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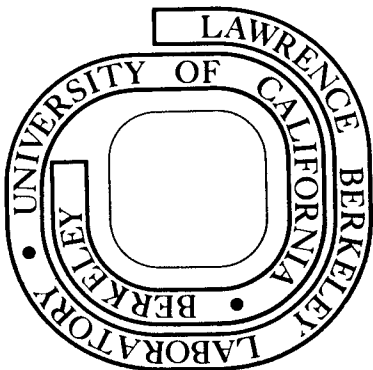
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CHEMICAL TRACK EFFECTS IN CONDENSED SYSTEMS AND
IMPLICATIONS FOR BIOLOGICAL DAMAGE

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INTRODUCTION

The chemical interests in particle tracks involve spatial distributions of reactive intermediates, chemical reactions, and products. Figure 1 shows our present concepts of the local space-time development following a small isolated energy loss in water [1-3], the ordinate gives radii in Å for distributions of the indicated species, and the abscissa is time in seconds; various important events which occur are noted.

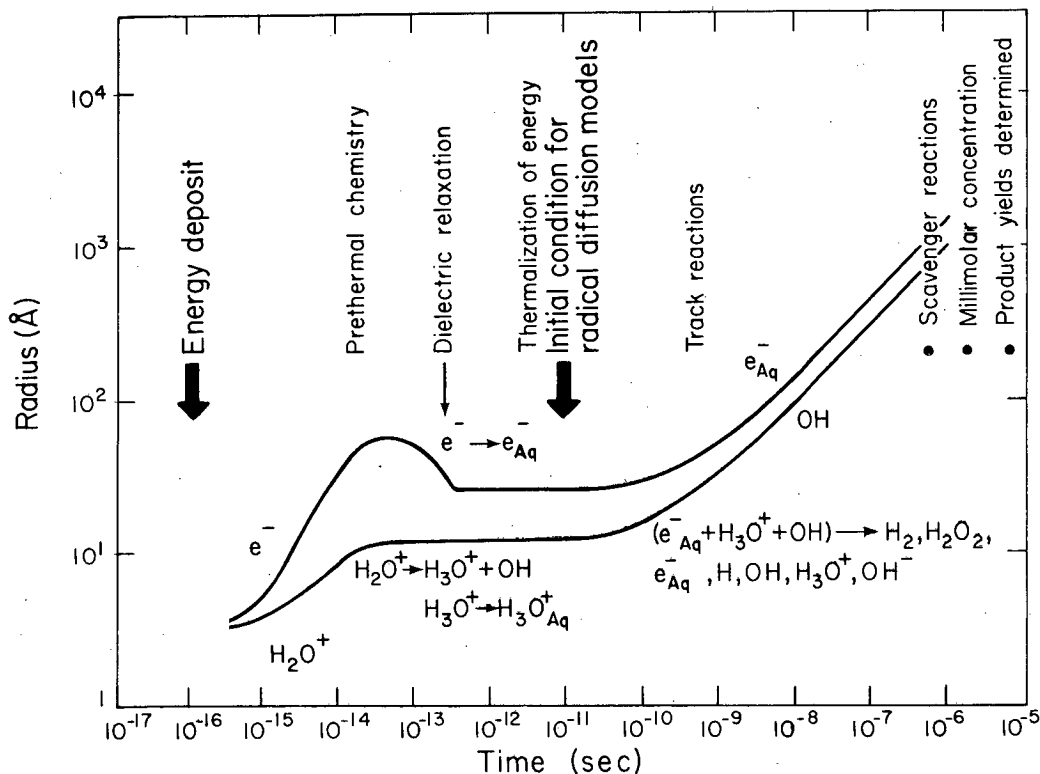


Fig. 1. Space-time development of small isolated energy deposit (spur) in a dilute aqueous system. In the prethermal time period ($t < 3 \times 10^{-12}$ sec), phenomena involve electronic motion for the most part; the ion-molecule reaction creating H_3O^+ and the longitudinal relaxation of H_2O require only proton motion. In the post-thermal period, the species that have already been created undergo diffusion-controlled reactions with each other (indicated by the parenthesis on the left of the equation).

