

Time-dependent aspects of electron degradation. II. General theory

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(Received 21 January 1988)

The well-known Spencer-Fano theory of electron-degradation spectra treats time-independent cases, in which the medium is subjected to stationary irradiation. We present a generalization to time-dependent cases, showing how to calculate the temporal behavior of the electron-degradation spectrum and of related quantities such as the yield of ions or excited states that are produced under nonstationary irradiation. The generalized theory indicates new aspects of electron-degradation phenomena, which are basic to radiation physics and chemistry as well as to applications such as gaseous electronics, upper-atmospheric physics, and astrophysics.

I. INTRODUCTION

The electron-degradation spectrum (or the track-length distribution) $y(T)$ is important in the microscopic analysis of radiation actions on matter. As originally defined by Spencer and Fano,¹ $y(T)dT$ represents the total track length of all the electrons having energies between T and $T+dT$ in a medium under stationary irradiation. We supposed that the medium consists of a single species of molecules at the number density n . We let $U(T)dt$ represent the number of source electrons having energies between T and $T+dT$. Then $y(T)$ obeys the Spencer-Fano equation of the form

$$nK_T y(T) + U(T) = 0, \quad (1)$$

where K_T is a linear integral operator having the dimension of the cross section (i.e., the length squared). More specifically, $K_T y(T)$ represents the net gain and loss of all the electrons at energy T , and may be expressed as

$$K_T y(T) = \int dT' y(T') \sigma(T' \rightarrow T) - y(T) \int dT'' \sigma(T \rightarrow T''), \quad (2)$$

where $\sigma(T_1 \rightarrow T_2)$ represents the cross section for all the processes in which an electron of energy T_1 collides with a molecule and an electron of energy T_2 emerges. The subscript T indicates that the cross-section operator K_T depends parametrically on T . Equation (1) can be solved by starting with the highest T and using descending values of T .

Knowledge of the degradation spectrum is crucial to the microscopic analysis of radiation actions. For example, the mean number $N_i(T_0)$ of ions generated as a result of the absorption of a single electron of energy T_0 is expressed as

$$N_i(T_0) = n \int_0^{T_0} dT y(T_0, T) \sigma_i(T), \quad (3)$$

where $\sigma_i(T)$ is the cross section for the ionization of the molecule by an electron of energy T , and $y(T_0, T)$ is the solution of Eq. (1) when the source is monoenergetic, i.e., when $U(T) = \delta(T - T_0)$. Recent developments in the

electron-degradation theory are summarized elsewhere.²

The purpose of the present article is to generalize the Spencer-Fano theory to time-dependent cases. This work was motivated by recent experiments³⁻⁷ that pertain to the behavior of subexcitation electrons and other transient species at short times after pulsed irradiation. To interpret some of the findings, one must develop a framework suitable for evaluating the time dependence of the electron-degradation spectrum and of the yield of transient species. One application has been reported in the first paper⁸ of the present series. Section II will present the general theory for a chemically pure medium, Sec. III the extension to chemical mixtures, and Sec. IV special cases where the continuous-slowning-down approximation is useful.

II. THEORY

Sections II A–II D will treat the basic concepts, and Secs. II E–II H will present additional comments.

A. The incremental electron degradation spectrum

We consider first a chemically pure and electrically neutral medium that consists of a single species of molecules at the number density n . The medium may be a gas, liquid, or solid. We use the term “molecule” to mean a structural unit appropriate for consideration of single-electron scattering. Our formalism applies to any neutral medium, including mixtures (which we treat in Sec. III).

We suppose that a *time-dependent* source of electrons is characterized by the function $u(T;t)$ as follows: $u(T;t)dTdt$ represents the number of source electrons introduced into the medium in the time interval between t and $t+dt$ that have kinetic energies between T and $T+dT$. The source electrons initiate the degradation process by colliding with molecules and produce secondary electrons through ionization.

We further suppose that $z(T;t)dTdt$ represents the increment, during the time interval between t and $t+dt$, of the track length of all the electrons having kinetic ener-

gies between T and $T+dT$. Then the function $z(T;t)$ obeys the equation

$$v_T^{-1} \partial z(T;t) / \partial t = n K_T z(T;t) + u(T;t), \quad (4)$$

where v_T is the speed of an electron of kinetic energy T . [See Sec. II H for further elaboration on the meaning of Eq. (4).]

The meaning of Eq. (4) is simple. Each side, when multiplied by dT , represents the rate of change in the number of electrons at energy T and time t . The reciprocal of the speed v_T is a necessary factor because the operator K_T is a cross section as defined by Eq. (2). We call $z(T;t)$ the *incremental electron-degradation spectrum*.

