

## Atomic Processes in Helium-Krypton and Helium-Xenon Mixtures\*

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The momentum transfer collision frequency of thermal electrons with neutrals in a decaying plasma established in helium-krypton and helium-xenon mixtures of known proportions was measured by microwave interferometer at gas temperatures of  $\sim 200$  to  $600^\circ\text{K}$ . The energy dependences of the momentum transfer cross sections of electrons with krypton and xenon atoms deduced from these measurements are best represented by  $Q_m(u) = 6.56 \times 10^{-16} - 2.79 \times 10^{-14} u^{1/2} + 3.14 \times 10^{-14} u$  and  $1.91 \times 10^{-14} - 8.30 \times 10^{-14} u^{1/2} + 9.40 \times 10^{-14} u$   $\text{cm}^2$ , respectively. Here  $u$  is the electron energy in electron volts. Mobilities of  $\text{Kr}^+$  and  $\text{Xe}^+$  in helium and their respective parent gas have also been determined, from the characteristic time constants of the electron density decay measured in the afterglow in the mixtures at low pressures, to be  $\mu(\text{Kr}^+ \text{ in He}) = 20.2 \pm 1.2$   $\text{cm}^2/\text{V-sec}$ ,  $\mu(\text{Kr}^+ \text{ in Kr}) = 1.01 \pm 0.06$ ,  $\mu(\text{Xe}^+ \text{ in He}) = 18 \pm 1.1$ , and  $\mu(\text{Xe}^+ \text{ in Xe}) = 0.55 \pm 0.03$  at  $\sim 300^\circ\text{K}$ . A study of the pressure dependence of the characteristic time constants of the electron density decay at fixed ratios of krypton to helium and xenon to helium concentrations yields the three-body conversion frequency of atomic krypton and xenon ions to their respective molecular ions.

### I. INTRODUCTION

THE employment of microwave technology in studying the fundamental atomic collision processes in a weakly ionized gas is well known.<sup>1</sup> Nevertheless, questions have been occasionally raised as to the assumption of thermal equilibrium of the electron gas with the neutrals at times in the afterglow the experiment was performed. In some cases, evidences<sup>2</sup> showed that the electron temperature could sustain at a level above that of the neutrals at times several hundred microseconds to a few milliseconds after removal of the excitation source. Since almost all physical parameters determined by microwave methods are related directly or indirectly to the electron temperature, it would be appropriate that the electron temperature is measured experimentally. In the present communication, the complete thermalization of the electrons with the neutrals in the He-Kr and He-Xe mixtures is demonstrated by a comparison of the microwave noise emitted from the plasma with that of a standard noise source as detected by a ruby maser. One of the reasons for mixing krypton and xenon with helium is to utilize the helium as a "recoil" gas<sup>2</sup> for the electrons. Quantitative and qualitative descriptions of various collisional processes are then obtained from the measurements made in the afterglow established in such mixtures. The problems of interest are: (1) The energy dependence of the momentum transfer cross sections of electrons with krypton

and xenon atoms at energies below Ramsauer minimum, (2) the mobilities of thermal  $\text{Kr}^+$  and  $\text{Xe}^+$  ions in helium and in their respective parent gas at room temperature (i.e.,  $\sim 300^\circ\text{K}$ ), (3) the three-body conversion frequency  $\nu_{\text{conv}}$  of atomic krypton and xenon ions to molecular ions<sup>3</sup> [see Eq. (7)], and (4) some qualitative evidence in supporting a suggested process of molecular krypton ions formation through collisions of high-lying, short-lived excited atoms with ground state atoms [see Eqs. (14) and (15)], by Hornbeck and Molnar<sup>4</sup> (HM).

