THE RADIATION CHEMISTRY OF
WATER AND AQUEOUS SOLUTIONS

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by

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Radiations: How Their Energy Is Dissipated

This book is an account of the chemical reactions brought about in water and its solutions by high-energy radiations.

Before coming to grips with the main topic, let us consider briefly what these radiations are and how they act. This is not the place for a detailed treatment of radiation physics, which may be found in many other books. Here we shall describe in a general way how liquid water takes up energy from the various kinds of radiation. All the radiations considered here give their energy up to matter through the action of fast charged particles, and we may divide the radiations into a light-particle group and a heavy-particle group, depending on whether the fast charged particles involved are electrons or atomic ions.

LIGHT-PARTICLE RADIATIONS

The penetrating electromagnetic waves—X-rays and γ-rays—are characterized by their wavelength. The quantum energy or energy per photon E of these rays is inversely proportional to the wavelength λ; $E\lambda = 12,400$ if E is given in ev and λ in Å.

X-rays are generated when high-voltage electrons are made to impinge on a metal target. The maximum quantum energy they can have is equal to the voltage imparted to the electrons which produced them, but most X-ray sources emit the bulk of their energy at considerably longer wavelengths. γ-Rays are emitted by nuclei during the process of radioactive decay. A given source emits γ-rays having only certain definite values of the quantum energy. Radiations of the longer wavelengths (lower energy) penetrate less readily into material and are spoken of as "soft" radiations; those of high energy penetrate farther and are called "hard." For a given radiation the rate of absorption in passing through matter is a constant: $dI/dx = -\mu$, where I is the intensity of the radiation, x is the distance penetrated into a material, and μ is the total absorption coefficient of the material for the particular ray. By integration of this equation we find $I = I_0 e^{-\mu x}$. Values of μ for rays of various wavelengths in water are shown in Fig. 1.1.
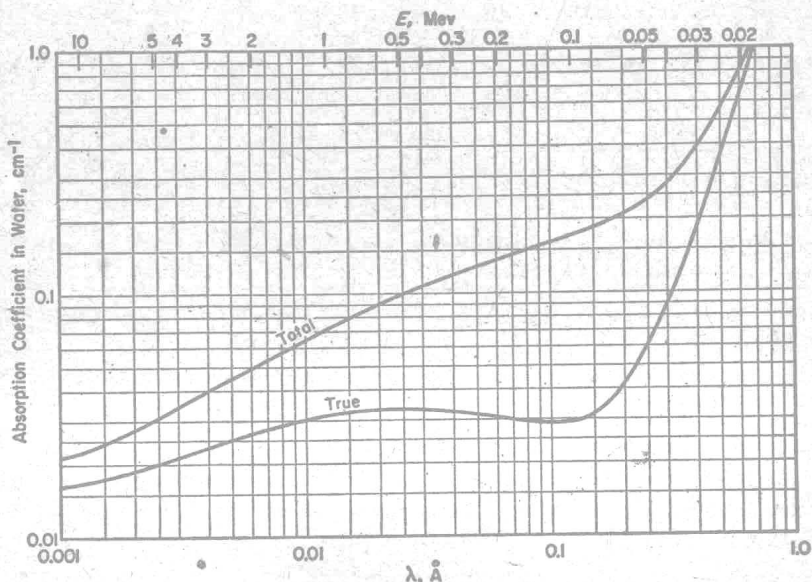
Fig. 1.1 "Total" and "true" absorption coefficients for X- or γ-rays in water as a function of wavelength (lower scale) or quantum energy (upper scale).

It is seen that soft X-rays of a few thousand electron volts are mostly absorbed in the first millimeter, whereas hard rays of 1 Mev or more can pass through several centimeters of water with reduction of only a small percentage of their intensity.

