

## **Radiation Chemistry: Yields of Chemical Species**

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## INTRODUCTION

Almost a century of research on the radiation effects due to heavy ions has passed since the isolation and use of radium in the Curie laboratory. (1) The early radiation chemistry studies were predominately performed with  $\alpha$ -particles because they were available and the chemical effects were large enough that they could be observed using the techniques of the time. Despite the experimental limitations, many fundamental processes in the radiolytic decomposition of water were identified. (2-7) The modern era of research on radiation effects began in the second half of the century as wartime efforts became public and equipment originally designed for military purposes became available for general research. Probably the most significant advancement in the field of radiation chemistry occurred following the announcement in 1960 that several facilities had achieved the capability of performing pulsed electron radiolysis. (8-10) This technique allows investigators to observe fast radiation chemical processes in real time. The vast majority of the experimental radiation chemistry studies involve the use of fast electrons or photons because of their relative ease of use and widespread availability. Nevertheless, a variety of heavy particle accelerators also became accessible to the radiation chemist in the second half of the century. These facilities made it possible to use a wide range of particle types and energies to examine the basic physical and chemical processes induced by the passage of heavy ions. In addition to the fundamental scientific aspects, many studies on the chemical effects of heavy particles have a variety of practical applications ranging from the nuclear power industry (11,12), space radiation effects (13), and medical therapy (14). Probably the most extensive use of heavy ion research in the near future will be in the environmental management of radioactive waste materials. (15)

A survey of the published literature shows that an increase in research on the practical aspects of heavy ion radiolysis has been coupled with a decrease in the number of publications examining fundamental properties. (16,17) A certain amount of a needs-driven approach to radiation effects is probably inevitable given current funding trends. However, there are few resources where new researchers in the field can find an updated overview of the fundamental radiolytic properties of heavy ions for application to their particular problem. Many of the observed radiation chemical effects for a given medium are due to the geometry of the physical energy deposition events, commonly referred to as the track structure. Heavy ion radiation effects are more determined by the basic relationships between physical and chemical processes than found with conventional radiation such as fast electrons or  $\gamma$ -rays. A few early theoretical studies (18-22) and years of experimentation (16) have formed much of the physical basis for the chemical effects of the track structure of heavy ions. Some of the fundamental aspects of this knowledge will be presented here. It is impossible to examine all of the details in depth, but rather a simple overview of the major effects responsible for the radiation chemistry will be given. The discussion will mainly address water and aqueous solutions as the target medium. However, most of the fundamental ideas are applicable to other liquids and some amorphous solids, but rarely gases.

## **HISTORICAL**

A short history of the radiation chemistry of water can be found in the article by Jonah (23) or the compilation of reminiscences by Kroh (24). A brief history of the experimental observations of track effects with heavy ions will be given here. Curie and Debierne (1) in 1901 were the first to study the radiolysis

of an aqueous solution with any type radiation when they observed the production of gases from solutions of radium salts. Giesel (25,26) and Ramsay (27-29) later determined that these gases were hydrogen and oxygen with the former in considerable excess. In 1910, Kernbaum found that the excess formation of molecular hydrogen could be associated with the production of  $\text{H}_2\text{O}_2$ . (30) The first true quantitative study of the radiolysis of water with  $\alpha$ -particles was performed by Duane and Scheuer in 1913. (31,32) Working in the Curie laboratory, they measured the production of hydrogen and oxygen in gaseous, liquid, and solid water with a radon source of a known activity.

The method by which the  $\alpha$ -particle-initiated chemical change remained unknown for several years although Cameron and Ramsay (29) thought that since  $\alpha$ -particles produced intense ionization in gases these processes should occur in water. Primitive techniques and impurities in the water hampered the early studies. However, it was realized that the differences between the products found with  $\alpha$ -particles and  $\beta$ -particles or X-rays were quite large. As late as 1933, Fricke (33) could detect no decomposition of pure, air-free water by X-rays, which is in contrast to the extensive production of hydrogen with  $\alpha$ -particles. Risse (34) was the first to suggest that water was decomposed into the radicals H and OH, which recombined in X-ray radiolysis with no apparent net decomposition of water. The radical theory of the radiolytic decomposition of water was firmly established by Weiss (35) in 1944, which was a major step toward understanding the experiments. However, several discrepancies still remained unexplained in the observations with different particles. Lefort (36) discovered that molecular hydrogen yield using  $\alpha$ -particles was essentially constant for a variety of different solutes. On the other hand, Miller (37) observed that certain product yields, which would later be found to be due to the radical chemistry, were much more dependent on solute concentrations with  $\alpha$ -particles

than with  $\gamma$ -rays. Once the fundamental products of water radiolysis were identified, researchers were then able to begin to explain observed differences in yields on track structure.

