The Estimation of the *G*-Values for the Ionization and Excitation of Noble Gases Irradiated by 100 keV Electrons

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The binary-encounter collision theory has been applied to the calculation of the *G*-values for the ionization and excitation of noble gases irradiated by 100 keV electrons. The *G*-values obtained were as follows in the order of He, Ne, Ar, Kr, and Xe: 2.27, 2.19, 2.81, 3.20, 3.45 for *G*(electrons), 0.85, 1.55, 1.92, 1.64, 1.51 for *G*(singlet states), and 0.17, 0.07, 0.13, 0.23, 0.39 for *G*(triplet states). The method of the calculation and the significance of the results were discussed.

One of the most attractive and challenging problems for radiation chemists is the non-empirical calculation or prediction of the *G*-values of products from the compounds they are concerned with. Such a calculation, however, has not been carried out except for helium gas, because there are too many unknown factors and not-established procedures. Even if the factors and the procedures are properly approximated, laborious calculations have to be performed. The calculation for helium was carried out by Erskine,[1] Miller,[2] and Platzman.[3] Since then, several calculations for the degradation spectra in a number of media were carried out, and some of the results were compared with the experimental data obtained largely in metallic media.[4] Recently, Alkhazov has recalculated the degradation spectrum of non-relativistic electrons in helium and discussed the yields of ionization and excitations.[5] This calculation may be the most detailed one for helium at present. His method, however, cannot be applied to other compounds, because several experimental values, which are known only for a limited number of gases, are used. From the point of view of radiation chemists, a more general method which is applicable to a variety of compounds is desirable even though the results are less accurate.

One of the present authors has recently shown[6] that, if the binary-encounter collision theory and the procedure for calculating the degradation spectrum of electrons are combined, the *G*-values of ionization and excitations can be calculated for practically all of the molecules. As an example, he showed the calculation for helium and the hydrogen molecule,[7] the results of which were in reasonable agreement with those estimated from the experimental work. This calculation was so laborious when it is applied to more complex atoms that we wrote a program for an electronic computer and carried out the calculations for the noble gases from He to Xe. The present paper will report the details of the calculation and will attempt to ascertain the limitations of this method.

Method of Calculation

Cross Sections for Ionization and Excitations. The most difficult problem in the calculation of the degradation spectrum of a high-energy electron is the accurate formulation of the cross sections for various energy-loss processes, especially when the energy of electrons is lower than 100 eV. However, if the binary-encounter collision theory is assumed to be applicable to any incident electron, the formulation is rather straightforward. Such a formulation has already been summarized by Vriens and reported in detail.[8] For the present purpose, the final expressions will be satisfactory.

According to the symmetrical model for the collision of a high-energy electron with an atomic electron, the energy loss of the incident electron may be estimated by means of the collisional cross section, where we ignore the radiative energy loss:

$$\begin{aligned}\sigma_E &= \sigma_{E,\mathrm{dir}} + \sigma_{E,\mathrm{exc}} \\ &= \frac{\pi e^4}{T+I_i+E_i}\left[\left(\frac{1}{E^2}+\frac{4E_i}{3E^3}\right)\right. \\ &\qquad \left. +\left\{\frac{1}{(T+I_i-E)^2}+\frac{1}{3(T+I_i-E)^3}\right\}\right] \qquad \text{(I)}\end{aligned}$$

for $T+I_i-E \geq 0$. Here, σ_E is the differential cross section per unit of energy for the energy loss (E) of the incident electron with the energy T, while E_i and I_i are, respectively, the average kinetic energy and the binding energy of the atomic electron under consideration. If the atomic electron is in the outermost shell of the atom, I_i is the ionization potential of the atom (I). The first term in the square bracket on the right-hand side of Eq. (I) corresponds to the direct excitation, and the second term, to the excitation induced by the exchange between the incident electron and an atomic electron. In the formulation of Vriens, there is another term, called "interference." This term results from the difference in the scattering angle between the direct and the exchange excitations. In the present calculation, though, we ignore it because the estimation is somewhat arbitrary when it is taken into account in the calculation[9] and because the contribution of this term to the whole calculation is very small, as will be shown later.

