I. INTRODUCTION

Since this is a symposium on "Very Early Effects," the time scale under consideration is from the passage of high energy radiation through the system to approximately one nanosecond thereafter. Until the development of pulse radiolysis a few years ago,\(^1\) essentially all chemical measurements were made in times of the order of minutes or greater after passage of the radiation through the system. Pulse radiolysis in its initial form shortened that gap to one microsecond. However, in the diffusion kinetics model\(^2\) all of the spur or track effects are over at those times. In this model a certain "initial" spatially inhomogeneous distribution of products is assumed at times of the order of 1 to 10 picoseconds (10\(^{-12}\) sec) after passage of the radiation. The model then predicts the time evolution of this system, and at about 0.1 to 1 microseconds later the spatially inhomogeneous stage is over, all reactive intermediates (free radicals and...
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solvated electrons) having disappeared by reaction among themselves or with scavengers. Until recently the only test of this model was its ability for predicting measurements made on a time scale of a microsecond or longer. Diffusion-kinetics was one of the few tools available, experimental or theoretical, that gave a detailed description of processes occurring in the time range of $10^{-11}$ to $10^{-6}$ seconds. Very recently the pulse radiolysis technique has been extended to the picosecond time scale and for the first time a more direct experimental test of the validity of the diffusion-kinetic model in predicting events on the $10^{-11}$ to $10^{-9}$ second time scale is available. Already some interesting discrepancies are becoming apparent and an interaction between theory and experiment promises to help elucidate the events occurring at those early stages of the radiolysis of aqueous solutions.

II. EXPERIMENTAL FACTS AT A MICROSECOND AND LONGER TIME SCALE

The basic experimental facts available about 15 years ago concerning the radiation chemistry of dilute aqueous solutions were the effect of linear energy transfer (L.E.T.) and of scavenger concentrations on the primary molecular and free radical yields as determined by experiments performed on a time scale of minutes and longer. These have been very well described in the book by Allen. Essentially, in going from radiations of low L.E.T. to radiations of high L.E.T. the free radical yields decrease and the molecular yields increase. This is depicted in Figures 1 and 2.
In Figure 1 it can be seen, for example, that the molecular yields of $\text{H}_2$ increase from about 0.45 molec/100 eV for 2 MeV electrons to about 1.1 molec/100 eV for $^{210}\text{Po}$ $\alpha$-particles. The corresponding solvated electron primary yields decrease from about 2.8 to about 0.5 molec/100 eV. The total observed yield for water disappearance decreases correspondingly from about 4.1 to about 2.8 molec/100 eV. The effect of scavenger concentration on molecular yields is indicated in Figure 3. Plots of $G_{R_2}/G_{R_2}^0$ against the logarithm of the scavenger concentration, obtained for different scavengers, can be made to coincide approximately, by horizontal translation. Here $R_2$ stands for either $\text{H}_2$ or $\text{H}_2\text{O}_2$, $G_{R_2}^0$ is the primary yield of $R_2$ in the limit of zero scavenger concentration and $G_{R_2}$ is the yield with scavenger present. The value of $p$ was made equal to one for $\text{NO}_2^-$ being the scavenger and $\text{H}_2$ the molecular product. For each scavenger-molecular product combination, $p$ was chosen so as to make all points fall on the same curve. These scavenger effects are independent of dose rate up to $10^8$ rad/sec. It can be seen from Figure 3 that an increase in scavenger concentration by about four orders of magnitude reduces the molecular yields by about 50%. The solid line is theoretical and will be explained in Section V.

