Degradation Spectra and the *G*-values for Ionization and Excitation of the Mixtures of Noble Gases

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Degradation spectra of electrons and the *W*-values in the mixtures of He–Ne, He–Ar, Ne–Ar, and Ne–Kr irradiated by 100 keV electrons have been calculated by using the binary-encounter theory and the theory of the degradation spectrum. On the basis of these calculations, the Jesse effect, the negative Jesse effect, and the non-metastable Penning effect have been reconsidered. It was shown that at least a part of the negative Jesse effect and the non-metastable Penning effect are explicable as due to the degradation spectra of electrons.

The yield of electrons in a binary mixture of noble gases irradiated by charged particles has been measured by several investigators. In some cases, a drastic change in the yield with the change of mixing ratio has been found. In 1952 Jesse and Sadauskis found that the yield of electrons, G_e, in helium is increased remarkably by the addition of a very small amount (~0.01%) of argon (the Jesse effect).[1] They attributed this increase to the well-known metastable Penning ionization. Hurst and his co-workers also found that the yield of electrons in argon is increased after the addition of foreign gases.[2] In order to explain this increase, they considered not only the metastable Penning ionization but also the resonance state Penning ionization which occurs through photon imprisonment. Kubota measured the yield of electrons in a helium–neon mixture, in which the metastable Penning ionization cannot energetically occur; however, he obtained a positive deviation as if the Penning ionization were occurring.[3] He attributed this deviation to the non-metastable Penning ionization. Klots observed an extraordinary behavior of the yield of electrons in the mixtures of Ne–Ar, Ne–Kr, and He–CH_4.[4] For example, when krypton is added to neon, the yield of electrons rapidly increases to a high value symptomatic of the Jesse effect, but then plummets to a minimum before finally climbing up again to the value characteristic of pure krypton (the negative Jesse effect). He interpreted this phenomenon in terms of the Hornbeck-Molnar process and some process competing with it. In this manner, the variation of the yield of electrons with the change of components in binary mixtures has been interpreted in terms of the metastable, resonance state, and non-metastable Penning ionizations and also of the Hornbeck-Molnar process. There is definite evidence for the metastable Penning ionization,[5,6] but no explicit evidence exists for the non-metastable Penning ionization and for the quenching of the Hornbeck-Molnar process.

Previously, we estimated the *G*-values for ionizations and excitations of pure noble gases irradiated by 100 keV electrons by a combination of the binary encounter collision theory and the theory of degradation spectrum.[7–11] The calculated *G*-values of electrons in pure noble gases are in fair accordance with the experimental values obtained by considering the double collision and the inner shell excitation. In that paper, we predicted that the yields for ionizations and excitations in the mixture greatly depend on the components, because the degradation spectra of electrons are quite dependent upon the type of noble gas.

In this paper, we apply the calculating method to estimate the *G*-values for ionizations in the mixtures of noble gases irradiated by 100 keV electrons and investigate the effect of the degradation spectra on the change of the yields of ionizations and excitations. We choose the mixtures of He–Ne, He–Ar, Ne–Ar, and Ne–Kr, because in these mixtures drastic changes of the *G*-values of electrons have been reported.

Method of Calculation

We consider a mixture of A and B gases. The basic procedure for the calculation on the mixture is analogous to that of a pure gas. The equations of the differential cross section, $\sigma_E\ (T)$, and of the cross section for ionization and excitation, $Q_s\ (T)$, are the same as those shown in the previous papers.[7,8] The cross sections for the double collisions and the inner shell excitations are also the same as those shown previously.[8]

Stopping Power. First we calculate the stopping power of the pure A gas, $S_A\ (T)$, and that of the pure B gas, $S_B\ (T)$, by use of the equation described previously.[7] Then, the stopping power of A–B mixture, $S_m\ (T)$, may be described as the combination of $S_A\ (T)$ and $S_B\ (T)$:

$$S_m(T) = \frac{p_A}{p_A+p_B}S_A(T) + \frac{p_B}{p_A+p_B}S_B(T) \tag{I}$$

for $T \geq E_{t,A}$. Here, $E_{t,A}$ is the energy of the lowest excited triplet state of the A gas and $E_{t,A} > E_{t,B}$ is assumed. $E_{t,B}$ is the energy of the lowest excited triplet state of the B gas. p_A and p_B are the partial pressures of each component. Equation (I) holds only in the energy range where both A- and B-components can contribute to the energy loss of the incident electron.