The early radium sources consisted of only about 100 mg of material and were very weak. With the new analytic techniques and the development of reliable and intense X-ray tubes in the 1930s, most subsequent radiation chemistry studies focused on the more penetrating particles. Accelerator-based radiolytic studies with heavy ions began to appear in the open literature in the 1940s as wartime efforts became public. (38) These instruments opened a whole new approach to radiation studies because of the high doses available and the wide range of particle types and energies. It was soon apparent that the particle ionization density had a direct effect on the chemistry. (39,40) Another major advance in understanding radiation effects occurred with the observation that the energy absorbed in the medium was more important than the energy loss by the incident particle. It was a radiation biologist (Zirkle, (41)) who first coined the term linear energy transfer, LET, to indicate this significance. The linear energy transfer is usually assumed to be equivalent to the rate of energy loss per unit path length of the incident particle or stopping power of the medium. However, this assumption can be in error, especially in heterogeneous systems or in selective nanometer sites. The high energies obtainable with accelerators enabled the examination of many systems over a wide range of LET. LET has continued to be a dominant parameter in the radiation chemistry of heavy ions, but it was soon apparent that LET was not the only factor that determined product yields. (37,42) The variation in product yields for two ions at the same LET was immediately and correctly ascribed to subtle differences in the particle track structures. (7,37,42)

## TRACKS AND SPURS

The stopping of heavy ions in matter proceeds by stochastic processes, whereas stopping power formulas give the average rate of energy loss per unit path length. The early cloud chamber pictures of Wilson in the 1920s (43,44) show that  $\beta$ -particle tracks are made up of isolated energy loss events due to discrete ionization processes. These events are well separated, except near the end of the tracks. The cloud chamber tracks of  $\alpha$ -particles appear as solid, continuous strings of ionization events. Early photochemical theories assumed that the ionization events were homogeneously distributed throughout the medium, but it was soon realized that ionizing radiation has a strong spatial component. (45) Theories developed in the 1940's and 1950's to describe radiation chemical events began to address the nonhomogeneous distributions of reactive species. (3,45,46)

The mean energy loss by a fast electron in water is about 60 eV and somewhat independent of the phase. (47) There is actually a wide range of possible collisions due to the passage of a fast electron in water, but the most probable events involve energy losses of less than 100 eV. Collisions involving this magnitude of energy loss will produce secondary electrons that further lead to an average of one or two ionizations. (48) Low-energy electrons have relatively large total elastic cross sections with a substantial backscattering component. (49-51) In simple terms, electrons of a few tens of eV do not go very far in liquid water and show a nearly isotropic angular distribution as they thermalize. (52) Following thermalization the electrons will eventually become hydrated adding another spatial delocalization from the initial energy loss event. The net result is that the initial energy loss event leads to a cluster, or spur, of two or three ionizations spatially localized. The concept of a spur in the liquid

phase of water is very old. (46) It is still the main concept used by radiation chemists to explain radiation effects with low LET radiation. The spur has no counterpart in the gas phase, which is the main source of confusion when applying gas phase theory and cross sections to the liquid phase.

Following the initial ionization events, water decomposes within a few picoseconds to give a spur composed of hydrated electrons, OH radicals, H atoms, H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. (7) In principal, the chemistry of any of these products can be used to probe the structure of the spur, but available experimental techniques and other factors have limited most of the investigations to examination of the hydrated electron. The nonhomogeneous distribution of hydrated electrons, and other water products, of the spur relaxes by diffusion and reaction with sibling radicals and molecules. Knowing the specific chemistry, the observed time decay of the hydrated electron can be used to estimate the average geometry of the spur. (53) Obviously, each spur is slightly different, but there are so many produced by even a single 1 MeV electron ( $> 10^4$ ) that the chemistry appears as an average over all spurs. Time decay measurements using low-energy multi-photon ionization just above the ionization potential of water have also been used to estimate the distribution of low-energy electrons in water. (54) These latter experiments agree well with the predicted results for the 'typical' spur produced by fast electrons. The observed time decay of the hydrated electron coupled with Monte Carlo calculations suggest that the 'typical' spur in electron radiolysis is well approximated by a Gaussian distribution with a characteristic radius of 4 – 5 nm. (55)