### II. EXPERIMENTAL APPARATUS

The gas-handling system is of standard high-vacuum type<sup>5</sup> baked at  $\sim 400^\circ\text{C}$  for more than 24 h prior to each sequence of experiments. An ultimate vacuum of the order of  $2$  to  $6 \times 10^{-10}$  mm Hg is attained. Gases are then introduced into the discharge tube, and the pressure is measured by a (capacity) null reading manometer.<sup>6</sup> The gases used are mass spectrometer controlled grade supplied by Linde Air Products Company. The discharge tube is made of thin wall (0.7 mm thick) Pyrex tubing of 22 mm outside diameter and 72 cm long with 6 cm tapering to a point at each end. The tube is housed coaxially in a 1-in.  $\times$  1-in. square waveguide which is connected to the standard  $x$ -band waveguide system through two 6-in. tapering sections. The gas is ionized by a variable high voltage dc pulse of several thousand volts and seven microseconds duration repeated at a frequency of 31.2 cps. The electrodes of the discharge tube are made out of high-purity titanium for its good gettering property for the atmospheric gases.<sup>7</sup>

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<sup>1</sup> The pertinent references can be found in the review articles of L. Goldstein, *Advance in Electronics and Electron Physics* (Academic Press Inc., New York, 1955) Vol. VIII, p. 473; S. C. Brown, *Basic Data of Plasma Physics* (Tech Press, Cambridge, Massachusetts, and John Wiley & Sons, Inc., New York, 1959).

<sup>2</sup> D. Formato and A. Gilardini, in *Proceedings of the Fourth International Conference on Ionization Phenomena in Gases, Uppsala, 1959*, edited by N. R. Nillson (North-Holland Publishing Company, Amsterdam, 1960), Vol. I, p. 99; M. A. Biondi, *Phys. Rev.* **90**, 730 (1953).

<sup>3</sup> This is similar to the three-body  $\text{He}_2^+$  formation process studied by A. V. Phelps and S. C. Brown, *Phys. Rev.* **86**, 102 (1952).

<sup>4</sup> J. A. Hornbeck and J. P. Molnar, *Phys. Rev.* **84**, 621 (1951).

<sup>5</sup> D. Alpert, *J. Appl. Phys.* **24**, 860 (1953).

<sup>6</sup> The design is originated from Westinghouse Research Laboratories, West Pittsburgh, Pennsylvania. A unique package is now marketed by Granville-Phillips Company, Boulder, Colorado.

<sup>7</sup> V. L. Stout and M. D. Gibbons, *J. Appl. Phys.* **26**, 1488 (1955).

Electron density variations and the effective electron collision frequency  $\nu_{\text{eff}}$  for momentum transfer are measured by microwave interferometry in the decaying plasma created in helium-krypton and helium-xenon mixtures. A schematic diagram of the microwave circuitry used in part of the experiment is shown in Fig. 1. A low-power ( $\sim 2 \mu\text{W}$ ), 9.03 or 8.53 kMc/sec probing signal (continuous or pulsed) is employed to measure the phase shifts and attenuations on the microwave due to the presence of plasma. The temperature of the discharge tube is monitored constantly by three copper-constantan thermocouples. The ruby maser is operated at a pump frequency of  $\sim 21\text{kMc/sec}$  and a signal frequency of 8.53 kMc/sec with a gain of  $\sim 25 \text{ dB}$ . A typical result is shown in Fig. 2.

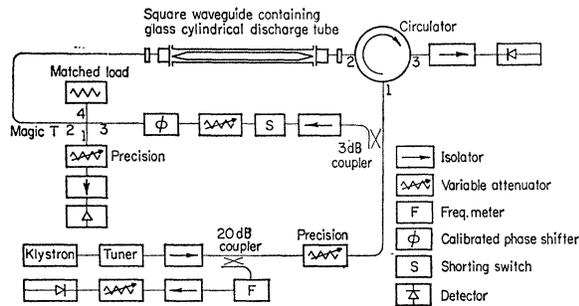


FIG. 1. Schematic diagram of one of the microwave circuitries employed in the present experiment.