Absorption of these rays proceeds by several quite different processes which may go on simultaneously, but with relative importance depending markedly on the wavelength. At the longer wavelengths most absorption occurs by the photoelectric effect, in which all the energy of the photon is given up to one electron in the material. This energy is much greater than the energy which binds the electron to its atom. The most tightly bound electrons in water, the K electrons of oxygen, require 532 ev to become ionized or removed from the molecule, while the quantum energy of the X-rays is many thousands of electron volts. All the excess energy, amounting to most of the energy of the photon, will therefore appear as kinetic energy of one electron; and the electron will consequently take off from its position and tear through the water like a super-speed bullet until slowed down by interaction of its electric charge with the water molecules.

At energies above a few kiloelectron volts, another process, the

Compton effect, becomes the most prominent. Here the photon interacts with an electron in the material, but instead of giving up all its energy to the electron, it gives up only a part; the remainder appears as a scattered photon of longer wavelength (lower energy). This scattered photon is usually sufficiently penetrating to escape altogether from a small absorber; therefore, although the original photon disappears and the original beam is thereby attenuated, not all the corresponding energy has gone into the sample but only that portion that was given to the electron involved. A resulting distinction is commonly made between the "total" absorption coefficient, corresponding to the fraction of photons reacting per unit path length, and the "true" absorption coefficient, equal to the total coefficient multiplied by the fraction of the energy which goes to the electron. This fraction may vary all the way from zero to unity for individual events; the relative probability of various fractional losses, and hence the average fraction, is a function of the primary wavelength.

At energies exceeding 1 Mev still another process becomes of importance; it is known as pair formation. When these high-energy photons pass very near an atomic nucleus, they may with a certain probability be converted to a positive and negative electron pair. This probability is greater the larger the charge on the nucleus and is consequently of much less importance in water than in materials containing heavy elements. In the experiments discussed in this book, pair formation is of negligible importance.

Because of the nature of the Compton effect and the simultaneous occurrence of the photoelectric effect, monochromatic radiation passing through water gives rise to electrons having a complicated spectrum of initial kinetic energies. Of course in practice the incoming X-ray or γ-ray photons themselves may possess a wide spectrum of energies, with the result that the actual energy distribution of generated electrons will be difficult to calculate precisely.

ENERGY LOSS OF ELECTRONS IN WATER

Whether the incident radiation is penetrating electromagnetic radiation, such as γ-rays, or such charged particle sources as β-rays or an electron beam from a high-voltage machine, the agency which affects the water is always the same, namely, a fast-moving electron. At the energies of interest these electrons may have speeds approaching the speed of light, and the relationship between their mass, velocity, and energy is affected by relativistic considerations.

A fast electron loses its energy gradually as it passes through matter

by reason of the interaction of its charge with the charges on the electrons and atoms of the material. As the moving charge passes by a molecule at a speed which may approach that of light, the electrons in the molecule receive a push from the field of the moving charge, the strength of which depends upon the nearness of the charge. Most of the electrons thus affected snap back into their normal positions and the molecules remain unaffected, but occasionally one electron will be left in a different state having more energy than normal. This excess energy will have been taken from the energy of the moving charge, which is slightly slowed down in the process. The accumulation of such energy losses eventually brings the moving charge to rest. The probability that a molecule will take up energy in this way will obviously be greater when the charge is moving more slowly, because the charge will then remain in the vicinity of the molecule for a longer time; thus the rate at which energy is lost increases as the particle is slowed down.

Frequently the energy taken up by an electron within the material is so great that this electron detaches itself from the molecule of which it was a part, leaving a positively charged ion and flying off with an energy that may be great enough to produce further ionizations in its turn. Such a secondary electron usually is ejected with an energy much less than primary, causing the ionizations it produces to lie much closer together than the ionizations along the track of the primary. The track of the fast electron is thus to be pictured as a series of clusters of secondary ionizations of variable size which are spaced along the track of the primary. The clusters lie closer together as the end of the primary track is approached.

