Course Instructor: **Prof. Rajeev Gupta**

Course Name: **Nuclear and Radiation Chemistry**

Paper Number – 4104

Section – B

Topic: **Radiolysis of Water**

Number of Classes: **Two (02)**

Radiolysis of Water

The major products of water radiolysis are free radicals ($H^{\bullet}$, $OH^{\bullet}$, $^{\bullet}OH_2$), positive ions (H_2O^+) and molecular products (H_2 and H_2O_2). Some of these are initially formed precursors which led to the other products by secondary reactions. The presence of dissolved O_2 or air in the water also affects the final yields of the products. Similarly, dissolved solutes also alter the products and yields.

(A) Ionic Products:

$$\gamma + H_2O \longrightarrow H_2O^* \longrightarrow H_2O^+ + e^-$$

$$e^- + H_2O \longrightarrow H_2O^* + e^- \longrightarrow H_2O^+ + 2e^-$$

$$e^- + H_2O \longrightarrow H^+ + {}^{\cdot}OH + 2e^- \longrightarrow H_2O^+ + 2e^-$$

$$e^- + H_2O \longrightarrow OH^+ + \dot{H} + 2e^- \longrightarrow \quad '' \quad ''$$

$$e^- + H_2O \longrightarrow O^+ + H_2 + 2e^-$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + {}^{\cdot}OH$$

The ionic products listed above are detected by mass spectrometer. H_2O^+ is the predominant product in such radiolysis reactions. The formation of -ve ion by e^- attachment is negligible; e^- prefer to recombine with +ve ions, or to get solvated.

$$e^- + H_2O \longrightarrow e^- \text{(aqueous)} \left\{ \begin{array}{l} \text{Mean life: 200-400 μs depending on pH} \\ G(e^-_{aq} : 2.8 \\ \text{Decay products: } H^{\bullet} + OH^-_{aq} \end{array} \right.$$

(B) Free Radical Products: The ionic products have all short lives, especially in an excited state they recombine to yield free radicals.

$$H_2O^+ + e^- \longrightarrow \cdot H + \cdot OH$$

$$H^+ + H_2O + e^- \longrightarrow H_3O^+ + e^- \longrightarrow 2H^\cdot + \cdot OH$$

$$OH^+ + H_2O + e^- \longrightarrow \cdot H + 2\cdot OH$$

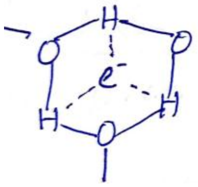
In the presence of dissolved O_2, Perhydroxyl radical is formed:

$$^\bullet H + O_2 \longrightarrow {}^\bullet HO_2$$

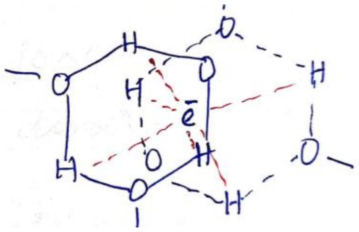
(C) Hydrated Electron (e^-):

$$\text{Naked } e^- + xH_2O \longrightarrow e^- \text{ (aqueous)}_x$$

Structure:



Or



Hydrated electrons is a distinct species associated with 3 or 4 or 6 water molecules, with a charge of 1- and a mean radius of 0.25 to 0.3 nm and with a characteristic spectrum.

Mean life: ~ 230 µs (pH ≃ 7), ~ 780 µs (pH > 7)

Decay products: $e^-_{aq} \longrightarrow H^\cdot + OH^-_{aq.}$; pK = 9.7

$\quad\quad\quad\quad\quad\quad\quad \hookrightarrow H_2\uparrow$

G(e^- aqeous) : 2.8

Potential, $E^\circ(e^-_{aq.} + H^+ \longrightarrow H^\cdot) = -2.77$ V (25°C)

A powerful Reducing agent.

The hydrated e^- is known to form a dimer which is less reactive, but decays slowly to H_2 accompanied by a marked increase in pH.

(D) Molecular Products due to Radical-Radical Interaction:

All the radicals being highly reactive, initiate series of reactions with dissolved solute, or they combine amongst themselves, resulting in stable products. .

$$\cdot H + \cdot OH \longrightarrow H_2O$$

$$\cdot H + \cdot H \longrightarrow H_2$$

$$\cdot OH + \cdot OH \longrightarrow H_2O_2$$

$$\cdot OH + \cdot HO_2 \longrightarrow H_2O + O_2$$

$$\cdot HO_2 + \cdot HO_2 \longrightarrow H_2O_2 + O_2$$

The actual yields of these molecular products vary with the nature of the ionizing radiation, the LET and the presence of dissolved solutes.

