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CALCULATION OF THE PRIMARY RADIATION CHEMICAL YIELDS IN HELIUM ON THE BASIS OF A CLASSICAL COLLISION THEORY

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An *ab initio* calculation of the primary radiolysis yields was examined. The method is based on the classical theory developed by Thomas in 1927 for the collision between two free moving electrons. The results of applying it to the irradiation of He with 100 keV-electrons are: $G_{ion} = 2.42$, $G_{ex}(n^1P) = 0.91$, and $G_{ex}(n^3S, n^3P) = 0.13$.

The transfer of radiation energy to the electronic system of individual atoms and molecules in matter results in the formation of excited and ionized atoms or molecules and electrons ejected in the ionization process. The ejected electrons in turn enter into exciting and ionizing collisions. The energy spectrum of the electrons, called the degradation or slowing-down spectrum, is represented by a function y(T) defined[1] by y(T)dT = total distance traversed by all electrons actually present in the irradiated medium while in the energy range T + dT and T. In the 'continuous slowing-down approximation' y(T) is, for one electron, the inverse of its stopping power,[1] i.e. $(dT/dx)^{-1}$. The number of the electrons of kinetic energy T may be calculated if we know the differential cross sections q(T,T') of an electron of kinetic energy T for ionization with production of a secondary electron having kinetic energy T' over a broad range of both T and T'. Successive generations of secondaries must be included in the calculation.

Once y(T) is calculated, the total number, N_s, of primary products of variety s formed in the complete absorption of an incident electron (the kinetic energy T_0) can be determined from:[2]

$$N_s = N \int_{T_s}^{T_0} q_s(T)y(T)dT \qquad (1)$$

Here N is the density of atoms in the medium, $q_s(T)$ is the probability that the product s will be formed in a collision with an electron of kinetic energy T, and T_s is the pertinent threshold energy. The G-value (number of events per 100 eV absorbed) is given by $100N_s/T_0$.

This letter will be confined, for simplicity, to the case of incident electrons with kinetic energy of 100 keV in He at the normal state (1 atm, 0 °C).

The Collision Model

The cross section formulae, used for calculating the stopping power, the slowing-down spectrum, and the total number of primary products, is the one derived by Thomas in 1927$^{3)}$ on the basis of a classical-mechanical treatment of atomic collisions. The approximations involved are:$^{4)}$

(i) the incident electron interacts with only one atomic electron at a time,

(ii) the interaction between the atomic electrons and nucleous can be disregarded during the collision.

In other words, the collision takes place in a region small compared to the atomic dimensions. Thomas considered the case that an electron of the kinetic energy T moves through a cloud of free target electrons moving in random directions with the same kinetic energy as in the atom.$^{3)}$ He gave for the differential cross section for transferring the energy ε to an atomic electron:

$$q_\varepsilon d\varepsilon = \frac{\pi e^4}{T + I + E_K}\left(\frac{1}{\varepsilon^2} + \frac{4E_K}{3\varepsilon^3}\right) d\varepsilon \qquad (2)$$

for $T + I \geq \varepsilon$. Here I is the ionization energy and E_K is the kinetic energy of the target electron. One may further assume$^{5)}$ that excitation of an atom to a level with excitation energy E_n occurs if $E_n \leq \varepsilon \leq E_{n+1}$ where E_{n+1} is the next higher level considered. Ionization would occur if ε is sufficient to remove the electron from the atom. The kinetic energy of the ejected electron is ε - I. These arguments would also apply to exchange excitations, for example triplet excitation of He.$^{6)}$

Results

Stopping power of He for electrons was calculated by integrating Eq. 2 multiplied by ε and N_e over a pertinent range of ε, N_e being the electron density of the medium. For numerical calculations of the slowing-down spectrum and of the total number of excitation and ionization events by way of Eq. 1, the total energy range 100 keV to zero eV is, for convenience, divided into such energy intervals as may be seen from the points on the curves in Fig. 1 or 2, and the integrations are replaced by the summations over the discrete energy intervals. This procedure is similar to that used by Oda and Nishimura.$^{7)}$

The input data used for the calculation are: T_0 = 100 keV, N = 0.269 $\times 10^{20}$ atoms/cm^3, I = 24.6 eV, $E_n(2^1P)$ = 21.2 eV, $E_n(2^3S)$ = 19.8 eV, and E_K = 39.5 eV.