The rate at which the moving electron loses energy is one quantity that is precisely known, at least for electrons of energy exceeding a few hundred electron volts. It is usually expressed as the amount lost per unit distance traveled and may be denoted by $-dE/dx$. This quantity is called *stopping power* by physicists, and *linear energy transfer* or LET by radiobiologists. For nonrelativistic electrons having energies below about 50,000 ev, the energy loss equation is

$$-\frac{dE}{dx} = \frac{2\pi e^4 NZ}{E} \ln \frac{E}{I} \sqrt{\frac{\varepsilon}{2}}$$

where e is the charge on the electron, E is the energy of the moving electron, NZ is the number of electrons per unit volume of irradiated material, ε is the base of the natural logarithms, and I is a number characteristic of each material which is sometimes called the *stopping potential*. An instructive elementary derivation of this formula is given

in a review article on radiation chemistry by N. Miller;[1] for a more complete discussion, see Bethe and Ashkin.[2]

As there is no precise theoretical method of determining the value of I for any given substance, it has to be found empirically. However, it is known to depend only on the nature of the atoms present and not on the way in which they are chemically combined (Bragg's Law); thus the stopping potential for water can be obtained from data on hydrogen and oxygen gases. The best value of I for water is 66 ev according to Schuler and Allen,[3] and 69 ev according to Burch.[4] Because of the form of the equation, a 5% change in I has a negligible effect on $-dE/dx$ when E is large enough for the formula to be used. Assuming $I = 66$ ev, the equation becomes

$$-\frac{dE}{dx} = \frac{1{,}019}{E} \log_{10} \frac{E}{56.6}$$

where E is in ev and $-dE/dx$ is in ev/Å. At higher energies the equation is somewhat modified to take into account the relativistic change of mass of the electron:

$$-\frac{dE}{dx} = \frac{2\pi e^4 NZ}{mv^2} \left[\ln \frac{mv^2 E}{2I^2(1-\beta^2)} - (2\sqrt{1-\beta^2} - 1 + \beta^2)\ln 2 + \right.$$

$$\left. (1 - \beta^2) + \frac{1}{8}(1 - \sqrt{1-\beta^2})^2 \right]$$

where $\beta = v/c$, the ratio of the velocity of the electron to the velocity of light. The relativistic corrections result in an increase in the rate of energy loss at high energy; therefore, with increasing energy the LET first decreases, attains a minimum value, and then slowly rises. The minimum value of 0.018 ev/Å is reached between 1 and 2 Mev.

At energies beyond the minimum, still other effects must be considered. The stopping power now depends upon the density of the medium (polarization effect) in a way which has been calculated by Sternheimer.[5] Furthermore, the generation of X-radiation (bremsstrahlung) becomes important. Figure 1.2 shows the LET for electrons in water as a function of electron energy. The value plotted does not in-

[1] Miller, N., Rev. Pure and Appl. Chem. Royal Australian Chem. Inst. 7, 123 (1957).

[2] Bethe, H. A., and Ashkin, J., in Segré, E., Experimental Nuclear Physics 1, 166, John Wiley & Sons, Inc., New York (1953).

[3] Schuler, R. H., and Allen, A. O., J. Am. Chem. Soc. 79, 1565 (1957).

[4] Burch, P. R., Rad. Res. 6, 289 (1957).

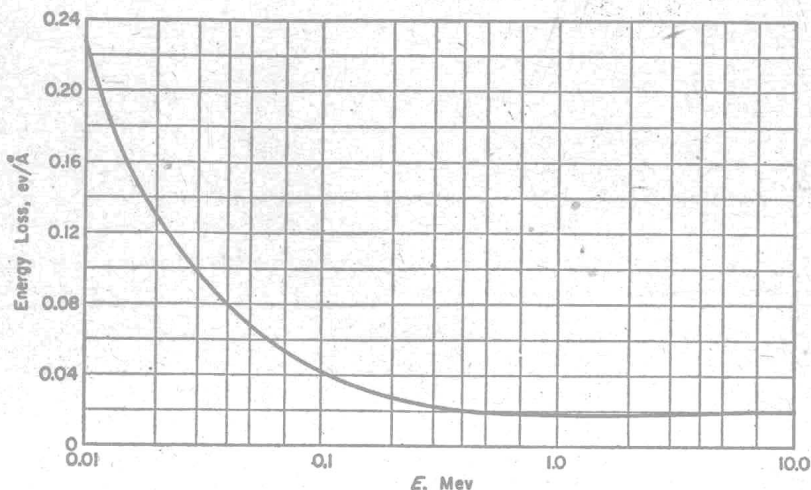[5] Sternheimer, R. M., Phys. Rev. 88, 851 (1952).