When the energy of the incident electrons is lower than $E_{t,A}$, the A-component cannot contribute to the energy loss and only the B-component participates in the energy loss of the electrons. That is, when $E_{t,B} \leq T < E_{t,A}$, the first term of the right-hand side of Eq. (I) disappears; when $T < E_{t,B}$, both terms disappear.

Degradation Spectrum. On the assumption of a continuous slowing down, the degradation spectrum of the incident electron in the mixture may be expressed in a manner similar to that described previously:[7]

$$y_1(T) = 1/S_m(T) \tag{II}$$

The degradation spectrum of the secondary electrons consists of two terms, which correspond respectively to the ionizations of the A- and B-components.

$$y_2(T) = \frac{p_A}{p_A+p_B}\frac{N}{S_m(T)}\sum_i n_{i,A}\int_T^{(T_0-I_{i,A})/2}\int_{2T_2+I_{i,A}}^{T_0} \times y_1(T_1)\sigma_A(T_1, T_2)dT_1dT_2 + \frac{p_B}{p_A+p_B}\frac{N}{S_m(T)}\sum_i n_{i,B}\int_T^{(T_0-I_{i,B})/2}\int_{2T_2+I_{i,B}}^{T_0} \times y_1(T_1)\sigma_B(T_1, T_2)dT_1dT_2 \qquad \text{(III)}$$

Here, N is the number of atoms in a unit volume, n_i is the number of electrons in the i-th shell, T_0 is the energy of the incident electrons, I_i is the binding energy of the electron in the i-th shell, and σ (T_1, T_2) is the differential cross section for the production of a secondary electron with the energy of T_2 in a collision between the atomic electron in the i-th shell and the incident electron with the energy of T_1. The suffixes A and B correspond to A- and B-components. Similar equations may be constructed for the electrons ejected in the later steps.

The total degradation spectrum, y (T), is the sum of the above spectra:

$$y(T) = \sum_k y_k(T) \qquad \text{(IV)}$$

The y (T) thus obtained contains the electrons produced in the ionization of the B-component in the collision with the electrons ejected from the A-component and *vice versa.*

Once y (T) is obtained, the yields of ionizations and excitations can be calculated by using the following equation:

$$N_s = \int_{T_s}^{T_0} Ty(T)Q_s(T)d\ln T \qquad \text{(V)}$$

$$G_s = 100N_s/T_0 \qquad \text{(VI)}$$

Here, N_s is the number of species produced in the s-process, T_s is the threshold energy for the s-process and G_s is the G-value of s-process.

The constants used for the calculation are the same as those reported in the previous paper.[7,8)]

Results

He–Ne Mixture. Figure 1 shows the component dependence of y (T) in the helium–neon mixture under a constant total pressure (1 atm). The y (T) in pure helium is completely separated from those calculated for the mixtures in the whole energy range.

In order to investigate the effect of the change of y (T) on the yield of ionization, the $T\,y(T)$ $Q_s(T)$'s for the ionization of helium and for that of neon are plotted as a function of ln T in Figs. 2A and 2B, respectively. The Ty(T) $Q_s(T)$ for helium in the 1:1 mixture is about 0.13 times that in pure helium, while that for neon is about 0.91 times that in pure neon; *i.e.*, the changes in the ionization yield do not compensate with each other.

Figures 3A and 3B show the G-values for the ionizations and excitations of helium and neon as a function of the parameter Z. This parameter was used by Kubota and equals the ratio of $p_{Ne}/(p_{Ne}+0.316\ p_{He})$.[3)] p_{Ne} and p_{He} are the partial pressures of neon and helium, and 0.316 is the ratio of the stopping powers of the two gases. As Fig. 3A shows, the decreasing curve of the G-value for the ionization of helium is concave, while the increasing curve for neon is convex, and the total G-values of ionization do not lie on a straight line. In this figure, the energy exchange between Ne and He is not taken into account.

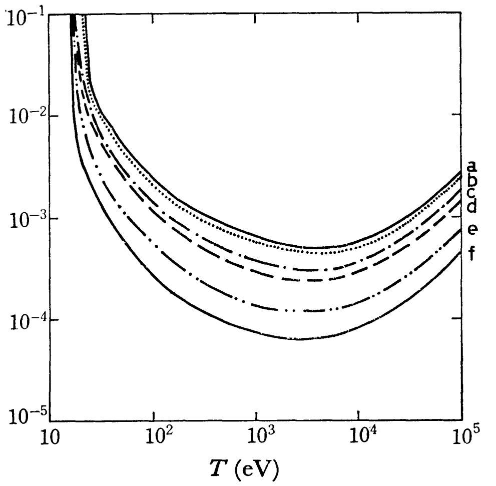

Fig. 1. The component dependence of $y(T)$ in the He–Ne mixture as a function of ln T.
a, $p_{Ne}/(p_{He}+p_{Ne})=0$; b, 0.038; c, 0.096; d, 0.162; e, 0.473; f, 1.0.