The average energy loss per unit track length of a 1 MeV electron is about 0.2 eV/nm. (47) With an average energy loss per collision event of 60 eV the mean separation of spurs is 300 nm, which is much too far apart for inter-spur reactions. (It is assumed throughout this article that incident particles are isolated

from each other, an assumption not necessarily correct at very high dose rates or with very short pulses of intense beams.) On the other hand, a 5 keV electron has an average LET of 3 eV/nm, which corresponds to an initial average separation of only one spur diameter. The spurs produced by an electron of this energy are not initially overlapping, but they will somewhat later as they develop in time. The resulting geometry leads to a short track as originally defined by Mozumder and Magee. (20) The tracks of heavy ions can be explained in much the same fashion. If the LET is greater than 3 eV/nm the spurs will be formed overlapping or will overlap shortly thereafter. At LET much less than 3 eV/nm the spurs will exist independently of each other and the observed chemistry of a heavy ion should become much like that of a fast electron. Experimentally it has been observed that radical and molecular yields with protons above about 20 MeV, 3 eV/nm, are virtually the same as with fast electrons. (56,57) It has been speculated that the charge on an ion may slightly alter the distribution of species within the spur (58), but no such process has been confirmed experimentally.

The column of species defined by the overlapping spurs along the path of a high LET particle make up what is commonly referred to as the track core. (21) Its physical parameters are difficult to quantify and it has no corresponding entity in the gas phase. No microdosimetry gas phase experiment will ever identify it, but that does not preclude the use of this concept in the liquid phase. Obviously, some energy loss collisions will be violent enough to form true  $\delta$ -rays, i.e. secondary electrons with enough energy to form tracks of their own. Various attempts have been made to separate the track core from the region of radiation effects due to secondary electrons (sometimes called the penumbra). (21,22,59,60) The main difficulty in any of these exercises is that the track is dynamic. It is constantly expanding in time due to diffusion of the reactive species and reactions initially associated with the track core may envelop those

due to the secondary electrons. Nevertheless, a large number of radiation chemical problems have been successfully addressed by treating each part of the track separately. (52,61-63) Refined Monte Carlo calculations will eventually elucidate the track structure, and the few published studies are quite promising. (64,65)

### **Special Very High LET Effects**

There are several specific effects that have been proposed to occur in particle tracks with very high rates of energy loss. These effects include the Coulomb explosion, thermal spike, and multiple ionization. Each of the special effects will be treated briefly.

The passage of a heavy ion in matter leads to a track of ionization events. A cation, or hole, is formed at or near the initial energy loss event while the electrons, being more mobile, are trapped at some distance away from the initial ionization event. At very high LET the local concentration of holes may become sufficiently large that they repel each other because of their positive charges. This "Coulomb explosion" has been used to explain some of the observed damage in insulators. (66,67) (Another type of Coulomb explosion occurs in the beams of intense radiation pulses, e.g. electron pulses from Febetrons. In this case the repulsion of charges follows similar physical laws, but it is the incident beam that expands, with different track consequences.) A simple calculation shows that the Coulomb repulsion for two cations with a typical water separation distance (0.3 nm) would involve about 4.8 eV of energy. (68) This energy must overcome any inherent inertial force to push the molecules apart, which is related to the viscosity of the medium. Viscous flow on a microscopic scale is essentially the movement of a molecule to a vacant neighboring site. It has been

argued that the creation of a vacant site is similar to the process of vaporization since comparable intermolecular bonds must be broken. (69) Empirically, the free energy of activation for viscous flow is found to be equal to the heat of vaporization divided by 2.45 or about 0.2 eV for water. (69) Clearly the repulsion energy of neighboring cations in water is sufficient to move them apart. A rigorous application of a Coulomb explosion model to water is required before more definitive statements can be made on any possible outcome. The most probable outcome of Coulomb explosions in liquids is to expand the track radially. The deposited energy per unit track length remains the same, but the density of energy deposition decreases from that normally expected for this particular incident particle. This 'broadening' of the track may account for the observed escape of radical products from the tracks of uranium ions in water. (70) A Coulomb explosion involving a large solute or nearby heterogeneous surface will have an as yet unexplored outcome.

