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By

Mitio Inokuti, D. A. Douthat & A. R. P. Rau

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# Degradation Spectra and Ionization Yields of Electrons in Gases<sup>\*</sup>

Mitio Inokuti

Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.

D. A. Douthat

Kennedy-King College, Chicago, Illinois 60621, U.S.A.

and

A.R.P. Rau

Department of Physics and Astronomy

Louisiana State University, Baton Rouge, Louisiana 70802, U.S.A

## Abstract

MASTER

Notable progress in the microscopic theory of electron degradation in gases recently made by Platzman, Fano, and co-workers is outlined. The theory consists of two principal components: First, the comprehensive cataloging of all major inelastic-collision cross sections for electrons (including secondary-electron energy distribution in a single ionizing collision), and second, the evaluation of cumulative consequences of individual electron collisions for the electrons themselves, as well as for target molecules (the so-called bookkeeping problem). Although current atomic physics offers a considerable volume of pertinent cross-section data, one must assess the data consistency and reliability through every possible means of critical analysis, and then to extrapolate the data to the ranges of variables (such as electron energy) left unexplored by individual measurements. It is precisely to this end that a series of plots devised by Platzman turns out to be especially powerful. By the use of realistic cross-section data thus established, the electron degradation spectra have been obtained through numerical solution of the Spencer-Fano equation for all electron energies down to the first ionization thresholds for a few concrete examples such as He and Ne. Remarkable systematics of the solutions thus obtained not only have led to the recognition of approximate scaling properties of the degradation spectra

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for different initial electron energies, but also point to new methods of more efficient treatment. At the same time, certain systematics of the ionization yields and their energy dependence on the initial electron energy have been recognized. Finally, we shall point out a close relation between the Spencer-Fano equation for the degradation spectra and the Fowler equation for the ionization and other yields; the two equations are tightly linked with each other by a set of variational principles.

## 1. Introduction

The purpose of this speech is to introduce to the microdosimetrist some developments recently accomplished by Platzman, Fano, and co-workers in the analysis of initial events in the action of ionizing radiations.<sup>\*</sup> These developments are primarily concerned with the distribution of initial events in energy transfer to molecules, and therefore only implicitly with their spatial distribution, i.e., the theme of microdosimetry. The reason for the emphasis on energy transfer is two-fold. First, the motivation for those developments is to characterize in detail the kinds and yields of chemical species (ions, excited states, radicals, etc.) that lead to radiation chemistry. To carry out the most detailed and sound analysis, we choose the simplest possible situation, i.e., gases in which we can take full advantage of the current knowledge about elementary processes provided by atomic physics. Second, the elucidation of the pure energy-transfer distribution is an essential prerequisite for the understanding of the combined spatial and energy-transfer distribution. In other words, one has no real hope of solving a complicated problem until one knows how to deal with a simpler problem that is a part of that complicated problem.

For definiteness, we shall discuss the basic case in which an electron of a fixed initial energy  $T$  enters a chemically pure gas of low density and completely stops within it. A typical problem is to calculate the number  $N_1(T)$  of ion pairs generated. The result may be expressed in terms of the average energy per ion pair

$$W(T) = T/N_1(T) , \quad (1)$$

or in terms of the so-called differential  $W$  value

$$\omega(T) = [dN_1(T)/dT]^{-1} . \quad (2)$$

The energy dependence of  $W(T)$  or  $\omega(T)$  is an important subject in microdosimetric measurements. We can also discuss the number  $N_s(T)$  of any specified initial products  $s$  other than ion pairs, for example, certain excited states or radicals of interest to the radiation chemistry.

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\*Fano (F75a) has recently written another article on the subject for a more general audience.

## 2. Cross Sections for Individual Collisions

The initial step of the analysis is the comprehensive cataloging of electron-collision cross sections for a molecule. By the word "comprehensive" we mean all major cross sections that account for say 99% of the stopping power at all energies on the absolute scale. To the best of our ability we must determine cross sections for every important energy-transfer process, not just for a few particular processes. To this end we search through all possible data sources, both experimental and theoretical, in the current atomic physics. This task is by no means straightforward because directly available data are seldom comprehensive. One reason for this circumstance is that our interest is sharply different from the interest of purely basic physicists who are looking for novel phenomena specific to a particular process, a particular energy, or a particular molecule. Actually, the need for the comprehensive determination of cross sections is not at all limited to radiation physics, but is common to most of the modelling studies of macroscopic phenomena, e.g., in plasma physics, chemical aeronomy, and laser development. An obvious facet of our approach is the inquiry into the possibility of competition among different processes. Every time someone brought up a new interesting process, Platzman used to ask, "Does that process effectively compete with all other possible processes?" This attitude is crucial to a successful solution of our problem.

Let us enumerate the kinds of cross sections we need to find. First of all, an electron of kinetic energy  $T$  may excite every discrete level  $n$  whose excitation energy  $E_n$  is smaller than  $T$ . The cross section for discrete excitation may be written as  $\sigma_n(T)$ . The label  $n$  is primarily an index of different electronic excitations (which are usually accompanied by some vibrational and rotational excitations). Purely vibrational and rotational excitations, as well as elastic collisions, contribute negligibly to the stopping power, except in the subexcitation range, (i.e., when  $T$  is lower than the first electronic excitation threshold), and are therefore irrelevant to the ionization yield.

Next, an electron with  $T > I$  may ionize the molecule whose (first) ionization threshold is  $I$ . The ionization may result from various values of

energy transfer  $E$  from the electron to the molecule. Suppose for simplicity that the molecule has the single ionization threshold  $I$  and always ionizes when  $E > I$ . Then the ionization will lead to a primary electron with energy  $T - E$  and a secondary electron with energy  $E - I$ . We may write the cross section for ionization with energy transfer between  $E$  and  $E + dE$  as  $[d\sigma_i(T, E)/dE]dE$ . The function is called the differential ionization cross section or the secondary-electron energy distribution. The total ionization cross section  $\sigma_i(T)$  is given by the integral

$$\sigma_i(T) = \int_I^{\frac{1}{2}(T+I)} \frac{d\sigma_i(T, E)}{dE} dE, \quad (3)$$

where the upper limit implies the customary convention that one calls the more energetic of the two electrons the primary and the less energetic the secondary. [In general, a molecule has many ionization thresholds corresponding to different ionic states, including multiply ionized states, and may not always ionize when  $E > I$  (P60, P61). Explicit enumeration of these complications is cumbersome but straightforward.]

The entirety of  $\sigma_n(T)$  and  $d\sigma_i(T, E)/dE$  for all  $n$ ,  $E$ , and  $T$  is sufficient for input to the pure energy-degradation problem. For treatment of spatial aspects, in contrast, we need much more detailed input data, i.e., angular distributions of secondary electrons, as well as of elastically and inelastically scattered electrons. Comprehensive cataloguing of these detailed data will require many variables and must depend upon far more fragmentary knowledge. This point already exemplifies the great challenge of theoretical microdosimetry.

For the pure degradation problem, the total inelastic-collision cross section

$$\sigma_{\text{tot}}(T) = \sigma_i(T) + \sum_n \sigma_n(T), \quad (4)$$

and the stopping cross section

$$\sigma_{\text{st}}(T) = \int_I^{\frac{1}{2}(T+I)} E \frac{d\sigma_i(T, E)}{dE} dE + \sum_n E_n \sigma_n(T) \quad (5)$$

are most important. Consideration of stochastic fluctuations requires also

also a sum with  $E^2$  and  $E_n^2$  in place of  $E$  and  $E_n$  in Eq. (5).

How do we determine the cross sections for a given molecule? Inspection of the literature readily shows that directly available data are limited in scope and reliability; absolute cross sections are in general hard to come by, both experimentally and theoretically, although the progress of research in this area in the last two decades is quite notable.

After much thought, Platzman devised an ingenious strategy (P67). His idea started with the recognition that electron collision cross sections are closely related among themselves, as well as to other properties, and are subject to a number of general constraints. This recognition points to many methods of testing the data reliability, and of extrapolating and interpolating data dependably. These methods rest on sound principles dictated by theory and use suitably chosen graphical plots of data. We shall illustrate the methods by quoting a few examples; exhaustive exposition is impossible in a limited time period, especially because the methods devolve upon many topics of atomic collision theory.