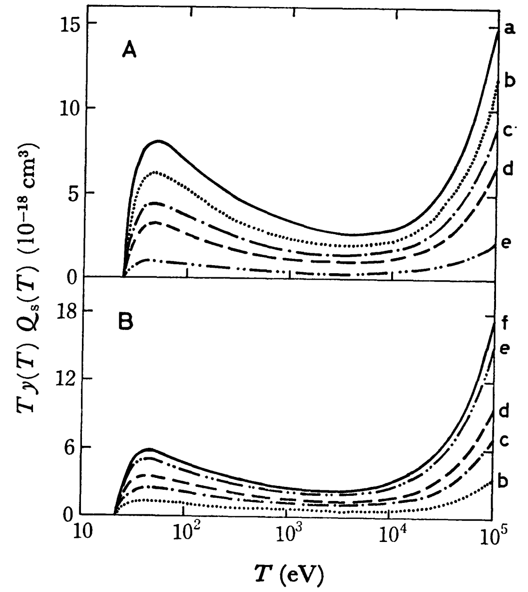

Fig. 2. The component dependence of $Ty(T)$ $Q_s(T)$ in the He–Ne mixture as a function of ln T.
A, ionization of He; B, ionization of Ne from the 2p shell.
a, $p_{Ne}/(p_{He}+p_{Ne})=0$; b, 0.038; c, 0.096; d, 0.162; e, 0.473; f, 1.0.

He–Ar Mixture. Figure 4 shows $y(T)$'s for the helium–argon mixtures. The curves are similar to those for the helium–neon mixtures shown in Fig. 1. Figures 5A and 5B show the component dependence of the $Ty(T)$ $Q_s(T)$'s for the ionization of helium and for that of argon from the 3p shell. The $Ty(T)$ $Q_s(T)$ for helium decreases smoothly with a decrease in the partial pressure of helium, while the $Ty(T)$ $Q_s(T)$ for argon behaves strangely in the electron energy range below

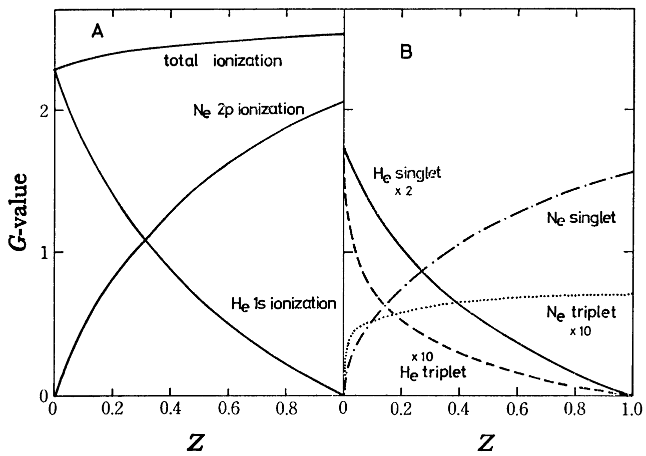

Fig. 3. The G-values for the ionizations and excitations of He and Ne in the He–Ne mixture as a function of Z. A, Ionization; B, excitation.

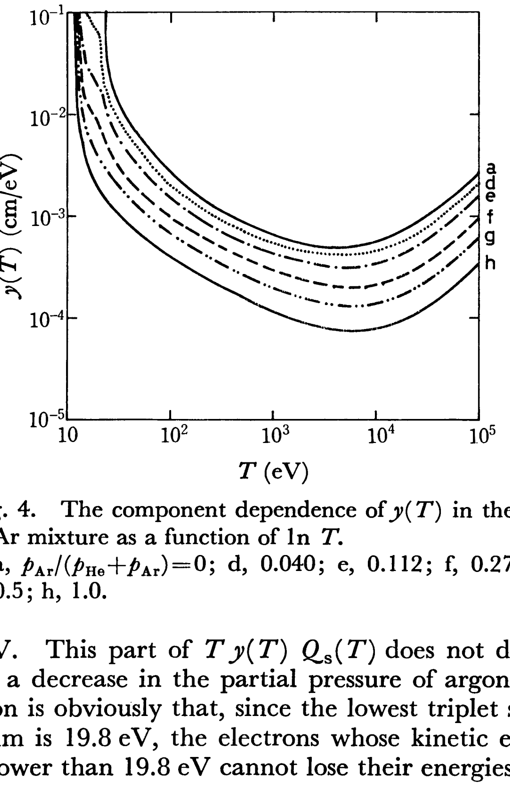

Fig. 4. The component dependence of $y(T)$ in the He–Ar mixture as a function of ln T.
a, $p_{Ar}/(p_{He}+p_{Ar})=0$; d, 0.040; e, 0.112; f, 0.274; g, 0.5; h, 1.0.