### III. MOMENTUM TRANSFER COLLISION CROSS SECTION

It has been shown<sup>8</sup> that the effective electron collision frequency for momentum transfer  $\nu_{\text{eff}}$ , under the influence of low-level dc or rf electric field, in a weakly ionized gas, is given by

$$\nu_{\text{eff}} = \nu_{em} + \nu_{ei}, \quad (1)$$

where  $\nu_{em}$  and  $\nu_{ei}$ <sup>9</sup> are the momentum transfer collision frequencies of electrons with neutrals and ions, re-

<sup>8</sup> V. L. Ginsburg and A. V. Gurevich, Usp. Fiz. Nauk **70**, 201 (1960) [translation: Soviet Phys.—Usp. **3**, 115 (1960)]; V. N. Kolesnikov and V. V. Obukhov-Denisov, Zh. Eksperim. i Teor. Fiz. **42**, 1901 (1962) [translation: Soviet Phys.—JETP, **15**, 692 (1962)]; C. L. Chen and M. Raether, Phys. Rev. **128**, 2679 (1962). Equation (1) is correct only when  $(\omega/\nu)^2 \gg 1$  where  $\omega$  is the radian frequency of the applied electric field and  $\nu$  is the momentum transfer collision frequency. In our experiment,  $(\omega/\nu)^2 \approx 100$ .

<sup>9</sup> A brief summary of the theoretical works in  $\nu_{ei}$  can be found in the article by J. M. Anderson and L. Goldstein, Phys. Rev. **100**, 1037 (1955). The formula for  $\nu_{ei}$  adopted in the present article is that by V. L. Ginsburg, J. Phys. U.S.S.R. **8**, 253 (1944) and has been shown approximately correct experimentally at 300°K by Anderson and Goldstein. The  $T_e^{-3/2}$  dependence in  $\nu_{ei}$  has not yet been established experimentally [see A. A. Dougal and L. Goldstein, Phys. Rev. **109**, 615 (1958)]. The influence on the interpretation of the present data is minute since  $\nu_{em} = \nu_{\text{eff}} - \nu_{ei}$  is always checked in the early and the very late afterglow where  $\nu_{ei}$  is presumably negligible.

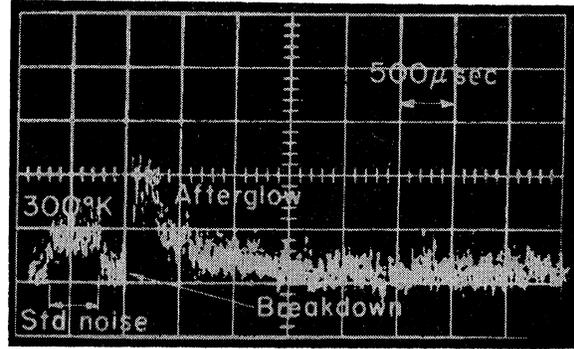


FIG. 2. A direct comparison of the noise emitted by the decaying plasma, created in He-Xe mixture of 54.6% Xe and a total gas pressure of 4.83 mm Hg, with that from a standard noise source of 300°K. The absorptivity of the plasma is checked with a  $\sim 2 \mu\text{W}$ , 8.53 kMc/sec coherent radiation and is found to be 1 up to 450  $\mu\text{sec}$  in the afterglow. The photograph shows that the electrons relax back to the gas temperature approximately 300  $\mu\text{sec}$  after termination of the pulse.

spectively. Furthermore,<sup>8</sup>

$$\nu_{em} = \frac{N_m}{3} \left( \frac{2}{\pi} \right)^{1/2} \left( \frac{m}{kT_e} \right)^{5/2} \int_0^\infty Q_m(v) v^5 \exp\left(-\frac{mv^2}{2kT_e}\right) dv. \quad (2)$$

Here  $N_m$  is the number densities of the neutrals,  $m$  is the electron mass,  $v$  the electron velocity, and  $T_e$  the electron temperature.  $k$  is the Boltzmann's constant and  $Q_m(v)$  is the momentum transfer cross section of electrons with the neutrals.