Some early models of radiation damage tried to equate energy loss by the incident ion with heat input into the medium. Most of the energy deposited by radiation will eventually be converted to low grade heat. (22) Various models suggest that if sufficient energy is quickly deposited in a small volume, such as in very high LET particle tracks, the local temperature will rise significantly above ambient. (22,71,72) Seitz (73) was the first to extensively develop the theory of thermal spikes for use in explaining the displacement of atoms in solids. Thermal spikes have been proposed to occur in various crystals (74,75) and in the bubble nucleation of water (76-80). The initial increase in temperature for low LET radiation is estimated to be a few tens of degrees, but Mozumder (22) calculates the increase can be  $10^4$  K in the tracks of fission fragments in water. A small temperature increase has been claimed in the fast electron radiolysis of very low-temperature glasses. (81) However, specific experiments designed to observe a

temperature increase in high-density gases (82) or in biological materials (83,84) have found no evidence of a temperature rise much above ambient. Theories on the thermal spike imply that energy is retained in a small volume for a fairly significant amount of time. However, energy is lost initially to electronic modes of the medium and it takes time for this energy to manifest itself as kinetic, vibrational, or rotational degrees of freedom. Energy degradation is competing with thermal diffusion with the result that the predicted spikes in temperature are much too fast to significantly affect the chemistry. Should a thermal spike occur in water, its consequences would be to increase reaction rates and radical diffusion rates. New decomposition modes for the water or any solutes may also be possible at extremely high temperatures. It should be stressed that no phenomena associated with thermal spikes in liquid water have been unambiguously observed.

Multiple ionization of a single molecule by the passage of ionizing particles has been observed in many circumstances. (85) Most of experiments have been performed with light ions in gases and vapors and it is found that the absolute cross section for double ionization is usually more than an order of magnitude less than for single ionization. Triple ionization is usually more than an order of magnitude less than double ionization. Uranium ions deposit more than  $10^4$  eV/nm at the end of their track in liquid water, which corresponds to about 5 keV per water molecule. Collisions with this amount of energy loss are possible for many types of particles, but for very high LET particles virtually every molecule along its path will receive large amounts of energy. More than one electron may be produced per medium molecule or all of the excess energy may go into the kinetic energy of one secondary electron. It has been proposed that multiple ionization is responsible for the large yields of  $\text{HO}_2$  produced in the heavy ion radiolysis of water at high LET. (86) Multiple ionization effects of high LET xenon

beams in water have been observed to increase the production of atomic oxygen above that found with low LET radiation. (87) Excess oxygen production at high LET may have severe consequences in radiation chemistry and biology. Predicting the outcome in liquid water from observations of oxygen production in the gas phase is difficult. Caging and other effects may significantly alter product yields between the two phases. Specifically designed experiments at high LET will be required to give more information on the role of multiple ionization effects in the radiolysis of liquid water.