One general constraint on the cross sections is their asymptotic behavior that prevails at high  $T$ . For example,  $\sigma_n(T)$  should behave as

$$\sigma_n(T) = A_n T^{-1} \ln T + B_n/T + C_n/T^2 + \dots, \quad (6)$$

where  $A_n$ ,  $B_n$ , and  $C_n$  are constant, according to the Bethe theory (B30,I71). In particular,  $A_n$  is equal to  $f_n/E_n$ , apart from a universal constant, where  $f_n$  is the optical oscillator strength for the transition to state  $n$ , and therefore is closely related to the photoabsorption spectrum. This connection arises because at high  $T$  glancing collisions predominate, and their influence upon the molecule is similar to that of light having a wide spectral distribution. The parameters  $B_n$  and  $C_n$  are more complicated in nature and depend upon hard collisions as well. For  $T > 10^4$  eV, Eq. (6) requires elementary modifications because of relativity effects, but  $\sigma_n(T)$  remains to be characterized by the same parameters,  $A_n$ ,  $B_n$ , and  $C_n$ . Equation (6) suggests that a plot of  $T\sigma_n(T)$  as a function of  $\ln T$  should approach straight-line behavior, as exemplified in Fig. 1. Such a plot is called the Fano plot (I71) after the original inventor (F54). The Fano plot is also useful for non-

asymptotic regions because  $T\sigma_n(T)$  approaches zero at the threshold  $T = E_n$  usually smoothly and monotonically so that one can interpolate the data much more easily and dependably than in a direct plot of  $\sigma_n(T)$  versus  $T$ . The asymptotic  $T$ -dependence of  $\sigma_i(T)$  and  $d\sigma_i(T, E)/dE$  at fixed  $E$  is also given by the same analytic form as Eq. (6), and therefore the Fano plot is useful for these cross sections (K75b).

Another important plot concerns the  $E$ -dependence of  $d\sigma_i(T, E)/dE$  at fixed  $T$ . Platzman pointed out that it is suitable to plot  $TE^2 d\sigma_i(T, E)/dE$  as a function of  $1/E$ , as exemplified in Fig. 2. The factor  $TE^2$  is in essence the reciprocal of the Rutherford cross section, and therefore  $TE^2 d\sigma_i(T, E)/dE$  represents the ratio of the differential ionization cross section to the Rutherford cross section which should apply for  $E \gg I$ , i.e., for collisions in which the electron binding is insignificant. Consequently, as  $E$  becomes large, the ratio should approach a value fixed by the number of molecular electrons effectively available for ionization, usually the number of outer-shell electrons. The Platzman plot is also related to the photoionization cross section, or equivalently, the oscillator-strength distribution  $df/dE$  for ionization. More specifically, the  $E$ -dependence of  $TE^2 d\sigma_i(T, E)/dE$  should resemble that of  $E df/dE$  for  $E \approx I$  and  $E \ll T$ , again owing to the dominance of glancing collisions. Finally, the choice of  $1/E$  as the abscissa makes the area under the curve equal to  $T\sigma_i(T)$  apart from a universal constant, and thus allows one to test quickly the consistency of  $d\sigma_i(T, E)/dE$  with usually better known  $\sigma_i(T)$ . The Platzman plot represents  $d\sigma_i(T, E)/dE$  data most concisely, and enables one to extrapolate and interpolate the data over  $E$ , as well as over  $T$ . Notice that the naive plot of  $d\sigma_i(T, E)/dE$  versus  $E$  usually requires use of the logarithmic scale on both the abscissa and the ordinate, and virtually defies any convincing extrapolation and interpolation. All these merits of the Platzman plot have been amply demonstrated by a series of work by Kim, who systematically and critically examined most of the recent experimental data on secondary-electron energy distributions (K72, K75a, b, c, KN75).

Other controls of data derive from sum rules (P67). For example, the optical oscillator-strength distribution, defined as a complete set of



$(E_n, f_n)$  for all  $n$  and  $df/dE$  for all  $E > I$ , obeys a number of theorems that relate the moments

$$S(\mu) = \int_I^{\infty} E^\mu (df/dE) dE + \sum_n E_n^\mu f_n \quad (7)$$

for different integers with various molecular properties. The best known of these theorems is the Thomas-Kuhn-Reiche sum rule:  $S(0)$  = the total number of molecular electrons. The electron collision cross sections also satisfy certain sum rules; the Bethe procedure of evaluating  $\sigma_{st}(T)$  of Eq. (5) at high  $T$  is an example. Likewise,  $\sigma_{tot}(T)$  of Eq. (4) can be evaluated reliably from certain molecular properties (IKP67, ISD75).

Another kind of consistency testing may be exemplified by a relation between  $\sigma_n(T)$  and  $d\sigma_i(T, E)/dE$  at the same  $T$ . In a class of discrete excited states (called Rydberg states), a single electron moves in a large orbit only slightly bound to the ion core. For very high states of this kind, the excited electron is hardly distinguishable from an electron ejected upon ionization with extremely low kinetic energy. This circumstance can be expressed rigorously by the quantum-defect theory (S70, F75b). In the simplest case where we consider a Rydberg series specified by a set of quantum numbers (such as angular momenta) and continuum states specified by the same set, we have the relation

$$(27.21 \text{ eV})^{-1} \lim_{n \rightarrow \infty} (n^*)^3 \sigma_n(T) = \lim_{E \rightarrow I} d\sigma_i(T, E)/dE, \quad (8)$$

where  $n^* = n - \delta$ ,  $n$  is the principal quantum number, and  $\delta$  is a constant called the quantum defect. An example of the use of this relation is seen in KI73.

As for the region of very low  $T$ , say within a few multiples of  $I$ , Platzman stressed the need for careful critique of measurements. For this purpose and others, he cultivated encyclopaedic knowledge of chemical physics and maintained close contacts with many workers over the whole world, often suggesting new and decisive experiments (F75a).

Examples of the comprehensive analysis of the cross-section data concern He (M56),  $H_2$  (G 75), Ne (S 75), and Ar (E 75).

### 3. Bookkeeping Problems

Once a complete set of cross sections for single collisions is established, we face the problem of evaluating cumulative consequences of many collisions. It is easy to get an idea of the number of electron collisions involved. Suppose that a 10-keV electron comes into a gas with  $W = 30$  eV, then the number of ion pairs is  $N_i = 333$ , which is also the number of ionizing collisions. The primary electron and all secondary electrons must undergo other inelastic collisions that excite discrete states, and the number of these collisions should be comparable to  $N_i$ . Consequently, the total number of inelastic collisions involved in the degradation down to  $T \approx 1$  is several hundred.

The most straightforward method of bookkeeping is the Monte-Carlo methods, which should be familiar to the audience from some papers (P 74, TP 74, and B74) at the preceding symposium. Indeed, Monte-Carlo calculations appear to be best at present for treating in detail the combined energy and spatial distributions of initial events.

But the pure degradation problem can be treated by analytical methods, which we may call methods of transport equations.

#### 3.1. The Fowler Equation

The most elementary approach uses an equation due to Fowler (F23) for  $N_i(T)$ . In the simplest case where a molecule has a single ionization threshold  $I$  and it invariably ionizes upon any energy transfer  $E > I$ , the Fowler equation takes the form\*

$$\sigma_{\text{tot}}(T) N_i(T) = \sigma_i(T) + \sum_n \sigma_n(T) N_i(T - E_n) + \int_I^{\frac{1}{2}(T+I)} dE \frac{d\sigma_i(T, E)}{dE} [N_i(T - E) + N_i(E - I)] . \quad (9)$$

The right-hand side divided by  $\sigma_{\text{tot}}(T)$  enumerates different contributions to  $N_i(T)$  classified according to the kind of first inelastic collision that an electron of energy  $T$  makes. When that collision leads to discrete excitation  $n$ , the scattered electron will have energy  $T - E_n$ . The number of ion pairs formed subsequently by that scattered electron and all its secondaries

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\*Consideration of many ionization thresholds, multiple ionization, and pre-ionization from superexcited states (P60, P62) leads to a generalized Fowler equation (I75).

is  $\sigma_n(T) N_1(T - E_n) / \sigma_{\text{tot}}(T)$ . The sum of this contribution over  $n$  corresponds to the second term in Eq. (9). When the first inelastic collision is ionizing,  $N_1(T)$  must increase by  $\sigma_i(T) / \sigma_{\text{tot}}(T)$ ; this contribution corresponds to the first term in Eq. (9). At the same time, that ionizing collision leads to an electron with energy  $T - E$  and another electron with energy  $E - I$ . The total contribution of these two electrons and their subsequent secondaries to  $N_1(T)$  is represented by the integral term of Eq. (9). Provided all the cross sections are specified, we can solve Eq. (9) by starting with the condition  $N_1(T) = 0$  for  $T < I$  and by ascending in  $T$ .

