

# Chapter 1

## An Incomplete History of Radiation Chemistry

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### 1. Introduction

Radiation chemistry, like all fields of science, has been strongly influenced by the techniques that were available to make measurements. As more and more sophisticated techniques become available, more and more sophisticated questions were posed and answered. In this short review of the history of radiation chemistry, I will select the various eras of radiation chemistry, as defined by the techniques available, and discuss the concepts and conclusions of the time. At the end, I will summarize where radiation chemistry is and what are the unanswered questions and new techniques that are needed to answer these questions. Much more on such topics will be found in the rest of the volume.

Radiation chemistry has developed very similarly to photochemistry. Max Matheson, one of the pioneers of radiation chemistry, said, "Radiation chemistry always trails photochemistry in time response." That trend continues today.

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The eras of radiation chemistry can be quickly summarized as:

- Experiments done with naturally occurring isotope sources,
- Experiments using high-power X-ray machines,
- Experiments using artificially produced isotope sources,
- Pulse radiolysis experiments,
- Sub-nanosecond pulse radiolysis experiments,
- Picosecond and femtosecond laser experiments,
- Future — true picosecond radiolysis experiments.

This outline, while useful, does not include two important subjects in the evolution of radiation chemistry: the role of theory and the role of modern heavy-ion-radiolysis experiments. One can describe different types of radiation by the rate at which they deposit energy going through a sample. The conventional term is linear energy transfer, abbreviated LET. High-LET radiation deposited energy densely along the path of the ionizing particle while low LET radiation deposited energy discretely along the path of the ionizing particle. Examples of low-LET particles are high-energy X-rays/gamma and electrons. High-LET particles include heavy ions, alpha particles and neutrons.

It is well to remember that much of the early progress was inhibited by the lack of the internet to facilitate transfer of early experimental knowledge. Of course, those experiments were also assisted because there was no internet to act as a massive time sink.

Please also excuse errors in summarizing the earlier experiments. Information about these was obtained by reading the literature and by reading review articles by the relevant authors, as I was not in the field yet. In particular, I will be making use of the information in *Early Developments in Radiation Chemistry* edited by Jerzy Kroh,<sup>1</sup> a book that collected the personal accounts of many of the most prominent radiation chemists of the middle of the 20th century, and *The Chemical Effects of Alpha Particles and Electrons* by Samuel C. Lind,<sup>2</sup> which discussed much of the radiation chemistry up to 1928.

## 2. The Period of Natural Isotopic Sources

The discussion in this section is primarily based on Lind's book.<sup>2</sup> Much of the early work in radiation chemistry was done either with radium sources and/or radon sources. These sources produced primarily alpha rays and weak beta rays. The lack of penetrating power of these particles made early experiments very difficult.

Many of the early experiments measured the effect of radiation on solids, such as the darkening of glass, the change in form of certain minerals, etc. These experiments required a considerable time (often weeks or months) and inherently were very difficult to quantify. No well-established techniques existed for measuring the amount of dose that was deposited in a liquid or solid target, so results varied from laboratory to laboratory.

While there was considerable confusion in the earliest experiments, it appears that most researchers had realized that radiation chemistry depended on the deposition of the energy in the solvent or dominant species and then a redistribution of the energy from the solvent. The exact nature of the early events where energy was deposited in the solvent (or dominant material) and then transferred to the compounds of interest was not known, but the similar products that one would get with different ratios of gases were strong indicators of the role of energy deposition in the solvent.

Early liquid phase experiments determined the formation of hydrogen and oxygen from the radiolysis of water along with the production of  $\text{H}_2\text{O}_2$ . The yield of hydrogen to oxygen was not two to one, so it was recognized that the third primary product was hydrogen peroxide. Yields were not well established, because one could not easily establish the dose that was deposited in the material.