By using Eq. (I), we can derive the total ionization cross section per atomic electron:

$$\begin{aligned}Q_{\mathrm{ion}} &= \frac{1}{2}\int_{I_i}^{T}\sigma_E \mathrm{d}E = \int_{I_i}^{(T+I_i)/2}\sigma_E \mathrm{d}E = \int_{I_i}^{T}\sigma_{E,\mathrm{dir}}\mathrm{d}E \\ &= \frac{\pi e^4}{T+I_i+E_i}\left[\left(\frac{1}{I_i}-\frac{1}{T}\right)+\frac{2E_i}{3}\left(\frac{1}{I_i^2}-\frac{1}{T^2}\right)\right] \qquad \text{(II)}\end{aligned}$$

The factor of 1/2 has to be introduced because we cannot distinguish the origin of the scattered electron, whether it is originally the incident electron or the atomic electron.

For the cross sections of excitations, we use the following formula according to the treatment of Vriens.[10)] Here, E_s and E_t are the energies of the lowest singlet and triplet levels respectively:

$$Q_{\mathrm{singl}} = Q_{\mathrm{de}} + \frac{1}{2}Q_{\mathrm{ee}}; \quad Q_{\mathrm{tripl}} = \frac{1}{2}Q'_{\mathrm{ee}} \tag{III}$$

Here,

$$\begin{aligned} Q_{\mathrm{de}} &= \int_{E_s}^{I} \sigma_{\mathrm{E,dir}} \mathrm{d}E \\ &= \frac{\pi e^4}{T+I+E_i}\left[\left(\frac{1}{E_s}-\frac{1}{I}\right)+\frac{2E_i}{3}\left(\frac{1}{E_s^2}-\frac{1}{I^2}\right)\right] \end{aligned}$$

for $T \geq I$, and

$$Q_{\mathrm{de}} = \int_{E_s}^{T} \sigma_{\mathrm{E,dir}} \mathrm{d}E$$

for $I > T \geq E_s$. When $T < E_s$, Q_{de} is set equal to zero.

$$\begin{aligned} Q_{\mathrm{ee}} &= \int_{E_s}^{I} \sigma_{\mathrm{E,exc}} \mathrm{d}E \\ &= \frac{\pi e^4}{T+I+E_i}\left[\left(\frac{1}{T}-\frac{1}{T+I-E_s}\right)\right. \\ &\quad \left. +\frac{2E_i}{3}\left\{\frac{1}{T^2}-\frac{1}{(T+I-E_s)^2}\right\}\right] \end{aligned}$$

for $T \geq I$, and similarly

$$Q_{\mathrm{ee}} = \int_{E_s}^{T} \sigma_{\mathrm{E,exc}} \mathrm{d}E$$

for $I > T \geq E_s$. When $T < E_s$, Q_{ee} is set equal to zero.

$$Q'_{\mathrm{ee}} = \int_{E_t}^{I} \sigma_{\mathrm{E,exc}} \mathrm{d}E$$

for $T > I$ and

$$Q'_{\mathrm{ee}} = \int_{E_t}^{T} \sigma_{\mathrm{E,exc}} \mathrm{d}E$$

for $I > T \geq E_t$. When $T < E_t$, Q'_{ee} is set equal to zero. These equations are very tentative, as Vriens has already mentioned, and should be replaced by better equations when they become available.

Stopping Power. In the present paper, we consider the energy loss resulting in the atomic excitation or ionization. Therefore, the stopping power of the medium which consists of a single kind of atom may be expressed as follows:

$$S(T) = N\left\{\sum_i n_i \int_{I_i}^{(T+I_i)/2} E\sigma_{\mathrm{E}} \mathrm{d}E + n\left(\int_{E_s}^{I} E\sigma_{\mathrm{E}} \mathrm{d}E + \frac{1}{2}\int_{E_t}^{E_s} E\sigma_{\mathrm{E,exc}} \mathrm{d}E\right)\right\} \tag{IV}$$

for $T \geq I$. Here, $S(T)$ is the stopping power, N is the number of atoms in a unit volume, n_i is the number of electrons in the i-th shell, and n is the number of electrons in the outermost shell. When the energy of the incident electron is smaller than I, the first term in Eq. (IV) disappears and the upper limit of the second integral should be replaced by T. Similarly, when $T < E_s$, the first and second terms dissappear and the E_s in the third integral should be replaced by T.

