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RADIATION CHEMISTRY OF HEAVY PARTICLE TRACKS
I. GENERAL CONSIDERATIONS*

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Abstract

The radiation chemistry of heavy particle tracks in dilute aqueous solution is considered in a unified manner. Emphasis is on the physical and chemical phenomena which are involved rather than on the construction of models to be used in actual calculations although the latter problem is discussed. A differential segment of a heavy particle track is composed of two parts which we call "core" and "penumbra"; elementary considerations show that all properties of such a differential track can be uniquely specified in terms of a two-parameter system, and we choose energy per nucleon (E) and atomic number (Z) as independent parameters. The nature of heavy-particle track processes varies with the magnitude of the energy deposit (LET), and we discuss three categories of track problems, for low-, intermediate-, and high-LET cases, respectively. Scavenger reactions normally terminate radical recombination in a track, and for heavy

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particle tracks we find a criterion involving the scavenger concentration for a convenient separation of core and penumbra into essentially noninteracting parts which can be treated independently. Problems of the core expansion in the three regions are considered and it is found that a versatile model can be constructed on concepts previously introduced by Ganguly and Magee. A model for the penumbra, based on the authors' electron track theory, is presented and discussed.

1. Introduction

High energy heavy particle tracks are all similar in structure.[1,2] The initial energy deposit has a compact "core" which contains somewhat more than half of the energy lost by the particle, and a diffuse "penumbra" which is composed of the tracks of knock-on electrons. The radiation chemistry of such particles contains a dichotomy of effects which arise, respectively, from the two parts of the track. At low energies the core always dominates, and at high energies the penumbra always becomes important.

Here we attempt a systematic treatment of the radiation chemistry of heavy particle tracks. Our considerations are actually restricted to the radiation chemistry of dilute aqueous solutions, but these systems allow the widest possible basis for comparison with earlier work - both experimental and theoretical.

The processes by which energy deposited in water by charged particles is utilized in the formation of chemically active species are not well known. Theoretical considerations[3] of these early events have been made, and experiments have been performed[4,5] in attempts to elucidate the early time period for electron irradiations. There is reason to believe that special phenomena arise from the larger energy densities which occur in heavy particle tracks, particularly those of high Z and small E. The initial "radical" yields may be different from those of electron tracks, and potentially important special effects could arise from the very high initial temperatures inevitably formed. They lead to weak shock waves and possibly local

expansions with bubble formation. Those effects are all neglected here and must be considered at a later time.

Early theoretical work on the radiation chemistry of water assumed that the chemically reactive intermediates are initially formed either in spurs, which are spherical, or in cylindrical in distributions.[6-11] It is actually not possible to take into account effects of knock-on electrons with such models, and later work made the attempt to do so.[12-18] A more sophisticated treatment of the radiation chemistry of electron tracks has been presented by the authors.[19]

At the present time heavy particle irradiations are available which display a very broad range of track structures[1,2] and a systematic treatment of the radiation chemistry of heavy particle tracks is thus necessary if experimental phenomena are to be understood.

We speak of radiation chemical yields in terms of two kinds of G-values: the integral yield, G, and the differential (or "local") yield, G'. These quantitites are both function of the same variables, such as type of particle, particle energy, the observed product, etc; the notation we employ is flexible, and any number of the variables may appear as arguments, e.g., the differential ferric yield for a particle of charge Z and energy E per nucleon in a solution with scavenger concentration c_s may be given as $G'(Fe^{+3};E)$ when the other conditions are understood, or $G'(Fe^{+3};E,Z,c_s)$ when the particle and concentration of solute (Fe^{+2}) need to be indicated explicitly. We are usually interested in the variation of a

particular yield with heavy particle energy and merely write G'(E), or G(E). The two kinds of G-values are related as follows:

$$G'(E) = \frac{d}{dE} EG(E) \quad . \tag{1}$$

From a theoretical point of view G'(E) is the more fundamental quantity to consider.

2. The Patterns of Energy Deposit

Consider the pattern of energy deposit in water by a fast heavy particle. The problem has been discussed by Chatterjee and Tobias.[20] They propose the use of the Bohr adiabatic criterion to get the radius of the cylinder about the particle trajectory in which the resonant electronic excitations occur.[21]

$$r_c = \frac{\beta c}{\Omega_p} \quad . \tag{2}$$

We call r_c the "core radius." In eq 2, β is the velocity of the particle in terms of the velocity of light, c; and Ω_p is the plasma frequency.[22] About half the energy is lost (in water) to excitation processes below 100 eV (resonant excitations), and half of the energy is lost to excitation processes above 100 eV (i.e., knock-on electrons).

The electronic excitation takes about 10^{-16} sec or less time, and there follows a period of transformations of the energy with creation of transient reactive species, etc.[2-4] One important sequence of events involves the transport of knock-on electrons from their loci of formation near the trajectory to the end of their ranges. Of course, some of the energy of these electrons is lost in the core, but most of it is used to create a region generally much larger than the core which we call the "penumbra". It has a radius which we designate as r_p. The total time for the penumbra formation may be as long as a pico second. However, the processes occurring and the local time ~~scale~~

scale for excitations created by secondary electrons are, for all practical purposes, the same as those of excitations created by the primary particle.

The distribution of energy in the penumbra has been studied by Chatterjee and Tobias.[20] These authors propose for the average initial energy densities in the track:

$$\rho_{core} = \frac{LET/2}{\pi r_c^2} + \frac{LET/2}{2\pi r_c^2 \ln(\sqrt{e}\, r_p/r_c)} \qquad r \leq r_c \quad , \qquad (3)$$

$$\rho_{pen}(r) = \frac{LET/2}{2\pi r^2 \ln(\sqrt{e}\, r_p/r_c)} \qquad r_c < r \leq r_p' \quad , \qquad (4)$$

Here, LET is the total energy loss per unit path length and r is the radial distance from the particle trajectory. The first term in eq 3 is the energy density due to the glancing collisions; the second term gives a contribution from the energy lost by the knock-on electrons in their penetration of the core. The energy density of eq 4 arises from knock-on electrons which are stopped between r_c and r_p.

It is clear that the track dimensions r_c and r_p depend only on the particle velocity β and not on charge or mass. The energy density, however, depends on the LET and thus on the particle charge. The general particle track, therefore, depends on two parameters which can be taken as energy per unit mass (E) and atomic number of particle (Z). The actual effective charge Z_{eff} is determined by the interaction of the particle with the medium; it depends on the velocity and cannot be set arbitrarily. Table I contains values of some of the track quantities which depend on the velocity only.

The last column of Table I gives λ, the ratio of the "initial" energy density in the core to that in the penumbra near r_c, and it shows that all concentrations of intermediates in the core are expected to be much larger than those in the penumbra. The actual location of the chemical intermediates formed by the resonant electronic excitations is not necessarily within the core of radius r_c; the early processes[2-4] involve subexcitation electron transport to distances of 20-50 A or so; although these electrons return toward their loci of formation before they become hydrated, the initial core radius for electrons is not likely to be much less than 30 A. In any case, however, the core has a much larger radical concentration than the adjacent penumbra.

The densities given by eqs 3 and 4 are <u>average</u> values, and the actual initial values may fluctuate greatly around them. For example, the core is comprised of spurs which contain, on the average, 40 eV; if the LET is small enough, the core is made up of a string of spurs rather than a continuous distribution of intermediates. The penumbra is made up of tracks of knock-on electrons, and it is always more inhomogeneous than the core. Here the individual tracks have their recombination reactions which take place early, and then the escaping radicals intermingle to form a density which has the approximate radial dependence given by eq 4. The extent and importance of the intermingling of the radicals from neighboring electron tracks of the penumbra depend upon the rate of the scavenger reaction in a manner considered in section 3.