Quantification of results first came in the radiolysis of gases. Conductivity-type experiments determined the number of ions that would be formed in a particular gas. The yield of products could then be compared with the amount of ionization. This ratio was referred to as  $M/N$ , where  $M$  was the yield of products and  $N$  was the number of ions that were formed by the radiation. It was believed that

when the ratio of products formed to the number of ions formed was much larger than one, that this was a measure of the size of clusters around the ions in the gas phase.

Early experiments in liquids were quite variable for many reasons. The conductivity technique, which was used in the gas phase to measure dose, was not applicable to the liquid phase. Reactions were measured using dissolved radium salts or radon gas as the ionization source. Some thought the chemistry was due to the reactions with radium; however, it was soon recognized that it was the emitted rays that caused the decomposition. Both radium and radon could cause radiation damage. Because the radon would be partitioned between the gas and liquid phase, the amount of energy that was deposited in the liquid depended critically on the experimental conditions such as the pressure and amount of headspace above the liquid. In addition, because the sources were weak, long irradiation times were necessary and products, such as hydrogen peroxide, could decompose.

In summary, in this first era of radiation chemistry it was discovered that the medium absorbs the energy and the result of this energy absorption leads to the initiation of the chemical reactions. The role of radium in these systems was not as a reactant or as a catalyst, but instead as a source of radiation. Most quantitative work was done with gases. It was learned that there was a close correspondence between the amount of ionization measured in a gas and the yield of chemical products. Solid and liquid-phase radiolysis studies were primarily qualitative.

### **3. X-Ray Generator in Radiation Chemistry**

In the late twenties, research started using powerful X-ray generators. With X-rays, it was then possible to use photons that would penetrate vessels and evenly irradiate a reasonable physical volume. With this capability and the development of small ionization chambers to measure X-ray dose, it now became possible to carry out quantitative radiolysis experiments in liquids.

Fricke demonstrated that the yield of  $\text{Fe}^{3+}$  in the radiolysis of ferrous sulfate was independent of the concentration of the ferrous

salt over a wide range.<sup>3</sup> This showed that the energy deposition was to the solvent, and was subsequently passed on to the ferrous ions. He determined the yields in air- and oxygen-saturated systems. This became the Fricke dosimeter, probably the most used dosimeter for the measurement of the amount of radiation. With this advancement, it then became possible to accurately and easily measure the total amount of radiation striking a system and thus to make meaningful quantitative measurements.

At the time, it was known that water could be decomposed by heat or by UV irradiation. However, irradiation by X-rays seemed to show no decomposition of very pure water. This led Hugo Fricke to conclude that radiation created two forms of excited water, which could react with additives in the system or decay back to normal water. Today we certainly know that radiation does decompose water.

It had been hypothesized that the biological effects would arise from the hydrogen peroxide formed in solution. Experimental measurements showed that this was not the case; the results of the ionizing radiation, and in Fricke's picture, the activated water molecules were the important species.

#### **4. Steady-State Radiolysis, the War Years and After**

During World War II, the atomic-bomb-development effort in the United States required a sudden increase in the knowledge of radiation chemistry. Water was going to be part of the reactors that were to produce plutonium to make bombs. Materials, including vacuum pumps, hoses, connectors and oils were to be exposed to very high levels of neutron and gamma radiation. Previous work was totally insufficient to understand the effects on these materials.

In the United States, a group under Milton Burton was formed to make these studies<sup>4</sup> while other research occurred in Canada and elsewhere. These research efforts made use of all radiation sources that were available. It was quickly realized that the experiments had to both be able to predict the effects of radiation on materials, and obtain a basic understanding of the chemistry and physics involved so that intelligent predictions could be made on new systems.