Degradation Spectrum. When a high-energy electron with the energy of T_0 passes through a medium, various types of ionizations take place and secondary electrons are ejected, the energies ranging from zero to $T_0 - I$. If the kinetic energy of the secondary electrons thus produced is higher than I, they will induce another ionization. From the point of view of the medium, there is a spectrum of the electrons which have a wide range of kinetic energies. Such a spectrum is called a degradation spectrum. Spencer and Fano may have been the first to discuss the quantitative method for the calculation of the degradation spectrum.[11)] Schneider and Cormack also investigated the method and performed the calculation for helium.[12)] This method was used by Oda and Nishimura to obtain the degradation spectrum produced by ^{60}Co-γ rays in water.[13)] Klots and Wright have also carried out the calculation on a simple atomic model and investigated the assumption of the continuous slowing-down which is involved in the calculation.[14)] The method used here is essentially the same as that used by Oda and Nishimura.

On the assumption of a continuous slowing-down, the degradation spectrum of the incident electron may be expressed in this form:

$$y_1(T) = 1/S(T) \tag{V}$$

On the way to the formation of this spectrum, the secondary electrons are ejected. To describe the degradation spectrum of these secondary electrons, it is more convenient to modify the differential cross section of ionization as follows:

$$\begin{aligned} \sigma(T_1 T_2) = \frac{\pi e^4}{T_1+I_i+E_i}&\left\{\left(\frac{1}{(T_2+I_i)^2}+\frac{4E_i}{3(T_2+I_i)^3}\right)\right. \\ &\left.+\left(\frac{1}{(T_1-T_2)^2}+\frac{4E_i}{3(T_1-T_2)^3}\right)\right\} \end{aligned} \tag{VI}$$

Here, $\sigma(T_1 T_2)$ is the differential cross section for the production of the secondary electron with the energy of T_2 in the collision between the incident electron with the energy of T_1 and an atomic electron in the i-th shell. Therefore, the degradation spectrum of the secondary electrons may be expressed in this form:

$$y_2(T) = \frac{N}{S(T)}\sum_i n_i \int_T^{1/2(T_0-I_i)} \int_{2T_2+I_i}^{T_0} y_1(T_1)\sigma(T_1 T_2) \mathrm{d}T_1 \mathrm{d}T_2 \tag{VII}$$

Here, the upper limit of the first integral, $1/2(T_0 - I_i)$, comes from the fact that the electrons having energies higher than this value are counted as primary. Similarly, the degradation spectrum of tertiary electrons is expressed as follows:

$$y_3(T) = \frac{N}{S(T)}\sum_i n_i \int_T^{1/4(T_0-3I_i)} \int_{2T_2+I_i}^{1/2(T_0-I_i)} y_2(T_1)\sigma(T_1 T_2) \mathrm{d}T_1 \mathrm{d}T_2 \tag{VIII}$$

Similar equations may be constructed for the electrons ejected in the later steps.

The total degradation spectrum is obviously the sum of the above spectra:

$$y(T) = \sum y_m(T) \tag{IX}$$

In the actual calculation, this series rapidly converges, and the sum of the first five terms is probably accurate enough, but in the following calculation we took the sum of the six terms.

G-*Values of Excitation and Ionization.* Once $y(T)$ is obtained, the calculation of the yields of excitation and ionization per incident electron is straightforward if we use the total cross section for each process:

$$N_s = Nn_i\int_{T_s}^{T_0} y(T)\cdot Q_s(T)\mathrm{d}T \qquad \text{(X)}$$

$$= Nn_i\int_{T_s}^{T_0} T\cdot y(T)\cdot Q_s(T)\mathrm{d}\ln T \qquad \text{(XI)}$$