The stopping power of heavy particles in matter has been investigated.[23,24] Figure 1 shows the LET for six selected particles[25] in water as a function of energy per unit mass (E). These curves were obtained using a recipe proposed by Blann.[26] Table II contains a summary of the effective charges (Z_{eff}) on particles in water as a function of E. The effective charge is given by[27]

$$Z_{eff} = Z[1 - \exp(-0.95\, v_r)] \quad , \tag{5}$$

where Z is the atomic number of the particle and v_r is the relative velocity given by $v_r = v/v_0 Z^{2/3}$; v is the particle velocity and v_0 is the average velocity of the electron in the H atom($v_0 = e^2/\hbar$). The stopping power (LET) of a particle with an energy per nucleon E is given in terms of the stopping power of the proton at the same energy[28]

$$\left(\frac{dE}{dx}\right)_{ion(Z_{eff})} = \left(\frac{dE}{dx}\right)_{proton} Z_{eff}^2 \quad . \tag{6}$$

The proton stopping power was calculated using the Bragg rule with data for the atomic targets H and O obtained from ref 24a. The data of ref 24a scatter very widely, and a considerable amount of smoothing was made; the low-energy stopping power of heavy particles cannot be considered as well known. Figure 2 contains curves of the stopping power of the particles H and He (obtained in the same way with data from ref 24b) in water for the lower energy region.

3. Overview of Heavy-Particle Track Problems

We by-pass all problems of the prethermal period ($t < 10^{-12}$ sec) of track development,[2-4] and consider as initial condition for the chemical processes of the track an assumed distribution of radicals formed by the deposited energy. With the problem simplified in this manner, treatment of the radiation chemistry of a heavy particle track still requires a system of partial differential equations for several species, with initial conditions given by the appropriate core and penumbra patterns. This procedure is too difficult to carry through, so we look for more simple intuitive models which can actually be elaborated with a reasonable amount of effort. A straightforward procedure using prescribed diffusion could, perhaps, be used to calculate the expansion of the core and its interaction with the adjacent penumbra; part of the penumbra will not interact with the core and, in any case, must be treated by the electron track theory. We need a scheme for making approximations which are reasonable on physical and chemical grounds and which allow track calculations to be carried out.

The most desirable approximation would be a separation of the track into two noninteracting parts: core and penumbra. Procedures exist for treating cylindrical tracks (core region) and for treating electron tracks (penumbra region); a natural type of approximation therefore is to assign appropriate fractions of the track energy to the two kinds of tracks. We examine the possibilities for this type of approximation.

In any irradiated systems there are always reaction sequences, and they depend upon the chemical composition. Radicals initially formed always react readily with one another to form molecular products, and they may also react with various molecules of the system. If the latter processes decrease the number of radicals, they are called "scavenger reactions." A simple example is the reaction

$$OH + Fe^{+2} \rightarrow OH^{-} + Fe^{+3}$$

which removes OH radicals from aqueous solutions. If a system has no scavenger at all initially present, radicals escape from tracks and build up a background concentration of radicals into which fresh tracks fall as the irradiation continues.[29] In such systems tracks have properties which vary with irradiation time. Systems which have scavengers present to destroy all newly-formed radicals as the tracks expand have track properties which are essentially independent of the extent of irradiation, and only these will be considered.

Let us consider a system which has radicals of one type only. At any point in a track, radicals recombine with a rate given by $2kc^2$ (because two radicals disappear) and react with the scavenger with a rate $k_s c_s c$, where c is the local radical concentration, c_s, the scavenger concentration, and k and k_s are rate constants. A radical concentration which we use as a reference is given by

$$c_1 = k_s c_s / 2k \quad , \tag{7}$$

and for this particular concentration the radical recombination and scavenger reaction rates are the same. If the radical concentration is larger than c_1, recombination is more important than scavenging, and if it is less than c_1, the reverse is true. The mean time for the scavenger reaction is given by

$$t_1 = (k_s c_s)^{-1} \quad , \tag{8}$$

and we use t_1 as a reference time. The track reactions cannot last for times appreciably larger than t_1. The distance, l_1, that a radical can diffuse in the time t_1, is given by

$$\langle l_1^2 \rangle = 4Dt_1 \quad . \tag{9}$$

Let us consider the changing phenomena in tracks as LET increases. At the lowest LET, particle tracks are closely related to high-energy electron tracks. In this range of LET, tracks are clearly separated into entities which develop independently;[19] and as LET varies, G'-values change because the spectrum of knock-on electrons changes (see eq 36).

As LET increases further, spurs (though initially separate in the track core) overlap (due to diffusion of radicals) before their "forward" reactions (i.e., radical combination reactions) are complete. And as LET continues to increase, the spurs are merged initially to form a cylindrical track. If we say that the average spur contains 40 eV and has a radius of 20 A, the initial merging

occurs when the energy deposit in the core is about 1 eV/A, or when the total LET is ≈2 eV/A. We call the region in which LET is less than 2 eV/A "Region I" (see Figure 1). In Region I, the cores of tracks are made up of spurs which are initially separate.

Other important "high-LET effects" are expected to arise from the "over-lapping" of the core and penumbra. Of course, the penumbra is composed of a statistical distribution of electron tracks; in the low-LET track they develop independently, but at higher LET (where they are deposited closer together), they overlap with each other and with the core before radical recombination is terminated by expansion. A measure of this kind of interaction is given by the average energy density in the track, and we can use the energy densities of Chatterjee and Tobias[20] given in eqs 3 and 4. Values of r_c and r_p are shown in Table I. It is interesting that the values of r_p in column 4 of Table I turn out to be related to the maximum electron energies in column 5 approximately as 1 Å per eV.

Let us consider the radical recombination in the penumbra of a track, using a one-radical model. The partial differential equation which applies is

$$\frac{\partial c}{\partial t} = D\nabla^2 c - 2kc^2 - k_s c_s c \quad , \tag{10}$$

where the c's are concentrations already defined and D is the diffusion coefficient. The first term on the right describes the diffusion, the second and third the radical recombination and scavenger reactions, respectively. In our exploratory consideration we take the scavenger reaction as a perturbation and look at the equation obtained by neglecting the last term of eq 10.

$$\frac{\partial c}{\partial t} = D\nabla^2 c - 2kc^2 \quad . \tag{10a}$$

The average initial radical concentration compatible with eq 4 is

$$c(r) = c_0 \left(\frac{r_0}{r}\right)^2 \quad , \tag{11}$$

where r_0 is an arbitrary reference radius, and c_0, the initial radical concentration at r_0, is to be obtained using eq 4; c_0 is proportional to LET. Use of eq 11 in eq 10a yields

$$\frac{\partial c}{\partial t} = \left[\frac{4D}{c_0 r_0^2} - 2k\right] c^2 \qquad t = 0 \quad . \tag{12}$$

This equation is valid only initially because at later times eq 11 does not generally hold. The diffusion and recombination terms in eq 12 have the same dependence on r, and this dependence is the same as c^2, i.e., r^{-4}. This means that, on the average, the rates of change in concentration because of diffusion and recombination have the same relative importance throughout the penumbra. There is a value of LET for each particle energy E for which the bracket is zero. The condition for zero bracket can be written

$$\frac{2k}{4D} c_o r_o^2 = 1 \tag{13}$$

A reasonable value for $2k/4\pi D$ to be used in a one-radical treatment of water is 5A. The value of $c_o r_o^2$ is somewhat more difficult to estimate. The energy density of eq 4 and the radical concentration of eq 11 correspond to average values, i.e., values which exist after the separate electron tracks of the penumbra intermingle. Thus the "initial" condition of eq 12 is a fictitious one in which the radicals escaping from the electron tracks of the penumbra form the average distribution of eq. 11. In track studies we have used 17 eV as the energy requirement for a radical pair.[19] The different significance of the "initial" condition in the penumbra, which actually occurs after the forward reaction of the electron tracks is more or less complete, means that a very different magnitude of energy per radical pair is required. We take 34 eV as the energy per radical pair. This choice of parameters allows a calculation of the position of zero bracket in eq 12 and it is indicated in Figure 1 by the line labelled $\alpha = 1$. The region below this line (and above Region I) is called "Region II"; the region above the line is called "Region III".