These are the basic experimental facts on a long time scale which, together with the more recent information on shorter times, must be considered by any theory which tries to describe the evolution of the system starting at times of the order of $10^{-11}$ seconds or earlier.
III. SIMPLE ONE-RADICAL DIFFUSION MODEL

The diffusion kinetic model in the radiation chemistry of dilute solutions has been reviewed previously.\(^2\) In its simplest form, it assumes that passage of the high energy radiation produces, in a time of the order of \(10^{-12}\) to \(10^{-11}\) seconds, a single kind of radical \(R\) which is inhomogeneously distributed in space. For radiations of low L.E.T., such as \(^{60}\)Co \(\gamma\)-rays, these radicals are distributed spherically around the molecule on which the low energy ionization event took place, and this group of radicals constitute what is called a spur. The radius of such a spur is of the order of magnitude of 10 to 100 Å and the amount of energy involved in its formation is of the order of magnitude of 100 eV. For radiations of high L.E.T., such as \(^{210}\)Po \(\alpha\)-particles, these spurs are assumed to overlap and form a cylindrical track. The spherical spur version of the model for low L.E.T. radiations was first proposed by Samuel and Magee,\(^5\) whereas the inhomogeneity associated to cylindrical tracks in aqueous systems was first proposed by Lea.\(^6\) In this simplified one-radical version of the model it is further assumed that a single kind of radical scavenger \(S\) was present in the medium. The radicals \(R\) are capable of diffusing toward each other and reacting to give molecules \(R_2\), or of diffusing away from each other and reacting with \(S\) to give product \(RS\). The corresponding mechanism is

\[
R + R \rightarrow R_2 \quad k_{RR} \quad (1)
\]

\[
R + S \rightarrow RS \quad k_{RS} \quad (2)
\]

\[
R + R \rightarrow R_2 \quad k_{RR} \quad (1)
\]

\[
R + S \rightarrow RS \quad k_{RS} \quad (2)
\]
The space-time evolution of the radicals is given by the diffusion-kinetic equations

\[
\frac{\partial c_R}{\partial t} = D_R \nabla^2 c_R - k_{RR} c^2_R - k_{RS} c_R c_S
\]  

(3a)

\[
\frac{\partial c_S}{\partial t} = D_S \nabla^2 c_S - k_{RS} c_R c_S
\]  

(3b)

where \( c_R \) and \( c_S \) are the local generalized concentrations (i.e., probability densities) of radicals R at a distance \( r \) from the center of the spur or the axis of the track at instant of time \( t \). \( D_R \) and \( D_S \) are the diffusion coefficients of the R and S, respectively, and the \( k \) are rate constants for the radical-radical and radical-scavenger reactions. \( \nabla^2 \) is the usual Laplacian operator and is given by

\[
\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{\alpha}{r} \frac{\partial}{\partial r}
\]  

(4)

where \( \alpha \) is 2 for spherical spurs and 1 for cylindrical tracks. The left hand side of Eq. (3a) represents the time rate of change of the concentration of radicals at a given position in the spur. The first term in the right hand side represents the net rate of diffusion per unit volume of radicals into that position (i.e., the difference between what diffuses in and what diffuses out per unit volume around that position); the second term represents the rate of disappearance of radicals (per unit volume) due to the recombination reaction (1); and the third term represents the corresponding decrease associated with
The radical-scavenger reaction. Equation (3a) is simply a conservation equation for radicals $R$ involving the diffusion and reaction processes. A similar interpretation is valid for Eq. (3b).

The initial spatial distribution of the radicals is usually assumed to be Gaussian and given by

$$c_R(r, 0, \theta) = c_R(0, 0) \exp\left(-\frac{r^2}{2 r_0^2}\right)$$  \hspace{1cm} (5)

where $r_0$ is the initial radius of the spur or track. In addition, the scavenger is assumed to be distributed homogeneously at $t = 0$.

It is not possible to solve Eqs. (3) analytically. However, with the use of digital computers it is possible to obtain accurate numerical solutions.\textsuperscript{2,8} Such solutions furnish the spatial distribution of radicals at any instant of time $t$.