Here, N_s is the number of the species produced in the s process, T_s is the threshold energy of the incident electron for the s process, and $Q_s(T)$ is the total cross section. According to the expression used by Platzman,[3] the results thus obtained can be shown, as they will be later, in the $T\cdot y(T)\cdot Q_s(T)$ *vs.* ln T plots, so that the area under the curve of $T\cdot y(T)\cdot Q_s(T)$ is proportional to the yield of the s process. Thus, we can estimate the G-values of each process by means of the equation:

$$G_s = \frac{100N_s}{T_0} \qquad \text{(XII)}$$

Constants Used for Calculation

In order to carry out the calculation, we have to know the constants which appear in the equations, the singlet and triplet excitation energies of the atom under consideration (E_s and E_t), the binding energies of the atomic electrons (I_i),[15] and their kinetic energies (E_i). Tables 1 and 2 summarize the values of E_s, E_t, and I_i used. The minimum I_i value for an atom is the ionization potential of the atom, for which the spectroscopic values may be better than those obtained by the technique of ESCA using X-rays.

Table 1. The lowest singlet and triplet levels (eV)

Atom	E_s	E_t
He	21.2	19.8
Ne	16.8	16.7
Ar	11.8	11.6
Kr	10.6	10.0
Xe	9.6	8.5

Table 2. The binding energy of electron, I_i (eV)

Shell	He	Ne	Ar	Kr	Xe
1s	24.581	867	3203	14326	34561
2s		45	320	1921	5453
2p		21.559	246	1701	4943
3s			25	289	1145
3p			15.755	219	968
3d				89	679
4s				24	208
4p				13.996	147
4d					63
5s					18
5p					12.127

Table 3. The kinetic energy of electron, E_i (eV)

Shell	He	Ne	Ar	Kr	Xe
1s	38.74	1265	4169	16884	38090
2s		37.59	169.6	789.9	1796
2p		112.8	667.3	3492	8445
3s			18.19	133.7	383.1
3p			32.27	294.5	897.2
3d				643.0	2412
4s				15.55	83.11
4p				23.18	151.3
4d					232.7
5s					12.29
5p					16.75
Total kinetic energy					
	77.48	3282	12911	64934	164238
−(Total energy)[a]					
	77.00	3456	14217	74211	195223

a) Ref. 16 and 17

Since we have no experimental data for E_i, we have to calculate them. For the noble gases from He to Kr[16] and later for Xe and Rn atoms,[17] Hartree-Fock SCF wave functions based on the single zeta Slater-type function for each electron have been reported. The value of E_i, therefore, may be calculated by using this equation:

$$E_i = -\frac{1}{2}\int \psi_i \nabla^{*2} \psi_i \mathrm{d}\tau \qquad \text{(XIII)}$$

Table 3 summarizes the calculated values. According to the virial theorem, the total kinetic energy should be equal to the −(total energy) of the atom. The calculated total kinetic energy and the total energy reported[16,17] are compared in Table 3. The agreement is satisfactory for the present calculation.

Results

Figures 1 and 2 show the $y(T)$ and $T\cdot y(T)\cdot Q_s(T)$ *vs.* ln T plots obtained with helium. Figure 2 is very similar to that presented by Platzman.[3]

Table 4 summarizes all of the G-values obtained in the present calculation. All the integrations were carried out by means of a computer, HITAC 8700, with a mesh of $(0.5)^{1/40}$ for the energy. With the increase in mesh, the G-values obtained decreased slightly. In the case of He, the G-value of ionization obtained with the mesh of $(0.5)^{1/80}$ was 2.26; this value agreed within 0.3% with the G-value listed in Table 4.

As has been stated in the previous section, a calculation including the interference term in the cross section

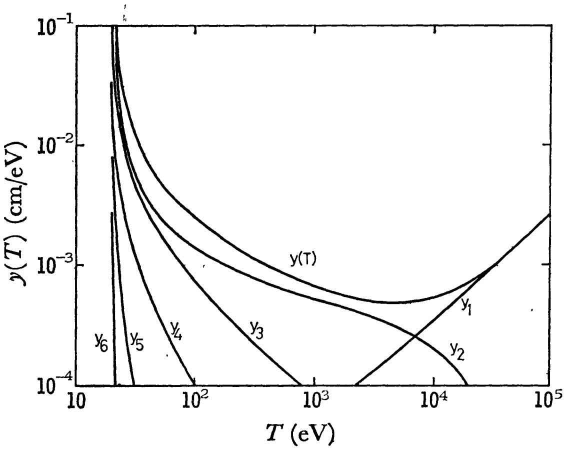

Fig. 1. Slowing-down spectrum in He.