The results are: G(total ionization) = 2.42, G(total singlet excitation) = 0.91, and G(total triplet excitation) = 0.13. The experimental measurements of W-value, the mean energy expended per ion pair, in pure He give G = 2.36 for the ionization.$^{8)}$ When such impurities as Xe, Kr, Ar, or H_2 are exist, the observed ionization yields are increased, e.g. G = 3.54 in the case of Xe as an impurity.$^{8)}$ This is partly due to Jesse effect (ionization of impurities by excited He-atoms) and partly due to ionization by subexcitation electrons.$^{2)}$ A quick estimate of the contribution from the latter was made as follows. The number of such subexcitation electrons as may have the kinetic energy higher than 12.1 eV (the ionization energy of Xe) is obtained from the present calculation. These electrons move through the medium until they collide with the impurity atom (Xe, for the present case) to ionize or else excite it. The ratio of the probabilities for ionization and excitation of Xe may be calculated using Eq. 2. This procedure gives G = 0.17 for the yield of the ionization of Xe by subexcitation electrons in He. Thus, the present method yields G = 2.42 + 0.91 + 0.13 + 0.17 = 3.63 for the total ionization yield in the case of He containing Xe as an impurity. The agreements with available experimental data are thus satisfactory.

Figure 2 illustrates the contributions of different portions of the electron slowing-down spectrum to the primary product yields. The values T × y(T) × $q_s(T)$ are plotted against log T so that the ordinate value is proportional to the yield stemming from that portion of the spectrum. It is noted that the main features of the curves are quite similar to those presented by Platzman.$^{2)}$ He constructed the curves semi-empirically by exploiting several sorts of experimental data on cross-sections and by using stopping power data given by McGinnies (based on the quantum-mechanical calculation) and, in some regions, by extra- or interpolations.

Applications to other atomic and molecular systems are now in progress.

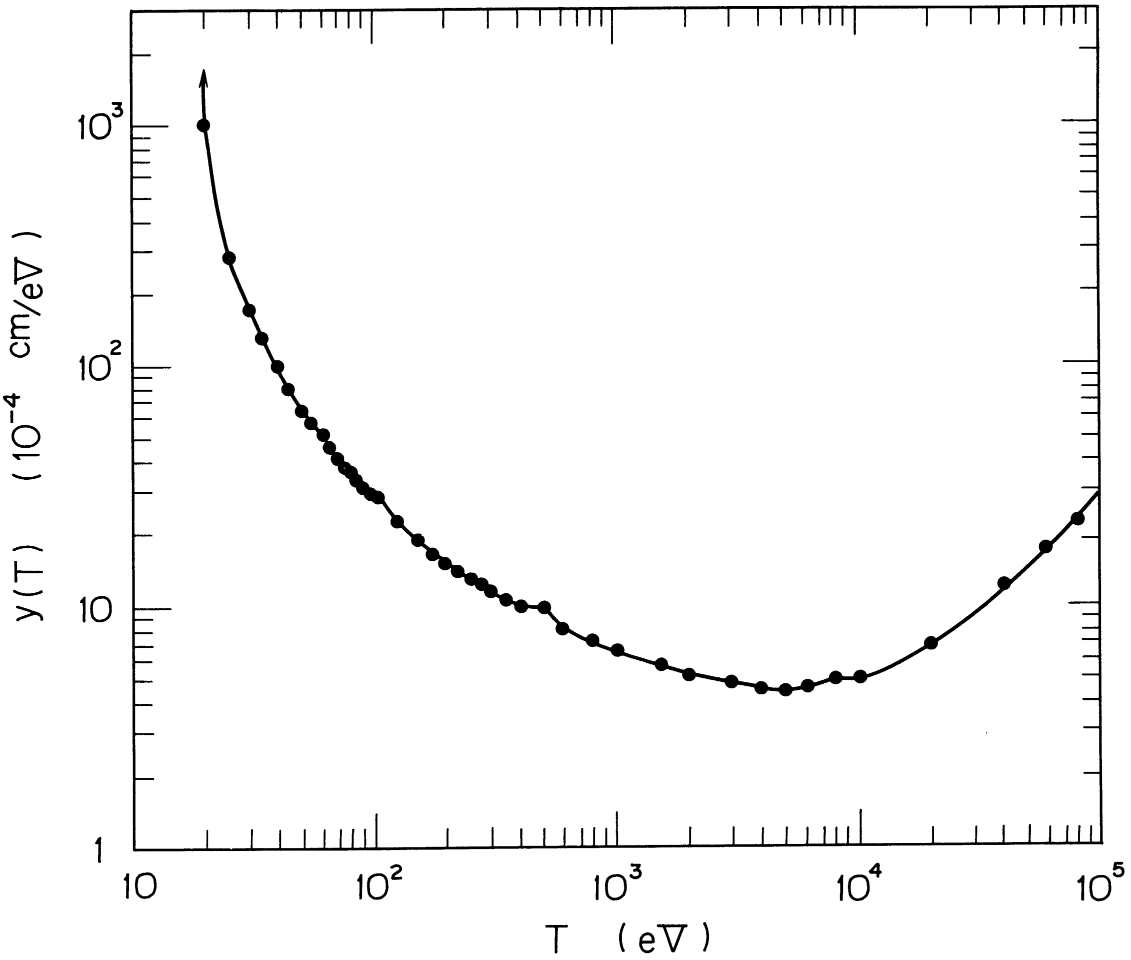

Fig. 1. Slowing-down spectrum for a 100 keV-electron in He (1 atm, 0 °C).