20 eV. This part of $Ty(T)$ $Q_s(T)$ does not decrease with a decrease in the partial pressure of argon. The reason is obviously that, since the lowest triplet state of helium is 19.8 eV, the electrons whose kinetic energies are lower than 19.8 eV cannot lose their energies in the collision with helium, but lose their energies only in the collision with argon.

Figures 6A and 6B show the G-values for ionizations and excitations of each component as a function of the parameter Z. This parameter equals 2.79 $p_{Ar}/(2.79 p_{Ar}+p_{He})$. Here, 2.79 is the ratio of the stopping powers of two gases in the treatment of Klots.[4] It is characteristic in Fig. 6B that the G-value for the triplet excitation of Ar in the mixture with helium is larger than that in pure argon. In this mixture, we must also consider the Penning ionization, which will be discussed later.

Ne–Ar Mixture. Figure 7 shows the component dependence of $y(T)$ in the neon–argon mixture. It is noticeable that the curves for $y(T)$ intersect at two points, where the energies of electrons are 56 and 10^4 eV.

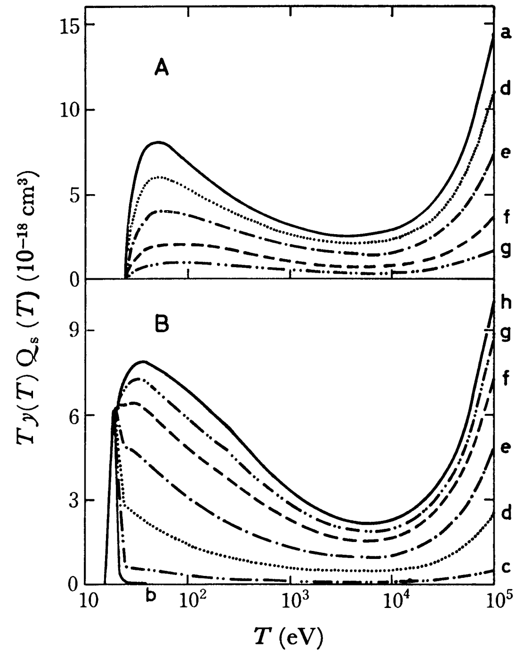

Fig. 5. The component dependence of $Ty(T)Q_s(T)$ in the He–Ar mixture as a function of ln T.
A, Ionization of He; B, ionization of Ar from the 3p shell.
a, $p_{Ar}/(p_{He}+p_{Ar})=0$; b, 0.001; c, 0.007; d, 0.040; e, 0.112; f, 0.274; g, 0.5; h, 1.0.

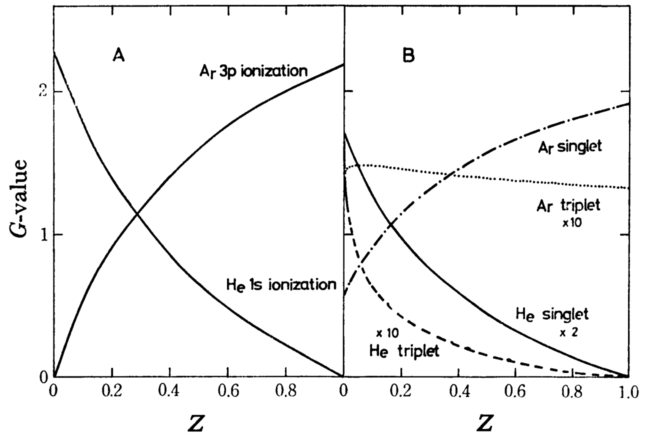

Fig. 6. The G-values for the ionizations and excitations of He and Ar in the He–Ar mixture as a function of Z. A, Ionization; B, excitation.

Such crossings were not obtained in the mixtures of helium–neon and helium–argon.

Figure 8 shows the component dependence of the T $y(T)$ $Q_s(T)$ for the ionization of argon from the 3p shell. There is a non-decreasing part at about 20 eV with the decrease in the partial pressure of argon. This is similar to the $Ty(T)$ $Q_s(T)$ for the ionization of argon in the He–Ar mixture.