Figures 3 and 4 show results of such calculations. We shall make several remarks on the properties of the solution of the Fowler equation.

First of all, results of numerical solutions in several examples (KEON 53, E54, M56, HM57, DG58, A71, J73, G75, E75) show an approximate behavior

$$N_1(T) \cong (T - U) / W_a \quad (10)$$

for  $T \gg I$ , where  $U$  and  $W_a$  are constants having the energy dimension. Inokuti (I75) attempted an interpretation of this observation. Equation (10) implies that, according to Eqs. (1) and (2),

$$W(T) \cong W_a / (1 - U/T) \quad (11)$$

and

$$\omega(T) \cong W_a \quad (12)$$

for  $T \gg I$ . Comparison of Eqs. (11) and (12) with measurements (G35, C69, S73, WB75, SH75) leads to no clear-cut conclusion at present. On one hand, measurements on air by Gerbes (G35) and by Cole (C69), as well as those on methane and the Rossi-Failla tissue-equivalent gas by Waker and Booz (WB74) show energy dependence of  $W(T)$  around  $T = 1$  keV, considerably stronger than that described by Eqs. (11) or (12). On the other hand, measurements on propane by Srdoč (S73) and on xenon by Samson and Haddad (SH75) show energy dependence consistent with Eqs. (11) or (12) down to lower  $T$ .

Tantalizingly, none of the gases experimentally studied have been theoretically treated in detail. Therefore, conclusive comparison of theory with experiment must await further development. Because good theoretical results are available for helium (M56, A71), molecular hydrogen (G75), neon (S75), and argon (E75), we recommend measurements on these gases.

As for  $W(T)$  at lower  $T$ , we expect to see a generally non-monotonic behavior reflecting complicated structures in electron-collision cross sections. As an illustration, Fig. 4 shows a theoretical result for He (M56), i.e., the simplest of all permanent gases, especially because of the absence of inner shells. In general, inner-shell ionization should give rise to some structures in  $W(T)$  in the neighborhood of each inner-shell threshold energy. Theoretical results on Ne (S75) and experimental results on methane and the Rossi-Failla gas (WB75) provide some insight into this problem area so far little explored.

Next, let us briefly consider  $W(T)$  at high  $T$  for different molecules. As Platzman (P61) already pointed out, the ratio  $W/I$  is 1.7–1.8 for all rare gases and 2.1–2.5 for commonly available molecular gases, according to experiments. The limited ranges of  $W/I$  might lead one to hazard a naive conclusion, e.g., that  $W/I$  should be 1.7–1.8 for all atoms. Actually, the limited ranges of the data are attributable to a limited variety of target species so far accessible to experimental study. To illustrate this point, we may quote results of theoretical calculations for atomic vapors for  $Z \leq 18$ , as shown in Fig. 5 (IDS75). Clearly, rare gases have minimal  $W/I$  values because of tight electronic structure. In contrast, alkalis and alkaline earths have large  $W/I$  values ranging over 2.0–3.2 because of loose electronic structure.

### 3.2. The Fano Factor

Fowler-type bookkeeping is also capable of treating statistical fluctuations of the number of ion pairs, a topic of great interest to the microdosimetrist. For the most detailed treatment, one sets up an equation satisfied by the probability  $P(T, n)$  that the incidence of an electron with energy  $T$  results in precisely  $n$  ion pairs in the gas under consideration. The equation for  $P(T, n)$  is a nonlinear integral equation discussed in KEON53 and LNST63. The connection of this equation with the Fowler equation is readily established; the average number  $N_i(T)$  of ion pairs is simply given as

$$N_i(T) = \sum_{n=0}^{\infty} n P(T, n) . \quad (13)$$

An important index of the statistical fluctuations of  $n$  is given by the mean square average

$$N_1^{(2)}(T) = \sum_{n=0}^{\infty} n^2 P(T, n) . \quad (14)$$

The function  $N_1^{(2)}(T)$  obeys a linear integral equation (KEON53) similar to the Fowler equation for  $N_1(T)$ . Further, it can be shown that the mean square deviation

$$(\Delta N)^2 \equiv [N_1(T)]^2 - N_1^{(2)}(T) \quad (15)$$

is proportional to  $N_1(T)$ , i.e.,

$$(\Delta N)^2 = F(T) N_1(T) \quad (16)$$

where  $F(T)$  is a function known as the Fano factor (F47). The Fano factor has been evaluated only for a few gases (F47, A71).

### 3.3. The Spencer-Fano Equation

Let us now turn to a different method of bookkeeping originally due to Spencer and Fano (SF54). In the Spencer-Fano theory, one looks at the energy distribution of all electrons, including primaries, secondaries, tertiaries, and so on, present in the gas. This distribution is most conveniently expressed in terms of the total pathlength  $y(T)dT$  of all the electrons having energies between  $T$  and  $T + dT$ , when the gas is subjected to a stationary flux  $S(T)$  of incident electrons. The function is called the degradation spectrum. It obeys an integral equation, which takes the form

$$\begin{aligned} \sigma_{\text{tot}}(T)y(T) = & \sum_n \sigma_n(T + E_n) y(T + E_n) \\ & + \int_I^{\infty} dE \frac{d\sigma_1(T + E, E)}{dE} y(T + E) \\ & + \int_{2T+I}^{\infty} dT' \frac{d\sigma_1(T', T + I)}{d(T + I)} y(T') + S(T) . \end{aligned} \quad (17)$$

in the simplest case of molecules with a single ionization energy  $I$ . The left-hand side of Eq. (17) is the number of electrons leaving a unit energy

interval around  $T$ , and the right-hand side is the number of electrons entering that interval, in a medium of unit molecular density. On the right-hand side, the first term accounts for energy losses by discrete excitations, and the second term for energy losses by ionizing collisions. The third term represents the production of secondary electrons by ionizing collisions.

When we have a unit flux of electrons with a single energy  $T_0$  incident upon a medium of molecular number density  $N$ , then we set

$$S(T) = N^{-1} \delta(T - T_0), \quad (18)$$

and designate the solution as  $y(T_0, T)$ , specifically including  $T_0$  as the second variable.

To solve the Spencer-Fano equation, Eq. (17), one starts with the highest possible  $T$  and descends in  $T$ . With the source term  $S(T)$  given by Eq. (18), we have\*

$$y(T_0, T) \cong [N \sigma_{st}(T)]^{-1} \quad (19)$$

for  $T_0 > T > T_0/2 \gg I$ , i.e., in the interval where secondary electrons do not contribute to  $y(T_0, T)$  and each energy loss is much smaller than the current electron energy  $T$ . Equation (19) is commonly referred to as the continuous-slowing-down approximation. Numerical solution of the Spencer-Fano equation is not easy because of the strong dependence of  $d\sigma_1(T, E)/dE$  on  $E$ , especially at low  $E$ . For this reason, Spencer and Fano (SF54) had to devise ingenious mathematical tricks in order to study  $y(T_0, T)$  even for high  $T$  and  $T_0$ , say above 10 keV. More recently Douthat (D75a, b) has succeeded in solving Eq. (17) for all  $T$  down to  $I$  in helium, using realistic cross-section data (Fig. 6).

Once  $y(T_0, T)$  is obtained, the number  $N_1(T_0)$  of ion pairs is readily evaluated as an integral

$$N_1(T_0) = N \int_I^{T_0} \sigma_1(T) y(T_0, T) dT. \quad (20)$$

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\* An elementary deviation of Eq. (19) is to expand all quantities on the right-hand side of Eq. (17) in powers of energy losses and to keep only the lowest-order terms. The assumption of small energy losses is too restrictive, however; Fano (F53) derives Eq. (19) on more general grounds.

One merit of the Spencer-Fano method is that the integrand of Eq. (20) gives an instructive breakdown of  $N_i(T_0)$  according to  $T$ . In this context it is suitable to plot  $T \sigma_i(T) y(T_0, T)$  against  $\ln T$ ; then the area under the curve corresponds to  $N_i(T)$ . Another merit of the same method is that the number  $N_s(T_0)$  of any other initial species  $s$  can be likewise computed; we just have to replace  $\sigma_i(T)$  by the appropriate cross section  $\sigma_s(T)$  for  $s$  in Eq. (20) to obtain  $N_s(T)$ .