For binary mixtures as in the present experiment,  $\nu_{em} = \nu_{em_1} + \nu_{em_2}$ , and

$$\frac{\nu_{em}}{p_t} = \left( \frac{\nu_{em_1}}{p_1} - \frac{\nu_{em_2}}{p_2} \right) \frac{p_1}{p_t} + \frac{\nu_{em_2}}{p_2}, \quad (3)$$

where  $p_t$  is the total gas pressure and is equal to the sum

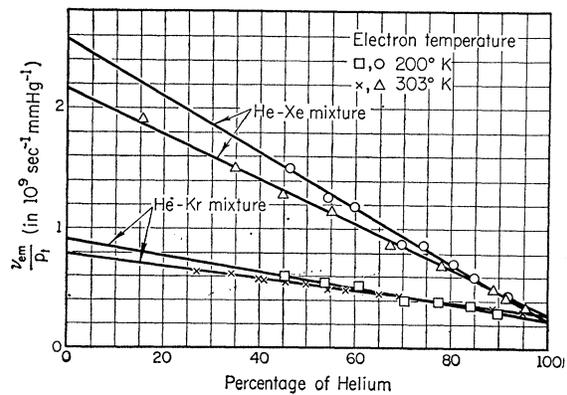


FIG. 3.  $\nu_{em}/p_t$  versus percentage of helium in helium-krypton and helium-xenon mixtures at 200 and 303°K. The straight-line behavior is predicted by Eq. (3) in the text under the condition of  $(\nu/\omega)^2 \ll 1$ . The two ordinates of  $\nu_{em}/p_t$  at 0 and 100% He give  $\nu_{em}(\text{Kr})/p(\text{Kr})$ ,  $\nu_{em}(\text{Xe})/p(\text{Xe})$ , and  $\nu_{em}(\text{He})/p(\text{He})$  at the temperatures indicated.

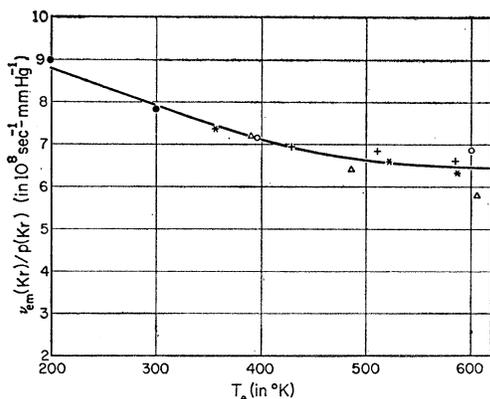


FIG. 4.  $\nu_{em}(\text{Kr})/p(\text{Kr})$  versus  $T_e$ . The various symbols on the graph represent the values of  $\nu_{em}(\text{Kr})/p(\text{Kr})$  deduced from different fractional krypton concentrations:  $\bullet$  from Fig. 3, \*41.6% Kr,  $\circ$  50.1% Kr,  $+$  58.8% Kr,  $\triangle$  73% Kr. The solid curve is the best fit to the experimental points according to Eq. (2) and assuming  $Q_m(v) = A + Bv + Cv^2$ .

of the partial pressures  $p_1$  and  $p_2$  of the mixtures. All pressures are hereafter referred to 0°C. Therefore, the ratio of measured electron-molecule collision frequency to the total gas pressure is a linear function of fractional concentration of one of the species. In our experiments,  $\nu_{ei}/\nu_{eff}$  is of the order of 1 to 10% in the afterglow in which  $\nu_{eff}$  is measured and<sup>9</sup>  $\nu_{ei}$  is subtracted out from  $\nu_{eff}$  to get  $\nu_{em}$ . The results are shown in Fig. 3. From the extrapolated values of  $\nu_{em}/p_i$  at  $p(\text{He})/p_i = 1$  and 0, the momentum transfer collision probability<sup>10</sup>  $\bar{P}_m$  of electrons with He, Kr, and Xe atoms are found to be: 18.9, 54.7, and 151  $\text{cm}^2/\text{cm}^3$ , respectively, at 303°K and 18.9, 77.5, and 221  $\text{cm}^2/\text{cm}^3$ , respectively, at 200°K. Thus, within experimental accuracy,  $\bar{P}_m(\text{He})$  and hence  $Q_m(v)$  for He is a constant in this range. This fact agrees with what has been found by other investigators<sup>11</sup> and is utilized later in deducing  $\nu_{em}(\text{Kr})/p(\text{Kr})$  and  $\nu_{em}(\text{Xe})/p(\text{Xe})$  from  $\nu_{off}/p_i$  measured at higher temperatures. The temperature dependence of  $\nu_{em}(\text{He})/p(\text{He})$  is taken to be