From a chemical point of view, the distribution in space of e_{aq}^- , H_3O^+ and OH at 10^{-11} sec is what is meant by "initial track structure." The radical diffusion model uses such distributions to calculate the reactions during track expansion and the radical reactions with scavengers; all of these processes are complete in a few microseconds, and the product yields are determined. The events which occur before thermalization (a few pico seconds) have not, of course, been observed directly. However, the ion-molecule reaction, which forms H_3O^+ and OH at $\approx 2 \times 10^{-14}$ sec (it is the fastest chemical process of radiation chemistry), and the hydration of the electron at the longitudinal relaxation time for water ($\approx 4 \times 10^{-13}$ sec) are widely accepted. In any case, the reactive intermediates are formed in the prethermal period. At thermalization, all of the deposited energy, except that which is tied up in dissociation of water to form the intermediates, is distributed as a local temperature rise in the track.

Biological systems are for the most part concentrated aqueous solutions, and many of the same processes (as those of Fig. 1) occur on irradiation of such systems. Reactions of the biological molecules can occur at any time, including the prethermal period.

Clearly, the tracks used by the chemist are related to the patterns of initial energy deposit obtained by purely physical considerations. The chemical "initial" patterns have lost a certain amount of the original detail--both in the distribution energy in species and in space. The chemist also has a cut-off in the size of pattern of interest; scavengers destroy radicals before they can move some maximum distance, such as 10^3 \AA or so in dilute aqueous systems.

The most important chemical track effects are the yields of chemical reactions, and they are understood in terms of the radical diffusion model [4-6].

OVERVIEW OF HEAVY PARTICLE TRACKS

Heavy particles lose approximately equal amounts of energy by means of two mechanisms which lead to distinctly different patterns of energy deposit. The first mechanism is a resonant process with individual losses in the range 0-100 eV; the result is the creation of chemical intermediates in a cylindrical region (called the "core") around the particle trajectory. The second mechanism is the knock-on process which creates recoil electrons in a spectrum from 100 eV to a maximum value, $E_{max} = 2mc^2\beta^2/(1-\beta^2)$, where β is the velocity of the particle, v , divided by the velocity of light, c , and m is the electron mass; the ejected electrons create intermediates in a region called the penumbra.

Figure 2 shows schematically the initial structure of a heavy particle track; 2a shows the track going into the page, and 2b shows it going horizontally. The cylindrical region is the core, and the knock-on electrons of the penumbra are indicated as lines. Approximately equal amounts of energy go into core and penumbra. The energy loss spectrum and the size of the penumbra depend upon the heavy particle velocity; particles with different LETs (because they have different effective nuclear charge, Z^*) have loss events spaced differently [7].

Calculation of chemical yields for the core made by using the radical diffusion model is relatively straightforward; the initial condition is a cylindrical distribution, and the track expansion occurs in cylindrical geometry. Treatment of the penumbra is a different type of problem, however. Initially, the knock-on electron tracks are so sparsely distributed that they do not interact on expansion. The