Douthat (75a) discovered an approximate scaling property of  $y(T_0, T)$ . When he plotted the product  $(T/T_0) \sigma_i(T) y(T_0, T) \ln(T_0/I)$  as a function of  $\ln(T/I)/\ln(T_0/I)$ , he obtained curves almost independent of  $T_0$ , as shown in Fig. 7. This observation explains the well-known empirical fact that  $W(T_0)$  is insensitive to  $T_0$  so long as  $T_0 \gg I$ .

Fano and Spencer (FS75) then gave a theoretical interpretation of the approximate scaling property. They first recast Eq. (20) by the use of Eq. (1) as

$$\frac{1}{W(T_0)} = \int_I^{T_0} \frac{dT}{T_0} y(T_0, T) N \sigma_{st}(T) \frac{1}{W_d(T)}, \quad (21)$$

where

$$\frac{1}{W_d(T)} = \frac{\sigma_i(T)}{\sigma_{st}(T)} \quad (22)$$

is the yield of ionization produced by an electron of energy  $T$  directly (i.e., rather than through its secondaries), per unit energy loss. Next, they introduce

$$\xi = \ln(T/I)/\ln(T_0/I) \quad (23)$$

as an independent variable, and

$$z(\xi) = [\ln(T_0/I)] (T/T_0) y(T_0, T) N \sigma_{st}(T) \quad (24)$$

as a dependent variable, both dimensionless. Then, Eq. (21) is transformed into a simple form

$$\frac{1}{W(T_0)} = \int_0^{\infty} d\xi z(\xi) \frac{1}{W_d(T)}. \quad (25)$$

The integrand of Eq. (25) depends only weakly upon  $T_0$ , in accordance with Douthat's observation. The function  $z(\xi)$  describes how much of the energy transferred in an ionizing collision to secondary electrons will be used once more by these secondary electrons for further ionization. In this sense, Fano and Spencer called  $\int_0^1 d\xi z(\xi)$  the recycling parameter, which ranges from 1.3-1.6 for  $T_0 = 2 - 100$  keV in helium. Furthermore, they transformed Eq. (17) into a new degradation equation which determines  $z(\xi)$  directly, and suggested a procedure of numerical solution. This method has now been used by Soong (S75), who treats electron degradation in neon specifically taking into account inner-shell phenomena such as Auger effects.

### 3.4. Variational Formulation

Finally, we shall point out a variational treatment that unifies the two major methods, i.e., the Fowler equation and the Spencer-Fano equation. Although variational methods in transport theory have been known for some time especially in the context of neutron transport in reactor physics (Po67, S74), we believe that our variational theory of electron degradation is new; indeed, what we present below is merely a sketch of our initial exploration.\*

Let us start with the Fowler equation, Eq. (9). We may write it in the form

$$\Omega_T N_i(T) = \sigma_i(T) , \quad (26)$$

where  $\Omega_T$  is an operator defined as

$$\begin{aligned} \Omega_T N_i(T) = & \sigma_{\text{tot}}(T) N_i(T) - \sum_n \sigma_n(T) N_i(T - E_n) \\ & - \int_1^{(T+1)/2} dE [d\sigma_i(T, E)/dE] [N_i(T - E) + N_i(E - 1)] . \end{aligned} \quad (27)$$

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\* Our approach follows the general method of constructing variational principles developed by Gerjuoy, Rau, and Spruch (GRS72,73).



Consider now an expression

$$V(T_0) \equiv N_{it}(T_0) - \int_I^{\infty} dT L_t(T_0, T) [\Omega_T N_{it}(T) - \sigma_1(T)] , \quad (28)$$

where  $N_{it}(T)$  is a trial, approximate, solution to Eq. (26), and  $L_t(T_0, T)$  is a trial function for a function  $L(T_0, T)$  to be specified later. If  $N_{it}(T)$  happens to be the exact solution of Eq. (26),  $V(T_0)$  obviously is the true value of  $N_1(T_0)$ . Suppose that

$$N_{it}(T) = N_1(T) + \delta N_1(T) , \quad (29)$$

and

$$L_t(T_0, T) = L(T_0, T) + \delta L(T_0, T) , \quad (30)$$

then

$$\begin{aligned} V(T_0) &= N_1(T_0) + \delta N_1(T_0) \\ &\quad - \int_I^{\infty} dT L_t(T_0, T) [\Omega_T N_1(T) - \sigma_1(T)] \\ &\quad - \int_I^{\infty} dT L(T_0, T) \Omega_T \delta N_1(T) \\ &\quad - \int_I^{\infty} dT \delta L(T_0, T) \Omega_T N_1(T) . \end{aligned} \quad (31)$$

The first integral on the right-hand side of this equation vanishes by definition, i.e., because of Eq. (26). We rewrite the second integral as

$$\int_I^{\infty} dT L(T_0, T) \Omega_T \delta N_1(T) = \int_I^{\infty} dT [\Omega_T^\dagger L(T_0, T)] \delta N_1(T) , \quad (32)$$

where we have introduced a new operator  $\Omega_T^\dagger$  acting on  $L(T_0, T)$ . (We shall later show an explicit form of  $\Omega_T^\dagger$ , which we call the adjoint of  $\Omega_T$ .) The third integral is small if  $L_t(T_0, T)$  and  $N_{it}(T_0)$  are close to the true solutions. We shall

write the third integral simply as  $O(\delta L \delta N)$ . Consequently, we have

$$V(T_0) = N_i(T_0) + \int_I^\infty dT [\delta(T - T_0) - \Omega_T^\dagger L(T_0, T)] \delta N_i(T) + O(\delta L \delta N) . \quad (33)$$

We are now led to choose  $L(T_0, T)$  [which we call the adjoint function  $N_i(T_0)$ ] as the solution of the equation

$$\Omega_T^\dagger L(T_0, T) = \delta(T - T_0) . \quad (34)$$

In other words, if  $L(T_0, T)$  is an approximate solution of Eq. (34), then  $V(T_0)$  given by Eq. (28) is a variational estimate of  $N_i(T_0)$ , better than the initial guess  $N_{it}(T_0)$ . In this sense, Eq. (28) is a variational principle for  $N_i(T_0)$ .

As for an explicit representation of the adjoint operator  $\Omega_T^\dagger$ , we can show through changes of variables and of integration orders that

$$\begin{aligned} \Omega_T^\dagger L(T_0, T) &= \sigma_{\text{tot}}(T) L(T_0, T) - \sum_n L(T_0, T + E_n) \sigma_n(T + E_n) \\ &\quad - \int_I^\infty dE \frac{d\sigma_i(T + E, E)}{dE} L(T_0, T + E) \\ &\quad - \int_{2T+I}^\infty dT' \frac{d\sigma_i(T', T + I)}{d(T + I)} L(T_0, T') . \end{aligned} \quad (35)$$

Comparison of Eq. (35) with Eq. (17) shows that Eq. (34) is nothing but the Spencer-Fano equation, and that we can identify  $L(T_0, T)$  with  $N_Y(T_0, T)$

If we multiply  $N_i(T)$  on both sides of Eq. (34), integrate over  $T$ , and use Eqs. (26) and (32), then we immediately obtain

$$\begin{aligned} N_i(T_0) &= \int_I^\infty dT N_i(T) \delta(T - T_0) \\ &= \int_I^\infty dT N_i(T) \Omega_T^\dagger L(T_0, T) \end{aligned}$$

$$\begin{aligned}
 &= \int_I^{\infty} dT [\Omega_T N_i(T)] L(T_0, T) \\
 &= \int_I^{\infty} dT \sigma_i(T) L(T_0, T) ,
 \end{aligned} \tag{36}$$

an expression equivalent to Eq. (20). Thus, we have established the equivalence of  $N_i(T_0)$  evaluated from the Fowler method and from the Spencer-Fano method (for the same set of cross-section data).

If we start the same procedure with the Fowler equation for the yield  $N_s(T_0)$  of any initial species (other than ions), then we still obtain the same and unique equation, Eq. (34), for  $L(T_0, T)$ . In other words, the Spencer-Fano degradation spectrum is the universal adjoint function of all  $N_s(T_0)$ .