Figures 9A and 9B show the G-values for the ionizations and excitations of each component. Here the parameter $Z=p_{Ar}/(p_{Ar}+0.75\,p_{Ne})$ is used as the abscissa, according to the treatment of Klots.[4] It is noticeable in Fig. 9A that the tendency of the change of the G-values for the ionizations in the Ne–Ar mixture is oppo-

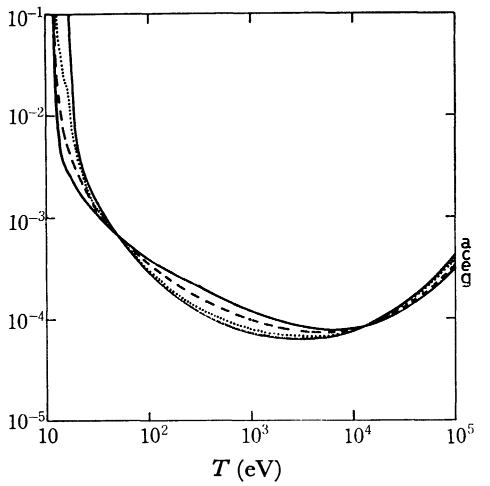

Fig. 7. The component dependence of $y(T)$ in the Ne–Ar mixture as a function of ln T.
a, $p_{Ar}/(p_{Ne}+p_{Ar})=0$; c, 0.165; e, 0.543; g, 1.0.

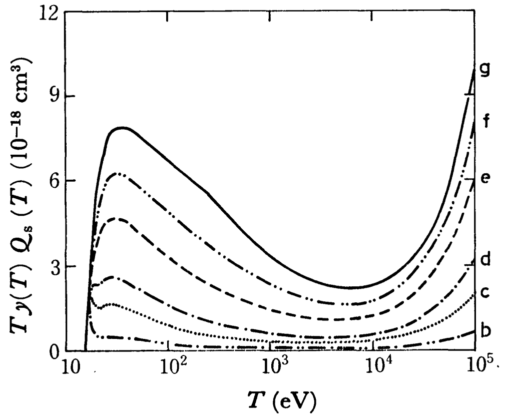

Fig. 8. The component dependence of $Ty(T)\ Q_s(T)$ for the ionization of Ar from the 3p shell in the Ne–Ar mixture as a function of ln T.
b, $p_{Ar}/(p_{Ne}+p_{Ar})=0.05$; C, 0.165; d, 0.274; e, 0.543; f, 0.760; g, 1.0.

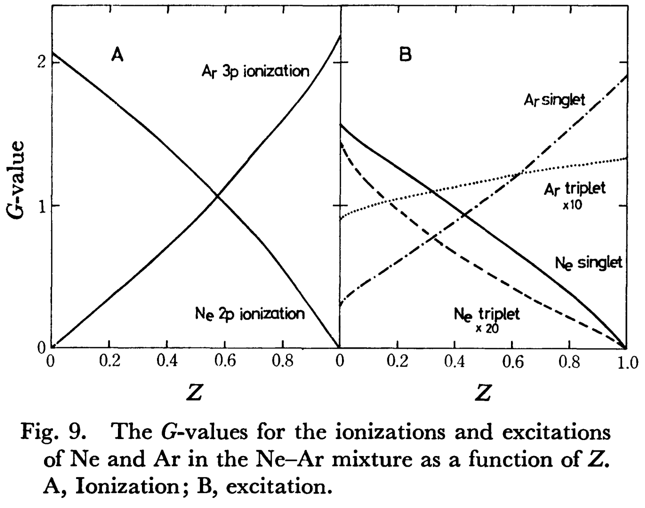

Fig. 9. The *G*-values for the ionizations and excitations of Ne and Ar in the Ne–Ar mixture as a function of *Z*.
A, Ionization; B, excitation.

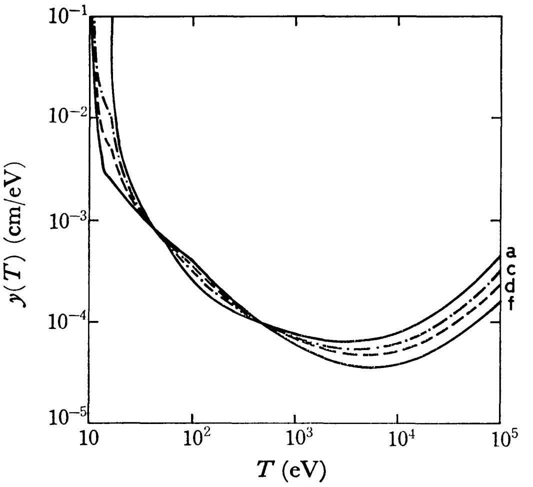

Fig. 10. The component dependence of $y(T)$ in the Ne–Kr mixture as a function of ln T.
a, $p_{Kr}/(p_{Ne}+p_{Kr})=0$; c, 0.234; d, 0.5; f, 1.0.