The first efforts were focused on pure water on the assumption that water was an important ingredient in most systems and would be the simplest to understand. Tremendous variability was found in the experimental results and pure water studies were curtailed and efforts were focused on systems closer to those of practical importance, water with ionic solutes. These results were significant in many ways. The experimental results were satisfying both practically and experimentally. The systems were reproducible and of significance to the development of the war effort.<sup>5</sup>

All of these efforts attempted to understand what role radiation played in the generation of the chemistry. In the usual confluence that often occurs in science, the role of radicals, and in particular the H and OH radicals was recognized in many places more or less simultaneously.<sup>5,6</sup> The first published description of the role of radicals was by Weiss in 1943<sup>6</sup> as the groups working on bomb production were not allowed to publish their work. These ideas were refined over time.

Allen first described the role of back reactions in the radiation chemistry of water.<sup>5</sup> This mechanism made clear the reason for the apparent lack of water decomposition in pure water that had been observed by Fricke and which led Fricke to suggest the dominant role of excited water in the radiation chemistry of water. Later on, this understanding of back reactions would be critical in allaying the fears of the “hydrogen bubble” that was suggested that could have occurred in the Three-Mile-Island reactor incident.<sup>7</sup> Early reports that suggested that there could be a serious consequence from the hydrogen formed by the radiation in the reactor incident were quickly corrected with the known understanding of the importance of back reactions.

Experiments during the war years showed the importance of the different types of radiation, alpha particles, neutrons, and beta particles and gamma rays. These studies also were part of the understanding of the role of back reactions in radiation chemistry.

The rise of reactors after the war led to one of the most important advances in radiation-chemical techniques, the Cobalt-60 and Strontium-90 sources. With a reactor, it is possible to create an

intense radiation source that made possible many of the advances that occurred over the next several decades. One interesting story is that told by Professor Kroh, who took a radiation source back to Poland in a lead pig. He stored it under his bed on the boat back from Canada.<sup>8</sup> The cobalt-60 source made relatively inexpensive, relatively simple source that could be used in many university environments. The source put out an energetic gamma ray that could easily and uniformly irradiate a liquid target. In the early days of radiation chemistry, the gamma-emitters were too weak to carry out sufficient chemistry for easy study. The alpha- and soft beta-emitters could not be conveniently used with liquids because the range was too short and it was thus difficult to measure radiation doses. The cobalt (and cesium) source solved these problems as Allen has discussed when he enumerated the advantages of isotope sources.<sup>9</sup>

The development of the sources led to studies in polymers, solids, organic systems, which were too numerous to mention. One only needs to look at the chapters by Dole, Willard and others in the book on the history of radiation chemistry to find the wide range of chemical systems that could be studied.<sup>1</sup>

Low temperatures that allowed one to trap long-lived species and electrons in glasses could be studied using spin resonance techniques.<sup>10</sup>

In the radiation chemistry of water, many steps of the process were clarified. The radical mechanism for the radiation chemistry of water was confirmed and the existence of multiple additional species other than H, OH and H<sub>2</sub>O<sub>2</sub>, such as HO<sub>2</sub>, O and other similar radicals were deduced. One additional complication became clear; there appeared to be two types of H atoms, with different reactivities. Dainton writes of having suggested that one of them might be an electron in solution; however, he was assured by James Franck that that species could not live for chemically significant times.<sup>11</sup> After several years, Dainton shook off this pronouncement and both he<sup>12</sup> and Czapski and Schwarz<sup>13</sup> measured the ionic-strength dependence of the reaction of the “H-atom” and showed that it had a negative charge.

## 5. A Slight Detour in Our “Tour Through Radiation-Chemistry Techniques”

At this point, I would like to discuss two techniques that do not conveniently fit the technique ordering/timeline for the advances in radiation chemistry. Use of high-LET radiation has been common since the beginning of radiation chemistry. As was mentioned earlier, high-LET radiation studies were common in early experiments because sufficient energy could be deposited to make it possible to observe reaction products. If low-LET sources were used, so little energy was deposited that the yield of products was too low to measure.<sup>2</sup>