For spherical spurs let $N(t)$, $N_{R_2}(t)$ and $N_R(t)$ be respectively the number of radicals remaining at time $t$ and the number of $R_2$ and RS molecules formed up to time $t$. For cylindrical tracks let these same symbols represent the equivalent linear densities, i.e., the number of radicals or molecules per unit length of track. Then,

$$N(t) = \int_0^\infty c_R(r, t) 2^\alpha \pi r^\alpha dr$$  \hspace{1cm} (6)

$$N_{R_2}(t) = \frac{1}{2} \int_0^t d\theta \int_0^\infty k_{RR} c_R^2 (r, \theta) 2^\alpha \pi r^\alpha dr$$  \hspace{1cm} (7)

$$N_R(t) = \int_0^t d\theta \int_0^\infty k_{RS} c_R (r, \theta) c_S (r, \theta) 2^\alpha \pi r^\alpha dr$$  \hspace{1cm} (8)
\[ N(t) + 2N_{R_2}(t) + N_R(t) = N(0) = N_0 \] (9)

Let the quantities \( N_{R_2}(\infty) \) and \( N_R(\infty) \) be represented by \( N_{R_2} \) and \( N_R \) respectively. \( \frac{2N_{R_2}}{N_0} \) and \( \frac{N_R}{N_0} \) represent the fraction of the initial number of radicals which have undergone reaction (1) and (2), respectively, and can be calculated numerically from Eqs. (7) and (8) once \( c_R(r,t) \) and \( c_S(r,t) \) have been obtained from the integration of the diffusion-kinetic Eqs. (3). They are related to the molecular and free radical yields and will be called the fractional molecular yield and the fractional radical yield respectively.

Figure 4 shows the behavior of \( \frac{N(t)}{N_0} \), \( \frac{N_{R_2}(t)}{N_0} \) and \( \frac{N_R(t)}{N_0} \) as a function of time for a representative spherical spur. From it it can be seen that at about \( 10^{-8} \) seconds the radical recombination reaction is practically over, whereas the radical-scavenger reaction has barely started; the latter is essentially over in about \( 10^{-6} \) seconds. Thus, the chemical history of this spur terminates in about 1 microsecond and the radical-radical and radical-scavenger reactions do not overlap in time. For higher scavenger concentrations, however, competition between these reactions does occur. It can also be seen from Figure 4 that a large fraction of the radical-radical reaction is over in \( 10^{-9} \) seconds and that to observe its time evolution it is necessary to make observations at times of the order of a few times \( 10^{-11} \) seconds after the passage of the high energy radiation through the medium.

This simple one-radical model explains qualitatively the L.E.T. effect and scavenger effect displayed in Figures 1, 2 and 3.
IV. **GENERALIZED MODEL**

In a more realistic model it is necessary to take into account the several types of reactive species formed as a result of the passage of high energy radiation through the aqueous solution. These are OH, $e^{-}_{aq}$, $H_3O^+_{aq}$ and H. A reasonable mechanism of formation of such species is the following one. The high energy radiation produces, directly or indirectly, ionization of water molecules.

\[ H_2O \rightarrow H_2O^+ + e^- \]  \hspace{1cm} (10)

The $H_2O^+$ ions then rapidly undergo a proton transfer reaction with neighboring water molecules, according to

\[ H_2O^+ + H_2O \rightarrow H_3O^+ + OH \]  \hspace{1cm} (11)

and become solvated into $H_3O^+_{aq}$. The electrons ejected in the ionization process would, in a majority of such events, have a low energy and after traveling a few tens of angstroms, become thermalized and get solvated into $e^-_{aq}$. According to such a model, the initial spacial distributions of OH and $H_3O^+_{aq}$ would be essentially the same, whereas that of the $e^-_{aq}$ would be more spread out. The processes just described would be the major ones. In addition, however, there could be some minor ones, such as the dissociation of excited and super-excited water molecules formed by electron impact:

\[ H_2O \rightarrow H_2O^* \]  \hspace{1cm} (12)
Allen has recently suggested, in order to explain the lack of material balance between oxidizing and reducing species, that an additional primary species, present in small amount, could be O atoms. This species could be formed from the dissociation of $\text{H}_2\text{O}^+$ according to

$$\text{H}_2\text{O}^+ \rightarrow \text{OH}^+ + \text{H}$$

Small amounts of such O atoms were included in some of the calculations described below.