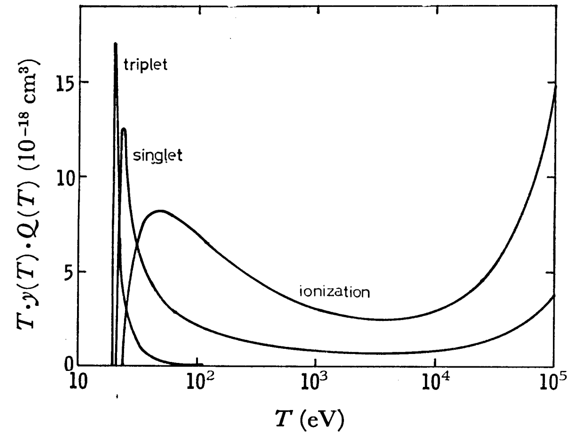

Fig. 2. Contribution of different portions of the electron slowing-down spectrum to the ionization and excitation in He.

Table 4. The G-values of excitations and ionizations

	He	Ne	Ar	Kr	Xe
Excitation					
singlet	0.85	1.55	1.92	1.64	1.51
triplet	0.17	0.07	0.13	0.23	0.39
Ionization					
shell					
1s	2.27	0.0038	0.00062	0.000031	0.0000043
2s		0.100	0.0081	0.00040	0.000086
2p		2.06	0.065	0.0024	0.00048
3s			0.25	0.0042	0.00066
3p			2.19	0.025	0.0032
3d				0.35	0.016
4s				0.17	0.0061
4p				1.78	0.038
4d					0.37
5s					0.27
5p					2.03

was also carried out. The G-value of ionization in He was 2.25. The difference from the G-value listed in Table 4 is within 1%.

The degradation spectra in Ne, Ar, Kr, and Xe are shown in Fig. 3. All of the spectra are alike, though there are small differences in the energy region lower than 100 eV. This difference might play an important role in a radiation-induced chemical reaction when these gases are used as the solvents.

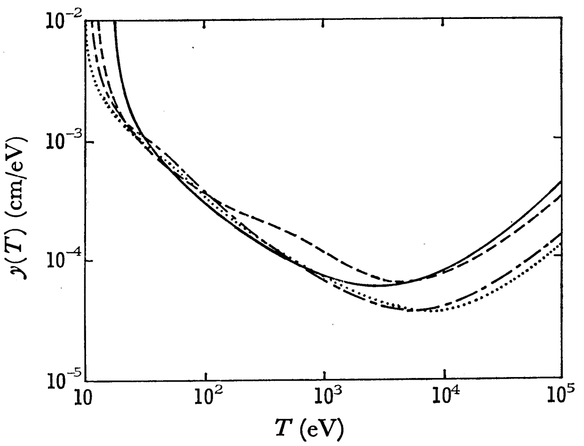

Fig. 3. Slowing-down spectra in Ne (——), Ar (– – –), Kr (-·-·-), and Xe (······).

Figures 4 to 7 show the $T \cdot y(T) \cdot Q_i(T)$ *vs.* ln T plots for Ne, Ar, Kr, and Xe. They clearly show that the

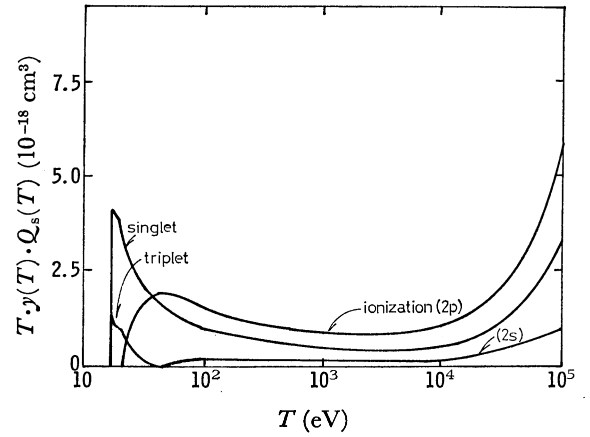

Fig. 4. Contribution of different portions of the electon slowing-down spectrum to the ionization and excitation in Ne.