Early on, the differences in the products from radiolysis of water were noticed. It was found, as mentioned above, that the radiolysis of pure water seemed to lead to almost no damage. If there were impurities in the water, radiation damage would occur. However, irradiation by high LET radiation would clearly lead to the formation of hydrogen. Further experiments showed that if one irradiated a sealed sample with high-LET radiation, and then the sample was irradiated with a low-LET source, the gas formed by the radiation would then disappear and it would appear as if there were no long-term decomposition. These data were part of the reason that A. O. Allen proposed the theory of radiation chemistry where back reactions occurred.<sup>9</sup>

The rise of heavy particle accelerators made it possible to study the radiation chemistry as a function of particle LET with machines such as the Lawrence Berkeley Bevatron and others that allowed the expansion of radiolysis to very heavy ions and *very high* LET.

The explanation for the differences of LET radiations arose out of the theoretical development in radiation chemistry. The basic theory is relatively simple; an ionizing particle goes through the solution, creating ions and excited states. These regions of excitation and ionization will be much closer together in high LET particles. In essence, in a simplified framework, high-LET particles make a cylindrical track of ionization, which can be approximated as two-dimensional diffusion. The low-LET particles create ionization regions



that are disjoint and can be approximated by spherical regions. There is a fundamental difference in the solution of these two problems; in cylindrical geometry, eventually everything will recombine, while in spherical geometry, there is a non-zero escape probability. In practice, we know that the escape yield is only a few percent for hydrocarbons, while for water at room temperature, the escape probability is 70%.

The simple description of the probability of energy deposition by high-energy particles is, unfortunately, not sufficient to describe the ultimate chemistry. One must also consider the energy loss from the secondary electrons created by the ionizing radiation, the distance that low energy electrons will travel and what species will be formed. These are not easily simulated using the simple physical principles that describe energy loss from high-energy electrons.

There were two thoughts on the ultimate fate of the electron. Samuels and Magee suggested that the electron would recombine very quickly with the positive ion, potentially leading to the formation of excited states.<sup>14</sup> Platzman suggested the electron would be thermalized and would associate with the water molecules in the solution to form a hydrated electron.<sup>15</sup> He even suggested where the electron would absorb. We know the resolution of this question — a hydrated electron was formed, presumably leading to different distance distributions for the electron. However, Platzman was not omniscient — he had suggested that the electron would have a lifetime of a few nanoseconds or so in water and as we know, with sufficient care, lifetimes into the millisecond range can be obtained.

The diffusion theory of radiation chemistry was developed by many authors in many places. A listing of many of these works is given in the review article by Kuppermann.<sup>16</sup> In the cited articles, the general basis of modern models of radiation chemistry was developed, except that the reactive species were the H atom and the OH radical. Distributions were estimated for the radical species, and even the role of scavengers was considered. With the advent of digital computers, these models could now be calculated in the complexity that might begin to reproduce the actual system. Flanders and Fricke started with integrating the equations (yes the same Fricke of biophysical radiation

chemistry fame).<sup>17</sup> Kuppermann and his collaborators did a large series of calculations, testing the importance of different parameters.<sup>18</sup> The possible parameters became more constrained with the identification of the hydrated electron (experimental work is discussed in the next section). The test for these calculations was to determine the yields of various products in the presence of variable concentrations of scavengers. Probably the seminal paper for this approach was by Schwarz in 1969, who calculated yields for various chemical systems using a form of modified prescribed diffusion.<sup>19</sup> Because of the speed of the calculations, the use of a prescribed diffusion model made it possible to survey a much larger range of parameters.

Models continued to develop including stochastic models and simplifications of the stochastic model, which provided insight into the fact that the systems are not continuous.

This excellent agreement with experimental data only lasted until sub-nanosecond pulse radiolysis experiments became common. We will return to this in Sec. 7.