When the source is monoenergetic at T_0 and is sharply pulsed at t_0 , we set

$$u(T;t) = \delta(T - T_0) \delta(t - t_0). \quad (5)$$

We call the solution of Eq. (4) with this $u(T;t)$ the *standard solution* and designate it as $z(T_0; T; t_0, t)$. The solution for an arbitrary $u(T;t)$ can be expressed as a superposition of the standard solutions, since Eq. (4) is linear.

To consider the yield of ions produced as a result of electron degradation initiated by the same source, we suppose that the increment of the yield during the time interval between t and $t+dt$ is written as $v_i(T_0; t, t_0) dt$. Then we may write

$$v_i(T_0; t, t_0) = n \int_I^{T_0} dT z(T_0, T; t_0, t) \sigma_i(T), \quad (6)$$

where $\sigma_i(T)$ is the total ionization cross section of the medium molecule for an electron of energy T , and the integration is over the T interval from the (first) ionization threshold I to the source energy T_0 .

The use of the term "incremental" might have given an impression that $z(T;t)$ at fixed T should invariably increase with t . This impression is false. Indeed, $z(T;t)$ may increase or decrease with t depending upon the sign of the right-hand side of Eq. (4). Notice that $K_T z(T;t)$ is either positive or negative depending upon the cross sections involved. Moreover, there are in general mechanisms for loss of electrons. For instance, the electron attachment to molecules leading to the production of negative ions certainly depletes electrons. This process often occurs in the subexcitation domain, which we shall treat at some depth in Sec. IV B. In our general theory, such a depletion effect is readily incorporated into the source term $u(T;t)$. Then $u(T;t)$ is in general a functional of $z(T;t)$. In the simplest case of the electron attachment for instance, $u(T;t)$ includes a term of the form $-n \sigma_{\text{att}}(T) z(T;t)$, where $\sigma_{\text{att}}(T)$ is the cross section for the attachment of electrons at energy T . Another example of the treatment of electron depletion effects is seen in paper I (Ref. 8) of the present series.

B. The cumulative electron degradation spectrum

Let us define the quantity

$$Z(T;t) = \int_{-\infty}^t dt' z(T;t'). \quad (7)$$

We write the lower limit of the t integration as $-\infty$; in

practice, the integral begins with the time at which $z(T;t')$ is nonzero. Then $Z(T;t) dT$ signifies the track-length of all electrons that are present at time t and have energies between T and $T+dT$. By combining Eqs. (4) and (7), we readily see that $Z(T;t)$ obeys the equation

$$v_T^{-1} \partial Z(T;t) / \partial t = n K_T Z(T;t) + U(T;t), \quad (8)$$

where $U(T;t)$ is the integrated source function defined as

$$U(T;t) = \int_{-\infty}^t dt' u(T;t'). \quad (9)$$

We call $Z(T;t)$ the *time-dependent cumulative electron-degradation spectrum*.

When the source is monoenergetic and pulsed [i.e., when $u(T;t)$ is given by Eq. (5)], we have

$$U(T;t) = \delta(T - T_0) \Theta(t - t_0), \quad (10)$$

where Θ represents the Heaviside function,

$$\Theta(t - t_0) = \begin{cases} 1 & \text{for } t_0 < t \\ 0 & \text{for } t < t_0. \end{cases} \quad (11)$$

We call the solution of Eq. (8) with this $U(T;t_0)$ the *standard solution*, and designate it as $Z(T_0; T; t_0, t)$.

The integral

$$N_i(T_0; t_0, t) = \int_{-\infty}^t dt' v_i(T_0; t', t_0) \quad (12)$$

represents the cumulative yield of ions, the total number of ions present at time t resulting from the monoenergetic pulsed source. The cumulative yield may be expressed alternatively as

$$N_i(T_0; t_0, t) = n \int_I^{T_0} dT Z(T_0, T; t_0, t) \sigma_i(T). \quad (13)$$

C. The connection with the stationary case

When the source term $u(T;t)$ is independent of time, the incremental spectrum $z(T;t)$ eventually approaches a stationary value, which we may denote as $z(T; \infty)$. This clearly satisfies Eq. (1), i.e., the Spencer-Fano equation in the stationary case, and thus may be equated with $y(T)$ of Spencer and Fano. At the same time, the incremental yield $v_i(T_0; t_0, t)$ approaches the yield $N_i(T_0)$ of the stationary case.

When the source term $u(T;t)$ vanishes after a period, the integrated source function $U(T;t)$ becomes independent of time. Then the cumulative spectrum $Z(T;t)$ eventually approaches a stationary value $Z(T; \infty)$, which may be equated with $y(T)$ of Spencer and Fano. At the same time, the cumulative yield $N_i(T_0; t_0, t)$ of ions approaches the yield $N_i(T_0)$ of the stationary case.

