and iodide/persulphate.

Also the study of redox reactions effected by using energy stored in the F and hole centres of γ-irradiated NaCl and KBrO₃ crystals is included. The reactions studied are

\[
\begin{align*}
\text{BrO}_3^- + I^- & \xrightarrow{\text{NaCl}^*} \text{IO}_3^- + \text{Br}^- \\
\text{BrO}_3^- + \text{NO}_2^- & \xrightarrow{\text{NaCl}^*} \text{NO}_3^- + \text{Br}^- \\
I^- & \xrightarrow{\text{KBrO}_3^*} \text{IO}_3^- + \text{Br}^- 
\end{align*}
\]