## 6. The Development of Pulse Radiolysis

In science, one builds models based on experimental data and one then attempts to verify these models. Experiments using isotope sources provided data that were explained with microscopic models. However, these models could only be indirectly tested because entities that took part in these reactions were too short-lived to be directly observed. Photochemistry had the same problems and to solve it, the techniques of sector photolysis and flash photolysis were developed. The attempts to create sector radiolysis were only marginally successful. The analog of flash photolysis, pulse radiolysis, was developed in three laboratories almost simultaneously and the first publications appeared within a month of each other.<sup>20-22</sup>

The early studies measured the radicals that occurred in various inorganic and organic systems, including the benzyl radical in cyclohexane, and  $I_2^-$  in water using spectrographic techniques. Soon, spectrophotometric techniques made the measurement of kinetics possible and techniques were expanded to include spin resonance

techniques, conductivity, resonance Raman and fluorescent techniques, to list just a few.

The observation and identification of the red spectrum of the hydrated electron was a major advance that occurred using pulse radiolysis. Keene may have first observed this absorption, and Matheson suggested that this observation might be the hydrated electron.<sup>23</sup> This observation was only an aside and, while written before the paper of Hart and Boag, was not published until after their paper. While chemical evidence had strongly suggested that the hydrated electron existed,<sup>12,13</sup> the publication of Hart and Boag<sup>24</sup> was the final confirming experiment that appeared to completely convince the community. The similarity to the electron spectrum in alkali metals, the chemical reactivity and the observation that its reactions were consistent with a negatively charged species certainly confirmed the identification.

The measurement and identification of the hydrated-electron spectrum led to a major increase in activity. It was now possible to directly measure the rate of hydrated-electron reactions with a large variety of inorganic and organic species. With these data, it was then possible to classify reactions in ways that had not been possible previously. It was possible to show that some reactions were diffusion controlled and to suggest that there were some reactions that were even faster than diffusion controlled (at least if one assumed normal reaction radii).<sup>25</sup> Conductivity measurements could directly measure the mobility of ions and could provide information that was unavailable in other ways.<sup>26</sup>

Spectra and kinetics were also determined for many other species. The solvated electron was observed and its spectrum was determined in a wide variety of solvents, from ethers and alcohols to hydrocarbons and even supercritical fluids. Other radicals, including the benzyl radical, the first species studied in pulse radiolysis, were observed. Excited states, both singlet and triplet, anions and cations, were determined for aromatic species. The number and variety of species is large. The importance of these studies was that it was now possible to observe the intermediate states in the radiation-chemical reactions and thus confirm or refute reaction mechanisms that had been proposed based on product yield data.

Radiation chemistry also made it possible to prepare radicals and ions of interest and study their properties. With the advent of pulse radiolysis, it was possible to directly explore the reactivity of such intermediates. In fact, many reactions that were suggested to be of importance in solar energy conversion could be more cleanly studied using radiation chemistry. Similarly, questions about the mobility of actinide species in the biosphere often depended on the reactivity of different oxidation states of materials such as plutonium. Thus, it was possible to show that plutonium oxides were unlikely to move quickly through water in the earth, because the soluble oxides were very reactive and the equilibrium values were far to the side of the insoluble compounds.

One particular example of the use of pulse radiolysis to general chemistry was the work of Miller and co-workers on the rates of electron-transfer reactions. These studies, which were begun using reactants captured in glasses, were able to show the distance dependence of the reaction of the electron with electron acceptors.<sup>27</sup> Further work, where molecular frameworks were able to fix the distance between electron donors and acceptors, showed the dependence of electron-transfer rate on the energetics of the reaction.<sup>28</sup> These studies were the first experimental confirmation of the electron transfer theory of Marcus.

One of the first experiments on the radiation chemistry of water was the work of the biophysicist, Hugo Fricke. With this background, it is not surprising that the new pulse radiolysis techniques were applied to biological molecules and biological chemistry. The reactions of the hydrated electron with amino acids, proteins, nucleic acids and DNA were studied in great detail. The spectra of the intermediates were also determined. The unfortunate situation is that most biological damage arises out of the reaction of OH radicals rather than the hydrated electron, so while the data on electron reactions are interesting, they are often not of great consequence in understanding biological damage. Rates for hydroxyl radical reactions can be determined by observing the formation of products, or by competition, where one observes the spectrum of the competing product. The direct measurement of the OH kinetics is difficult

because the OH radical is weak and absorbs in the ultraviolet in a region where most species absorb.