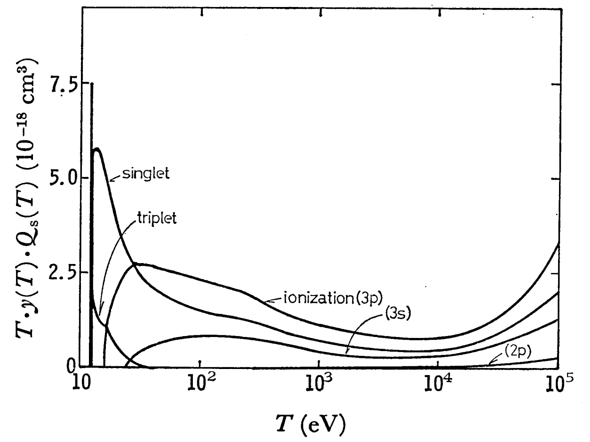

Fig. 5. Contribution of different portions of the electron slowing-down spectrum to the ionization and excitation in Ar.

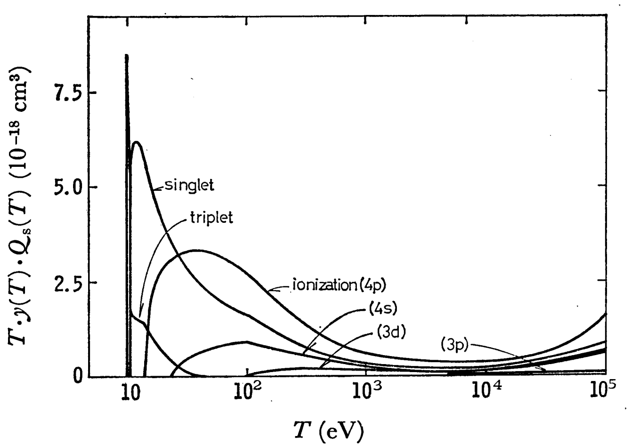

Fig. 6. Contribution of different portions of the electron slowing-down spectrum to the ionization and excitation in Kr.

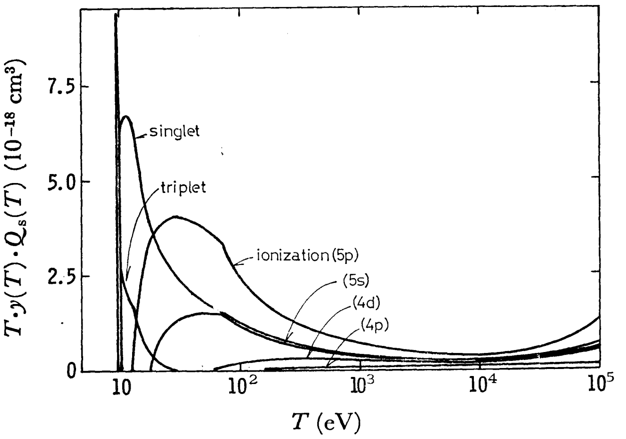

Fig. 7. Contribution of different portions of the electron slowing-down spectrum to the ionization and excitation in Xe.

ionizations from the inner shells become more important with an increase in the atomic number. Consequently, in order to estimate the G-values of electrons, we have to consider the Auger effect. For example, an excited Ar ion with the ejection of the 2p electron has energy enough for the auto-ionization:

$$\mathrm{Ar^+(2p)} \longrightarrow \mathrm{Ar^{5+}} + 4\mathrm{e^-} \qquad (1)$$