Chain Reactions: Molecular-Radical Interactions

$$\cdot H + H_2O_2 \longrightarrow \cdot OH + H_2O$$

$$\cdot HO + H_2 \longrightarrow \cdot H + H_2O$$

Chain reactions are postulated specially in explaining abnormally high yields of certain radiolytic products, e.g. Radiolysis of aqueous benzene-O_2; aq $CHCl_3$-O_2 and organic halogen compounds etc.

The yields of Radicals and Molecular Products:

Since in the radiolysis of H_2O, not only water molecules are dissociated, but some of these molecules (H_2O) are reformed.

G-H_2O(initial) = G-H_2O + G-H_2 + G-H_2O_2

Where, G-H_2O(initial) : No. of H_2O molecules initially dissociated

G-H_2O : Water molecules Converted into radicals and molecular products

The value of G-H_2O is independent of the nature of the radiation employed. The radical yields are highest for LOW LET radiation (e.g. γ or electrons). While the molecular yields are greatest for HIGH LET radiations (e.g. α, heavy ions, fission fragments).

DOSIMETRY

Units of radiation:

GRAY: The gray is the SI unit of dose.

1 grey (Gy) = 1 J/kg = 100 rads

It is necessary to include a unit for the “RATE” of the energy absorption. This is the “dose rate” i.e., dose absorbed/sec, in units of rad/sec or Gy/sec.

Dosimetry = Measuring dose (radiation energy absorbed)

Chemical Dosimetry: The Chemical reactions induced by radiation, ex. $Fe^{2+} \longrightarrow Fe^{3+}$ or $Ce^{4+} \longrightarrow Ce^{3+}$

Fricke Dosimeter: The most common chemical dosimeter is the F.D., which consists of an aqueous solution of approximately following composition:

0.001 M $Fe(NH_4)(SO_4)$ (Mohr’s Salt solution)

0.001 M NaCl

0.001 H_2SO_4

The amount of Fe^{3+} formed through radiation is determined spectrophotometrically, and the dose absorbed in Gy calculated by the equation:

$$D(Gy) = A/\{\varepsilon\rho G(Fe^{3+})\}\ J/Kg$$

A = Change in absorbance

(Fe^{3+}) = Yield of Fe^{3+} in mol/j

ε = Molar extinction coefficient (= 217.4 m^2/mol at 304 nm or 2174 m^{-1} cm^{-1})

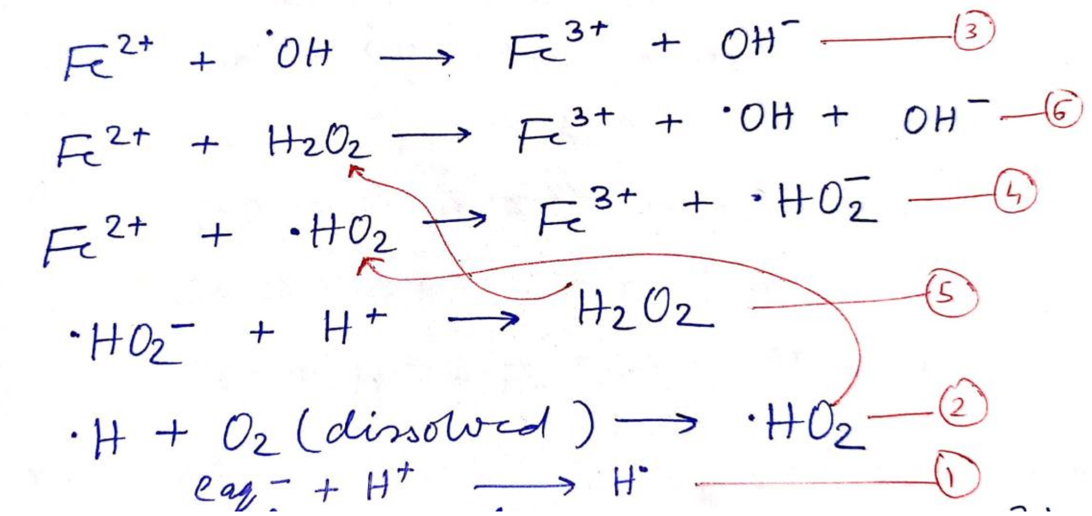
x = Length of the cell in meter

ρ = Density of the solution (= 1024 kg/m^3 at 15-25 °C)

The G values depends somewhat on the LET value of the radiation. The F.D. is independent of dose rate up to dose value of about 2×10^6 Gy/sec and can be used in the range of 1-500 Gy.