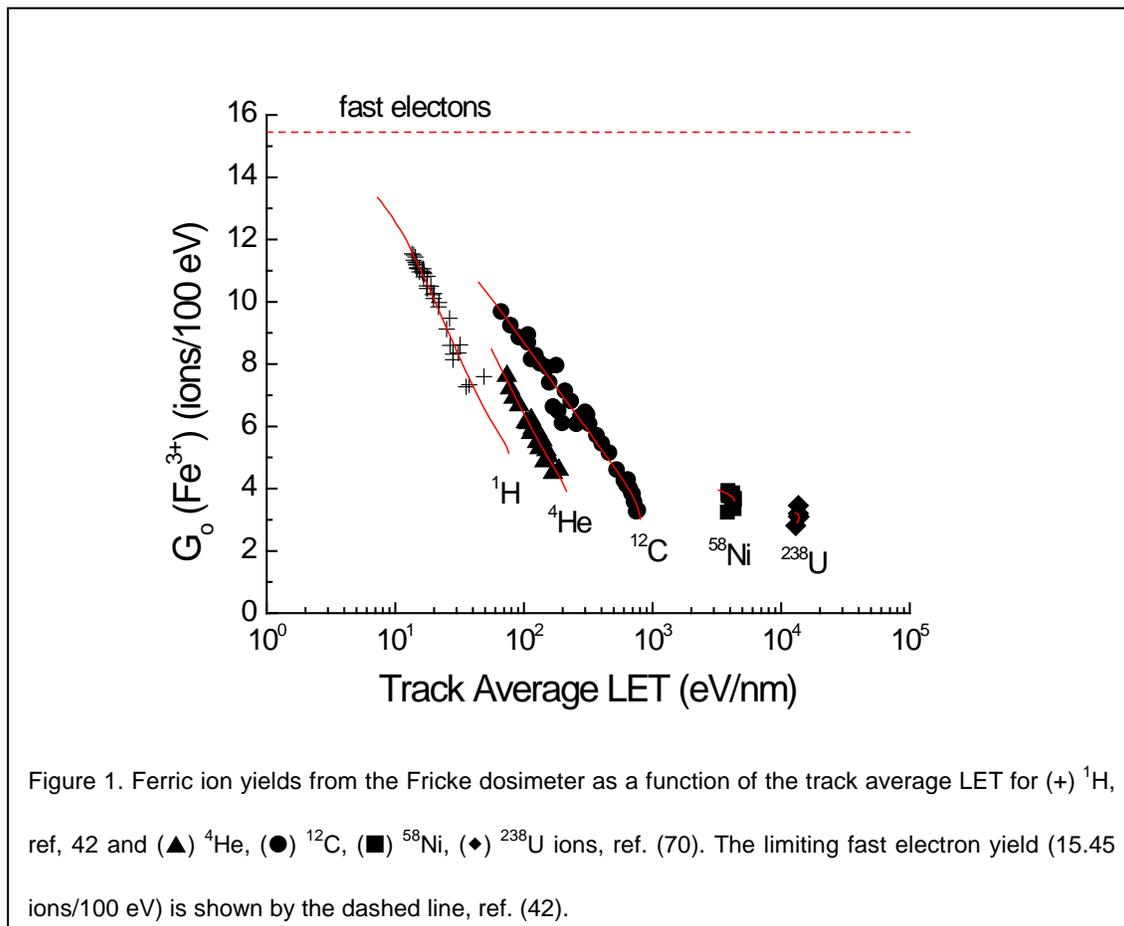
## **CHEMICAL EFFECTS OF TRACK STRUCTURE**

As discussed above, the earliest experiments showed that there were differences in product yields for various particles in liquid water. Increasing particle LET results in an increase in the yields of molecular products such as  $H_2$  and  $H_2O_2$  and a corresponding decrease in the yields of radicals such as  $e_{aq}^-$ ,  $H$  and  $OH$ . (7,88) The nonhomogeneous distribution of reactive species initially produced by the energy deposition relaxes in time toward a homogeneous distribution. In pure water a competition is quickly established between radical-radical combination reactions among the sibling radicals and radical diffusion into the bulk medium. Increasing the particle LET increases the probability of radical-radical combination reactions with a corresponding increase in molecular products. It has always been assumed that the initial decomposition of water is independent of particle type. (39) There are experimental results that seem to support this conclusion. Pulsed experiments with protons find the short time yield of the hydrated electron is similar to that found with fast electrons. (89,90) In addition,  $W$ -values, the average energy required per ion pair, for high-energy particles in a given medium are nearly independent of the particle type. (91) Ion

pairs are the main initial species formed in radiolytic decomposition of water so one would expect similar yields for the products due to these species. In special circumstances the initial product yield may be dependent on particle type, e.g. low-energy particles with large contributions from nuclear scattering processes or very high LET particles with high probabilities of causing multiple ionization of the medium molecules. For the most part, observed variations in product yields with particle type or energy are due to effects of track structure on the radiation chemistry.

Product yields with heavy ions are generally presented as a function of the LET of the irradiating particle. However, LET is not the sole parameter that describes the track structure and thereby the observed yields. (7,37,42) Many experimental observations have shown that for two incident particles at the same LET radical yields are greater and molecular yields are lower for the ion with a higher nuclear charge. (37,42,58,70) Figure 1 shows an example of the LET effect on the oxidation of ferrous ions in the Fricke dosimeter. (42,70) The Fricke dosimeter is an acidic aqueous solution of ferrous sulfate in which the radicals produced in the water decomposition oxidize the ferrous ions to ferric ions. It is the most studied single aqueous system with heavy ions because of its use as a chemical dosimeter and as a benchmark for new experiments. Although the chemistry of the ferrous ion involves multiple reactions, ferric ion yields are mainly dependent on the yields of hydrated electrons and H atoms. Radical yields decrease with increasing LET due to enhanced intra-track reactions resulting in a decrease in ferric ion yields from the Fricke solution. This decrease is almost an order of magnitude from fast electrons to uranium ions. Chemical yields in other systems may change by more, or less, and decrease, or increase, depending on the specific chemistry. Many of the expected track effects are observable with this system. High-energy protons give about the same ferric ion

yields as fast electrons because they both deposit energy in isolated spurs. It is readily seen that LET is not the definitive parameter for describing ferric ion yields. In fact, rarely is one single parameter sufficient for describing product yields.