A remark is in order on the meaning of the stationary spectra. Our entire treatment is limited to electron energies T above a fixed value that corresponds to the lowest threshold E_{min} for the excitation process that we explicitly include in the K_T operator. The stationary spectra, $Z(T; \infty)$ and $z(T; \infty)$, are defined for $T > E_{\text{min}}$. A treatment of the region below E_{min} , to cover the electron thermalization, is outside the scope of the present article.

D. The time-dependent Fowler equation

Much earlier than the Spencer-Fano work, Fowler⁹ showed how to calculate $N_i(T)$ directly in the stationary case. Therefore, it is customary to call an equation for the yield a Fowler equation. Rau, Inokuti, and Douthat¹⁰ showed the precise connection between the Spencer-Fano equation and the Fowler equation. Before treating time-dependent cases, we will recapitulate the main point of Rau, Inokuti and Douthat.

We set the source $U(T)=\delta(T-T_0)$ in Eq. (1). Then we take an inner product with $N_i(T)$. In other words, we multiply Eq. (1) by $N_i(T)$ and integrate the result over the T interval $I \leq T < \infty$. Then we obtain

$$n \int dT N_i(T) K_T y(T_0, T) + \int dT N_i(T) \delta(T - T_0) = 0. \quad (14)$$

We rewrite the first integral as

$$\int dT N_i(T) K_T y(T_0, T) = \int dT [K_T^\dagger N_i(T)] y(T_0, T). \quad (15)$$

Here we have introduced a new operator K_T^\dagger that acts on $N_i(T)$. The operator K_T^\dagger is the adjoint of K_T , and its existence has been established for a large class of linear operators and function spaces.¹¹

The second term of Eq. (14) is readily equated with $N_i(T_0)$, which is given by Eq. (3). Thus, we have

$$n \int dT [K_T^\dagger N_i(T) + \sigma_i(T)] y(T_0, T) = 0. \quad (16)$$

The relation holds for every value of T_0 . So long as $y(T_0, T)$ is a well-behaved function of T , we must have

$$K_T^\dagger N_i(T) + \sigma_i(T) = 0 \quad (17)$$

at every value of energy T . This is the Fowler equation. A general form of the operator K_T^\dagger adjoint to K_T of Eq. (2) is

$$K_T^\dagger N_i(T) = \int dT' N_i(T') \sigma(T \rightarrow T') - N_i(T) \int dT'' \sigma(T \rightarrow T''). \quad (18)$$

To derive this result, one inserts Eq. (3) into Eq. (15), and changes the order of repeated integrations.

The physical meaning of Eq. (17) is that the quantity $K_T^\dagger N_i(T) + \sigma_i(T)$ represents the net change of the number of ions due to all collisions experienced by an electron of kinetic energy T . In particular, the first term on the right-hand side of Eq. (18) represents the production of ions by all succeeding collisions. The Fowler equation is solved by starting with the obvious condition $N_i(T) = 0$ at $T = I$ and *ascending in T* . This is in contrast to the Spencer-Fano equation, Eq. (1), which is solved by *descending in T* .

We now treat the time-dependent equation, Eq. (4). We set the source term as $u(T; t) = \delta(T - T_0) \delta(t - t_0)$ and take an inner product of Eq. (4) with $v_i(T; t_0, t)$, defined by Eq. (6). The inner product is in the combined

space of T and t . In other words, we take integrals over $-\infty < t < \infty$ and $I < T < \infty$. Thus, we write

$$\begin{aligned} & \int dt \int dT v_i(T; t_0, t) v_T^{-1} \partial z(T_0, T; t_0, t) / \partial t \\ &= n \int dt \int dT v_i(T; t_0, t) K_T z(T_0, T; t_0, t) \\ &+ \int dt \int dT v_i(T; t_0, t) \delta(T - T_0) \delta(t - t_0). \end{aligned} \quad (19)$$

We treat the right-hand side virtually in the same way as the stationary case. We rewrite the first term as

$$\begin{aligned} & n \int dt \int dT v_i(T; t_0, t) K_T z(T_0, T; t_0, t) \\ &= n \int dt \int dT [K_T^\dagger v_i(T; t_0, t)] z(T_0, T; t_0, t). \end{aligned} \quad (20)$$

Using Eq. (6), we write the second term as

$$\begin{aligned} & \int dt \int dT v_i(T; t_0, t) \delta(T - T_0) \delta(t - t_0) \\ &= n \int dt \int dT \delta(t - t_0) \sigma_i(T) z(T_0, T; t_0, t). \end{aligned} \quad (21)$$

The left-hand side of Eq. (19) shows a new aspect. We integrate the left side by parts in t . The resulting boundary terms may be dropped with the assumption that the incremental spectrum vanishes at $t \rightarrow -\infty$ and $t \rightarrow \infty$. This is justified as long as the source acts for a finite time. Thus, we have

$$\begin{aligned} & \int dt \int dT v_i(T; t_0, t) v_T^{-1} \partial z(T_0, T; t_0, t) / \partial t \\ &= - \int dt \int dT v_T^{-1} \partial v_i(T; t_0, t) / \partial t z(T_0, T; t_0, t). \end{aligned} \quad (22)$$

