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The thesis is divided into three chapters.

Chapter I presents a review of the work done on the primary radiolytic products of water, their physical and chemical properties and the dependence of molecular and radical yields on various factors.

Chapter II includes the experimental details regarding the preparation of samples, the irradiation facility used and the analytical methods employed for determining radiolytic yields of different species obtained in various systems investigated. These include (1) pure substances such as KBrO₃, K₂C₂O₄ and (2) binary mixtures such as I⁻/BrO₃, I₂/BrO₅, C₂O₄²⁻/BrO₅, C₂O₄²⁻/IO₃ and I⁻/C₂O₄²⁻. These binary mixtures are so chosen that they do not react at room temperature though a reaction between these is thermodynamically possible, they react on exposure to γ-radiation. Following are some of the important observations.

(1) The yields of the product(s) vary linearly with the dose in the case of both pure solutions and their binary mixtures. Over a certain range of dose depending upon composition of
mixture and the relative concentrations of the reactants. G values of the products are calculated from the linear portions of the curves.

(2) The radiolytic yields of Br\(^-\) and I\(^-\) ions are greater in the mixed solutions as compared to their yields in pure solution. Thus in pure solution of KBrO\(_3\) \(G(\text{Br}^-)\) is 1.0 and in the binary mixtures such as I\(^-\)/BrO\(_3\)\(^-\) and C\(_2\)O\(_4\)\(^2-\)/BrO\(_3\)\(^-\) values for \(G(\text{Br}^-)\) are 3.4 and 2.8 respectively. And in case of solution of pure iodate \(G(\text{I}^-) = 0.35\) whereas in the mixture C\(_2\)O\(_4\)\(^2-\)/IO\(_3\)\(^-\) \(G(\text{I}^-)\) is 7.5. (The G values quoted are maximum values observed, except in case of C\(_2\)O\(_4\)\(^2-\)/IO\(_3\)\(^-\) mixture).

(3) During the action of \(\gamma\) radiation of these dilute solutions, of single solute or binary redox mixtures, most of the photons are absorbed by water molecules. Mechanisms consistent with the observed results are expressed in terms of the primary radiolytic products (prop) of water in all the systems studied.

The maximum G values of the stable products on the basis of the proposed mechanisms are:

(i) In pure bromate solution

\[
G(\text{Br}^-) = 1/3 \cdot g_{\text{aq}}^{-} + H
\]

(ii) In pure iodate solution

\[
G(\text{I}^-) = 1/2 \cdot (g_{\text{aq}}^{-} + H - \text{OH})
\]
(iii) In pure oxalate solution

\[ G(-C_2O_4^{2-}) = G_{\text{OH}} \]

(4) The results obtained in the radiolysis of binary redox systems are explained on the basis of reactivities of prp with solute ions, their concentrations and the transients produced thereby. The transients are highly reactive and are responsible for the oxidation of I\(^-\) to IO\(_3^-\)/C\(_2\)O\(_4^{2-}\) to HCO\(_3^-\). A large sequence of reactions is involved in the radiolysis of the mixed solutions. The quantitative correlation of the G values of the stable products and the primary radiolytic product of water are established on the basis of probable mechanisms proposed. The yields of the products in the different systems are given by the following expressions.

(i) I\(^-\)/BrO\(_3^-\) system

\[ G(\text{IO}_3^-) = G(\text{Br}^-) = G_{\text{aq}} + H \]

(ii) C\(_2\)O\(_4^{2-}\)/Br\(_3^-\) system

\[ G(\text{Br}^-) = G_{\text{aq}} \]

\[ G(-C_2O_4^{2-}) = G_{\text{aq}} + G_{\text{OH}} + 1/2 \text{H}_2 \]

(iii) C\(_2\)O\(_4^{2-}\)/IO\(_3^-\) system

\[ G(I^-) = n(G_{\text{aq}} - H - G_{\text{OH}}) \]

\[ G(-C_2O_4^{2-}) = 2G(I^-) \]
(iv) $I^-/O_2^2-$ system

$$G(IO_3^-) = \frac{1}{5}(O_2^{aq} + H + O_{OH})$$

(5) In the radiolysis of the aqueous solution of $I^-/BrO_3^-$, Anber and Neta had proposed that the Br(IV) species formed oxidizes the iodide ion to iodine at the same time a reduction of iodine to iodide ions also takes place by the same species. Our experiments with the same system have enabled us to show that Br(IV) species is a strong oxidant and it oxidizes, not only iodide to iodine, but iodine to iodate through triiodide ion, there being no reduction of $I_2$ to $I^-$.

The results obtained in the system are used to calculate the second order rate constant for the reaction

$$I_3^- + BrO_3^- \rightarrow I_2^- + Br^- + BrO_3^-$$

the value obtained is $1.9 \times 10^{12} \text{ M}^{-1}\text{s}^{-1}$.

(6) During the radiolysis of the aqueous solution of $C_2O_4^{2-}/BrO_3^-$ it is found that oxalate and bromate ions disappear in the mole proportion of 2:1 for any given dose.

(7) In the presence of oxalate ions the iodate ions are reduced to iodide ions, on radiolysis. The iodide yield is found to increase linearly with the oxalate ion concentration. This abnormal behaviour observed is explained by postulating a chain mechanism which includes the reaction of OH radical with $IO_3^-$
(oxidant) even in the presence of $\text{C}_2\text{O}_4^{2-}$ on reductant, which is expected to react with $\text{OH}$ normally. Independent evidence for the reaction between iodate ion and $\text{OH}$ radical is also presented.

(8) The persulphate ion is found to oxidize iodine to iodate under $\gamma$-irradiation getting reduced itself to $\text{SO}_4^{2-}$ ion.

Chapter III deals with the use of energy stored in the $F$ and hole centres of $\gamma$-irradiated $\text{NaCl}$ and $\text{KBrO}_3$ crystals in effecting the redox reaction like

$$\text{BrO}_3^- + \text{I}^- \xrightleftharpoons{[\text{NaCl}]^*} \text{IO}_3^- + \text{Br}^-$$

$$\text{NO}_2^- + \text{BrO}_3^- \xrightleftharpoons{[\text{NaCl}]^*} \text{NO}_3^- + \text{Br}^-$$

$$\text{I}^- \xrightleftharpoons{[\text{KBrO}_3]^*} \text{IO}_3^- + \text{Br}^-$$

in aqueous solution, which otherwise do not react unless exposed to $\gamma$ radiation directly. The redox yields obtained in the reactions are used in calculating the concentration of the $F$ and hole centres produced in the $\gamma$-irradiated crystals. The results obtained agree with those obtained earlier in the studies on aquoluminescence, the emission during the dissolution of irradiated crystals in water. The chapter also includes a brief survey of the related literature.