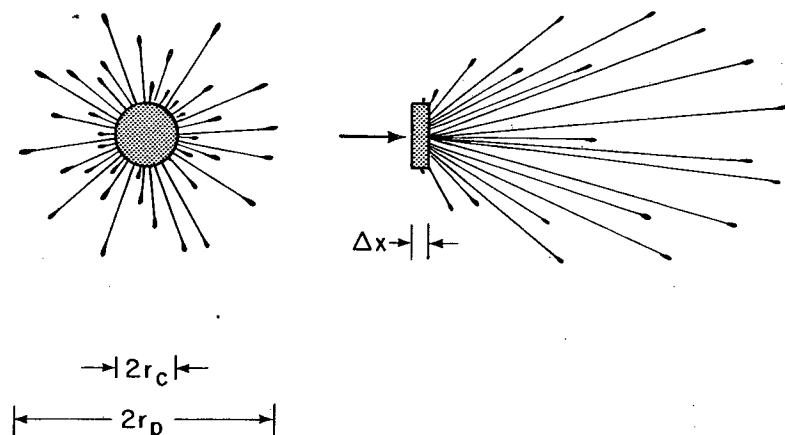


Fig. 2. (a) Schematic representation of initial condition (before radical diffusion starts) for heavy particle track going into the page; the radius of the core, r_c , is typically 10-80 Å; the radius of the penumbra, r_p , is typically 1-100 microns. The knock-on electron tracks are indicated by lines, although they actually are composed of strings of spurs which are as large in diameter as the core; the track ends are indicated; branch tracks occur too, but they are not shown. (b) Schematic representation of initial condition for the same heavy particle track going parallel to page; the locus of the transients created in a section of track ΔX in length is given. The core energy is located in a region shaped like a pill box of radius, r_c , and height, ΔX ; the locus of knock-on electrons which form the penumbra is shown. The actual amount of energy (and also the number of electrons) depends upon the LET (v and Z of the particle). Most segments of track of a few Å length would have one or no knock-on electrons.

(XBL 794-1325)

basic problem is to obtain the chemical yield arising from electron tracks which start with arbitrary energy. This problem has been considered [5]. Electron tracks are similar to heavy particle tracks in having cores and penumbras; the cores of high energy electron tracks reach a limiting form of widely spaced spurs resembling a string of beads. The penumbra is composed of the knock-on electron tracks. A basic equation, valid in the high energy region, has been found for $G_e(E)$, the yield of an arbitrary product formed per 100 eV of energy loss for an electron which starts with the energy E . The equation is

$$\frac{d}{dE} EG_e(E) = (1-f)G_{sp} + \left(f \int_{E_0}^{\frac{E}{2}} G_e(\epsilon) W_e(E, \epsilon) d\epsilon \middle/ \int_{E_0}^{\frac{E}{2}} W_e(E, \epsilon) d\epsilon \right) \quad (1)$$

where G_{sp} is the average G value for the isolated resonant energy losses of the core; f is the fraction of energy which goes into knock-on electrons; and $W_e(E, \epsilon)$ is the fraction of knock-on energy per unit energy interval for an electron of energy E to form knock-on electrons with energy ϵ . This equation has been used along with an electron track model in the low energy region to obtain $G_e(E)$ values [5]; the special problem of the yields below 100 eV has been considered [2].

The yield of any radiation product can be used in Eq. (1). G values for the water decomposition products OH, H, H₂O₂, and H₂ have been obtained, and are shown in Fig. 3. G values for the best known of all aqueous systems, the Fricke dosimeter, were also calculated, and are shown in the figure. The Fricke yield is related to the water decomposition yields as follows: $G_e(\text{Fe}^{+3};E) = 3G_e(\text{H};E) + G_e(\text{OH};E) + 2G_e(\text{H}_2\text{O}_2;E)$. As we see from Fig. 3, the Fricke G value tends to parallel the radical yields. The figure also shows that radical and molecular yields tend to vary in opposite directions, one having a maximum, where the other has a minimum.