Combining Eqs. (19)–(22), we arrive at

$$\begin{aligned} & \int dt \int dT [-v_T^{-1} \partial v_i(T; t_0, t) / \partial t] z(T_0, T; t_0, t) \\ &= \int dt \int dT [n K_T^\dagger v_i(T; t_0, t) \\ &+ n \delta(t - t_0) \sigma_i(T)] z(T_0, T; t_0, t). \end{aligned} \quad (23)$$

For this equation to hold, we must have

$$-v_T^{-1} \partial v_i(T; t_0, t) / \partial t = n K_T^\dagger v_i(T; t_0, t) + n \delta(t - t_0) \sigma_i(T) \quad (24)$$

at every t and T . This is the desired Fowler equation for the incremental yield.

The physical meaning of Eq. (24) is that the time t runs from ∞ to $-\infty$, as is always the case with the adjoint of an equation that contains the time derivative of any odd order. An example is the well-known partial differential equation for diffusion; its adjoint is the same equation with the time direction reversed.¹¹ Thus, the incremental ion yield $v_i(T; t_0, t)$ satisfies Eq. (24) with $-t$ corresponding to the physical time.

Similarly, we can derive an equation for the cumulative ion yield, as defined by Eqs. (12) and (13). The result is

$$-v_T^{-1} \partial N_i(T; t_0, t) / \partial t = n K_T^\dagger N_i(T; t_0, t) + n \sigma_i(T), \quad (25)$$

in which $-t$ again represents the physical time.

To prevent misunderstanding, we may introduce the physical time $\hat{t} = -t$, which runs from $-\infty$ to $+\infty$, and rewrite Eqs. (24) and (25) as follows:

$$v_T^{-1} \partial v_i(T; \hat{t}_0, \hat{t}) / \partial \hat{t} = n K_T^\dagger v_i(T; \hat{t}_0, \hat{t}) + n \delta(\hat{t} - \hat{t}_0) \sigma_i(T) \quad (26)$$

and

$$v_T^{-1} \partial N_i(T; \hat{t}_0, \hat{t}) / \partial \hat{t} = n K_T^\dagger N_i(T; \hat{t}_0, \hat{t}) + n \sigma_i(T). \quad (27)$$

These equations are to be used in numerical work.

E. Yields of excited species

For simplicity, we have thus far discussed the yield of ions. However, discussing the yield of any excited species s is straightforward. We let the cross section for the production of s by a collision of an electron of energy T be $\sigma_s(T)$. Then the incremental yield $v_s(T_0; t_0, t)$ is given by

$$v_s(T_0; t_0, t) = n \int_{t_0}^t dT z(T_0, T; t_0, t) \sigma_s(T), \quad (28)$$

and the cumulative yield $N_s(T_0; t_0, t)$ by

$$N_s(T_0; t_0, t) = n \int_{t_0}^t dT Z(T_0, T; t_0, t) \sigma_s(T). \quad (29)$$

These expressions are formally similar to Eqs. (6) and (13); the only difference is the replacement of $\sigma_i(T)$ with $\sigma_s(T)$. Likewise, $v_s(T_0; t_0, t)$ and $N_s(T_0; t_0, t)$ satisfy Fowler equations formally similar to Eqs. (24)–(27).

F. Formal solutions

The equations for the incremental cumulative spectra, as well as those for the ion yields, are all linear differential equations of the first order in t . Therefore, we can write their solutions. For instance, we can write the solution of Eq. (4) as

$$z(T; t) = \int_{-\infty}^t dt' D(t, t') u(T; t'), \quad (30)$$

where $D(t, t')$ is an operator defined as

$$\begin{aligned} K_T(T) = & \int dT' y(T') \left[q(T'; T) + \int dT_2 q(T'; T, T_2) + \int dT_1 q(T'; T_1, T) \right. \\ & + \int dT_2 \int dT_3 q(T'; T, T_2, T_3) + \int dT_1 \int dT_3 q(T'; T_1, T, T_3) \\ & \left. + \int dT_1 \int dT_2 q(T'; T_1, T_2, T) + \cdots \right] \\ & - y(T) \left[\int dT_1 q(T; T_1) + \int dT_1 \int dT_2 q(T; T_1, T_2) + \int dT_1 \int dT_2 \int dT_3 q(T; T_1, T_2, T_3) + \cdots \right]. \quad (33) \end{aligned}$$