It is also possible to begin with the Spencer-Fano equation, Eq. (34), and to look for a variational principle for  $L(T_0, T)$ . Then we consider an expression

$$\begin{aligned}
 V(T_0, T) &\equiv L_t(T_0, T) \\
 &- \int_I^{\infty} dT' [\Omega_{T'}^\dagger L(T_0, T') - \delta(T' - T)] M_t(T_0, T') ,
 \end{aligned} \tag{37}$$

where  $M_t(T_0, T)$  is a trial function for the adjoint of  $L(T_0, T)$ . Then we can show through the same procedure as before [i.e., the steps from Eq. (28) to Eq. (34)] that  $M(T_0, T)$  should satisfy

$$\Omega_T M(T_0, T) = \delta(T - T_0) . \tag{38}$$

If we replace  $T$  by  $T'$  in this equation, multiply  $L(T, T')$  on both sides, and integrate over  $T$ , then we obtain

$$\begin{aligned}
 L(T, T_0) &= \int_I^{\infty} dT' L(T, T') \delta(T' - T_0) \\
 &= \int_I^{\infty} dT' L(T, T') \Omega_{T'} M(T_0, T') \\
 &= \int_I^{\infty} dT' [\Omega_{T'}^\dagger L(T, T')] M(T_0, T') \\
 &= \int_I^{\infty} dT' \delta(T - T') M(T_0, T') = M(T_0, T) ,
 \end{aligned} \tag{39}$$

by the use of Eq. (34). Thus, we see the adjoint  $M(T_0, T)$  of the function  $L(T_0, T)$  is  $L(T, T_0)$ . Note the interchange of  $T_0$  and  $T$ .

We are now beginning to explore numerical applications of the theory.

#### 4. Concluding Remarks

Having summarized the theory of the yields of initial species, we now wish to reconsider the meaning of the term "initial species." Our treatment so far concerns the earliest stage of radiation action — the physical stage, in Platzman's words (HP61) — in which new species such as ions are generated by collisions of energetic electrons or other particles. These are the species we call initial species.

In most of the measurements of  $W$  values, for example, gas pressures are rather high — at least a few Torr and sometimes an order of one atmosphere or even higher. Under these pressures, thermal collisions of the initial species with other molecules are quite frequent, and may cause some interconversion among different species. In other words, the usual  $W$  measurements score the number of ions at a time later than the thermal-collision time; during the time period, some of the excited species may convert into ions. Platzman called attention to such additional ionizations on many occasions and called it collateral ionization. For example, Gerhart (G75) obtained  $W = 40$  eV for the initial ionization in molecular hydrogen by an electron with 1 keV. In contrast, experiments at high pressures give  $W = 36.5 - 37.5$  eV; there are about 10% more ionizations other than initial ionization. In this example, collateral ionization comes from excited hydrogen atoms formed by dissociation of hydrogen molecules. Gerhart evaluated the number of excited hydrogen atoms  $H^*$  also, and showed that the process



accounts for the 10% difference between the theoretical value and the experimental value of  $W$ . More specifically, Gerhart suggests that about 50% of the  $2^2S$  and  $2^2P$  states of atomic hydrogen make  $H_3^+$  at one atmosphere through reaction (40). To be sure, collateral ionization is just an example of many processes in which excited species change their identity during the so-called

physico-chemical stage (HP61). Similar considerations apply to other effects, for example, luminescence, often used as a means of dosimetry. Because of long time periods ( $10^{-9}$  sec or longer) involved, most of the luminescence observed comes from excited species that have had many thermal collisions or have undergone molecular internal conversion.

Full elucidation of conversion processes of initial species must await a major step forward. In this respect the progress of pulse radiolysis toward shorter time and the advent of short-time laser techniques for detection of various species give us much hope.

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### Figure Captions

- Fig. 1. An example of the Fano plot (reproduced from K75b with permission of the author and the publisher). The data represent the total ionization cross section  $\sigma_1$  of helium, as well as of molecular nitrogen, as a function of incident electron energy  $T$ . The abscissa variable  $\ln[\beta^2/(1-\beta^2)] - \beta^2$ , where  $\beta c$  is the electron speed, is suitable in the relativistic domain (F54), and reduces to  $\ln T$  minus a constant  $\ln(mc^2/2)$  in the nonrelativistic domain, i.e.,  $T < 10$  keV. The ordinate variable is  $\beta^2 \sigma_1 / (4\pi a_0^2 \alpha^2)$ , where  $a_0 = 0.529 \times 10^{-8}$  cm is the atomic unit of length and  $\alpha = 1/137$  is the fine-structure constant. This variable reduces to  $T \sigma_1$ , apart from a universal constant, in the nonrelativistic domain. Note the asymptotic approach to the straight-line behavior at high energies and the gradual approach to zero at low energies.
- Fig. 2. An example of the Platzman plot (reproduced from K75c with permission of the author and the publisher). In the top half (a), the data show the differential ionization cross section  $d\sigma_1(T, E)/dE$  of nitrogen by impact of electrons with  $T = 500$  eV. The abscissa scale is  $R/E$ , where  $R = 13.6$  eV is the Rydberg unit of energy, and the  $R/E$  values increase on going from right to left. The corresponding secondary electron energy  $E - I$  is shown on the top horizontal scale. The ordinate scale is  $TE^2 [d\sigma_1(T, E)/dE] / (4\pi a_0^2 R^2)$  where  $a_0 = 0.529 \times 10^{-8}$  cm is the atomic unit of length. The flat curve labeled "MOTT" represents hard-collision contributions evaluated by the Mott formula. In the bottom half (b), the optical oscillator-strength density  $df/dE$  is shown. The abscissa scale  $R/E$  is the same as in (a). The ordinate scale  $E df/dE$  is suitable for comparison with  $TE^2 [d\sigma_1(T, E)/dE]$  at fixed  $T$ . Note the similarity in the shapes of the curves (a) and (b).

- Fig. 3. An example of the numerical solution of the Fowler equation (reproduced from I75 with permission of the publisher). The average number  $N_1(T)$  of ions produced in helium by the incidence of an electron with energy  $T$  is plotted as a function of  $T$ . The data were taken from M56. The broken straight line shows an extrapolation of the high-energy linear behavior, and intercepts the horizontal axis at about  $T = 14$  eV.
- Fig. 4.  $W(T) = T/N_1(T)$  for helium. The data are the same as in Fig. 3.
- Fig. 5. The ratio  $W/I$  for 10-keV electrons in atomic vapors plotted as a function of atomic number  $Z$  (from IDS75). The values  $W_F$  were evaluated from Fano's theory (F46), and  $W_a$  from the theory of I75, by use of somewhat schematic cross-section data. Squares show better theoretical results (DG58, M56, E75) and circles show generally quoted experimental results (available for rare gases only).
- Fig. 6. Degradation spectra for helium gas at  $0^\circ$  C and one atmosphere (reproduced from D75a with permission of the publisher). The abscissa scale is  $\ln(T/R)$ , where  $R = 13.6$  eV is the Rydberg unit of energy. Each curve represents  $y(T_0, T)$  in the notation of the text at the three values of incident electron energy  $T_0$ .
- Fig. 7. A scale plot of the same degradation spectra as in Fig. 6 (reproduced from D75a with permission of the publisher). The abscissa variable is  $\ln(T/I)/\ln(T_0/I)$ , and the ordinate variable is  $(T/T_0)N\sigma_i(T)y(T_0, T)\ln(T_0/I)$  in the notation of the text.