The geometrical distribution of these primary species depends, in the diffusion model, on the quality of the ionizing radiation being used. For example, let us consider the case of $^{60}\text{Co} \gamma$-rays. The interaction of such high-energy photons with the water molecules produces mainly Compton recoil electrons having initial energies which vary over a wide range. These proceed to further ionize molecules producing secondary electrons, which can produce tertiary ones, etc. The L.E.T. of the high-energy electrons is low and, within the framework of the diffusion model, produces in general "local" depositions of energy of the order of 100 eV, generating spherically symmetrical "spurs" which are sufficiently distant from each other so as not to interact. However, a certain fraction of the electrons have low energy and produce spurs which do overlap, and if there are sufficient numbers of these they form cylindrical

$$\text{H}_2\text{O}^* \rightarrow \text{H} + \text{OH}$$ (13)
tracks. Furthermore, as a high-energy electron slows down, it also produces spurs which overlap. Therefore, one must consider the whole distribution of interspur distances corresponding to this spectrum of energy degradation before a meaningful comparison with experiments can be made. However, this distribution is dominated; in the case of $^{60}$Co $\gamma$-rays, by isolated spherical spurs. The initial distribution of primary reactive species within these spurs is assumed to be a Gaussian function of the distance to its center.

Let us now consider a radiation of high L.E.T., such as $^{210}$Po $\alpha$-particles. Here the primary interaction produces local ionizations corresponding to a long string of overlapping spurs which form a cylindrical track, along which the density of reactive species increases as the particle slows down. In addition, energetic secondary electrons can be ejected, forming their own tracks, some of which correspond to a lower L.E.T. than that of the initial $\alpha$-particle, corresponding to a cylinder along which the initial radical density varies relatively slowly with distance. Similarly to spherical spurs, it is usually assumed that this initial radical density is a Gaussian function of the distance to the track axis.

As stated above, these primary reactive species are distributed inhomogeneously with high initial concentrations in the center of spurs or along the axis of tracks. They then proceed to react with each other, or to diffuse away from each other and to react with solutes initially present. The high degree of initial spacial inhomogeneity of the reactive species, and the consequent competition between recombination with each other and diffusion away
from each other, followed by reaction with solutes, is the real essence of the diffusion model.

The initial distribution of the most prominent reactive species, OH, $\cdot e_{aq}$ and $\cdot H_3O_{aq}$ are depicted in Figure 5.

In this generalized situation Eqs. (3) are extended to include all of the appropriate reactions that the reactive species undergo and furthermore there is one equation per reactive species. The numerical investigation of the simple one-radical model described in the previous section has shown$^8$ that one may assume that the scavengers are homogeneously distributed throughout the medium at all times without significant error, i.e., that the effect of scavenger depletion in the spur or track is very small. As a result, equations corresponding to (3b) can be neglected and the $c_s$ in equations corresponding to (3a) can be taken as constant. A realistic mechanism for which diffusion kinetic calculations have been performed$^9$ is given in Table I together with corresponding rate constants. The several $S$ and $P$ stand for scavenger and product. Since very little is known about the rate constants of O atoms in aqueous solutions, they are arbitrarily set at $6 \times 10^9$ M$^{-1}$ sec$^{-1}$. The number of O atoms initially present was assumed to be less than 4% of the initial number of radicals. Therefore exclusion of these atoms would produce only a minor change in the main yields. The diffusion coefficients, $D_i$, initial Gaussian radii, $r_{oi}$, and initial number of radicals per spur, $N_{oi}$, are given in Table II. This mechanism and initial conditions and the corresponding diffusion-kinetic equations were used to calculate the effect of L.E.T. on radical and molecular yields. Account
TABLE I