The first group of terms represents the increase of electrons at energy T and the second group of terms the decrease of electrons at energy T , resulting from all the collisions. Integration of Eq. (33) over T , followed by suitable changes of variables, gives

$$\begin{aligned} \int dT K_1 y(T) = & \int dT y(T) \left[\int dT_1 \int dT_2 q(T; T_1, T_2) + 2 \int dT_1 \int dT_2 \int dT_3 q(T; T_1, T_2, T_3) \right. \\ & \left. + 3 \int dT_1 \int dT_2 \int dT_3 \int dT_4 q(T; T_1, T_2, T_3, T_4) + \cdots \right]. \quad (34) \end{aligned}$$

We note that the result does not include $q(T; T_1)$, and that it represents the multiplication of the electrons due to ioniz-

$$D(t, t') = \exp[(t - t') n v_T K_T] v_T. \quad (31)$$

To derive this solution, we merely need to recognize that $\exp(-t n v_T K_T) v_T$ is an integrating factor for Eq. (4). (This operator cannot be written as $v_T \exp(-t n v_T K_T)$, because K_T and v_T are not commutable.)

Similarly, the solution of Eq. (8) is written as

$$Z(T; t) = \int_{-\infty}^t dt' D(t, t') U(T, t'). \quad (32)$$

Formal solutions are also possible for the equations [Eqs. (26) and (27)] for the yields of ions. The formal solutions may not be suitable for numerical studies, but they are useful for analytical studies. We recall that $Z(T; t)$ in the limit $t \rightarrow \infty$ is the Spencer-Fano degradation spectrum in the stationary case. Equation (32) provides a new avenue toward an approach to the stationary problem.

G. Detailed expression for the cross-section operator

The operator K_T is defined by Eq. (2) in a compact form. For some considerations (e.g., those in Sec. IIH), it is useful to write a more detailed form. Let $q(T; T_1) dT_1$ be the cross section for the collision in which an electron of energy T leads to an electron of energy between T_1 and $T_1 + dT_1$, and no other electron; this collision is an excitation process. We let $q(T; T_1, T_2) dT_1 dT_2$ be the cross section for the collision in which an electron of energy T leads to an electron of energy between T_1 and $T_1 + dT_1$ and a second electron of energy between T_2 and $T_2 + dT_2$; this collision is a single ionization process. Then we let $q(T; T_1, T_2, T_3) dT_1 dT_2 dT_3$ be the cross section for the collision in which an electron of energy T leads to an electron of energy between T_1 and $T_1 + dT_1$, a second electron of energy between T_2 and $T_2 + dT_2$, and a third electron of energy between T_3 and $T_3 + dT_3$; this collision is a double ionization process. Likewise, we can define the cross section $q(T; T_1, T_2, \dots) dT_1 dT_2 \dots$ of a higher multiple ionization process. Then, we may express the K_T operator as

ing collisions.

It is straightforward to show that the adjoint of K_T is given by

$$K_T^\dagger N(T) = \int dT_1 q(T; T_1) N(T_1) + \int dT_1 \int dT_2 q(T; T_1, T_2) [N(T_1) + N(T_2)] \\ + \int dT_1 \int dT_2 \int dT_3 q(T; T_1, T_2, T_3) [N(T_1) + N(T_2) + N(T_3)] + \cdots \quad (35)$$

To prove this, we insert Eq. (33) into Eq. (15) and change the order of repeated integrations.

Equations (33)–(35) indicate the precise meaning of the operators K_T and K_T^\dagger , and the operands $y(T)$ and $N(T)$ represent any well-behaved functions.

H. Connection of the degradation spectrum with the electron energy distribution

A more general treatment of the electron behavior in gaseous or condensed media requires the solution of the Boltzmann equation for the density distribution function, $f(\mathbf{r}, \mathbf{v}_T; t)$, which describes the electron flow in the phase space.¹² Specifically, $f(\mathbf{r}, \mathbf{v}_T; t) d\mathbf{r} d\mathbf{v}_T$ represents the number of electrons having velocities in the range between \mathbf{v}_T and $\mathbf{v}_T + d\mathbf{v}_T$ and positions in the range between \mathbf{r} and $\mathbf{r} + d\mathbf{r}$ at time t . When the position is irrelevant, we may define an electron energy distribution function,

$$\rho(T; t) = (2T/m)^{1/2} F(T; t), \quad (36)$$

by integrating f over both the configuration space and the electron direction. In other words,

$$F(T; t) = \int d\mathbf{r} \int \sin\theta_v d\theta_v \int d\phi_v f(\mathbf{r}, \mathbf{v}_T; t). \quad (37)$$

This integration reduces the Boltzmann equation to an energy-transport equation,

$$\partial\rho(T; t)/\partial t = nK_T v_T \rho(T; t) + u(T; t), \quad (38)$$

where $u(T; t)$ is the same source term as in Eq. (4). Comparison with Eq. (4) shows that

$$z(T; t) = v_T \rho(T; t), \quad (39)$$

which we take to be the elementary definition of z . Although the dimension of z in Eq. (39) is $\text{length} \times \text{energy}^{-1} \times \text{time}^1$ by its connection with the Boltzmann equation, it is evident that these units may be changed by altering the definition of ρ in Eq. (38). For example, if we give ρ in units of concentration $\times \text{energy}^{-1}$, then z must have units of $\text{length}^{-2} \times \text{energy}^{-1} \times \text{time}^{-1}$ and u must be changed accordingly. An essentially equivalent point of view is given in Ref. 1, where the units of z are dictated by the units of the source term without reference to Eq. (38).