The stopping power predicts to a first approximation that for two different types of particles to have the same LET the one with the higher charge will have a higher velocity. A higher incident particle velocity produces a larger radial distribution of energy deposition in part because the distribution of secondary electrons increases with an increase in the initial particle velocity. Even though both particles are depositing the same amount of energy per unit path length the higher Z particle is losing that energy in a larger volume, which leads to a less dense track of reactive species. Several modeling studies have tried to quantify

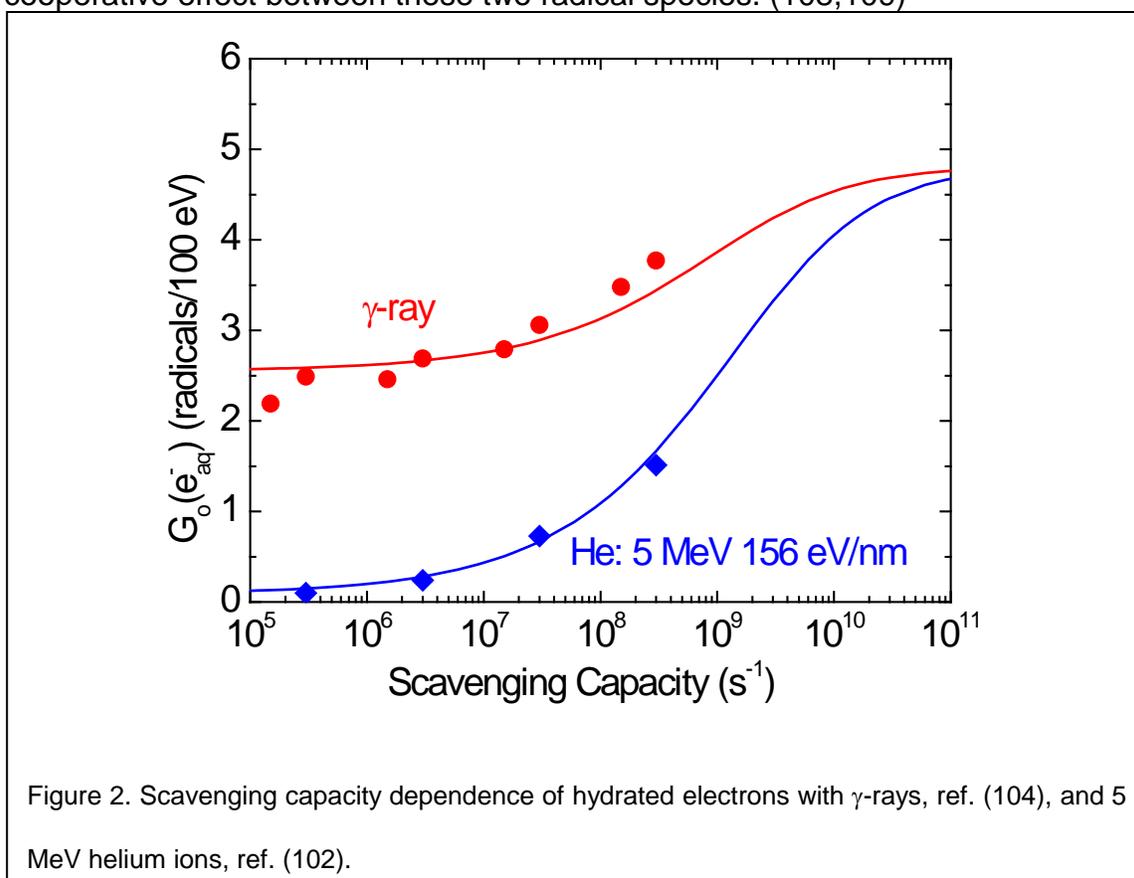
the observed LET dependence using simple radiation chemical mechanisms, but the results are not conclusive. (61,62,92) Different media and even different products in a given media can exhibit a variety of dependences on particle Z at a given LET. Nevertheless, LET still remains the most useful single parameter for describing radiation damage and it is perfectly valid for a given type of particle. Difficulties arise when the data for one particle is substituted for another in a particular application.