Equation 12 gives the initial $\frac{\partial c}{\partial t}$ in the penumbra for the partial differential eq 10a. Consider the early development in time of this equation in the penumbra for r values sufficiently distance from r_c or r_p. If the bracket is positive, diffusion dominates recombination initially; if the bracket is negative, recombination dominates diffusion initially. An examination of $\partial c/\partial t$ for small values of the time shows that, as time increases, $\partial c/\partial t$ becomes more

positive if it is initially positive and more negative if it is initially negative. We call Region II "a region of diffusion domination," and Region III "a region of recombination domination."

The importance of the scavenging reaction depends on the radical concentration as compared with c_1 (eq 7). The values of the radii (r_1) for the six representatives particles for which $c = c_1$ are given in Figure 3.[31] We call this the radius of the "chemical core" because it is based on a chemical reaction criterion, whereas the core radius r_c was based on a physical criterion. Figure 3 shows that r_1 is equal to r_c at high particle energies; as particle energy decreases, r_1 increases and r_p decreases; at some energy, r_1 becomes equal to r_p; for smaller values of E, $r_1 = r_p$.

The fraction of the total energy of the tracks enclosed within the radius r_1 for this particular set of parameters is shown in Figure 4 for each of the six representative particles. At values of E for which r_1 is equal to or less than the core radius r_c, the fraction of energy in the core is about 0.52; at values of E for which r_1 is equal to r_p (or $k_s c_s/2k$ is less than the radical concentration at $r = r_p$), $F_{core} = 1$.

Use of eqs 7-9 and 11 allows us to write

$$r_1^2 = \frac{2kc_o r_o^2}{4D} l_1^2 \tag{14}$$

This relationship shows that both r_1 and l_1 vary in the same way with scavenger concentration. We also see that for the condition of zero bracket in eq. 12 (i.e., $\alpha = 1$),

$$r_1^2 = l_1^2 \tag{14a}$$

In the application of eq 10 to the portion of the track with $r > r_1$, to a good approximation we can neglect the recombination term $2kc^2$. The consideration leading to eq 12 shows that the diffusion and recombination terms are of comparable importance, so the diffusion term can also be neglected; thus, the equation

$$\frac{\partial c}{\partial t} = -k_s c_s c \tag{15}$$

appears to be a reasonable approximation. This means that the scavenger reacts completely with the radicals, and thus the yields are just the same as for the separate tracks which form the penumbra.

This treatment suggests that the "chemical core" (i.e., the portion contained within $r = r_1$) reacts in a typical kind of track process, and the "chemical penumbra" (the portion beyond $r = r_1$) reacts as if the electron tracks were isolated. Thus, the approximate separation of the heavy particle track into two noninteracting parts is reasonable. In sections 4, 5 and 6 we consider various aspects of the core expansion problem; in section 7, we consider the penumbra problem.

4. The Low-LET Chemical Core

The problem considered here is the overlapping of spurs along a track as expansion occurs and the treatment is similar to that of Ganguly and Magee.[7] A one-radical model is used for simplicity but an application of the methods developed here in a companion paper[30] employs a multi radical treatment.

In one-radical prescribed diffusion the concentration of radicals in a track of N spurs is given by

$$c(r,z,t) = \sum_{i=1}^{N} \nu_i \frac{\exp - \left[\dfrac{r^2+(z-z_i)^2}{r_i^2 + 4Dt}\right]}{[\pi(r_i^2+4Dt)]^{3/2}} ; \tag{16}$$

the N spurs have centers located at positions on the z axis at z_1, z_2, $z_3 \ldots z_i \ldots z_N$; the $i^{\underline{th}}$ spur has ν_i radicals and a radius parameter r_i. If we use this concentration in the partial differential eq 10a and first integrate over all space, we get

$$\frac{d}{dt}\sum_i \nu_i = -2k\left[\sum_{i=1}^{N} \frac{\nu_i^2}{[2\pi(r_i^2+4Dt)]^{3/2}} + \sum_{\substack{i=1\\ j\neq i}}^{N} \frac{\nu_i\nu_j \exp - \dfrac{(z_i - z_j)^2}{r_i^2 + r_j^2 + 8Dt}}{[\pi(r_i^2+r_j^2+8Dt)]^{3/2}}\right] , \tag{17}$$

which is an equation summed over all the N spurs.[32]

In prescribed diffusion the ν_i are considered as function of time to be determined. We write a system of n ordinary differential equations.

$$\frac{d}{dt}\nu_i = -2k\left[\frac{\nu_i^2}{[2\pi(r_i^2 + 4Dt)]^{3/2}} + \nu_i \sum_{j\neq i} \frac{\nu_j \exp - \dfrac{(z_j - z_i)^2}{r_i^2 + r_j^2 + 8Dt}}{\left[\pi(r_i^2 + r_j^2 + 8Dt)\right]^{3/2}}\right] \quad i = 1,2,3\ldots N, \quad (18)$$

In justification of these equations we note that all possible spur-spur interaction terms are included, and summation of both sides of eqs 18 over i leads to eq 17.

A rigorous treatment of this set of equations has not been made but the following approximation leads to a result which has intuitive appeal. Consider the equation for an interior spur, the ith, and approximate the summation (in eqs. 18) by an integration. We are interested in the average value of $\frac{d}{dt}\nu_i$, and take the probability that the jth spur occurs in the interval dz_j as (dz_j/Z_1), where Z_1 is a parameter which depends on the LET. Substitution of the appropriate integral gives

$$\frac{d\nu_i}{dt} = -2k\left[\frac{\nu_i^2}{\left[2\pi(r_i^2 + 4Dt)\right]^{3/2}} + \nu_i\left\langle\frac{\nu_j}{\left[\pi(r_i^2 + r_j^2 + 8Dt)\right] Z_1}\right\rangle\right] \quad (19)$$

It is clear that the first term of eq 19 gives the ordinary prescribed diffusion result for a spur, and the second term gives its interaction with the other spurs; the bracket ⟨ ⟩ on the second term indicates an

average over the spur distribution function. Equation 19 applies to a spur of any size. Spurs are created by resonant energy losses in the range 0-100 eV, and with 17 eV required to form a radical pair, ν_i varies from 2 to 12; in order to get the track yield, this expression must be averaged over the spur distribution function. Although a distribution function for spurs has been proposed,[33] we do not consider this average explicity at this time, but for simplicity, propose that the following equation applies to the low-LET average spur which has ν radicals

$$\frac{d\nu}{dt} = -\frac{2k\ \nu^2}{[2\pi(r^2 + 4Dt)]^{3/2}} \left[1 + \frac{[2\pi(r^2+4Dt)]^{1/2}}{Z_1}\right] , \qquad (20)$$

where we choose ν as the average number of radicals in a spur and the average r^2 parameter so that the correct spur yields are obtained (e.g., 18.4[19] for the Fe^{+3} yield of the Fricke system); the parameter Z_1 varies inversely with LET, and the proportionality constant can be adjusted for agreement with the experiment.