Mechanism

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant (10^{10} \text{ M}^{-1} \text{ sec}^{-1})</th>
<th>Reaction number</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH + OH  (\rightarrow) H(_2)O(_2)</td>
<td>1.0</td>
<td>16</td>
</tr>
<tr>
<td>OH + e(<em>{aq}) (\rightarrow) OH(</em>{aq})</td>
<td>3.0</td>
<td>17</td>
</tr>
<tr>
<td>e(<em>{aq}) + e(</em>{aq}) (\rightarrow) H(<em>2) + 2 OH(</em>{aq})</td>
<td>1.0</td>
<td>18</td>
</tr>
<tr>
<td>e(_{aq}) + H(<em>3)O(</em>{aq}) (\rightarrow) H + H(_2)O</td>
<td>2.3</td>
<td>19</td>
</tr>
<tr>
<td>OH(_{aq}) + H(<em>3)O(</em>{aq}) (\rightarrow) 2 H(_2)O</td>
<td>14.3</td>
<td>20</td>
</tr>
<tr>
<td>H + OH  (\rightarrow) H(_2)O</td>
<td>3.2</td>
<td>21</td>
</tr>
<tr>
<td>H + e(_{aq}) (\rightarrow) H(<em>2) + OH(</em>{aq})</td>
<td>3.0</td>
<td>22</td>
</tr>
<tr>
<td>H + H  (\rightarrow) H(_2)</td>
<td>2.6</td>
<td>23</td>
</tr>
<tr>
<td>e(_{aq}) + H(_2)O(<em>2) (\rightarrow) OH(</em>{aq}) + OH</td>
<td>1.23</td>
<td>24</td>
</tr>
<tr>
<td>H + H(_2)O(_2) (\rightarrow) OH + H(_2)O</td>
<td>0.016</td>
<td>25</td>
</tr>
<tr>
<td>OH + S  (\rightarrow) P</td>
<td>0.6</td>
<td>26</td>
</tr>
<tr>
<td>e(_{aq}) + S' (\rightarrow) P'</td>
<td>0.6</td>
<td>27</td>
</tr>
<tr>
<td>H + S'' (\rightarrow) P''</td>
<td>0.6</td>
<td>28</td>
</tr>
<tr>
<td>O + H(_2)O(_2) (\rightarrow) O(_2) + H(_2)O</td>
<td>0.6</td>
<td>29</td>
</tr>
<tr>
<td>O + H(_2)O(_2) (\rightarrow) OH + HO(_2)</td>
<td>0.6</td>
<td>30</td>
</tr>
<tr>
<td>O + e(<em>{aq}) (\rightarrow) OH + OH(</em>{aq})</td>
<td>0.6</td>
<td>31</td>
</tr>
<tr>
<td>O + OH(_{aq}) (\rightarrow) HO(<em>2)(</em>{aq})</td>
<td>0.6</td>
<td>32</td>
</tr>
<tr>
<td>O + H  (\rightarrow) OH</td>
<td>0.6</td>
<td>33</td>
</tr>
<tr>
<td>O + OH  (\rightarrow) HO(_2)</td>
<td>0.6</td>
<td>34</td>
</tr>
<tr>
<td>O + S'' (\rightarrow) P''</td>
<td>0.6</td>
<td>35</td>
</tr>
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</table>
### TABLE II