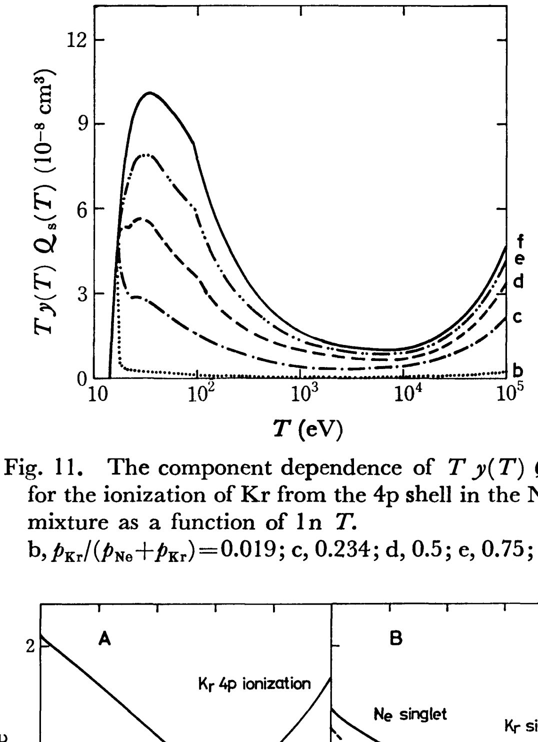

Fig. 11. The component dependence of $T\ y(T)\ Q_s(T)$ for the ionization of Kr from the 4p shell in the Ne–Kr mixture as a function of ln T.
b, $p_{Kr}/(p_{Ne}+p_{Kr})=0.019$; c, 0.234; d, 0.5; e, 0.75; f, 1.0.

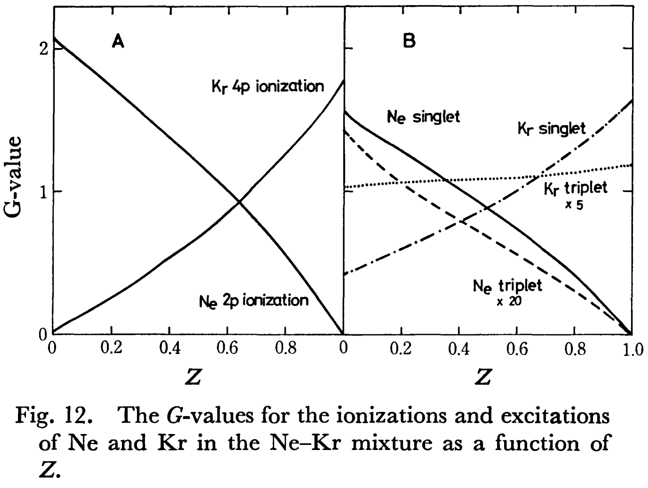

Fig. 12. The *G*-values for the ionizations and excitations of Ne and Kr in the Ne–Kr mixture as a function of *Z*.
A, Ionization; B, excitation.

site to that in the He–Ar mixture: *i.e.*, the curve of the *G*-value for the ionization of neon, whose ionization potential is higher than that of argon, is convex, while the curve for the ionization of argon is concave. The situation of the excitations in the Ne–Ar mixture is also quite different from that in the He–Ne and He–Ar mixtures. For example, the change of the *G*-values for singlet excitation of neon shows an S-shaped curve.

Ne–Kr Mixture. The $y(T)$'s and $Ty(T)\ Q_s(T)$'s for the Ne–Kr mixture are similar to those for the Ne–Ar mixture. These are shown in Figs. 10 and 11. Figures 12A and 12B show the *G*-values for the ionizations and excitations of each component. The abscissa is the parameter *Z*, which is equal to $p_{Kr}/(p_{Kr}+0.465\ p_{Ne})$ according to the treatment of Klots.4) The general tendency of each curve is similar to that for the Ne–Ar mixture.