When the parameter Z_1 in eq 20 gets so small with the increase of LET that the second term in the bracket is much larger than unity, we get

$$\frac{d\nu}{dt} \cong -\frac{2k\ \nu^2}{[2\pi(r^2 + 4Dt)]\ Z_1} , \qquad (21)$$

and we can write the equation in terms of the variable $\nu/Z_1 = N$, the number of radicals per unit distance

$$\frac{dN}{dt} \cong -\frac{2k\ N^2}{[2\pi(r^2 + 4Dt)]} \quad , \tag{22}$$

which is the ordinary prescribed diffusion equation for cylindrical symmetry (without consideration of scavenger reaction or interaction with penumbra). Equation 20 therefore, has a convenient form which allows the low-LET core equation to remain valid as LET increases. This equation contains the essence of the Ganguly-Magee track treatment; here, however, we recognize that only part of the track is involved. This treatment can also be extended to apply to a multi-radical case, and in the companion paper this is done and the G'-value for the Fricke dosimeter is calculated. We note that the yield of the core depends only on LET_{core} (because the penumbra is neglected).

5. The Medium-LET Chemical Core (Region II)

In Region II the spurs in the track core are initially merged, and the main problem for calculation of track yields is the interaction of the core with the penumbra. This is a region of "diffusion domination" in the penumbra, as noted in section 3. The radical concentration increases initially at all positions in the penumbra as the net result of diffusion and recombination; this means that the outward diffusion of radicals from small radii is more important than radical loss by recombination, and a model in which the core expands into the penumbra is indicated. Consider a one-radical model of the core expansion in sharp-boundary prescribed diffusion. The core volume per unit length of track increases with time as

$$V(t) = \pi(r_c^2 + 4Dt) \quad . \tag{23}$$

Say that the number of radicals in this volume per unit length of track is N(t); it changes with time because of two processes: a decrease because of recombination, and an increase arising from the engulfing of the penumbra. Thus

$$\frac{dN(t)}{dt} = -2k\left(\frac{N}{V}\right)^2 V + c\frac{dV}{dt} \quad , \tag{24}$$

where c is the local concentration in the penumbra given by eq 11; c is actually increasing with time but, in this treatment, we take it to be time independent and equal to the initial value. Equation 24 can be transformed into

$$\frac{dN}{dx} = -\kappa N^2 + \gamma \tag{25}$$

in which we use the new independent variable $x = \ln V/V_o$, and the quantities $\kappa = 2k/4\pi D$ and $\gamma = \pi r_o^2 c_o$ are introduced; $V_o = \pi r_o^2$.

Equation 25 is a form of the Riccati equation and has an analytical solution of the desired type

$$N(x) = \sqrt{\frac{\gamma}{\kappa}}\left[\frac{1 + \sigma e^{-2\alpha x}}{1 - \sigma e^{-2\alpha x}}\right] , \tag{26}$$

where $\alpha = \sqrt{\gamma\kappa}$ and $\sigma = (N_o - \sqrt{\gamma/\kappa})\ (N_o + \sqrt{\gamma/\kappa})^{-1}$. When $x = o$, $N(x) = N_o$, the initial number of radicals per unit length in the core. .

The condition for the vanishing of the bracket in eq 12 is $\alpha = 1$. In Region II near this limit, α is almost unity (somewhat smaller) and, for modest expansion ratios, the asymptotic form of eq 26 is reached, i.e.,

$$N(x) \approx \sqrt{\frac{\gamma}{\kappa}} \quad . \tag{27}$$

The picture we obtain from this analytical solution is that of a core in a steady state as it sweeps through the penumbra; at each instant of time there is just enough recombination to balance the addition of radicals through engulfment.

When the condition $\alpha = 1$ is satisfied, the asymptotic number of radicals per unit length in the core is

$$N_\infty = \sqrt{\frac{\gamma}{\kappa}} = \gamma = \frac{1}{\kappa} \quad , \tag{28}$$

and the concentration of radicals decreases in time as

$$c_{core} = \frac{N_\infty}{V} \approx \frac{1}{\kappa 4\pi Dt} = \frac{1}{2kt} \quad , \tag{29}$$

which is the same as the time dependence of radical concentration in a homogeneous system that recombines with the rate constant $\underline{k}$ (see eq 34). The actual value of $N = \kappa^{-1} = 4\pi D/2k \approx 4\pi D/2x4\pi Da \approx 1/2a$, where we have used the diffusion limited form of the rate constant with the parameter $\underline{a}$ as the reaction radius; if $2\underline{a}$ is taken as 5A $N = 0.2$. Under the condition $\alpha = 1$, for any particle, at least several radicals will have been formed per A in the core and the part of the penumbra engulfed; thus, the recombination is nearly complete.

In this region the core maintains a concentration higher than the penumbra it is engulfing. When the core concentration drops to its lowest value, i.e., $k_s c_s/2k$, we assume that the recombination stops and all remaining radicals react with the scavenger.

Let us consider the validity of the assumption that the core and penumbra do not interact. We shall not make a general treatment but limit the discussion to the situation at the boundary between Regions II and III where $\alpha = 1$. Here the bracket of eq 12 vanishes and $l_1 = r_1$. Since $\left(\frac{\partial c}{\partial t}\right)_{r=r_1} = 0$, a calculation of the flux from the core into the penumbra is simple because we can take $c(r,t) = c(r,o)$. The outward flux of radicals per unit track length through $r = r_1$, is equal to

$$J = 2\pi r_1 \; D\left(\frac{\partial c}{\partial r}\right)_{r=r_1} = 4\pi D c_1 \tag{30}$$

This flux integrated over the time $(k_s c_s)^{-1}$ over which the track reaction occurs gives

$$J(k_s c_s)^{-1} = \frac{4\pi D}{2k} = \kappa^{-1} \approx 0.2 \tag{31}$$

Examination of this condition for the heavy particle tracks of C, Ne and Ar for $\alpha = 1$ shows that about 10 radicals are formed per A in each case, and this means that only 2 percent of the radicals leave the chemical core before the scavenger reaction takes over.

The treatment of this section is based on eq. 24 and an analytical solution is obtained because of the r^{-2} dependence assumed for the radical concentration in the penumbra. (The average initial concentration has this r dependence). Equation 24 is again obtained if we start with eq. 22 and add the same penumbra engulfment term. Thus the Ganguly-Magee model of the core can be used in region II if the penumbra engulfment is added. In actual calculations using a numerical procedure it is convenient to use this model and it has several advantages. A multiradical reaction scheme can be used and the geometry of the core changes from a string of spurs to a cylinder automatically. This technique is used in the model calculation of the companion paper.[30]

6. The High-LET Chemical Core (Region III)

In the extreme case of recombination domination, the equation in the one-radical approximation is

$$\frac{dc}{dt} = -\ 2kc^2 \quad , \tag{32}$$

which has the solution

$$c(t) = \frac{c(o)}{1 + 2k\ c(o)t} \tag{33}$$

The long-time limit of eq 33 is

$$c(t) = \frac{1}{2kt} \quad , \tag{34}$$

and we see that this limit does not depend upon the initial concentration; all high concentrations of radicals reach the same absolute value at long times. The measure of the time to reach the limiting form, however, does depend upon the initial concentration; the half time is

$$t_{1/2} = \frac{1}{2kc(o)} \quad , \tag{35}$$

In section 5 the consideration of the core expansion for the case in which the bracket of eq 12 is zero led to a core concentration given by eq 34 (see eq 29). This result suggests that a simple recombination model for the high-LET track should have good validity.

The low-LET limit for this model is the vanishing of the bracket in eq 12 (see the line $\alpha = 1$ on Figure 1). The size of the core is determined essentially by the condition $c(o) = k_s c_s/2k$.

