# CHAPTER I

INTRODUCTION

FREE RADICAL MODEL OF WATER RADIOLYSIS

1.1   Radiolysis of water yields primary free radical and molecular products. Several models have been proposed by radiation chemists. Most of them are similar and the yield of primary products formed have been extensively investigated. The simple model of radiolysis of water (1) can be represented in the following sequence of re-actions. Incident radiation of sufficient energy (usually γ-rays or X-rays) produces the following overall change in water:

$$H_2O \xrightarrow{\ h\nu\ } H_2O^* \longrightarrow H + OH \ \ldots\ldots\ldots\ldots\ldots (1)$$
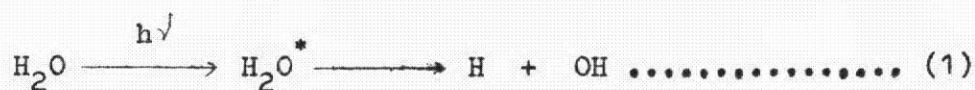
In the primary ionizations, the charged species

$$H_2O \xrightarrow{\ \ \ } e^- + H_2O^+ \qquad\qquad \ldots\ldots\ldots\ldots\ldots (2)$$

are formed. These react as follows:

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \qquad \ldots\ldots\ldots\ldots\ldots (3)$$

The electrons produced in the ionization of water can be recaptured by polar ions $H_2O^+ + H_3O^+$ i.e.

$$H_2O^+ + e^- \longrightarrow H_2O^* \qquad\qquad \ldots\ldots\ldots\ldots\ldots (4)$$

and $H_3O^+ + e^- \longrightarrow H_3O$ .... (5)
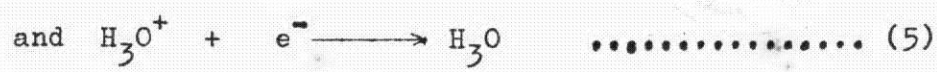
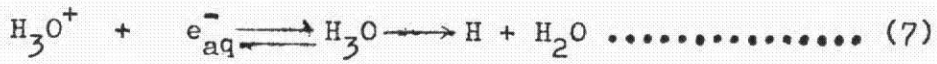The unstable, partially solvated entity of H_3O can undergo two thermal dissociations,

$$H_3O \longrightarrow \begin{cases} \longrightarrow H + H_2O \\ \longrightarrow e^-_{aq} + H_3O^+ \end{cases} \qquad \text{................... (6)}$$

And it is possible that

$$H_3O^+ + e^-_{aq} \rightleftharpoons H_3O \longrightarrow H + H_2O \text{ .... (7)}$$
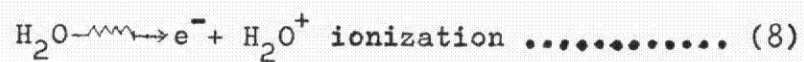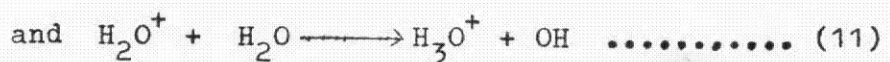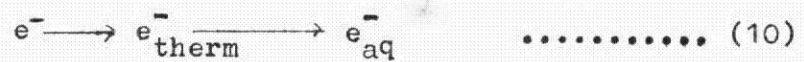
The overall process of water radiolysis can briefly be divided into 3 stages:

1) The physical stage: the incident radiation produces,

$$H_2O \rightsquigarrow e^- + H_2O^+ \text{ ionization .... (8)}$$

and $H_2O \rightsquigarrow H_2O^* \qquad$ excitation .... (9)
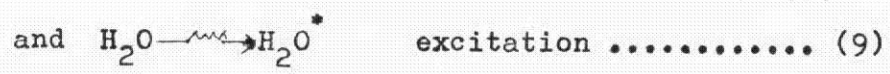
2) The physicochemical stage: electrons ejected in the ionization process become thermalized and hydrated,

$$e^- \longrightarrow e^-_{therm} \longrightarrow e^-_{aq} \qquad \text{.......... (10)}$$

and $H_2O^+ + H_2O \longrightarrow H_3O^+ + OH$ .... (11)

and the H_3O^+ becomes hydrated, $H_3O^+_{aq}$.

Thermalization of an electron ejected in the ionization is the last step in the energy loss process along the medium it traverses, where its kinetic energy (E) is almost equal to thermal energy (kT).