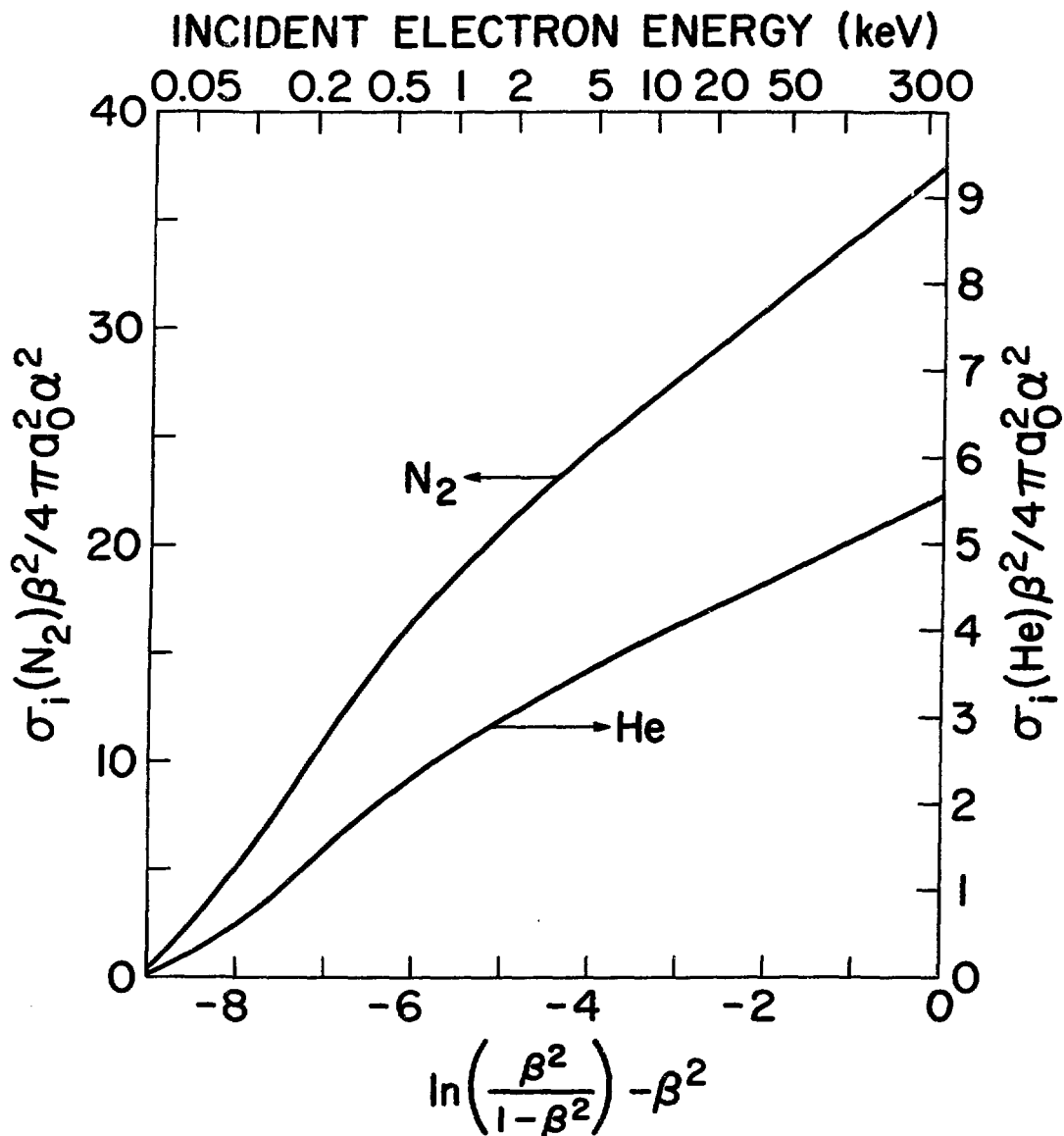


Fig. 1

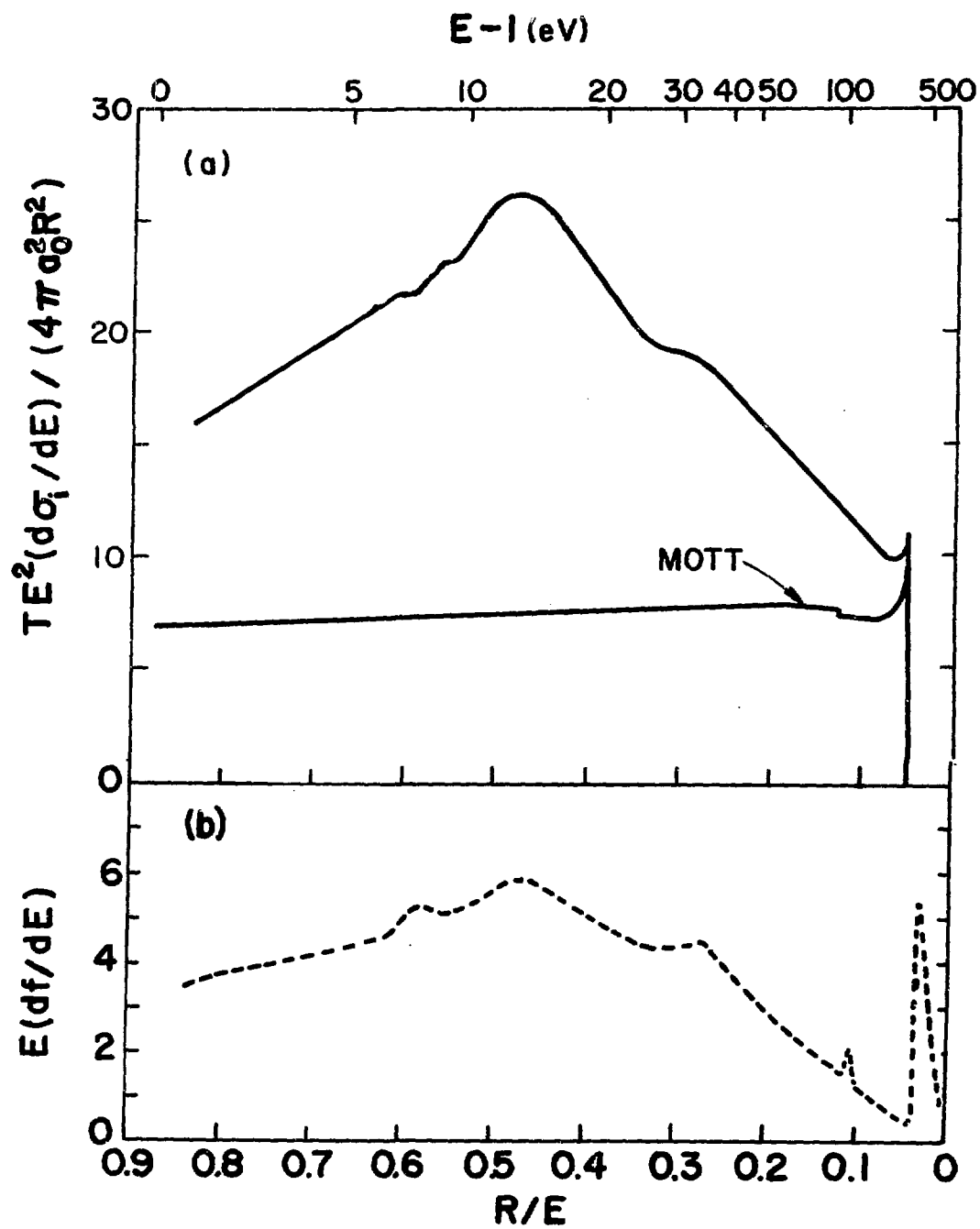


Fig. 2