In a quantitative sense there is little difference between the use of the equations of this section and the prescribed diffusion model described in sections 4 and 5. The recombination is almost complete in any case and this result is obtained by either procedure. In the model calculation of the companion paper[30] we use the same prescribed diffusion model for the core in all three regions. The most serious questions in region III have to do with the initial radical yields and with special phenomena which may alter the reactions.

7. Heavy Particle Track Model

If $G_e(\varepsilon)$, the G-value of a radiation chemical products is known as a function of energy for electron tracks, the G'-values of the same product for low-LET particles can be obtained by elementary operations.[19] We have

$$G'(E) = (1-f)G_{sp} + f\frac{\int_{\varepsilon_0}^{\varepsilon_{max}} G_e(\varepsilon)w(E,\varepsilon)d\varepsilon}{\int_{\varepsilon_0}^{\varepsilon_{max}} w(E,\varepsilon)d\varepsilon} \tag{36}$$

where G'(E) is the differential yield per 100 eV of the particle with energy E; G_{sp} is the isolated spur yield of the product; $G_e(\varepsilon)$ is the G-value for the product of an electron track which starts with energy ε; $w(E,\varepsilon)$ is the fraction of energy lost by the particle of energy E in creation of knock-on electrons per unit energy interval at ε; ε_0 is 100 eV, the low energy limit of knock-on electrons; $\varepsilon_{max} = 2\ mc^2\beta^2/1-\beta^2$, the maximum knock-on electron energy; f is the fraction of energy expended in the creation of knock-on electrons.

In practice, eq 36 applied only to protons, deuterons, and α particles at LET's below 0.2 - 0.3 eV/A or so. We should perhaps note that all spur properties, such as energy distribution, are expected to be independent of the particle which creates them. The condition for validity of eq 36 is the nonoverlapping of the spurs along the track core as they expand and react with the scavenger. We can write a more general relationship for the track yield

$$G'(E) = F_{core}(E)G'_{core}(E) + [1 - F_{core}(E)]G'_{pen}(E) \quad , \tag{37}$$

where $G'_{core}(E)$ is to be obtained according to the appropriate model of sections 4-6, and $G'_{pen}(E)$ is to be obtained by a modification of the integral expression of eq 36. The basic electron yield curve as a function of energy must be used, and the electron spectrum of the electrons which are absorbed in the region $r_1 \leq r \leq r_p$ must be used. Let us consider the following expression for the penumbra yield

$$G'_{pen}(E) = \frac{\int_{\varepsilon_1}^{\varepsilon_{max}} G_e(\varepsilon')w(E,\varepsilon)d\varepsilon}{\int_{\varepsilon_1}^{\varepsilon_{max}} w(E,\varepsilon)d\varepsilon} \quad . \tag{38}$$

All of the knock-on electrons originate on the track axis and go into the chemical core region $r \leq r_1$; ε_1 is the minimum energy which allows them to reach r_1 and must be taken as the lower limit of the integral. The penetration of electrons in the penumbra is a statistical problem which has been considered by Chatterjee and Tobias.[20] These authors found that the value of r_p is essentially proportional to ε_{max}. This result means that on the average the penetration of an electron is linear in energy. Thus we take

$$\varepsilon' = \varepsilon - \varepsilon_1 \tag{39}$$

as the appropriate argument in the electron yield expression i.e., $G_e(\varepsilon')$, because the electrons which go beyond r_1 leave this amount of energy in the penumbra.

With this prescription for $G_{pen}(E)$, the model for the chemical yield of the heavy particle track is complete. The discussions of the physical and chemical phenomena are based on simplified systems (e.g., one radical models), but the approximation of separation of the track into two independent parts is probably a more general result. In any case, use of this approximation allows the construction of elaborate models including complete reaction mechanisms.

8. Discussion

There are many facets of the track problem in radiation chemistry and the heavy particle track involves all of them. The general heavy particle track has two diverse regions (core and penumbra) which must be treated explicitly, including their interaction. Considerations of this paper using one-radical models suggest that a meaningful separation can be made of the track into two parts which develop independently. This type of approximation is very practical in terms of calculational procedures and it is used in a companion paper[30] to calculate yields of the Fricke dosimeter. A multi radical treatment is actually used and comparison with experiment is encouraging.

The high energy low Z particles (H and He) have tracks which are actually very well understood. Their yields are related in a fairly rigorous way to the yields of electron tracks.

At the other extreme, low energy high Z particles, the situation is less satisfactory. We believe that a valid model for such a track is a cylindrical core, but there are serious problems. The large initial energy densities in such tracks introduce phenomena into the picture which we have neglected and which may have important effects. On very general grounds we know that high temperatures and high pressures are created and that a weak shock wave is formed. Following the shock wave, the temperature is still high, further expansion occurs, and the possibility exists that a bubble is formed around the track core. Such a bubble cannot be very large, but its effects are

entirely unknown and further investigation is clearly needed. Perhaps a more important effect is the variation of the yields of transient intermediates with energy density. It has been suggested that more radicals per unit energy are created in the higher energy densities, but no mechanisms have been proposed. In all model calculations (such as those of the companion paper[30]) it is assumed that the initial yields of intermediates is constant, independent of energy density.

The radiation chemical yields discussed here are in all cases final yields and the time dependences of the transient intermediates, although explicitly a part of any model, have not been given. Numerous investigations of the time dependence of the products (such as hydrated electrons) formed in electron pulses have been made.[5] Similar results are not generally available for heavy particle irradiations, but eventually they will be. A limited study of the time dependence of hydrated electron in pulses of H and He has been made by Naleway et al.[18] We expect to extend this study at a future time to include the time dependence of intermediates in the general heavy particle track.

References and Notes

1. A. Chatterjee and J. L. Magee, Sixth Symposium on Microdosimetry, J. Booz and H. G. Ebert, Eds., Vol. I, 1978, p. 283.

2. J. L. Magee and A. Chatterjee, Proceedings of Sixth International Congress of Radiation Research, S. Okada, M. Imamura, T. Terashima, and H. Yamaguchi, Eds., 1979, p. 166.

3. J. L. Magee and A. Mozumder, Int. J. Radiat. Phys. and Chem. 7, 83 (1975).

4. T. Sawai and W. H. Hamill, J. Phys. Chem. 74, 3914 (1970); J. Chem. Phys. 52, 3843 (1970); H. Ogura and W. H. Hamill, J. Phys. Chem. 77, (1973).

5. J. W. Hunt in "Advances in Radiation Chemistry," M. Burton and J. L. Magee, Eds., Wiley-Interscience, 1976, p. 185.

6. A. H. Samuel and J. L. Magee, J. Chem. Phys., 21, 1080 (1953).

7. A. K. Ganguly and J. L. Magee, J. Chem. Phys., 25, 129 (1956).

8. H. A. Schwarz, J. Am. Chem. Soc., 77, 4960 (1955).

9. P. J. Dyne and J. M. Kennedy, Can. J. Chem., 36, 1518 (1958).

10. A. Kuppermann and G. G. Belford, J. Chem. Phys., 1412, 1427 (1962).

11. A. Kuppermann (a) in "Actions Chim. Biol. Radiat.," M. Haissinsky, Ed., Masson and Cie, Vol. 5, 1961, p. 85; (b) in "Radiation Research," G. Silini, Ed., North Holland Publishing Co., Amsterdam, 1967, p. 212.