It can attach to neutral molecules, undergo a charge neutralization process and interact with the environment. Hydration is the process after thermalization when water molecules of high dielectric constant surrounding the electron align themselves in the electric field of the latter.

The dissociation of excited water molecules gives the hydrogen atom and hydroxyl radical as main products

$$H_2O^* \longrightarrow H + OH \quad \ldots\ldots\ldots\ldots\ldots (12)$$

It also gives a low yield of e^-_{aq} and, eventually, H_2.

3) The chemical stage: primary species (e^-_{aq}, OH, $H_3O^+_{aq}$ and H) diffuse away from the origin and chemical reactions which attain chemical equilibrium occur.

These phenomena take place in a time period of about 10^{-9} sec after the passage of high energy radiation.

From the model we have mentioned, primary products of water radiolysis can be divided into two main types:-

1) Short-lived Reducing Species:-

(a) <u>The hydrated electron</u> (e^-_{aq})

The simplest elementary negative ion in aqueous solutions is the hydrated electron. The evidence for its existence is the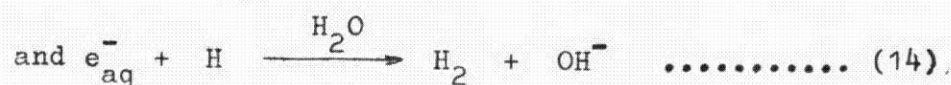 o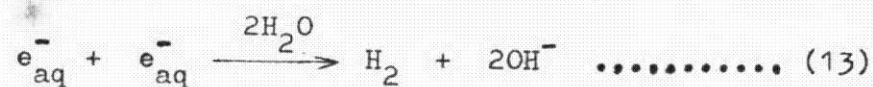bservation of the transient absorption spectrum (λ_{max} = 720 nm) in pulse radiolyzed aqueous solutions (2). It is known as a very reactive species and its half-life is very short in the range of microseconds.

(b) <u>The hydrogen atom</u> (H)

The role of H atoms in radiolysis of aqueous solutions is considerably less than that of the hydrated electron. This situation results from the fact that, at the beginning of the chemical stage of radiolysis, the amount of H atoms is substantially less than that of e_{aq}^-, and that their reactivity is in general considerably weaker.

(c) <u>Molecular hydrogen</u> (H_2)

This reducing species is one of the molecular products in water radiolysis. The origin of the primary molecular hydrogen may be sought in the recombination of e_{aq}^-, i.e.,

$$e_{aq}^- + e_{aq}^- \xrightarrow{2H_2O} H_2 + 2OH^- \quad \dots\dots\dots\dots (13)$$

$$\text{and } e_{aq}^- + H \xrightarrow{H_2O} H_2 + OH^- \quad \dots\dots\dots\dots (14).$$

Also the recombination of H atoms

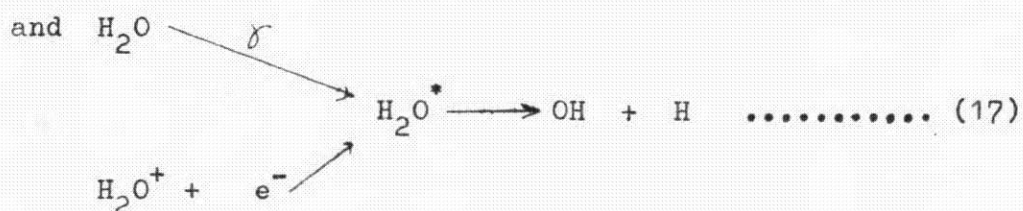$$H + H \longrightarrow H_2 \quad \dots\dots\dots\dots (15)$$

If these reactions are indeed the only source of H_2, then a sufficient increase in concentration of an efficient scavenger for hydrated electrons must also lead to an effective decrease in yield of molecular hydrogen.