One consequence of Eq. (38) is noteworthy. If we integrate both sides of that equation over T with the use of Eq. (34), the result is

$$d/dt \int dT \rho(T; t) = n \int dT v_T y(T) \left[\int dT_1 \int dT_2 q(T; T_1, T_2) + 2 \int dT_1 \int dT_2 \int dT_3 q(T; T_1, T_2, T_3) \right. \\ \left. + 3 \int dT_1 \int dT_2 \int dT_3 \int dT_4 q(T; T_1, T_2, T_3, T_4) + \cdots \right] + \int dT u(T; t). \quad (40)$$

This equation shows the rate of increase of the total electron number due to ionizing collisions and to the source term.

III. EXTENSION TO MIXTURES

Virtually all the problems of practical interest in radiation physics, chemistry, and biology concern mixtures that contain various chemical species. Therefore, the theory must be extended to treat mixtures.

We let the medium consist of $n^{(1)}$ molecules per unit volume of species 1, $n^{(2)}$ molecules per unit volume of species 2, and so on. We define

$$nK_T = \sum_{\lambda} n^{(\lambda)} K_T^{(\lambda)}, \quad (41)$$

where

$$n = \sum_{\lambda} n^{(\lambda)} \quad (42)$$

is the total number density of molecules. The symbol $K_T^{(\lambda)}$ is the cross-section operator for the molecule of species λ , defined as in Eq. (2), but referring to collisions only with species λ . Then, the Spencer-Fano equation [Eq. (1)], as well as the time-dependent equation [Eq. (4)], is valid. The solution of the Spencer-Fano equation depends upon the composition, i.e., the whole set of $n^{(\lambda)}$.

The expression for the yield of ions, Eq. (3), must be generalized. The yield $N_i^{(\lambda)}(T_0)$ of ions of molecules of species λ is written as

$$N_i^{(\lambda)}(T_0) = n^{(\lambda)} \int_0^{T_0} dT y(T_0, T) \sigma_i^{(\lambda)}(T), \quad (43)$$

where $\sigma_i^{(\lambda)}(T)$ is the cross section for the ionization of a molecule of species λ by an electron of energy T . Writing an expression for the time-dependent yield is likewise straightforward.

The general structure of the Fowler equation for the

yield is formally the same as for a chemically pure medium. However, an expression for the adjoint of the operator nK_T is complicated. It includes all the terms representing a series of processes in which an electron collides first with a λ molecule and next with λ' molecule. The Fowler equation for binary mixtures has been written in detail by Eggarter,¹³ as well as by Kimura and Inokuti,¹⁴ who also gave numerical solutions for Ar-H₂ mixtures.

IV. THE CONTINUOUS-SLOWING-DOWN APPROXIMATION

A. Generalities

Under certain conditions we may greatly simplify the cross-section operator. An example occurs in the interval $T_0/2 < T < T_0$, where the source energy T_0 is much higher than most of the possible energy-transfer values. In this interval, no secondary electrons are produced because by definition the highest energy of a secondary electron resulting from a primary electron of energy T is $(T - I)/2$, I being the ionization threshold.

For convenience, let us write the energy transfer as a discrete variable E_j . Then we may rewrite Eq. (2) as

$$K_T y(T) = \sum_j \sigma_j(T + E_j) y(T + E_j) - \sum_j \sigma_j(T) y(T), \quad (44)$$

where $\sigma_j(T)$ is the cross section for the collision in which an electron of energy T transfers energy E_j to the medium. The sum over j includes the integration over the ionization continuum, which usually dominates in practice. We assume that $E_j \ll T$ and retain only the terms linear in E_j . Then we obtain

$$K_T y(T) = \partial/\partial T [s(T) y(T)], \quad (45)$$

where $s(T)$ is the stopping cross section

$$s(T) = \sum_j E_j \sigma_j(T). \quad (46)$$

Now K_T is a first-order differential operator. This simplification is known as the continuous-slowing-down approximation (CSDA).

Within the CSDA, the Spencer-Fano equation for the stationary monoenergetic source becomes

$$n \partial/\partial T [s(T) y(T_0, T)] + \delta(T - T_0) = 0. \quad (47)$$

From this we see that $y(T_0, T)$ is the reciprocal of the stopping power $ns(T)$. Historically, Spencer and Fano¹ looked for a quantity that replaces the reciprocal stopping power to remove the limitation of the CSDA, and thus arrived at the degradation spectrum.