Discussion

He–Ne Mixture. Since the lowest excited states of helium are located at 19.8 (^{3}S) and 21.2 eV (^{1}P) and the ionization potential of neon is known to be 21.56 eV, the so-called Penning ionization cannot energetically occur in this mixture. Consequently, Haeberli *et al.* expected that the *W*-values in this mixture should satisfy this equation:12)

$$1/W_m = (1/W_A - 1/W_B)Z + 1/W_B \qquad (1)$$

Here, $Z=[p_A+(S_B/S_A)\ p_B]^{-1}\ p_A$. A and B stand for He and Ne in the present case, and S_A and S_B for the stopping powers of the two gases. However, Kubota observed that the experimental results do not satisfy Eq. 1: *i.e.*, the total *G*-value of ionization deviates positively from the straight line expected from Eq. 1.3) He explained this positive deviation as due to the non-metastable Penning ionization. According to the present calculation, however, a similar positive deviation can be obtained as the result of the change of $y(T)$. This is shown in Fig. 3.

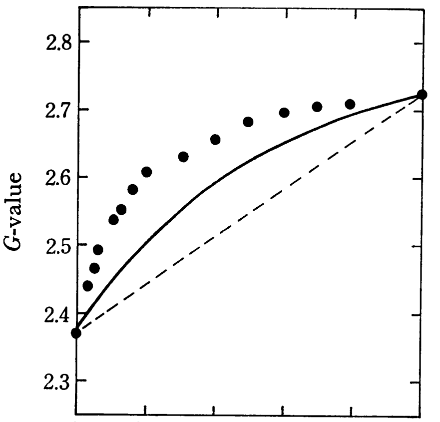

Fig. 13. The total *G*-value of electrons in the He–Ne mixture as a function of *Z*.
—, Calculated; ●, Kubota's experimental.

In order to check the deviation quantitatively, Kubota's experimental results are reproduced in Fig. 13 together with the calculated curve. The absolute *G*-values for ionizations in pure states calculated and experimentally obtained do not coincide with each other. Therefore, the following correction has been made for the calculated *G*-values:

$$G_{ion}' = G(A^+)f_A + G(B^+)f_B \qquad (2)$$

Here, $G(A^+)$ and $G(B^+)$ are the calculated *G*-values of A^+ ion and B^+ ion in a mixture and f_A and f_B are the ratios of the experimentally obtained *G*-values to the calculated *G*-values in the pure states of A and B.

As Fig. 13 shows, about a half of positive deviation can be explained as the result of the change of $y(T)$. It may be obvious from this figure that the non-metastable Penning ionization is not a unique explanation for the deviation from the straight line expected from Eq. 1.

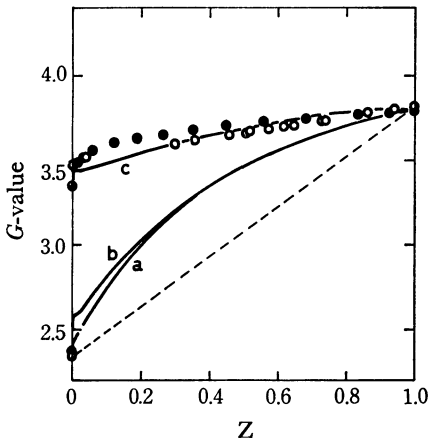

Fig. 14. The total *G*-value of electrons in the He–Ar mixture as a function of *Z*.
—, Calculated; ●, Kubota's experimental; ○, Klots' experimental.

He–Ar Mixture. There are two sets of experimental data for this mixture: one is that of Klots,4) the other of Kubota.3) They are reproduced in Fig. 14, together with the calculated curve. The curve a was obtained in a manner similar to that used in the case of the He–Ne mixture. In this mixture, we have to consider the Penning ionization, because the ionization potential of argon (15.7 eV) is much lower than the energy of the lowest triplet state of helium (19.8 eV).

If the metastable Penning ionization is taken into account:

$$He(^3S)^* + Ar \longrightarrow He + Ar^+ + e^- \qquad (3)$$

the calculated *G*-values increase to the curve b. The curve c was drawn by taking into account the so-called resonance state-Penning ionization.

$$He(^1P)^{**} + Ar \longrightarrow He + Ar^+ + e^- \qquad (4)$$

The radiative lifetime of the He(^{1}P)** is very short; however, the photon imprisonment will prolong its apparent lifetime.13) The agreement between experimental plots and the calculated curve is very good.