Several practical details may not be readily apparent in the presentation of the data in Figure 1. This figure gives the track average yield,  $G_o$ , as a function of the track average LET. High LET particles generally have a short range in water. For example a 10 MeV proton (LET = 4.7 eV/nm) has a range in water of 1.2 mm while a 10 MeV carbon ion (LET = 700 eV/nm) has a range of 13  $\mu$ m. Both particles would be completely stopped in the solution in most practical applications. The chemistry measured in such a configuration is an average over all particle energies from the incident particle energy,  $E_o$ , to zero. Track segment yields are the chemical yields in a discrete segment of particle path length. Within this small segment of track the energy, LET, and other parameters of the particle are well defined and constant. Model calculations normally predict track segment yields while experiments usually, but not always, give track average yields. The difference between track average and track segment yields can sometimes be significant, up to 20-30% in the case of the Fricke dosimeter. The formal definition of the track segment yield is  $G_i = d(G_o E_o)/dE_o = G_o + E_o dG_o/dE_o$ . It can be seen that track segment yields are similar to track average yields as the initial particle energy approaches zero or if the track average yield is independent of energy. It is not uncommon for track segment yields to be similar to track average yields, but such an equality should not be assumed.

One of the biggest challenges for experimentalists and theoreticians is determining the temporal history of products in water radiolysis with heavy ions. Not only does the time dependence put severe limitations on track models they can be vital for predicting radiation damage in concentrated systems that cannot be probed directly. Several early pulsed heavy ion experiments (89,90,93-95) have been joined with new studies (96-100) to directly give water product yields at specific times. Except for the work of Burns and coworkers who used water jets, these experiments are limited to determining the product yields on the  $\mu\text{s}$  time domain. The major difficulty with pulsed experiments is the need for relatively large doses in narrow pulses and the very short particle range. These limitations restrict the number of systems that can be examined and the time scales. Competition kinetics can be used to define the time scale in these high LET experiments. Solutes that are radical scavengers will stop the competition between radical reaction and diffusion at a time characteristic of the particular scavenging reaction. By changing the solute concentration one can effectively probe the chemistry in the particle track at different times. Even most of the pulsed experiments rely on scavengers to stop the chemistry at short times so product yields can be observed with pulses at longer times.