B. Subexcitation electrons

Another energy region in which the CSDA is often justifiable is $T < E_1$, where E_1 is the lowest electronic-excitation threshold of the medium. In this energy region no secondary electrons are produced. Moreover, elec-

trons in this region experience much feebler moderation than those at $T > E_1$, and therefore warrant separate consideration. Platzman¹⁵ called these subexcitation electrons and pointed out their roles, e.g., in exciting impurity molecules that have excitation energies lower than E_1 . They are numerous because their total number is equal to the total energy of ions produced in any initially neutral medium. Subexcitation electrons are precursors for some radiation-chemical products such as solvated electrons and negative ions. The behavior of subexcitation electrons is also important in some atmospheric and astrophysical problems, as exemplified by the recent work of Douthat.¹⁶ Our initial application of the time-dependent theory was an analysis of the behavior of subexcitation electrons in rare gases admixed with trace nitrogen.⁸

The moderation of subexcitation electrons occurs through vibrational excitation, rotational excitation, and elastic scattering upon collisions with molecules in a gas, or through the excitation of phonons and other low-energy quanta in condensed matter. Here we consider the case of a pure gas in some detail. For a summary of current cross-section data, see the work of Stephens and Robicheaux.¹⁷

The mean energy loss per collision due to vibrational excitation is ordinarily not much greater than the vibrational quantum, typically about 0.1 eV, because the excitation of many quanta in a single collision is highly unlikely. (Exceptions arise at resonance energies at which an incident electron is temporarily captured by a molecule; then probabilities are substantial for multiquantum excitation.¹⁷) Thus, with respect to vibrational excitation, the fractional energy loss per collision may be taken as small, provided that the electron energy T greatly exceeds 0.1 eV.

The mean energy loss due to rotational excitation is much smaller, i.e., typically of the order of meV. Therefore, the fractional energy loss per collision is even smaller. (For gas at room temperature, there are also possibilities that rotational deexcitation of a molecule may result in an energy gain of an electron. What counts for our purpose is the net energy loss, which, for brevity, we call the energy loss due to rotational excitation.)

Therefore, the energy losses due to vibrational and rotational excitation may be treated within the CSDA so long as $0.1 \text{ eV} \ll T < E_1$, as in Sec. IV A. Specifically, the contributions to $K_T y(T)$ are expressed in the same form as Eq. (45), and $s(T)$, the stopping power due to vibrational and rotational excitation, is given in the same way as Eq. (46).

Each energy loss due to elastic collisions with molecules is even smaller, and therefore the CSDA is even more justifiable as long as the electron energy T is much higher than the translational energy of molecules in thermal motion. Here we treat contribution to $K_T y(T)$ from elastic collisions.

We suppose that an electron of energy T collides elastically with a molecule. Then the molecule receives translational kinetic energy Δ , which depends upon the angle θ of electron scattering. We know¹² that the mean value $\bar{\Delta}$ is given by

$$\bar{\Delta} = \lambda(1 - \overline{\cos\theta})T, \quad (48)$$

where $\lambda = 2m/M$ (twice the ratio of the electron mass to the molecular mass). Explicitly, we may write the probability of energy transfer values between Δ and $\Delta + d\Delta$ as $p(T, \Delta)d\Delta$; then we may write

$$\int d\Delta \Delta p(T, \Delta) = \lambda(1 - \overline{\cos\theta})T, \quad (49)$$

where

$$\int d\Delta p(T, \Delta) = 1. \quad (50)$$

The mean value of $1 - \cos\theta$ is often expressed as the ratio of the momentum-transfer cross section $\sigma_m(T)$ to the total elastic scattering cross section $\sigma_e(T)$.

Thus, we may express the contribution of elastic collision to the K_T operator as

$$\begin{aligned} K_T y(T) \Big|_{\text{elastic}} &= \int d\Delta \sigma_e(T + \Delta) p(T + \Delta, \Delta) y(T + \Delta) \\ &\quad - \int d\Delta \sigma_e(T) p(T, \Delta) y(T) \\ &= \partial/\partial T \left[\sigma_e(T) \int d\Delta \Delta p(T, \Delta) y(T) \right] \end{aligned} \quad (51)$$

within the CSDA. We use Eq. (49) to obtain

$$K_T y(T) \Big|_{\text{elastic}} = \partial/\partial T [\lambda T \sigma_m(T) y(T)]. \quad (52)$$

Combining this with the vibrational and rotational contributions, we arrive at the total expression

$$K_T y(T) = \partial/\partial T [s(T) y(T)], \quad (53)$$

where $s(T)$ is the stopping cross section for subexcitation electrons, defined as

$$s(T) = \lambda T \sigma_m(T) + \sum_r E_r \sigma_r(T) + \sum_v E_v \sigma_v(r). \quad (54)$$

Here the second term represents the stopping cross section due to rotational excitation, and the third term the stopping cross section due to vibrational excitation.