$$\nu_{em}(\text{He})/p(\text{He}) = 1.56 \times 10^7 T_e^{1/2} \text{ sec}^{-1} \text{ mm Hg}^{-1}. \quad (4)$$

By subtracting electron-ion<sup>9</sup> and electron-helium [as calculated from Eq. (4)] contributions from  $\nu_{eff}$ , the resulting momentum transfer collision frequency of electrons with Kr and Xe atoms as a function of electron temperature is shown in Figs. 4 and 5. The velocity dependence of the momentum transfer cross section  $Q_m(v)$  is determined from a best fit to the experimental

<sup>10</sup> It is easily shown from the rf electrical conductivity that  $\nu_{eff} = \frac{2}{3} N_m Q_m(v)$ , where  $Q_m$  is the effective momentum transfer cross section and  $(v) = (8kT_e/\pi m)^{1/2}$ . Then, the effective momentum transfer collision probability  $\bar{P}_m$  is given by  $\bar{P}_m = \frac{2}{3} \nu_{eff}/(v)$ . A more rigorous proof of it is given by R. C. Hwa, Progress Report on Research in Physical Electronics, Electrical Engineering Research Laboratory, University of Illinois, Urbana, Illinois, 1955 (unpublished).

<sup>11</sup> L. Gould and S. C. Brown, Phys. Rev. **95**, 897 (1954); J. L. Pack and A. V. Phelps, *ibid.* **121**, 798 (1961).

points by assuming  $Q_m(v) = A + Bv + Cv^2 \text{ cm}^2$  in Eq. (2). The solid curves on Figs. 4 and 5 are the best fits. The derived energy dependence of the cross sections are

$$Q_m(u) = 6.56 \times 10^{-15} - 2.79 \times 10^{-14} u^{1/2} + 3.14 \times 10^{-14} u \text{ cm}^2 \quad (5)$$

for krypton and

$$Q_m(u) = 1.91 \times 10^{-14} - 8.30 \times 10^{-14} u^{1/2} + 9.40 \times 10^{-14} u \text{ cm}^2 \quad (6)$$

for xenon. Here  $u$  is the electron energy in electron volts.

Recently, Pack, Volshall, and Phelps (PVP)<sup>12</sup> have deduced  $Q_m(u)$  from their electron mobility studies in Kr and Xe. Their results together with the present one are shown in Figs. 6 and 7, in which PVP's notation are preserved. O'Malley<sup>13</sup> has adopted "atomic effective range formulas"<sup>14</sup> to analyze Ramsauer-Kollath (RK) scattering experiments.<sup>15</sup> In this analysis, the parameters of the theory are so chosen to fit RK experimental cross sections. These calculations were extrapolated to zero energy and are also shown in Figs. 6 and 7. All agree fairly well with each other in shape but not in absolute value. The disagreements can be attributed partly to the approximations and experimental errors in each case.