Above we talked about the diffusion models that were used to explain the chemical products that occur after irradiation with low-LET radiation. It was pointed out that models, in addition to making specific predictions about the yield of products, also made predictions about the time dependence of products. For low-LET radiation, these models suggested that the primary non-homogeneous reactions would occur in the 30–300-ps-time scale and that there would be continuing decays at longer times. Experimental data, for example by Buxton<sup>29</sup> and Thomas<sup>30</sup> suggested that the data were not inconsistent with these suggestions.

## 7. Sub-nanosecond Pulse Radiolysis

To address the questions of non-homogeneous/spur kinetics, John Hunt and his group at Toronto developed a sub-nanosecond pulse-radiolysis system.<sup>31</sup> In their stroboscopic pulse radiolysis system, they could observe from about 30 to 350 ps after the pulse with a time resolution of about 10 ps. Their results showed no significant decay of the electron between 30 and 350 ps, which was not consistent with the diffusion-kinetic models of spur decay in radiation chemistry.

The foray into sub-nanosecond pulse radiolysis was continued by Matheson and Jonah at Argonne,<sup>32</sup> Tabata and co-workers in Tokyo,<sup>33</sup> and Katayama and co-workers in Hokkaido.<sup>34</sup> The experiments at Argonne measured the decay of the hydrated electron both from about 100 ps to 4 ns and from 1 ns to 40 ns.<sup>35</sup> These results clearly showed that the decay measured was approximately a factor of 10 slower than that predicted by theory. The decay profiles are very similar to those determined using a linac-laser combination about 15 years later.<sup>36</sup> The decay of the OH radical was also considerably slower than what theory predicted,<sup>37</sup> which is, of course, no surprise that the two should decay at similar rates.

Hamill had suggested that there was a precursor of the hydrated electron that could be scavenged and called this species the dry electron.<sup>38</sup> Work by the Hunt group with his stroboscopic pulse radiolysis

system determined a large number of such apparent reactions and found a good correlation between the rate of precursor scavenging and the rate of the reaction of the hydrated electron.<sup>39</sup> The only example that they found that did not correlate was the proton — the reaction of the electron with the proton was very fast; however there was no apparent reaction of the electron precursor. The Argonne group, guided by the studies of Miller in “tunneling” reactions, attempted to find species that the rate of the dry electron and the hydrated electron did not correlate. Probably the clearest example was the selenate anion.<sup>40</sup>

Czapski and Peled<sup>41</sup> pointed out that many of these apparent cases of precursor reactions could be equally well explained by the radiation-chemical analog of photochemical “static scavenging”, which in the photochemical case was when an excited state is formed within the reaction radius of a quencher. Such a process would be expected to depend exponentially on concentration, which is indeed what is observed. Most systems in water could be explained that way; however, selenate and electrons in alcohols would not be consistent with such an explanation.

The sub-nanosecond pulse radiolysis techniques have made it possible to study the initial yields of singlets and triplets in the radiolysis of aromatic systems, the decay of electrons in non-polar media, fast electron transfer reactions and solvation experiments.

Other techniques have been used for getting sub-nanosecond time resolution. These include the fast conductivity experiments of the electron in non-polar media.<sup>42</sup> Streak camera detection has been used for the measurement of fluorescence from scintillators in hydrocarbon solutions. These experiments probe the role of the transfer of energy from solvent excited states to scintillators in comparison with the role of ion-recombination to form the scintillator excited states.<sup>43</sup>

Recently, laser-driven photocathode accelerators and lasers coupled with compressed pulses have been able to produce electron pulses in the vicinity of 5–10 ps.<sup>44–46</sup> This has enabled one to improve on the time resolution available from the original Hunt experiments but without the limitations of the multiple pulses. These short times have been used for measuring electron transfer reactions, electrons in

rare gas and supercritical fluids and transport and lifetimes of triplet states. Work at ELYSE has included the measurement of solvation of the electron polyols.