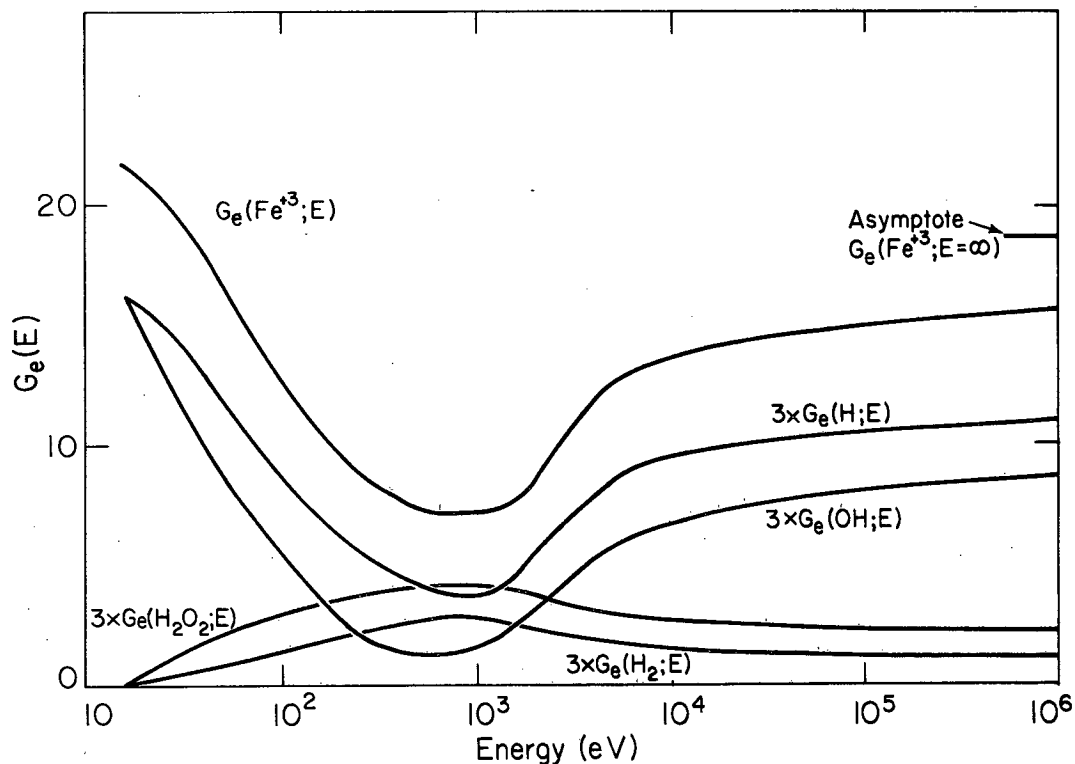


Fig. 3. $G_e(E)$ values in acid solution of the water decomposition products and Fe^{+3} of the Fricke dosimeter for electrons starting with energies in the range 0- 10^6 eV. The electrons are completely degraded in the system. The asymptotic yield of Fe^{+3} is also the spur yield.

(XBL 794-1327)

The use of a radical diffusion model, consisting of a cylindrical expansion for the core radicals and penumbra electron yields obtained with the use of Eq. (1), allows us to calculate the chemical yields of heavy particle tracks.

SUMMARY OF HEAVY PARTICLE RADICAL DIFFUSION CALCULATIONS

Figure 4 shows G values for the Fricke dosimeter over a wide range of energies for a representative set of particles. The equations used and the calculation procedures have been described [6]: the most important points are that prescribed diffusion is used, and the initial dissociation of water is assumed to require 17 eV. All of the water decomposition products have been obtained, and the Fricke yields are given as the most understandable results in terms of comparison with other data.