Diffusion coefficients and initial conditions

<table>
<thead>
<tr>
<th>i</th>
<th>Species</th>
<th>( D_i ) (10^{-5} \text{ cm}^2/\text{sec})</th>
<th>( r_{0i} ) (Å)</th>
<th>( N_{0i} ) (radic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OH</td>
<td>2</td>
<td>6.25</td>
<td>2.10</td>
</tr>
<tr>
<td>2</td>
<td>( e_{aq}^- )</td>
<td>4.5</td>
<td>18.75</td>
<td>2.08</td>
</tr>
<tr>
<td>3</td>
<td>( H_2O_{aq}^+ )</td>
<td>10</td>
<td>6.25</td>
<td>2.08</td>
</tr>
<tr>
<td>4</td>
<td>O</td>
<td>2</td>
<td>6.25</td>
<td>0.08</td>
</tr>
<tr>
<td>5</td>
<td>H</td>
<td>8</td>
<td>6.25</td>
<td>0.18</td>
</tr>
<tr>
<td>6</td>
<td>( OH_{aq}^- )</td>
<td>2</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>( H_2O_2 )</td>
<td>1.4</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
was taken of the spectrum of energy degradation. The results obtained are represented by the points and full lines of Figures 1 and 2. The dashed lines are experimental. As can be seen the agreement is quite satisfactory.

V. PUZZLES IN COMPARISON WITH EXPERIMENTS AT TIMES OF 1 MICROSECOND AND GREATER

As pointed out in the previous section, the agreement between theory and experiment over a large L.E.T. range is sufficiently satisfactory so as to not present any substantial puzzles. However, until relatively recently some discrepancies did remain associated with the effect of scavenger concentration and of pH on primary yields as well as on the isotope separation factors. We shall proceed to discuss these puzzles.

Effect of Scavenger Concentration

The solid curve in Figure 3 is the diffusion-kinetic theoretical curve for H₂ obtained from the mechanism and parameters described in the previous section, i.e., the same parameters which furnished good agreement with L.E.T. effects. The only change is that the rate constant of reaction (27) was made equal to \(0.46 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}\) which is the experimental value for the reaction of \(e^-_{\text{aq}}\) with \(\text{NO}_2^-\) solutions. The spectrum of energy degradation was taken into account in the exact same way as for the L.E.T. effects. As can be seen, the agreement between theory and experiment is quite good.
up to scavenger concentrations of about 0.3 M. However, it is evident that the curvature of the theoretical curve is somewhat more pronounced than that of the experimental one. This discrepancy can be removed by assuming that a certain fraction of the molecular products do not have free radical precursors, but come from a first order disappearance of excited water molecules. Observation of Figure 3 indicates that at a scavenger concentration of about 10 M essentially all of the radicals should have been eliminated and, therefore, that the remaining H₂ yield, equal to about 1/5 of its value at low concentration, could be due to an H₂O* precursor. This problem has been analyzed more quantitatively by Schwartz, who concluded that the fraction of the molecular H₂ yield not coming from a free-radical precursor should be about 1/3 rather than 1/5. In any event, the discrepancy between theory and experiment is thereby eliminated.

Effect of pH

The mechanism in Table I includes in it the effect of pH due to the presence of reactions 19 and 20. When experiments are done in acid solutions, reaction 19 transforms most of the solvated electrons into H atoms, increasing the extent of reactions 21 and 23. Calculations of primary yields in acid solutions were done by Schwarz, who found that there was good agreement with the total H atom plus solvated electron yields but that the H₂ yields were high by 10 to 20%, when using the same parameters which gave...
good agreement in neutral solutions. Since in the latter the contribution of reactions 21 and 23 was relatively small, an upward change in the diffusion coefficient for H atoms would not affect the neutral yields but bring about better agreement with the acid yields. It seems, therefore, that no real disagreement exists between theory and experiment for acid solutions.