* In a common modification, the solution also contains NaSCN, leading to the formation of the intensity red complex ion $[Fe(SCN)_6]^{3-}$ upon irradiation.

The quantitative oxidation of Fe^{2+} to Fe^{3+} on irradiation can be explained by simple mechanism:



The yield of the final product Fe^{3+} is related to the radical and molecular yield by the expression:

$$G(Fe^{3+})_{air} = 2G_{H2O2} + 3G_H + G_{OH}$$

$$= (2\times0.8)+(3\times3.7)+2.9$$

$$= 15.6$$

The average value of $G(Fe^{3+})$ in Fricke dosimeter for 1.25 MeV (mean) γ from ^{60}Co, 2 MeV electrons and for 0.7 MeV β from ^{32}P is 15.5.

Factors which alter the Fe^{3+} yield:

The yield of Fe^{3+} depends on the molecular and radical yields in the radiolysis of Fricke solution. The factors which alters the yields of $H^{\bullet}$, $OH^{\bullet}$, H_2O_2 will therefore alter the ferric ion yield. The LET of the incident radiation is considered to be one of such factors.

- $G(Fe^{3+})_{air}$ decreases with increase in the LET values of the incident radiation.4
- **Organic Impurities:** The presence of organic impurities also increases the yield of Fe^{3+} ion in the irradiation of the aerated solutions.

$$\cdot OH + RH \longrightarrow R\cdot + H_2O$$

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

$$ROO\cdot + H^+ + Fe^{2+} \longrightarrow Fe^{3+} + ROOH$$

$$ROOH + Fe^{2+} \longrightarrow Fe^{3+} + RO\cdot + OH^-$$

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

$^{\bullet}OH$ radical starts a chain reaction after reacting with organic compound and so the yield of the Fe^{3+} also increases. For Ex. The $G(Fe^{3+})_{air}$ is about 75 in presence of EtOH and about 250 in case of adding formic acid.

- **Role of Cl^- Ion:** The addition of Cl^- ion to the acidified air-saturated Fricke solution also favours the yield of Fe^{3+} ion. In this case Cl atom replaces the $^{\bullet}OH$ radical and oxidize Fe^{2+} ion or react with organic impurity.
  To protect the oxidation of the Fe^{2+} against the sensitization by organic impurities, Cl^- ion is added to the dosimeter solution.
  Thus, of these reactions the 1 + 2 predominate over 3 pointing to the fact that the overall result of adding
  Cl^- ion is that each hydroxyl radical oxidizes only ONE ferrous ion. Although, in such a case, the yield is not spuriously high, the normal yield of the Fe^{3+} ion is not affected by organic impurities. Basically, Cl^- ion inhibits the oxidation of Fe^{3+} by trace organic impurities.

1

$$\cdot OH + Cl^- + H^+ \longrightarrow Cl^{\cdot} + OH \qquad \longrightarrow$$

2

$$Cl^{\cdot} + Fe^{2+} \longrightarrow Fe^{3+} + Cl^- \qquad \longrightarrow$$

3

OR

$$Cl^{\cdot} + RH \longrightarrow R^{\cdot} + HCl \qquad \longrightarrow$$

- **In Absence of dissolved O_2:**

  In this situation the reaction $^{\bullet}H + O_2 \longrightarrow HO_2^{\bullet}$ does not take place, but following reaction occurs leading to the oxidation of the acidified ferrous sulphate solution.

  $$^{\bullet}H + H^+ + Fe^{2+} \longrightarrow Fe^{3+} + H_2$$

  The reaction, $H^+ + {}^{\bullet}HO_2 + Fe^{2+} \longrightarrow Fe^{3+} + H_2O_2$ also does not takes place. In such a case of "evacuated or anaerobic sample", the yield of Fe^{3+} ion is given by

  $$G(Fe^{3+})_{vacuum} = 2G_{H2O2} + 3G_H + G_{OH}$$

  $$= 2(0.8)+3.7+2.9$$

  $$= 8.2$$

which is much lower than that in the presence of the dissolved O_2 ($G(Fe^{3+})_{air} = 15.6$)

» So, basically the presence of oxygen favours the ferric ion yield in the radiolysis of Fricke Solution.