C. Time-dependent degradation spectra

Within the CSDA, the equation for the incremental degradation spectrum takes the form

$$v_T^{-1} \partial z(T; t) / \partial t = n \partial/\partial T [s(T) z(T; t)] + u(T; t). \quad (55)$$

$$s(T) z(T; t) = s(g(\tau - t)) z(g(\tau - t); 0) + \int_0^t dt' v_{g(\tau - t + t')} s(g(\tau - t + t')) u(g(\tau - t + t'); t'). \quad (63)$$

Another special case is the standard solution $z(T_0; T; t_0, t)$, i.e., the solution for the source term given by Eq. (5). We easily write

$$\begin{aligned} s(T) z(T_0, T; t_0, t) &= v_{g(\tau - t + t_0)} s(g(\tau - t + t_0)) \\ &\quad \times \delta(g(\tau - t + t_0) - T_0). \end{aligned} \quad (64)$$

This is a linear partial differential equation of the first order in both t and T . Therefore, we can always solve it analytically by use of an elementary method.

To be specific, we multiply both sides by $v_T s(T)$ and obtain

$$\begin{aligned} \partial/\partial t [s(T) z(T; t)] &= n v_T s(T) \partial/\partial T [s(T) z(T; t)] \\ &\quad + v_T s(T) u(T; t). \end{aligned} \quad (56)$$

Here we introduce a new variable τ such that

$$-dT/d\tau = n v_T s(T). \quad (57)$$

In other words, we use

$$\tau = \int_T^{E_1} [n v_T s(T')]^{-1} dT' \quad (58)$$

instead of T . The variable represents the time for an electron of initial energy E_1 (the highest energy of subexcitation electrons) to reach energy T within the CSDA. We may call τ the CSDA time. Now Eq. (56) takes a compact form

$$(\partial/\partial t + \partial/\partial \tau) s(T) z(T; t) = w(\tau; t), \quad (59)$$

where we have defined $w(\tau; t)$ as

$$w(\tau; t) = v_T s(T) u(T; t). \quad (60)$$

The precise meaning of the definition is the following: to determine $w(\tau; t)$ at given value of τ , we first find a corresponding value of T , which we write $g(\tau)$, by inverting Eq. (58), and then evaluate the right-hand side of Eq. (60). The inversion is always possible and unique because τ is a single-valued monotonic function of T .

The general solution of Eq. (59) is

$$s(T) z(T; t) = \phi(\tau - t) + \int_0^t dt' w(\tau - t + t', t'), \quad (61)$$

where ϕ is any differentiable function of the combined variable $\tau - t$. The correctness of Eq. (61) is most easily seen by inserting it into Eq. (59).

The function ϕ is determined if $z(T; t)$ at a particular time (e.g., at $t=0$) is given. In this event, we have $\phi(\tau) = s(T) z(T; 0)$, or more precisely,

$$\phi(\tau) = s(g(\tau)) z(g(\tau); 0). \quad (62)$$

The particular solution in this case is then

The standard solution for the cumulative spectrum is then written as

$$\begin{aligned} Z(T_0, T; t) &= \int_{-\infty}^t dt' z(T_0 T; t_0, t) \\ &= \Theta(t - \tau) / [n s(T)]. \end{aligned} \quad (65)$$

This result is consistent with the solution of the steady-state equation, Eq. (47), as it should be.

The foregoing illustrates our general conclusion. Whenever the CSDA is applicable, the equation for the incremental spectrum or the cumulative spectrum is a partial differential equation of the first order in T and t ; therefore, it is solvable analytically. In the initial application⁸ of the method, we treated an even more general case in which some of the subexcitation electrons collided with impurity molecules, caused their electronic excitation, and thus were removed from the energy domain of interest. In this case, the partial differential equation corresponding to Eq. (55) had an additional term of the form $-k(T)z(T;t)$, where $k(T)$ is proportional to the cross section for the impurity excitation. However, the equation was still analytically solvable.

V. CONCLUDING REMARKS

We have shown a general theory of time-dependent aspects of electron degradation. An application has been already published.⁸ Other applications are seen in papers III and IV of the present series (Refs. 18 and 19). Further work now in progress will amply illustrate the rich physics that the general theory implies.

ACKNOWLEDGMENTS

This work was supported in part by the U.S. Department of Energy, Office of Health and Environmental Research, under Contract No. W-31-109-Eng-38, and by the Office of Basic Energy Sciences. We thank U. Fano and M. C. Sauer, Jr. for valuable comments on an earlier manuscript.

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