Fig. 1.2 LET for electrons in water. The value plotted is the rate of energy loss due to ionization and excitation, including the polarization correction (density effect) but not including radiation losses.

clude radiation losses, since they do not contribute to energy deposition in the water.

Electrons frequently change direction as they pass through matter owing to collisions with atomic nuclei, and the loss of energy with distance refers to the distance traveled by the electron along its actual path, not to the distance between its starting and terminating points, which may be much shorter. Because of this scattering, an initially parallel beam of electrons of the same energy entering a material will fan outward and the electrons will come to rest after penetrating a variety of distances into the material. A complete mathematical account of the scattering of an initially homogeneous beam of electrons has yet to be worked out.

Ordinary X-ray machines generally have peak voltages from 15 to 250 kv. A large number of electrostatic generators and resonance transformers are now to be found operating at voltages of 1,000 to 5,000 kv (1–5 Mv), and may be used to produce either X-rays or beams of electrons or, in some cases, protons. β-Rays and γ-rays from radioactive substances usually have maximum energies in the range of from 0.3 to 3 Mev or 300 to 3,000 kev. Only one important isotope, tritium, has β-rays of much lower energy, 18 kev maximum and 5.5 kev average. A few electron-synchotron machines exist that can accelerate electrons to voltages of 20 to 30 Mv and produce X-rays with correspondingly high

energy. Generally the effects of electrons of different energies are found to vary with their LET, as expected from Fig. 1.2. In particular, no important change is found as we go from electron energies of 1 Mev toward higher energies, since LET changes very little. Chemical effects of the softer X-rays in aqueous systems may be appreciably different from those of harder X-rays because of LET effects.

Of equal or greater interest than the mean LET value is the question of how much energy the electron loses in each event. Theory [6] indicates that the probability of any given energy loss is greatest for small energy loss and decreases exponentially with increasing energy. Only for energy losses exceeding a few hundred volts does the theory give this probability accurately. At lower energies the probability depends upon the binding of the electrons in the material and becomes difficult to calculate. Attempts have been made to count the individual droplets in low-pressure cloud-chamber photographs, and thus to find the mean number of individual ionization events associated with each primary loss. From such data Pollard [7] has concluded that the average energy loss per primary event is 110 ev, but this number may be in error by as much as 30%. Besides, the true value may be quite different in liquid water than in the gas of a cloud chamber.

Energy losses less than the ionization potential of a molecule must appear only as molecular excitation. If the energy loss greatly exceeds the ionization potential, another fast electron will be produced which will carry the excess energy and may have energy enough to create further ionizations in its turn. Along with these secondary and tertiary ionizations, excitations will likewise occur. Thus an average primary event involving 110 ev will result in a little cluster of ionizations and excitations, produced by the secondary electron generated in the primary ionization, lying within a few angstroms of each other. Since the path of the secondary electron is frequently deviated by collisions, the ions will not be strung out in a line but will be clustered within a more or less spherical region. These groups are sometimes referred to as *spurs* on the main track of the primary electron. The French use the more accurately graphic term *grappes,* meaning "a bunch of fruit or flowers, like grapes, carried on the branches of a single primary stem." If the secondary has an average of several hundred or more electron volts, it will produce a true track, diverging in direction from the primary; it is then called a *delta-ray.*

[6] Moller, C., *Ann. Physik* 14, 531 (1932).
[7] Pollard, E., *Advances in Biological and Medical Physics* 3, 153 (1953).