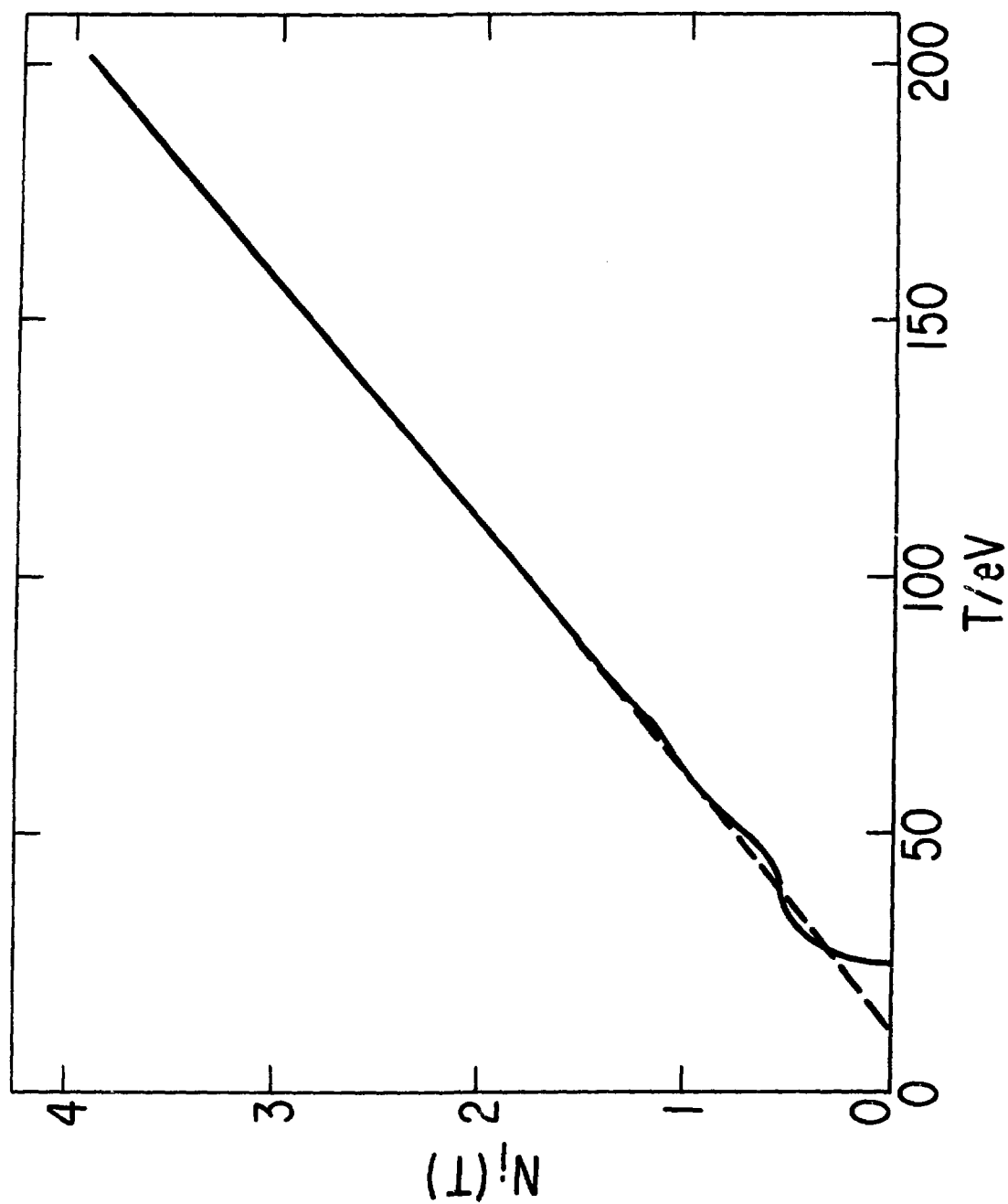


Fig. 3

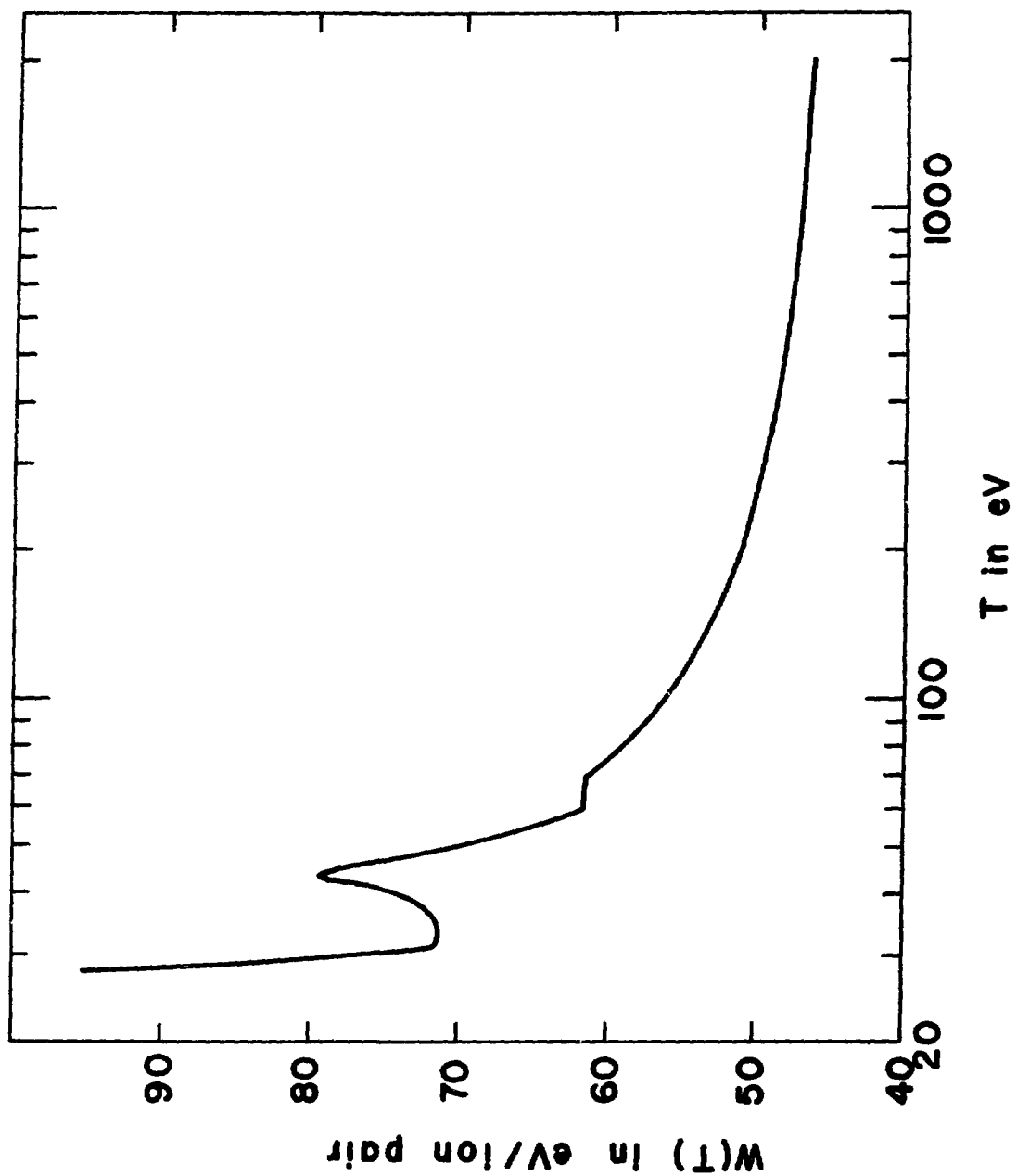


Fig. 4

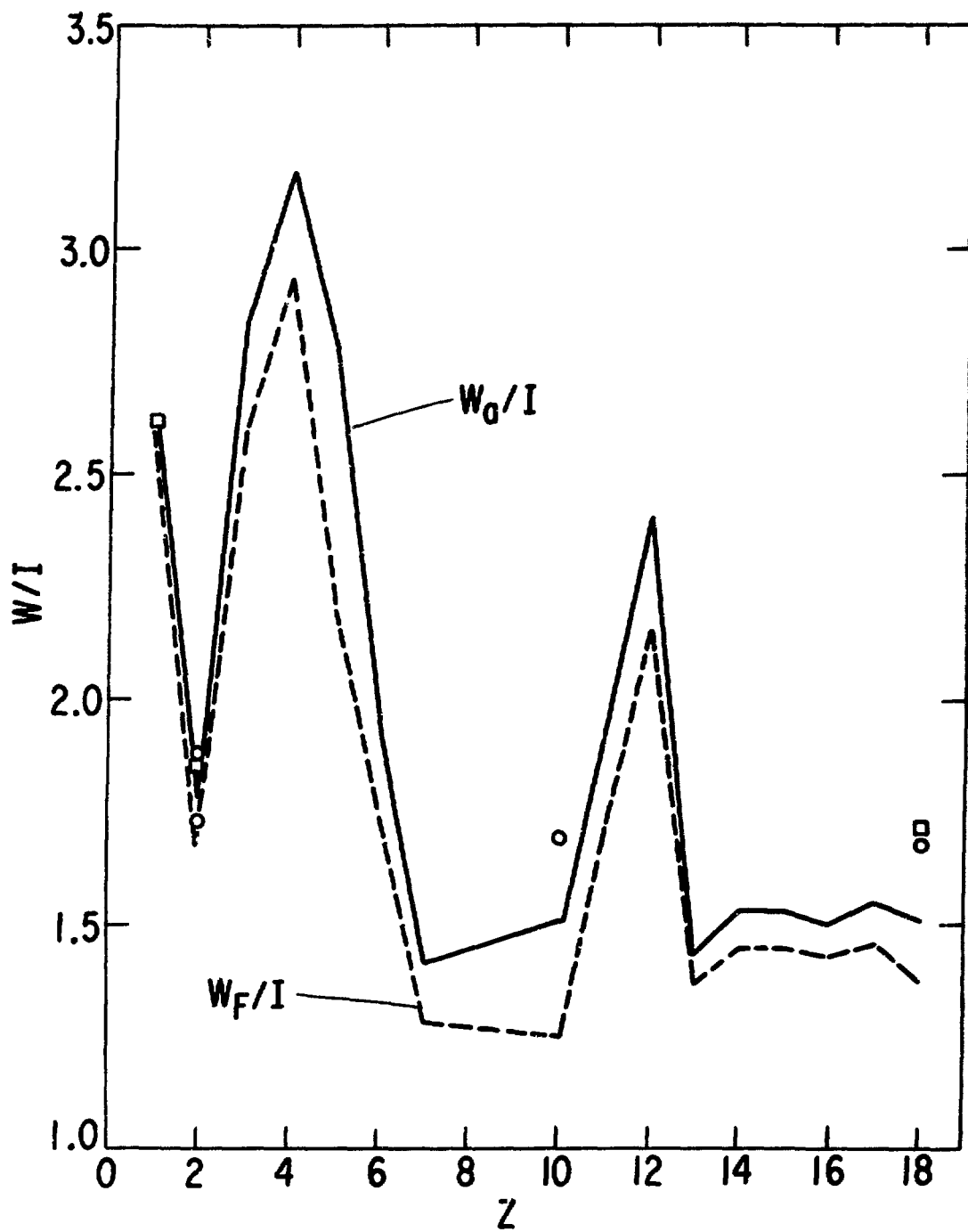