Isotope Separation Factors

Anbar and Meyerstein\(^{14}\) have studied isotope factors in dilute HDO solutions and have determined the separation factors \((\text{H/D})_{\text{gas}} / (\text{H/D})_{\text{liq}}\) for the molecular H\(_2\) yields and for reactions 18, 22 and 23 of Table I as a function of acid concentration. The separation factor for reaction 18 was found to be \(4.7 \pm 0.2\) and that for reaction 23 was \(2.7\) in neutral solutions and \(3.4\) in \(0.2\ M\) acid solutions. The separation factor for reaction 22 was \(1.6\) and \(1.7\) for these two solutions, respectively. However, in the radiolysis of solutions containing \(25\%\) deuterium, the separation factor for the molecular H\(_2\) yield was essentially independent of pH over the pH range of 1 through 11 and equal to about 2.22. This was very puzzling initially, since it seemed to indicate that reactions 18, 22 and 23 could not be the initial contributors to the molecular H\(_2\) yield. However, Schwarz\(^{13}\) has shown that a separation factor of 1.8 for the part of the molecular H\(_2\) yield which does not have a free-radical precursor would give agreement with Anbar and Meyerstein's results in neutral solutions. Assuming this separation factor to be independent of pH, which is very reasonable, he was then able to
calculate the dependence of the separation factor for the total molecular $H_2$ yield as a function of pH and show that there was good agreement with all of Anbar and Meyerstein's data. The reason for the pH independence observed was that the mixtures of reactions 18 and 22 have an average isotope effect which is coincidently equal to that of reaction 23 in acid solutions. Therefore, the puzzle of the separation factors has also been solved.

VI. PUZZLES IN THE TIME RANGE OF $10^{-11}$ TO $10^{-8}$ SECONDS

Recently Hunt and co-workers$^3$ have developed pulse radiolysis techniques which permit observations of reactive intermediates in the radiolysis of aqueous solutions on a time scale of 20 picoseconds. The technique uses the fine structure electron pulses (of 10 picoseconds duration) produced by a 30 MeV beam from a linear accelerator to produce transient species. The Čerenkov light associated with these pulses is used to detect the solvated electrons produced. A stroboscopic effect is created by varying the time delay between the Čerenkov light flashes and the fine structure pulses. This is achieved by deflecting the light around a path of variable length. A change of 3.3 mm in the length of this path corresponds to a change in the time delay of 1 picosecond. With this technique they have studied the decay of the solvated electron signal in a .75 M and 1.50 M perchloric acid solution.$^{3b}$ During the 350 picoseconds which separate the fine structure pulses, that signal increases to its maximum value in about 10 picoseconds and then decays exponentially with time according to a pseudo first order reaction. The process
responsible for this decay is reaction 19. The resulting bimolecular rate constant, extrapolated to low acid concentration, agrees well with those measured at a microsecond time scale. It might be superficially thought that the exponential decay is characteristic of pseudo first-order reactions for a spatially homogeneous distribution of reagents and, therefore, that it might be inconsistent with the spur model. However, this is not the case. In acid solutions at the concentrations used, reaction 19 is extremely important and overwhelms reaction 18. In the absence of reaction 18, reaction 19 would show a pseudo first-order behavior, with an exponential decay of the $e_{aq}^-$, regardless of whether the latter are distributed homogeneously or inhomogeneously. A detailed analysis of the diffusion-kinetic calculations shows that in spite of the presence of reaction 18 during the lifetime of the spur, the decay of $e_{aq}^-$ is still exponential at the acid concentrations considered. The effect of bimolecular reaction 18 is to increase somewhat the apparent first-order rate constant obtained from the exponential decay. This increase has been observed experimentally by Hunt, et al. However, an additional factor contributes to the increase in the apparent rate constant for reaction 18 as the acid concentration decreases. This is the acid effect and it probably overwhelms the diffusion-kinetic effect just described. In any event, there is no disagreement between the time rate of change of the solvated electron in acid solutions on a time scale of $10^{-14}$ seconds and diffusion-kinetics.