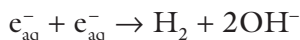
## 8. Laser-Simulated Radiation Chemistry

Pulse radiolysis was modeled after flash photolysis. The time resolution of laser flash photolysis has always been better than for pulse radiolysis. There are multiple reasons for this effect. (1) Flash photolysis equipment is cheaper than electron accelerators so there have been many more practitioners of the art. (2) Photons do not repel each other so it is possible to focus a larger number of them in a small volume over a short time period than it is possible to do for electrons. (3) The velocity of relativistic electrons in a dense material is much higher than photons in the same material so sample thicknesses must be much thinner for pulse radiolytic experiments than for flash photolytic experiments, thus meaning that signals would be smaller.

Experimenters began applying high-power lasers to creating electrons, the prototypical radiolytically produced species, and studying their structure chemistry, excited states and photochemistry. First, the absorption of the hydrated electron was measured; these results could be interpreted to give an idea of the separation of the electron from its geminate positive ion.<sup>47-49</sup> These distances appeared to depend on the energy of the photons used to create the electron.<sup>50</sup> Much more effort was spent studying the properties of the hydrated electron. Barbara and his co-workers, in particular, studied the role of excited states and structure in the hydrated electron.

Much of the work has been focused on “what is the hydrated electron” and what gives rise to the spectrum. These experiments have suggested that the spectrum of the hydrated electron cannot be clearly shown to be inhomogeneous, i.e. made up of multiple components that do not interconnect on the experimental lifetime. Theoretical studies had suggested that the ground-state spectrum would be made up of three s-p transitions of different energies that would interconvert on the experimental time scale; however, this was not clearly shown by the experimental work.<sup>51</sup>

There is clear evidence that the spectrum of the hydrated electron is best described as a charged particle in a cavity in solution, the simplest anion.<sup>52-54</sup> The spectrum and the reactivity are very consistent with such an interpretation. However, there is also clear evidence that this is not the best description of the electron. There is no obvious way to reconcile the reaction



with a cavity model for the electron. Several authors, primarily Tuttle and co-workers<sup>55</sup> and Robinson and co-workers<sup>56</sup> have suggested that the electron as a molecular anion is a better or at least a viable alternative. These problems have led to considerable effort to create a model that consistently explains the spectral data and the reaction data; however, in general their solutions have failed to explain the spectra of the electron.

I think it is fair to say that these techniques have given tremendous information about the structure of the species, in particular the hydrated electron, that is generated by ionizing radiation, but little new information on the chemistry that evolves.

## 9. The Future

Recently, new techniques such as laser-driven photocathode accelerators<sup>44-46</sup> have increased the time resolution available for radiation-chemical studies. They have been of great use in studying fast electron-transfer processes, but are not the one-to-two orders of magnitude improvement that would be needed to explore some of the fundamental questions of electron-precursor reactions and initial distribution of radiolytically produced species. Newer techniques, such as the laser-wakefield accelerator, have the potential to answer these sorts of questions; however, they have not reached their maximum potential.<sup>57,58</sup>

Radiation chemistry has become a mature field of study. Much of the work today makes use of these techniques to study chemical, physical and biological problems rather than studying the fundamental



processes of radiation chemistry. There are still questions that need to be answered such as the identity of electron precursors, the role of spatial distributions, particularly at elevated temperatures. However, much more important are questions of how reactions occur and what the role of temperature and media are on the reactions; questions that are not exclusively, or possibly even primarily radiation chemical but are really more chemical and physical.

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