RADIATION UNITS

X-rays are usually measured by means of ionization chambers, the number of ions formed in a given quantity of air being proportional to the total amount of radiation incident on the chamber. The practical unit for measuring X-rays, called the *roentgen*, was taken as the amount of X-radiation which would produce one electrostatic unit of ions of either sign per cubic centimeter of air under normal temperature and pressure. This unit, usually called "r", is widely used but bears no simple relationship to the fundamental physical quantities involved in the radiation, such as the energy flux or the number of photons. What is worse from the practical viewpoint, the r does not even bear a simple relationship to the amount of energy deposited in the material being irradiated. The energy deposition, usually called the *radiation dose*, is conveniently expressed in the basic units of ergs per gram. Now 1 r, corresponding to a certain number of ions in air, also corresponds to a definite amount of energy absorbed by, or dose given to, the air, because the energy per ion pair formed in air is essentially constant and equal to 34 ev for all qualities of X-ray. The energy received by any other substance from exposure to 1 r is proportional to the absorption coefficient of that substance. The ratio of the absorption coefficients of water and air varies with the wavelength of the X-ray, so that 1 r of soft X-rays will give a somewhat different dose to water than 1 r of hard X-rays or γ-rays. Actually 1 r of γ-rays contributes to water a dose of 97.3 ergs per gram according to the latest measurements. Since most users of radiation, including radiation chemists, are interested chiefly in radiation doses, a new unit of radiation dose called the *rad* has recently been defined as equal to 100 ergs per gram deposited from the radiation in the substance of interest. It is seen that within a few percent, 1 r of γ-radiation will deliver 1 rad which all the water, or to living tissue that is largely composed of water. Hence, for many purposes the two units can be used almost interchangeably, but they are conceptually quite distinct.

Radiation chemists are accustomed to thinking of energies in terms of electron volts rather than ergs. The common method of expressing radiation chemical yields is to give the number of molecules of material formed or destroyed for each 100 ev deposited in the substance. This number is called "G." Radiation chemists frequently express their dose as electron volts per gram even though this commonly leads to very large numbers, such as 10^{20}. To convert these units we note that 1 r of γ-rays deposits 6.08×10^{13} ev per gram of water, whereas 1 rad equals
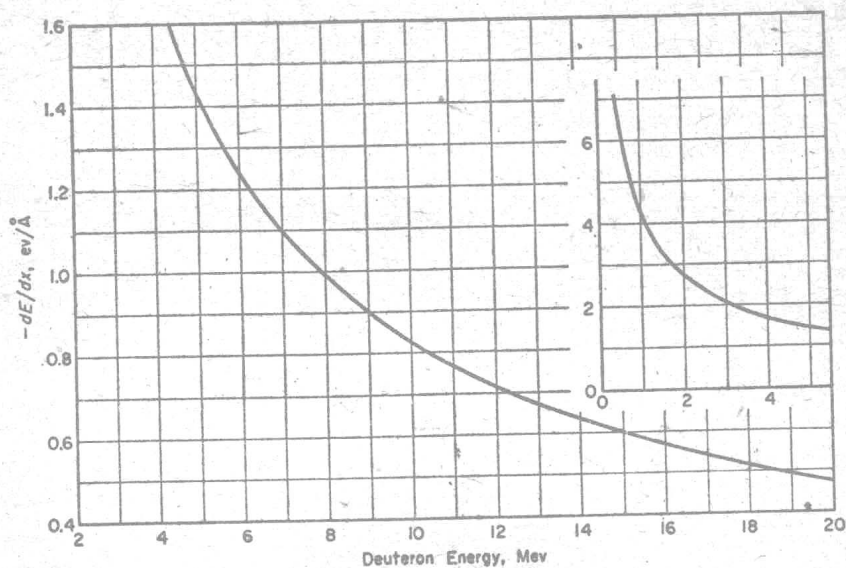
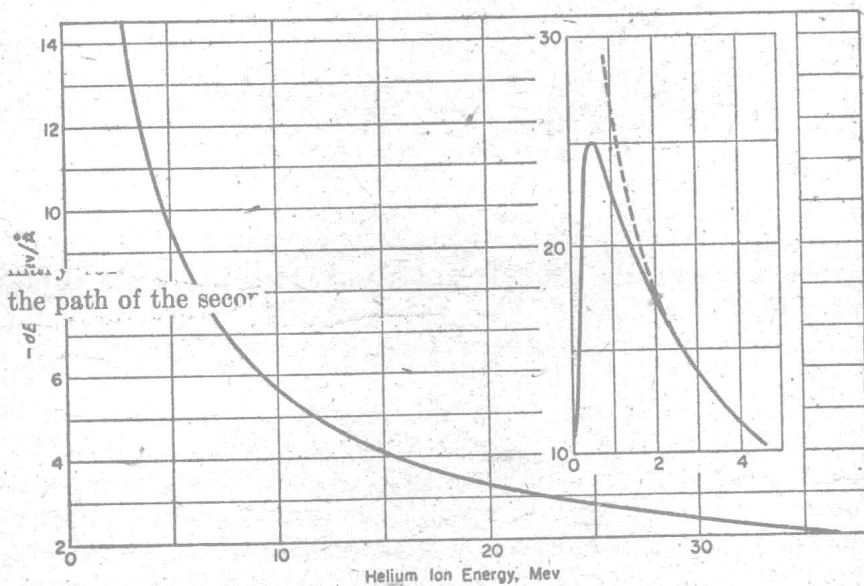Fig. 1.3 LET for deuterons in water.