To calculate the total G-value of electrons, the ionization from the 2p shell in Ar should be taken as corresponding to 5e$^-$. Here, the yield of the fluorescence, which is often observed with the Auger effect, is ignored. For such a calculation, we need exact data for the multiple-ionizations of the noble gases. Most of the data we need are not available. Therefore, the G-values of electrons were estimated by using a tentative equation:

$$G(\mathrm{e^-}) = \sum_i f_i G_i(\mathrm{M^+}) \qquad \text{(XIV)}$$

Here, f_i is the largest integer which satisfies the equation:

$$I_i/I \geq \sum_{x=1}^{f_i} x \qquad \text{(XV)}^{18)}$$

and $G_i(\mathrm{M^+})$ is the G-value of the M$^+$(i-th shell) ion. Table 5 shows the results, together with the W-values calculated from the G-values and the W-values reported previously.[3,5] We believe that the agreement is satisfactory.

It may be worthwhile to notice here that the G-values of the electrons calculated here do not contain any contribution from the Hornbeck-Molnar process:[19]

$$\mathrm{M^* + M \longrightarrow M_2^+ + e^-} \qquad (2)$$

Here, M* represents the excited state of a noble gas.

TABLE 5. THE G-VALUES OF ELECTRONS AND THE W-VALUES OBTAINED THEORETICALLY AND EXPERIMENTALLY

Atom	Theoretical			
	present work		others	Experimental[3]
	G_e	W	W	W
He	2.27	44.05	46.5[2] 46.45±1.0[5]	42.3
Ne	2.19	45.66		36.3
Ar	2.81	35.59		26.4
Kr	3.20	31.25		24.2
Xe	3.45	28.99		22.0

Discussion

For fast collisions ($T \geq 10^4$ eV), it is well known that the binary-encounter collision theory is an approximation to the Bethe theory,[8,20] because the model used for the binary-encounter collision theory can deal only with close collisions, not with distant collisions. However, since the energy distribution of secondary electrons is mainly determined by the close collisions, the binary-encounter collision theory may not be a bad approximation for the estimation of the degradation spectrum. On the other hand, the Bethe theory, although it is a quantum mechanical treatment, cannot properly estimate the close collisions within the Born approximation. Moreover, special treatment has to be applied to take the exchange effect into account.[20]

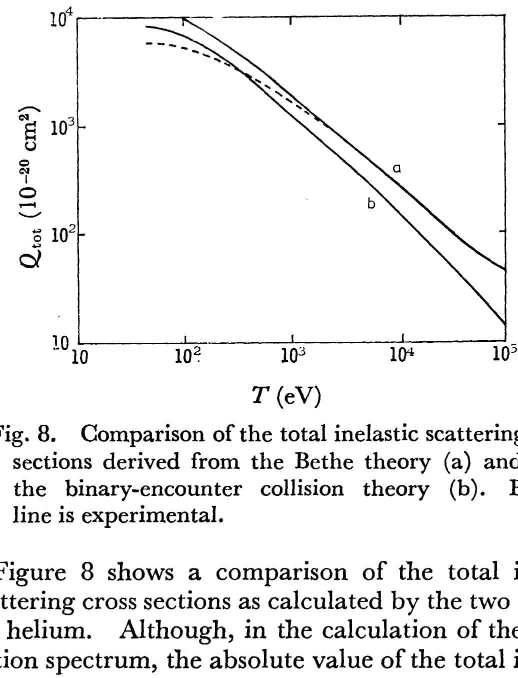

Fig. 8. Comparison of the total inelastic scattering cross sections derived from the Bethe theory (a) and from the binary-encounter collision theory (b). Broken line is experimental.

Figure 8 shows a comparison of the total inelastic scattering cross sections as calculated by the two theories for helium. Although, in the calculation of the degradation spectrum, the absolute value of the total inelastic scattering cross section does not directly affect the final result, the comparison of these values may be worthwhile in order to compare the two theories.