On the other hand diffusion-kinetics makes a definite prediction for neutral solutions which could be tested by experimental
observation. As can be seen from Figure 4 there should be a decay of approximately 35% on the solvated electron concentration in going from \(10^{-11}\) seconds to about \(10^{-8}\) seconds due to inhomogeneous reactions during the spur stage of solvated electrons with other solvated electrons, hydroxyls and hydrogen atoms. These reactions are essentially over by the time a scavenger present in millimolar concentrations or less starts reacting with the solvated electron. Since \(G_{e_{\text{aq}}} = 2.8 \text{ molec/100 eV}\), this should be the value measured at times of the order of \(10^{-8}\) seconds or longer. However, for times of the order of 20 picoseconds, Figure 4 would predict a value of 4.3 molec/100 eV. The more accurate calculations described in Section IV also predicts a value of 4.6 molec/100 eV. This difference is sufficiently large so that it should be possible to measure it. This measurement is somewhat difficult to make with the University of Toronto's linear accelerator employed by Hunt, et al., because it puts out about 40 fine structure pulses over a period of 12 nanoseconds and this tends to blur the time resolution of the experiments for species living more than 350 picoseconds. To make a good direct observation of the decay of solvated electrons from \(10^{-11}\) to \(10^{-8}\) seconds it would be necessary to do experiments using a small number of 10 picosecond electron pulses, preferably one to two.

Nevertheless, Bronskill has been able, by relating the measured dose to the observed \(e_{\text{aq}}^{-}\) absorption signal at 30 picoseconds, to make an estimate of the absolute \(G_{e_{\text{aq}}}^{-}\) at that time. The result is \(3.2 \pm 0.5 \text{ molec/100 eV}\). Unfortunately, the experimental
uncertainty of this determination spans a wide interval. If the 3.2 value is confirmed in a more accurate determination, this would present a very severe puzzle for the diffusion model and could require a significant revision of either the model or the mechanism leading to the assumed initial conditions. Another interesting experimental observation\textsuperscript{17} is that most $e_{aq}^-$ scavengers are capable of reducing the yield of $e_{aq}^-$ at 10 picosecond times. This suggests that these scavengers are capable of reacting with a precursor of $e_{aq}^-$. Such a precursor has up to now not been included in the diffusion-kinetic model. Sawai and Hamill\textsuperscript{18} have suggested that $H_2O^+$, which they call the dry hole, is also a scavengable species. Therefore, as a result of these observations, it may be necessary to add two additional reactive intermediates to the diffusion model. In conclusion, measurements made during the last two years on a time scale of 10 picoseconds have brought about new experimental information which has created new puzzles which when solved should substantially increase our understanding of the very early effects in the radiolysis of aqueous solutions.
REFERENCES


FIGURE LEGENDS

Figure 1 Variation of $G_{e_{aq}}^-$, $G_{OH}^-$, $G_{H_2O_2}$, $G_H$ and $G_{H_2}$ with average L.E.T. The points and full lines represent theoretical calculations, corresponding to the radiations indicated. The dashed lines are experimental.\(^{11}\)

Figure 2 Variation of $G_{-H_2O}$ with average L.E.T. The points and full line represent theoretical calculations corresponding to the radiations indicated. The dashed line is experimental.\(^{11}\)

Figure 3 Variation of $G_{R_2}/G_{R_2}^0$ with $p_{CS_0}$ for $^{60}$Co $\gamma$-rays. The points are experimental.\(^{12}\) The solid curve is theoretical and is explained in the text.

Figure 4 Variation of $N(t)/N_0$, $2N_{R_2}(t)/N_0$, and $N_{R_2}(t)/N_0$ with time for a spherical spur. Gaussian initial distribution. $N_0 = 12$ radicals, $r_0 = 10$ Å, $D_R = 4 \times 10^{-5}$ cm$^2$/sec, $D_S = 4 \times 10^{-6}$ cm$^2$/sec, $k_{RR} = k_{RS} = 6 \times 10^9$ M$^{-1}$ sec$^{-1}$, $c_{S_0} = 10^{-3}$ M.

Figure 5 Initial distribution of OH, H$_3$O$^+$ and $e_{aq}^-$ in a typical spherical spur.
Figure 5
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By ___________________________

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