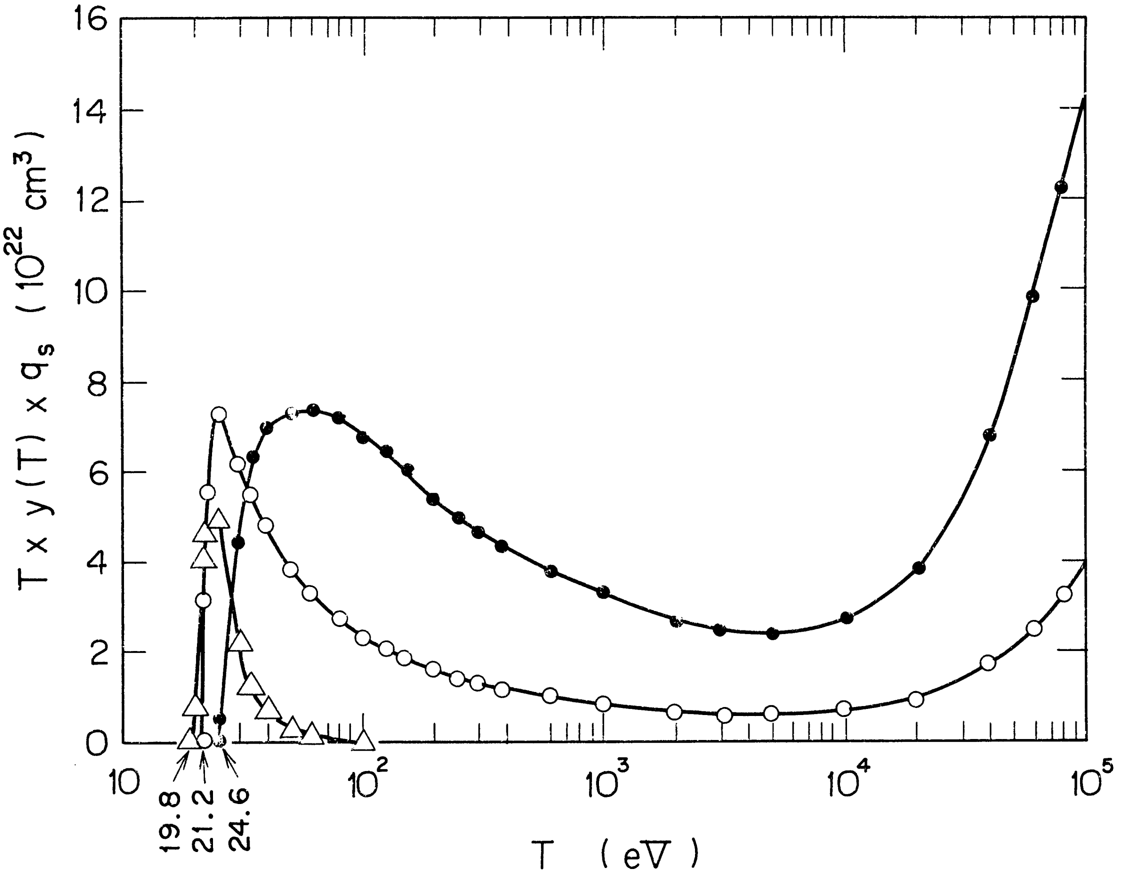

Fig. 2. Contribution of different portions of the electron slowing-down spectrum to the total ionization and excitations: 100 keV-electron in He.
● : Ionization, ○ : Singlet excitation, △ : Triplet excitation.

References

1) L. V. Spencer and U. Fano, Phys. Rev., 93, 1172 (1954).
2) R. L. Platzman, Int. J. Appl. Radiat. Isotopes, 10, 116 (1961).
3) L. H. Thomas, Proc. Camb. Phil. Soc., 23, 829 (1927).
4) L. Vriens, "Case Studies in Atomic Collision Physics I," ed. by E. W. McDaniel et al., North-Holland, Amsterdam(1969), p. 335.
5) M. Gryzinski, Phys. Rev., 115, 374 (1959).
6) L. Vriens, Proc. Phys. Soc., 89, 13 (1966).
7) N. Oda and F. Nishimura, Bull. Tokyo Inst. Techn., 54, 137 (1963).
8) W. P. Jesse and J. Sadaukis, Phys. Rev., 100, 1755 (1955).

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