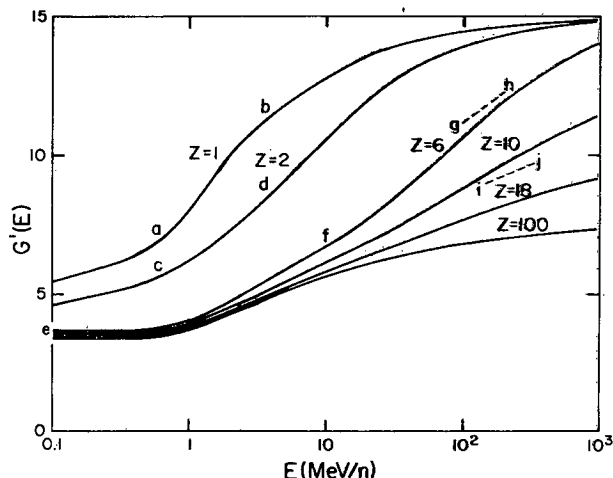


Fig. 4. $G'(E)$ values for six particles ($Z=1, 2, 6, 10, 18$, and 100) vs. E (MeV/AMU). $G'(E)$ is the differential yield (sometimes called "local" yield) for a particle of energy E , and applies to a small section of the particle track. In the regions marked a and b (for $Z=1$), c and d (for $Z=2$), and e and f (for $Z=6$), experimental results agree reasonably well with present calculations. Comparison could not be made at other energies for lack of experimental data. Experimental data are taken from Hart, Ramler, and Rocklin [8] for $Z=1$, Schuler and Allen [9] for $Z=2$, and from Schuler [10] for $Z=6$. Lines g to h and i to j indicate the approximate location of experimental points for carbon ($Z=6$) and argon ($Z=18$) obtained by Jayko et al. [11]. (XBL 794-1324)

The G values for the proton and helium are obtained over most of the energy range directly from the electron theory without any additional adjustment of parameters. In the small energy region (around 1 MeV per nucleon), it is clear that there is a saturation effect, and approximately the same yields are expected for all particles of $Z > 6$; the same saturation-type effect to a somewhat lesser degree occurs at higher energies, and there is very little difference between Ar ($Z=18$) and Fm ($Z=100$), even in the range of energies above 100 MeV per nucleon.

A weakness in the present situation regarding heavy particle tracks is our lack of knowledge of the phenomena that occur at extremely high energy deposits (say, 1000 eV per Å). Significantly elevated temperatures must be formed, and these are probably accompanied with shock waves, and possibly bubble formation.

APPLICATION TO BIOLOGY

The survival of cultured cells after irradiation depends in such a striking manner on certain parameters of the radiation that target theories to explain the effects have been very appealing. Such theories (if taken literally) seem to imply that the deposit of energy in the proper location of the cell can guarantee its death, i.e., there is an all-or-none effect, dependent solely on absorption of energy. It is clear that before death is registered, many processes of a chemical and biological nature occur. Any biological system is also a chemical system, and one can expect it to behave in its first response to radiation as an ordinary non-

living system. Another type of over-simplified model (as contrasted with the "target" theory) would have some chemical effect produced soon after irradiation as determining cell survival in an all-or-none manner.

A radical diffusion model for cell survival has been investigated [12], and seems to be able to furnish survival curves with many of the correct properties. In this model it is assumed that there is a particular type of lesion of DNA formed by a purely chemical process which can provide the certain lethality. Figure 5 presents a schema of the model.

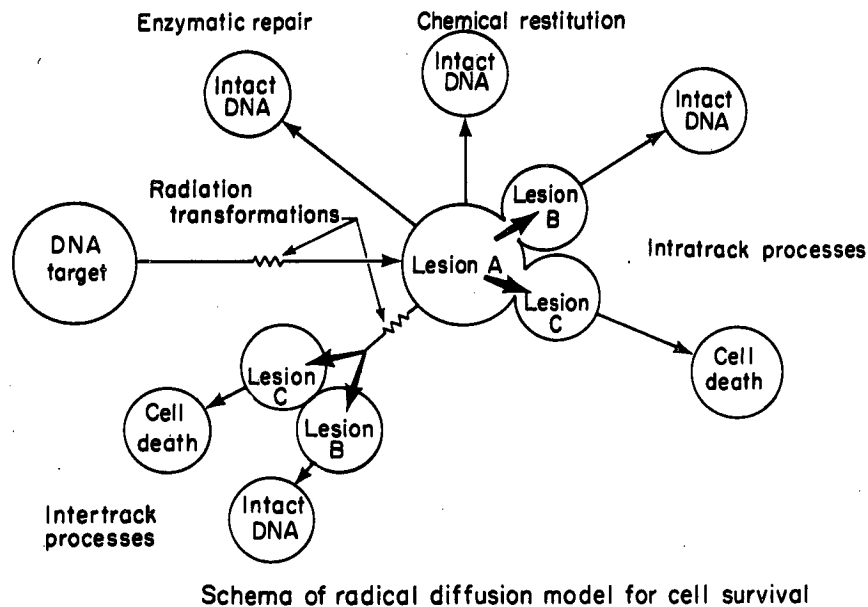


Fig. 5. Schema of radical diffusion model for cell survival. The symbols are defined and discussed in the text. (XBL 794-1323)