12. A. Mozumder and J. L. Magee, Radiat. Res., 20, 203 (1966).

13. A. Mozumder and J. L. Magee, Radiat. Res., 20, 215 (1966).

14. P. J. R. Burch, Radiat. Res., 11, 481 (1959).

15. J. Santor and J. Bednar, Adv. Chem. Ser., No. 81, 523 (1968).

16. W. G. Burns in "Charged Particle Tracks in Solids and Liquids," G. E. Adams, D. K. Bewley, and J. W. boag, Eds., The Institute of Physics and the Physical Society, London, 1970, p. 143.

17. H. A. Schwarz, J. Phys. Chem., 73, 1928 (1969).

18. C. A. Naleway, M. C. Sauer, C. D. Jonah and K. H. Schmidt, Radiat. Res. 77, 47 (1979).

19. J. L. Magee and A. Chatterjee, J. Phys. Chem., 82, 2219 (1978).

20. A. Chatterjee and C. A. Tobias, Environ. Radiat. Biophys. and Chem., in press.

21. A More sophisticated treatment of this problem has been presented by A. Mozumder, J. Chem. Phys., 60, 1145 (1974).

22. The plasma frequency, strictly speaking, applies to an electron gas. It is $\omega_p = (4\pi ne^2/m)^{1/2}$, where n is the number density of electrons, e the charge on the electron, and m the electron mass. In his introduction of the adiabatic criterion, Bohr used the lowest transition frequency.

23. L. C. Northcliffe and R. F. Schilling, Nucl. Data, A7, 233 (1970).

24. "The Stopping Power and Ranges of Ions in Matter." Organized by J. F. Ziegler, Pergamon Press, 1977. (a) Vol. 3., "Hydrogen Stopping Powers and Ranges in All Elements," by H. H. Anderson and J. F. Ziegler; (b) Vol. 4, "Helium Stopping Powers and Ranges in All Elements," by J. F. Ziegler.

25. These particles were selected to cover the entire heavy particle spectrum; H, D and He have been widely used for many years; C, Ne and Ar are the principal particles accelerated in the BEVALAC; Fm has atomic number 100 and is representative of the very heavy particles.

26. The authors thank Professor Blann for this personal communication.

27. T. E. Pierce and Marshall Blann, Phys. Rev., 173, 390 (1968).

28. Equation 5 differs from the equation given in the abstract of ref 27 in that a correction for the effective proton charge is omitted.

29. J. L. Magee, J. Am. Chem. Soc., 73, 3270 (1951).

30. A. Chatterjee and J. L. Magee, this Journal, following paper.

31. These r_1 values were calculated using eqs. 4 and 7, with 34 eV required to form a radical pair and with $k_s c_s = 3x10^6$ and $2k = 2x10^{10}$.

32. A more sophisticated discussion of the general particle track and the prescribed diffusion approximation is given by L. Monchick, J. L. Magee and A. H. Samuel, J. Chem. Phys. 26, 935 (1957).

33. J. L. Magee and A. Chatterjee, Radiat. Phys. and Chem, 15, 125 (1980).

Table I. Track Parameters Independent of Particle Charge

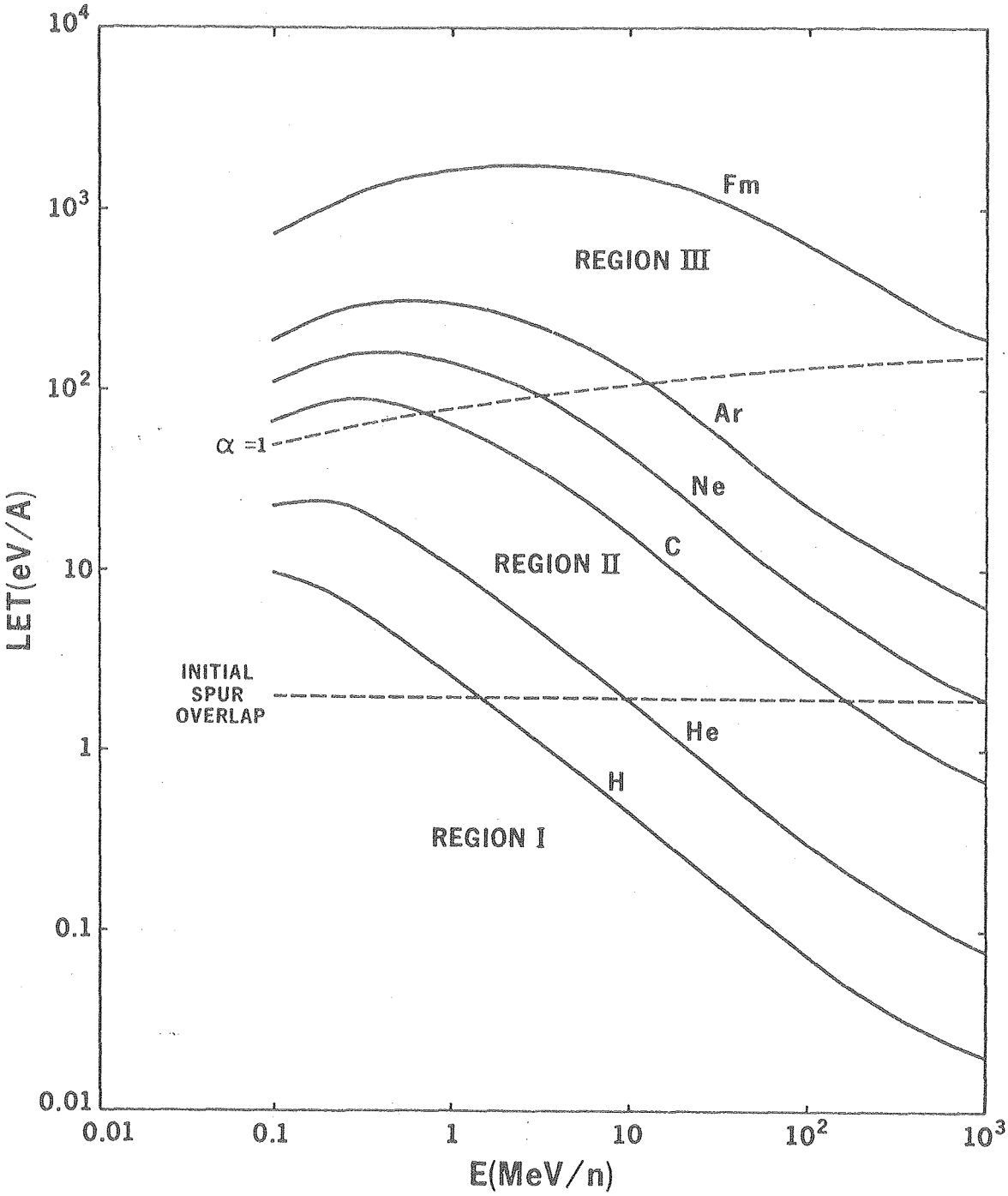
Energy(MeV/n)	β	r_c Core Radius(A)	r_p Penumbra Radius(A)	ε_{max}(eV)	λ
1000	0.876	90.16	2.7×10^6	3.4×10^6	23.42
800	0.843	86.75	2.4×10^6	2.5×10^6	22.46
600	0.794	81.69	2.1×10^6	1.7×10^6	22.31
400	0.715	73.54	1.6×10^6	1.1×10^6	21.98
200	0.568	58.43	8.4×10^5	4.9×10^5	21.15
100	0.430	44.21	3.9×10^5	2.3×10^5	20.17
80	0.390	40.12	3.0×10^5	1.8×10^5	19.84
60	0.343	35.26	2.1×10^5	1.4×10^5	19.38
40	0.284	29.23	1.3×10^5	0.9×10^5	18.80
20	0.204	20.99	5.3×10^4	4.4×10^4	17.67
10	0.145	14.96	2.1×10^4	2.2×10^4	16.49
8	0.130	13.40	1.6×10^4	1.8×10^4	16.17
6	0.113	11.63	1.1×10^4	1.3×10^4	15.70
4	0.092	9.51	6.2×10^3	8.8×10^3	14.96
2	0.065	6.73	2.4×10^3	4.4×10^3	13.75
1	0.046	4.77	9.6×10^2	2.2×10^3	12.61
0.8	0.041	4.26	7.1×10^2	1.8×10^3	12.23
0.6	0.036	3.69	4.8×10^2	1.3×10^3	11.74
0.4	0.029	3.02	2.8×10^2	8.8×10^2	11.06
0.2	0.021	2.13	1.1×10^2	4.4×10^2	9.89
0.1	0.015	1.51	4.3×10^1	2.2×10^2	8.70