Ne–Ar Mixture. In the case of this mixture, Klots did not show the experimental data in his paper, but did report the parameters obtained by his interpretation.4) Using his parameters, the curve for the ionization has been reproduced in Fig. 15. The curves a,b, and c have been drawn by using the calculated values in a manner similar to that in curves a,b, and c in Fig. 14. The calculated curve does not agree at all with the curve obtained experimentally. However, there is another

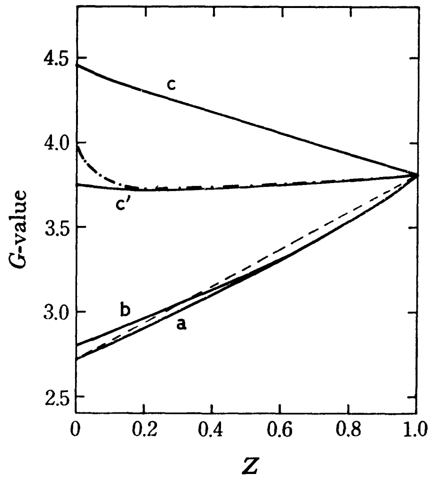

Fig. 15. The total *G*-value of electrons in the Ne–Ar mixture as a function of *Z*.
—, Calculated; —·—, Klots' experimental.

problem we have to consider here: *i.e.*, the ratio between the calculated *G*-value and the experimentally obtained *G*-value for the excitation is not necessarily equal to the ratio for the ionization, f_A or f_B. If the ratio between the calculated *G*-value and the experimental one for the singlet excitation of the A gas, Ne in the present case, is assumed to be 0.58, then the curve c′ in Fig. 15 can be obtained. In spite of this modification, the agreement between experiment and calculation could not be attained, especially in the range of small partial pressure of Ne. This disagreement might reflect some invalidity in the present explanation; however, a detailed inspection of the following mixture suggests that our explanation is one of the possibilities.

Ne–Kr Mixture. Klots' experimental data is reproduced in Fig. 16. The curves a, b, and c were drawn in a manner similar to that used in the case of the Ne–Ar mixture. Although the curve c does not agree at all with the experimental data, a small bump observed at a very small concentration of Kr is reproduced in the curve c. In the interpretation by Klots, this bump comes from the incomplete quenching of the excited state of Ne by Kr atoms. However, the small bump in the curve c is the result of a calculation in which the incomplete quenching was not taken into account.

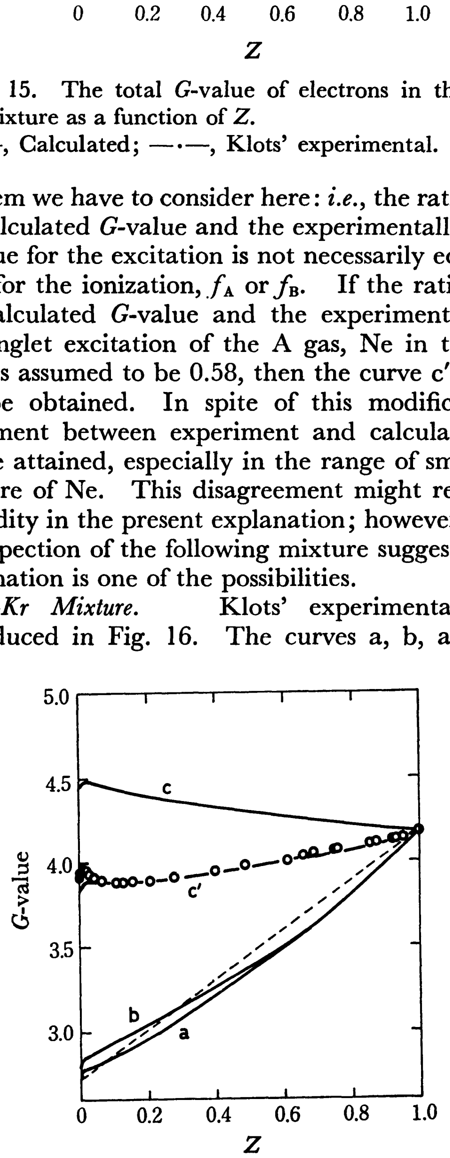

Fig. 16. The total *G*-value of electrons in the Ne–Kr mixture as a function of *Z*.
—, Calculated; ○, Klots' experimental.

As was done in the case of the Ne–Ar mixture, if the ratio between the experimentally obtained *G*-value and the calculated one for the singlet excitation of Ne is assumed to be 0.63, the curve c′ can be obtained. The experimental plots lie close to the curve c′.

Conclusion

In order to explain the change of the *W*-values in binary rare gas mixtures with the change of the mixing ratio, unestablished processes such as the non-metastable Penning ionization and the quenching of the Hornbeck-Molnar process have so far been proposed. As has been shown above, we can explain some of the change of the *W*-values which accompanies the change of the mixing ratio in terms of the change of the degradation spectra. Consequently, it may be conclude that, when we discuss the *W*-value of a binary mixture, we have to consider the degradation spectrum in detail.

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