The a curve in Fig. 8 was drawn by using the Bethe asymptotic cross section theoretically estimated by Inokuti *et al.*:[21]

$$Q_{\mathrm{tot}} = \frac{1}{\beta^2}\left\{1.410\left[\ln\left(\frac{\beta^2}{1-\beta^2}\right)-\beta^2\right]+15.118\right\}\times 10^{-20}\,\mathrm{cm}^2 \qquad \text{(XVI)}$$

Here, β is the ratio of the velocity of the incident electron and the velocity of light. The b curve was drawn by means of the equation used for the present calculation:

$$Q_{\mathrm{tot}} = \sum_i n_i Q_{\mathrm{ion}} + n(Q_{\mathrm{singl}} + Q_{\mathrm{tripl}}) \qquad \text{(XVII)}$$

Obviously, the present method underestimates the cross sections, especially at higher energies. On the other hand, the Bethe asymptotic cross section deviates from the experimental value at lower energies of the incident electron and gives too high values.[22] The total inelastic scattering cross section obtained by the binary-encounter collision theory seems to compensate itself between higher energies and lower energies.

For noble gases other than He and Ne,[23] no theoretical cross sections are obtained by the Bethe theory. However, experimental values for 0.1—2.7 MeV electrons have been reported in the forms of M^2 and C in the following equation:[24]

$$Q = 4\pi\left(\frac{\hbar}{mc}\right)^2(M^2x_1+Cx_2) \qquad \text{(XVIII)}$$

Here, $4\pi(\hbar/mc)^2 = 1.874\times10^{-20}$ cm^2 and

$$x_1 = \beta^{-2}\ln[\beta^2/(1-\beta^2)]-1,\quad x_2 = \beta^{-2}$$

Table 6. Comparison of the binary-encounter collision theory with the experiment in the total inelastic scattering cross section of electrons at the energy of 10^5 eV

Atom	$Q_{\text{tot}}\times10^{20}$cm^2 calculated	$Q_{\text{tot}}\times10^{20}$cm^2 experimental
He	13.62	45.09
Ne	132.0	107.6
Ar	106.2	225.3
Kr	145.2	305.9
Xe	143.6	433.5

In Table 6, the total inelastic scattering cross sections of the electrons at the energy of 10^5 eV as calculated by the binary-encounter collision theory are compared with the experimental values. Obviously, most of the cross sections calculated are smaller than the experimental values. In the case of Ne, though, the binary-encounter collision theory predicted a cross section larger than the experimental value. This anomaly seems to result from the overestimation of $E_i(2p)$. The discrepancy in the cross section shown in Table 6 as an example may be one of the most serious shortcomings of the present calculation, although this discrepancy is not directly reflected in the final *G*-values.

Table 7. The ratios of the *G*-value of excitation and the *G*-value of electrons

Atom	$G_{\text{exc}}/G(\text{e}^-)$
He	0.45
Ne	0.74
Ar	0.73
Kr	0.59
Xe	0.55

We believe that the *G*-values of ionization, at least the relative values of each process, shown in Table 4 are reliable; however, the *G*-values of excitations are much less reliable. Platzman assumed $G_{\text{exc}}/G(\text{e}^-)=0.4$ for all noble gases.[3] The ratios calculated by the present method are listed in Table 7. The reliability of these ratios may be discussed in comparison with the experimental data for the mixture of noble gases, in which such Penning ionization as:

$$\text{He}^* + \text{Ar} \longrightarrow \text{He} + \text{Ar}^+ + \text{e}^- \qquad (3)$$

occur. Such data, however, are not abundant. By using the α particles from ^{239}Pu as the exciting source. Klots measured the *W*-values of a mixture of two noble gases. From his data,[25] the *G*-values of the excited states of He and Ne can be estimated; they are shown in Table 8. The calculated *G*-values of excitations are not so bad as had been expected.

Table 8. The sum of $G(\text{e}^-)$ and G_{exc}. Comparison with the value calculated from Klots' data

Atom	present	Klots' data
He	3.29	3.50∼3.66
Ne	3.81	3.98∼4.01

In conclusion, we would like to summarize two of our conclusions of the present calculation, points which are often overlooked by experimental radiation chemists, including us: 1) the ionization from inner shells cannot be ignored even in the molecules composed of atoms with low atomic numbers, and 2) the yields of the forbidden states, the triplet states in the present calculation, are very much dependent upon the $y(T)$ at low energies; *i.e.*, the yield greatly depends on the solvent in which the chemical reactions are taking place.

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