Table II. Root Mean Square Charge States

E(MeV/N)	Fermium	Argon	Neon	Carbon	Helium	Hydrogen
1000	99.50	18.00	10.00	6.00	2.00	1.00
800	99.39	18.00	10.00	6.00	2.00	1.00
600	99.17	18.00	10.00	6.00	2.00	1.00
400	98.67	18.00	10.00	6.00	2.00	1.00
200	96.76	18.00	10.00	6.00	2.00	1.00
100	92.54	17.99	10.00	6.00	2.00	1.00
80	90.51	17.99	10.00	6.00	2.00	1.00
60	87.38	17.97	10.00	6.00	2.00	1.00
40	82.02	17.92	10.00	6.00	2.00	1.00
20	70.84	17.62	9.97	6.00	2.00	1.00
10	58.45	16.86	9.83	5.98	2.00	1.00
8	54.47	16.47	9.74	5.96	2.00	1.00
6	49.47	15.88	9.58	5.93	2.00	1.00
4	42.78	14.87	9.25	5.84	2.00	1.00
2	32.65	12.79	8.40	5.55	1.99	1.00
1	24.40	10.52	7.27	5.03	1.96	1.00
0.8	22.14	9.79	6.87	4.83	1.93	1.00
0.6	19.49	8.88	6.34	4.54	1.89	0.99
0.4	16.22	7.67	5.60	4.11	1.82	0.98
0.2	11.77	5.85	4.41	3.35	1.63	0.93
0.1	8.47	4.36	3.37	2.63	1.40	0.85

Figure Legends

1. The stopping power (in eV/A) of six selected particles in H_2O vs specific energy (in MeV per nucleon). See text for definition of low-, medium- and high-LET regions (Regions I, II and III, respectively). Data are from Ziegler.[24]
2. The stopping power (in eV/A) of H and He in H_2O vs specific energy (in MeV/n). Data are from Ziegler.[24]
3. Chemical core radii $r_1(E)$ (in A) for the six selected particles vs specific energy E(in MeV/n). At low energies, all values of $r_1(E)$ are equal to the penumbra radius, r_p; at high energies, all values of $r_1(E)$ become equal to the physical core radius, r_c. Of course, r_c and r_p are common for all particles.
4. The fraction of track energy contained initially within the chemical core radius $r_1(E)$ for the six particles vs the specific energy E.