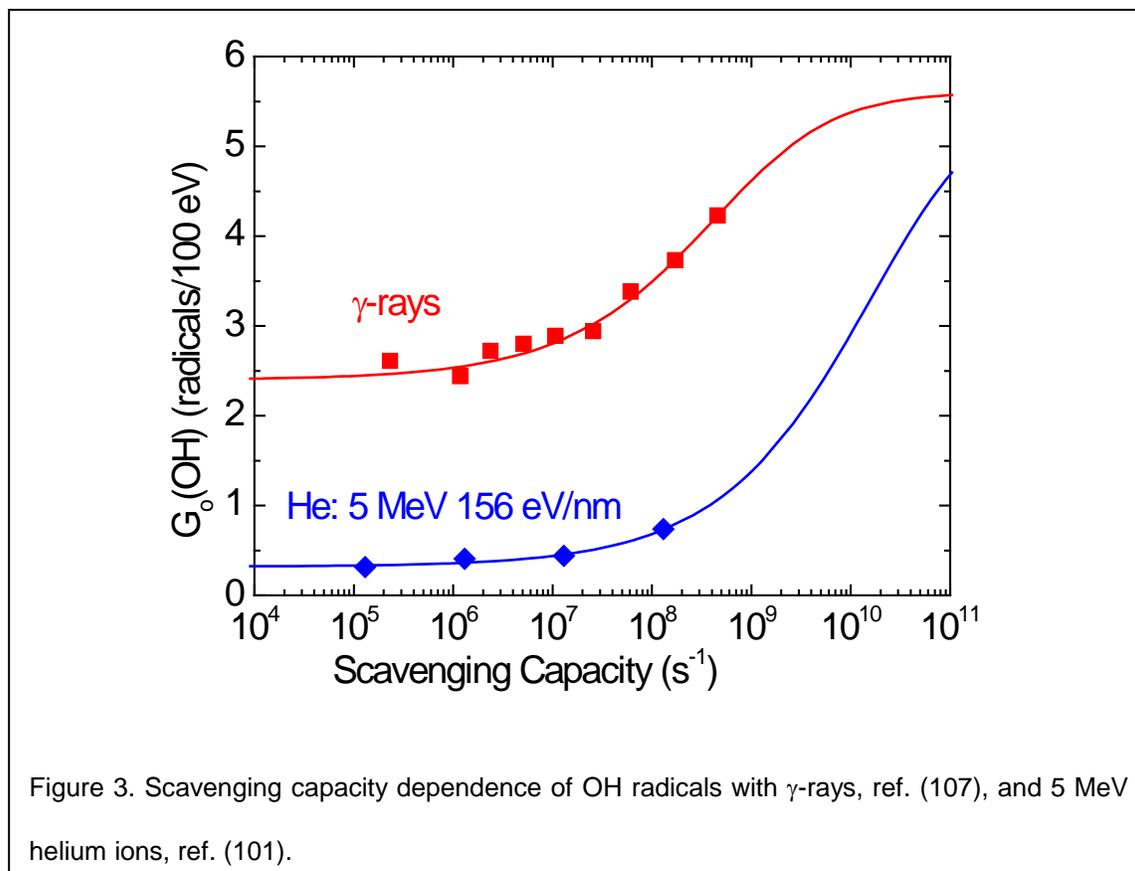
Several experiments using scavenger techniques have been able to determine the temporal variation of radicals and molecular products in the particle tracks from nanoseconds to microseconds. (101-103) The dependence of the hydrated electron on its scavenging capacity is shown in figure 2 for  $\gamma$ -rays and 5 MeV helium ions. (102,104) In these particular experiments the reaction of glycylglycine with the hydrated electron to give ammonia was used as a quantitative measurement of the yield of the hydrated electron. The scavenging capacity,  $s$ , is defined as the product of the solute (glycylglycine) concentration,  $[S]$ , and the rate coefficient of the scavenging reaction,  $k_s$ . For a given radical or

molecular product and a particular radiation type, the scavenging capacity is a universal parameter for all solutes. (105,106) The shape of the curves in a graph such as in figure 2 represents the chemistry of that particular product, which in turn is dependent on the track structure. The scavenging lifetime,  $\ln 2/s$ , is a good measure of the time dependence of that particular species in **pure water**. (107) It should be noted that it is possible to alter the yield of one radical, for instance the hydrated electron, by scavenging another, e.g. OH radicals, because of the cooperative effect between these two radical species. (108,109)



Hydrated electrons are produced with a yield of about 5 radicals/100 eV within a few ps and then decay in time by reaction with themselves and their sibling as the track or spur evolves in time. At long times, small scavenging capacities, the hydrated electron yield approaches a nearly constant value with  $\gamma$ -rays as the initial nonhomogeneous distribution of reactive species relaxes to a

near homogeneous one. This long time or escape yield is usually quoted as the yield with  $\gamma$ -rays. Many experimental conditions involve low scavenger concentrations and it is perfectly valid in some circumstances to consider a constant yield of hydrated electrons or other water products with  $\gamma$ -rays. However, at higher solute concentrations and in nearly all cases for helium ions it is impossible to specify a unique radical yield. It is only correct to define a yield at a given time or for a specific scavenging capacity. Because the hydrated electron yields have a different scavenging capacity dependence for  $\gamma$ -rays and for helium ions it is invalid to consider the “effectiveness” of one radiation to the other. At no time, except at zero and possibly extremely long times, is the ratio of hydrated electron yields for  $\gamma$ -rays to that for helium ions constant.



The scavenger capacity dependences of OH radicals for  $\gamma$ -rays and 5 MeV helium ions are shown in figure 3. (101,107) In general, the trends for OH

radicals are similar to that for hydrated electrons. There is a decrease in OH radical yields with decreasing scavenger capacity, increasing time. However, the results with OH radicals for helium ions seem to reach a limiting value at low scavenging capacity, unlike that found with hydrated electrons. The reason for this observation is due to reaction of hydrated electrons with hydrogen peroxide within the track to produce OH radicals. This reaction occurs in the spurs of  $\gamma$ -ray, but to a much less extent. Virtually all of the reactions within the tracks of heavy ions are also occurring in the spurs of  $\gamma$ -rays. It is dependence of the second order reactions on the concentrations of reactants due to the LET that can cause large differences in the product yields.

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