We note at first that radiation creates much damage in DNA, but that most of it is repaired. We lump all of the initially radiation-damaged DNA into "lesion A"; this damaged DNA interacts first with its environment, some of it is immediately repaired (chemical restitution), and some of it is transformed in ways which leave it as "lesion A." Reaction of lesion A with other radicals produced by the radiation transforms it into lesion B with inevitable repair, and into lesion C with inevitable death; along the horizontal line the radicals are produced in the same track, and the arrows descending to the lower left show that the radicals are produced in other tracks.

This model requires that a radical produced by the radiation survives long enough to react with lesions created in other tracks. It is clear that the primary radicals formed in water cannot fulfill this requirement, so we call the effective radicals "secondary radicals." They could be any radicals formed by the primary intermediates or their progeny.

This chemical model is constructed explicitly to involve particle tracks and time. Survival curves in terms of single particle-kill probabilities are obtained in their most general form; here, of course, the properties of the track appear explicitly. As applied to irradiations of short enough duration with low LET radiation, where the tracks are so tenuous that the individual track entities can be taken as occurring randomly in space, the survival curve can be written in a very simple form:

$$-\ln N/N_0 = f_2 \eta D + (f_2(1-f_1)\eta \lambda) (e^{-\lambda D} - 1) \quad , \quad (2)$$

where

- N is the number of surviving cells from an original population of N_0 .
- D is the dose in rads.
- η is the number of A-type lesions created per rad of radiation.
- λ is the average number of secondary radical reactions with A-type lesions per rad.
- f_1 is the probability that a secondary radical will be produced and react with an A-type lesion created in the same track entity.
- f_2 is the fraction of A-type lesions which react with secondary radicals and which are thereby transformed into C-type lesions.

Equation (2) has reasonable properties. For small D, it has the linear quadratic form which is widely used by radiation biologists; if we call the coefficients α and β , they are $\alpha = f_2 f_1 \eta$, $\beta = f_2(1-f_1/2)\eta\lambda$. For large D, Eq. (2) is a simple exponential function with $D_0^{-1} = f_2 \eta$ and an extrapolation number $n_0 = \exp f_2(1-f_1)\eta/\lambda$. All of these quantities, except f_2 , are explicitly derived from radical diffusion considerations. There is no way f_2 can be obtained from theory at the present time.

The more general form of cell survival curve that involves the particle tracks explicitly also involves parameters that have definite meaning in terms of radical diffusion. The simplest form is a linear quadratic expression with

$$\alpha = \frac{p}{c \text{LET}} \quad , \quad \beta = \frac{(1-p)^2 \gamma}{2c^2 (\text{LET})^2} \quad ,$$

where

- p is the single particle kill probability.
- γ is a track overlap function which involves both space and time.
- c is a geometrical factor.

It appears to be possible to explain how biological phenomena vary with particle properties by using the same theoretical basis which explains chemical yields. In such treatments, phenomena which follow the initial energy deposit are considered for very long time periods, and the corresponding distances which chemical intermediates travel are large.

SUMMARY

Much is known concerning the energy deposited by high energy particles in condensed systems, e.g. water. The chemical processes following the energy deposit are also known--at least in an approximate way--including most of the phenomena in space and time. There is actually no theory of the very early (prethermal) effects, and the phenomena themselves are not known when the energy density is very high.

A model which attempts to explain cell survival in terms of radical diffusion processes has been introduced. Further study of this model will allow a more explicit assessment of the role of chemistry and its relationship with strictly biological phenomena.

Acknowledgment

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