2) Oxidizing Species:—

(a) <u>The hydroxyl radical</u> (OH)

This radical is one of the most powerful oxidizing short-lived species. It can oxidize most inorganic ions which can

exist in higher valence states. The origin of the hydroxyl is out-
lined in the following reactions:

$$H_2O^+ \quad + \quad H_2O \longrightarrow OH \quad + \quad H_3O^+ \dots\dots\dots \text{(16)}$$

and

$$H_2O \searrow \gamma$$
$$H_2O^* \longrightarrow OH + H \quad \dots\dots\dots \text{(17)}$$
$$H_2O^+ + e^- \nearrow$$

(b) <u>Hydrogen peroxide</u>(H_2O_2)

Recombination of hydroxyl radicals is the most
probable source of primary hydrogen peroxide

$$OH \quad + \quad OH \longrightarrow H_2O_2 \quad \dots\dots\dots \text{(18)}$$
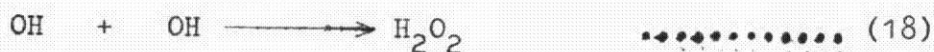
1.2 Radiation-Chemical Yields

The common unit in chemical radiolysis is the radiation
chemical yield, G_R, of free radicals. It is defined (3) as the
number of free radicals escaping initial recombination and available
for chemical reaction per 100 eV of energy put into the solution
by the radiation; similarly a molecular yield, G_M, is defined as
the number of molecules found, per 100 eV energy input, in the
solution at equilibrium.

1.3 Diffusion-Kinetic Model

In a classical chemical reaction, active species are homogeneously distributed in the reaction volume. This is not the case for a chemical reaction induced by radiation where we considered the spatial distributions of primary events; primary active species are produced along the path of an ionizing ray only. Classical chemical kinetics, which takes into account changes in concentration of reacting substances as a function of time is inadequate for a kinetic interpretation of the reactions of active species which are initially distributed inhomogeneously. This is why the diffusion-kinetic model has been proposed for chemical reactions in the early stages of water radiolysis. It takes into account the inhomogeneous distribution which varies with time as the active species diffuse away from their point of origin, reacting with each other or with substances present in solution.

The model is formulated in terms of a system of nonlinear differential equations. Its purpose is only to present some aspects of the model which contribute to a better understanding of water radiolysis: the visualization of events which still escape a direct experimental observation, as well as the possibility of correlating the experimental data on the effect of reactivity with the yields of primary products of water radiolysis.

One assumption is that primary species diffuse away from the place of energy deposition (i.e., from spurs) according to

Fick's macroscopic diffusion law, $\dfrac{\partial C_i}{\partial t} = D_i \nabla^2 C_i$

C_i = the concentration of the species i at time t

D_i = the diffusion constant

and ∇^2 = the Laplacian transform

The eqation is

$$\frac{\partial^2 C_i}{\partial t . \partial r} = D_i \frac{\partial}{\partial t} \left[\frac{\partial C_i}{\partial X} + \frac{\partial C_i}{\partial Y} + \frac{\partial C_i}{\partial Z} \right]$$

The concentration in the diffusion-kinetic model means $C(r,t)$, the probability density of finding a particle at a position in the system determined by vector r at time t after the onset of the chemical stage. The mathematical use of this equation is beyond the scope of this work. However, the model is frequently referred to in the literature when interpreting the results obtained in radiation chemistry.

1.4 Chemical Reactivity of e^-_{aq}

The chemical behaviour of hydrated electron should be different from that of "free" thermalized electrons in the same medium. Secondary electrons produced under radiolytic conditions will thermalize within 10^{-13} sec., whereas they will not undergo hydration before 10^{-11} sec., thus, any reactions with electrons of half-life shorter than 10^{-11} sec. will take place with nonhydrated electrons[2].

Recently Hamill (4) has suggested a model which includes chemical reactions of e_{dry}^- with several e_{aq}^- scavengers. This concept contrasts to the diffusion model which has been assumed that all radicals and ions formed react only after thermalization and solvation of these species have been completed. E. Peled and G. Czapski (5) have studied the effect of several solutes on $G_{e_{aq}^-}$. They found no evidence of prehydration scavenging of e_{aq}^- for other solutes studied except glycine and alanine which are known as poor scavengers of e_{aq}^-. These amino acids decrease $G_{e_{aq}^-}$ substantially. This effect suggests that they may react with some precursor of the e_{aq}^-. Z.D. Draganic' and I.G. Draganic' (6)(7) have also worked on primary yields of water radiolysis including $G_{e_{aq}^-}$. As yet, no conclusion can be drawn from their work but a better understanding of the reaction between the e_{aq}^- precursor and the solutes used, can be obtained.

This present study is an extension of the work of Draganic' and Draganic' (7) mentioned. The competition reactions of amino acids (glycine + alanine) and nitrate ions for e_{aq}^- in the presence of sodium formate have been studied for lower nitrate concentrations in order to obtain more knowledge about the reactions of amino acids with the electrons produced in the radiolysis of water.