Fig. 5

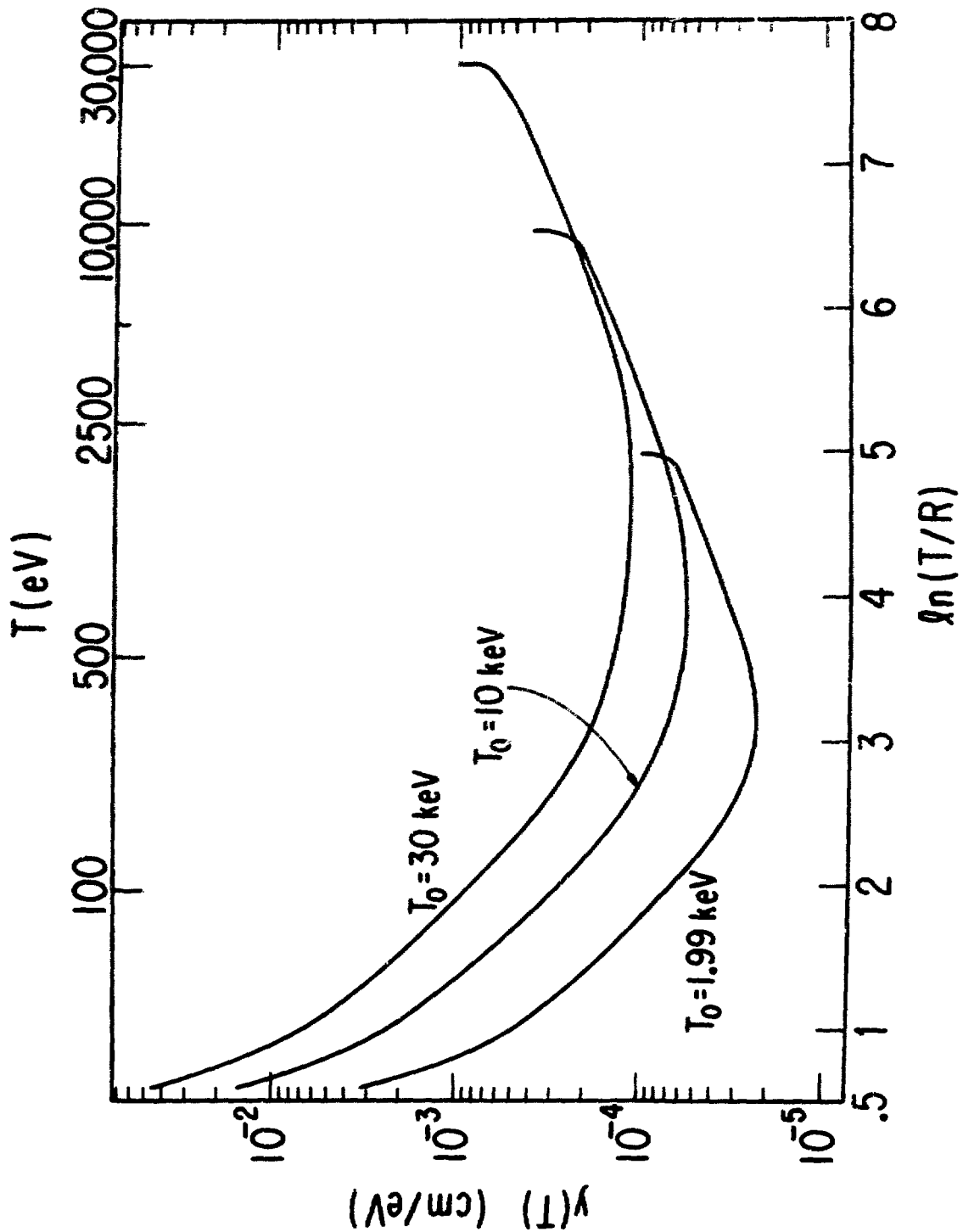


Fig. 6



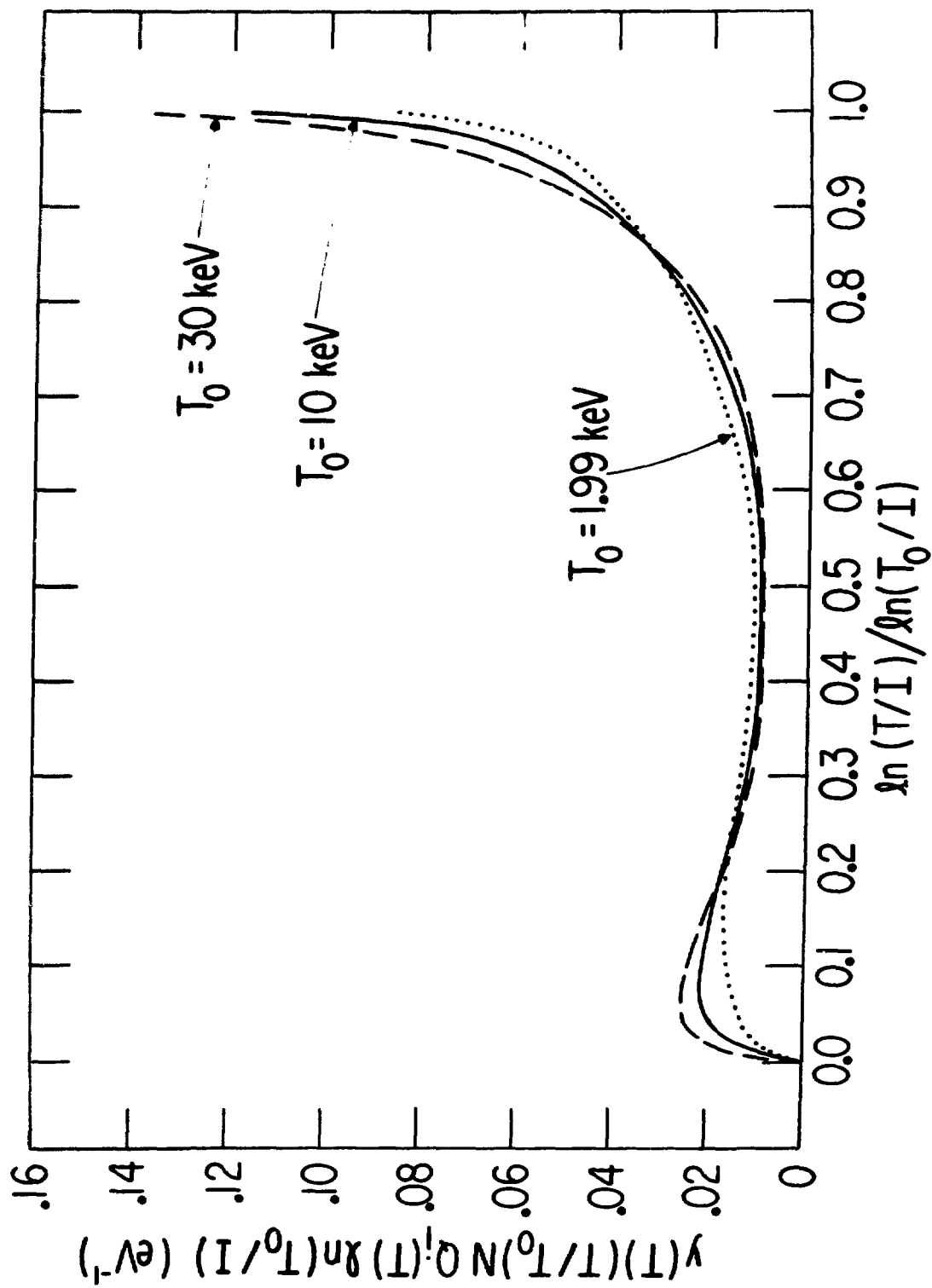


Fig. 7