the path of the secon

Fig. 1.4 LET for ~~~ium ions (α-rays) in water.

100 Å

Fig. 1.5 Schematic picture of water decomposition by charged particles. Each dot represents deposition of 20 ev, or approximately one water molecule decomposed. Upper line, 40 kev electron, LET 0.08 ev/Å. Middle, 18 Mev deuteron, 0.5 ev/Å. Bottom, 5.5 Mev α-ray, 9 ev/Å. A 1-Mev electron would on the average show no events in the length here depicted. (Extended to next page.)

6.24×10^{13} ev per gram. A dose of 1,000 r of γ-rays will produce a concentration change of 1.010 micromoles per liter (μM) of dissolved substance in water if $G = 1$, and proportionately more if G is higher.

HEAVY PARTICLES

The loss of energy of a charged particle through ionization or excitation of the material it traverses depends only on its speed and the magnitude of its charge and not on the sign of the charge. Since a proton weighs 1,836 times as much as an electron and an α-particle or He^{++} ion 7,296 times as much, their speed will be correspondingly slower than that of an electron of equal energy. The equations for LET of protons and α-particles are similar to those of electrons:

$$-\frac{dE}{dx} = \frac{2\pi e^4 z^2 NZ}{E} \frac{M}{m} \ln \frac{4E}{I} \frac{m}{M}$$

where M and z are the mass and number of unit charges of the moving ion. This reduces for water, assuming $I = 66$ ev to

$$-\frac{dE}{dx} = \frac{1.870}{E} \log_{10} \frac{E}{0.0605}$$

for protons and

$$-\frac{dE}{dx} = \frac{29.735}{E} \log_{10} \frac{E}{0.1203}$$

for α-particles, where E is now in Mev, although $- dE/dx$ is still in ev/Å. The rate of energy loss for a deuteron, which is sometimes of interest because of the use of the cyclotron as a radiation source, is equal to that of a proton of half the deuteron's energy. At very low speeds the equation predicts that the LET should become indefinitely large. In fact, when a proton falls below 1 Mev in energy it may capture an electron from the material and become a fast moving neutral H atom. After the neutral atom has proceeded a short distance it may lose the electron again and the resulting proton may lose some more energy be-