XBL 7911-12802

Fig. 1

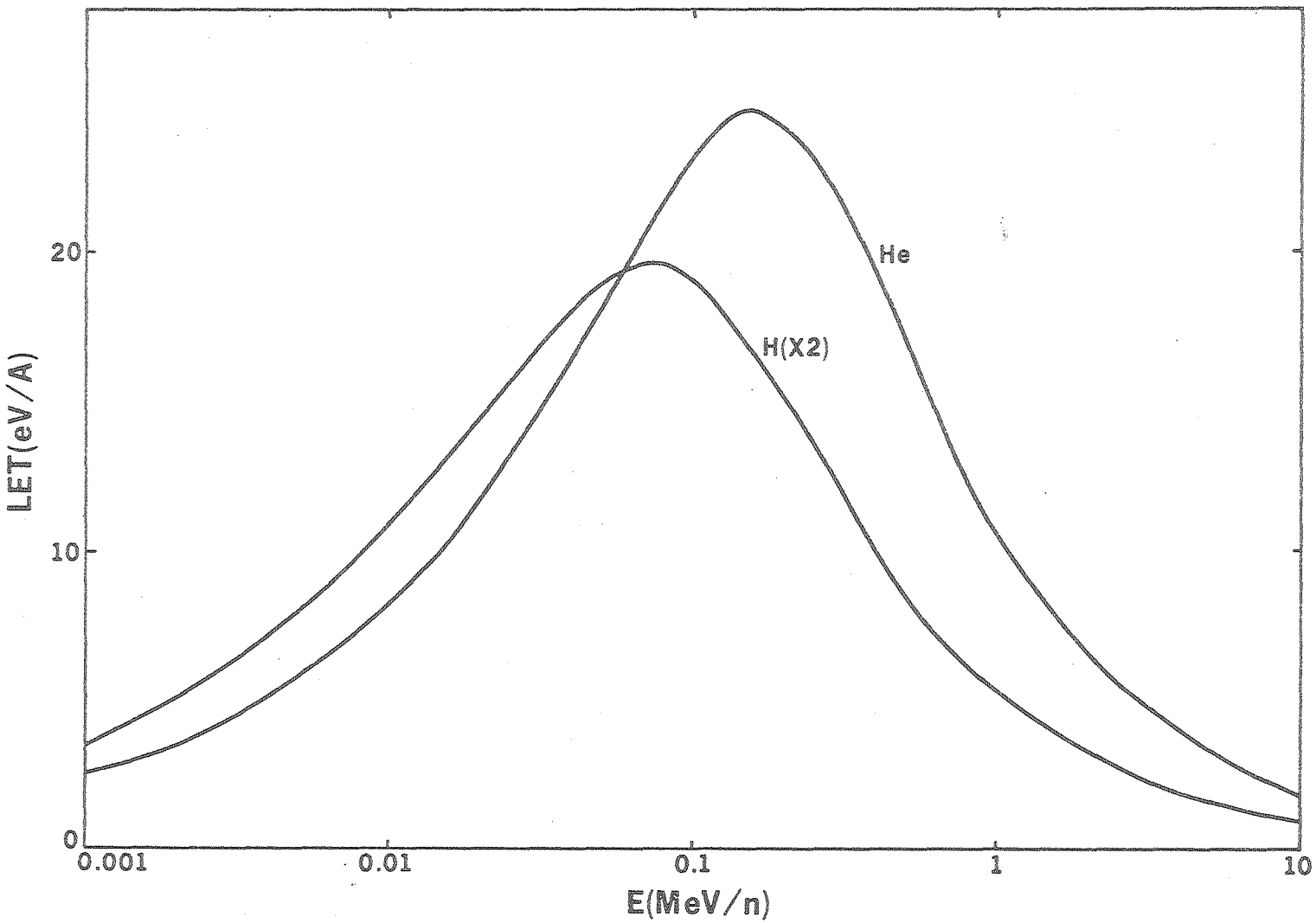


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Fig. 2

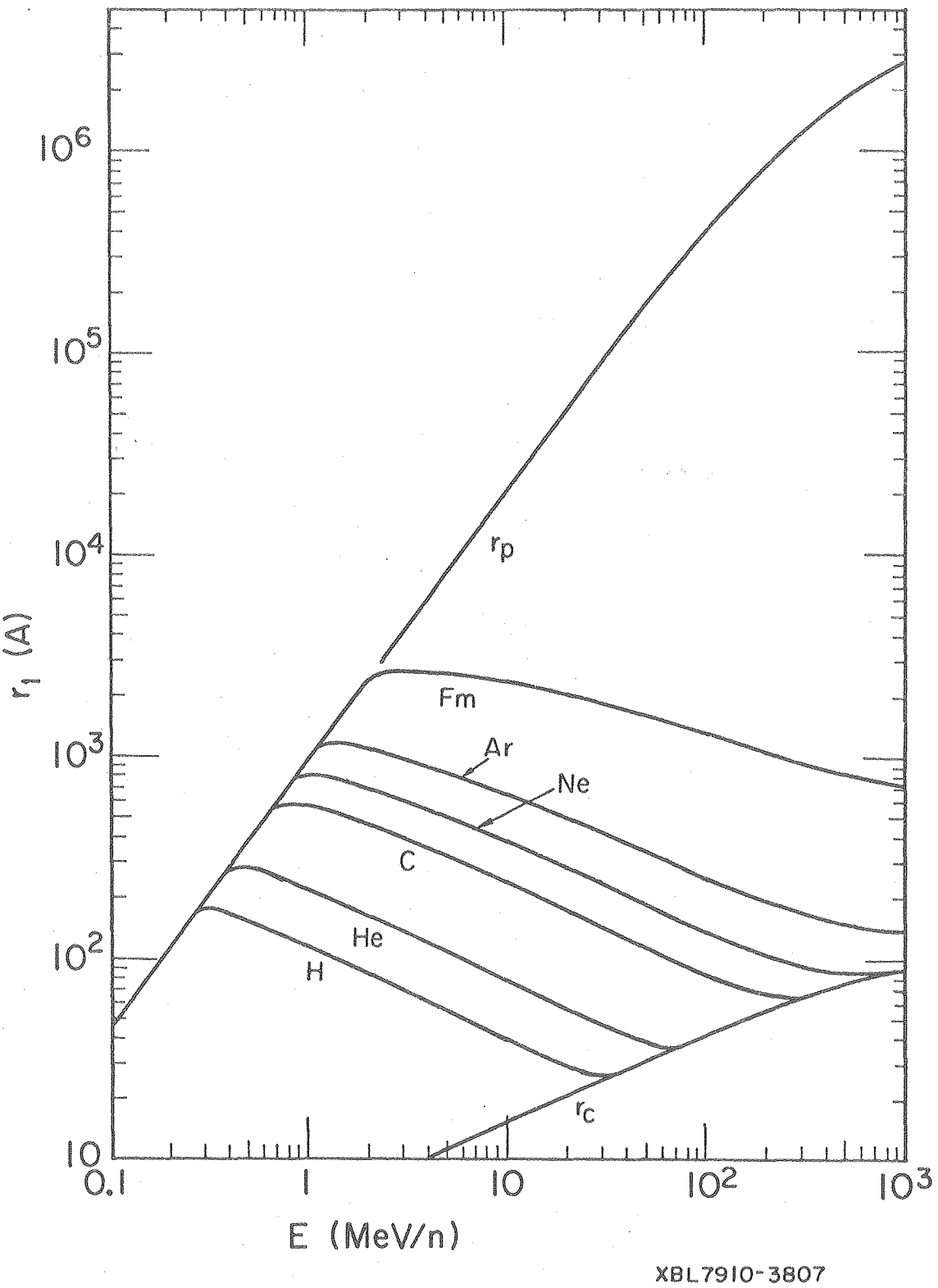
10^6
10^5
10^4
10^3
10^2
10
r_1 (Å)
r_p
Fm
Ar
Ne
C
He
H
r_c
0.1
1
10
10^2
10^3
E (MeV/n)
XBL7910-3807

Fig. 3

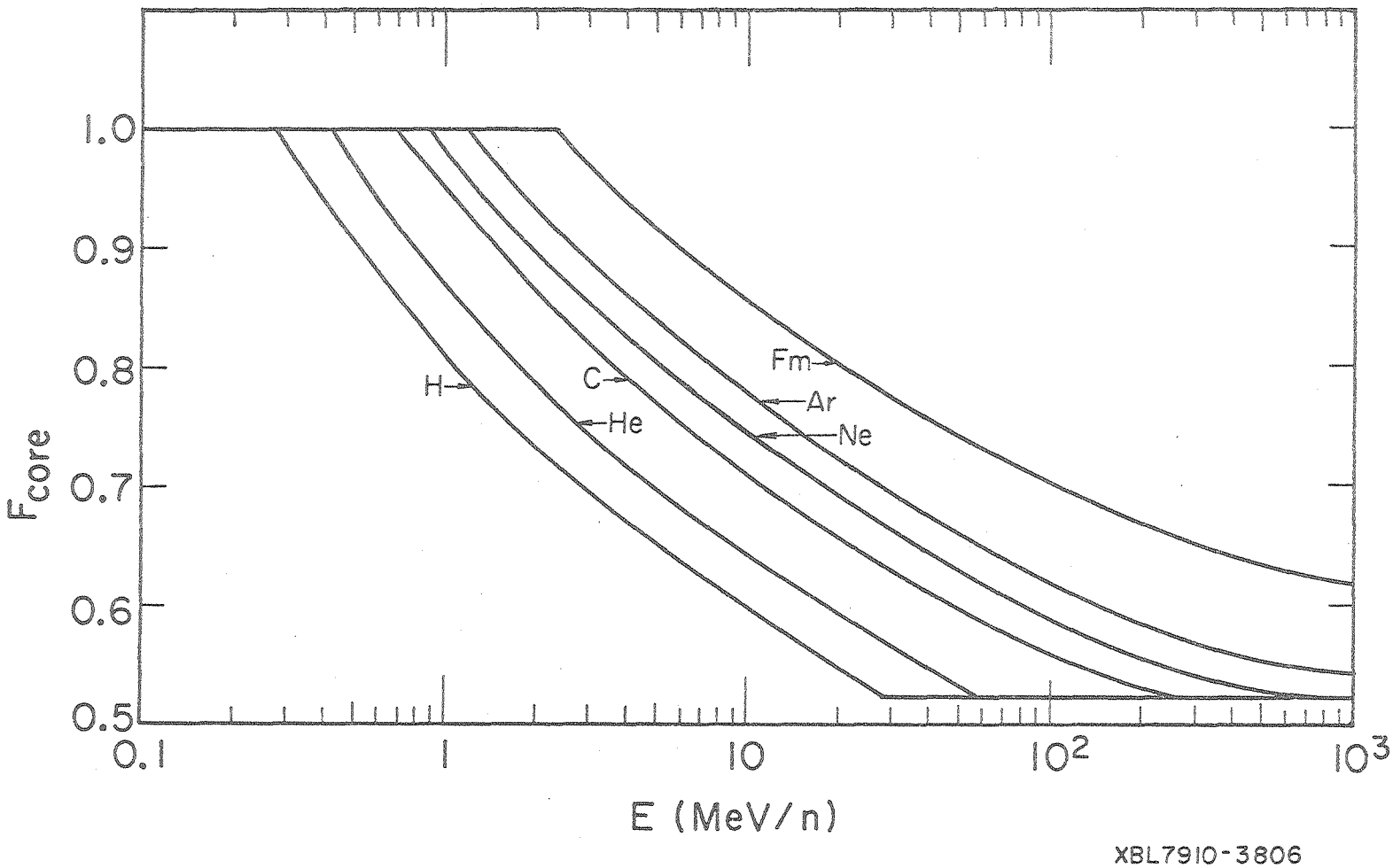
1.0
0.9
0.8
0.7
0.6
0.5
F_{core}
0.1
1
10
10^2
10^3
E (MeV/n)
H
He
C
Ne
Ar
Fm
XBL7910-3806

Fig. 4