#### IV. ION MOBILITIES AND CONVERSION FREQUENCIES

The main electron loss process in the afterglow of a low pressure, weakly ionized noble gaseous discharge is ambipolar diffusion.<sup>16</sup> For the present experiments

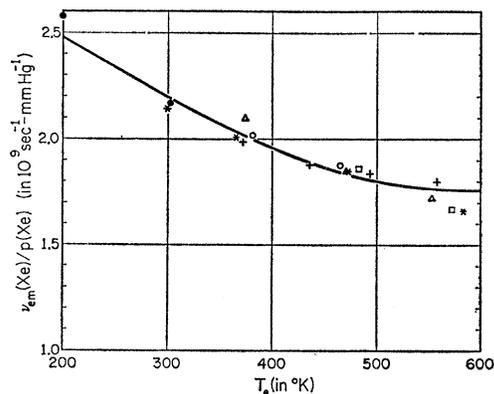


FIG. 5.  $\nu_{em}(\text{Xe})/p(\text{Xe})$  versus  $T_e$ . The various symbols on the graph represent the values of  $\nu_{em}(\text{Xe})/p(\text{Xe})$  deduced from different fractional xenon concentrations:  $\bullet$  from Fig. 3,  $+$  50% Xe,  $\circ$  58.8% Xe,  $\square$  73.4% Xe,  $\triangle$  84.9% Xe, \*93% Xe. The solid curve is the best fit to the experimental points according to Eq. (2) and assuming  $Q_m(v) = A + Bv + Cv^2$ .

<sup>12</sup> J. L. Pack, R. E. Voshall, and A. V. Phelps, Phys. Rev. **127**, 798 (1962).

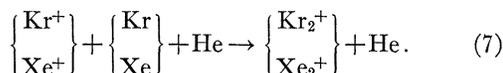
<sup>13</sup> T. F. O'Malley, Phys. Rev. **130**, 1020 (1963).

<sup>14</sup> T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. **2**, 491 (1961); Phys. Rev. **125**, 1300 (1962).

<sup>15</sup> C. Ramsauer and R. Kollath, Ann. Physik **12**, 837 (1932).

<sup>16</sup> M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949); W. P. Allis and D. J. Rose, *ibid.* **93**, 84 (1954); I. B. Bernstein and T. Holstein, *ibid.* **94**, 1475 (1954).

(helium-krypton or helium-xenon mixtures of various proportions) the ions created in the active discharge are believed to be atomic krypton or xenon ions when suitable breakdown voltage pulse is employed.<sup>17</sup> This is supported by the spectral examination of the discharge in He-Kr mixtures with a Bausch and Lomb Littrow No. 5402 Spectrograph which has a dispersion of 7.7 Å/mm at 3670 Å and 45.5 Å/mm at 6700 Å. It is found that no band spectra of any kind and only atomic krypton lines are presented. HM noticed in their mass spectrometric studies of molecular ions in noble gases that Kr<sub>2</sub><sup>+</sup> and Xe<sub>2</sub><sup>+</sup> ions are much more difficult to be formed than He<sub>2</sub><sup>+</sup>, Ne<sub>2</sub><sup>+</sup>, and Ar<sub>2</sub><sup>+</sup> through collisions of high-lying, short-lived excited states with the ground state atoms. Therefore, at low gas pressures and careful breakdown condition,<sup>17</sup> the molecular ions formed by this process can be ignored. However, Kr<sup>+</sup> or Xe<sup>+</sup> ions created in the active discharge, while diffusing through the mixture to the walls in a decaying plasma, experience not only elastical scatterings from helium and their parent gas atom, but also may change their identities to molecular ions through three-body collisions:



$$D_a \bar{p}(\text{He}) = \frac{T_e}{7.63} \frac{\mu(\text{Kr}^+ \text{ in He})}{1 + [\bar{p}(\text{Kr})/\bar{p}(\text{He})][\mu(\text{Kr}^+ \text{ in He})/\mu(\text{Kr}^+ \text{ in Kr})]} + \Lambda^2 C_{\text{conv}} \bar{p}^2(\text{He}) \bar{p}(\text{Kr}), \quad (11)$$

where  $\mu(\text{Kr}^+ \text{ in He})$  and  $\mu(\text{Kr}^+ \text{ in Kr})$  are the mobilities of atomic krypton ions in helium and in krypton, respectively, referred to 0°C and 760 mm Hg gas pressure.  $\bar{p}(\text{Kr})$  and  $\bar{p}(\text{He})$  are the partial pressures of krypton and helium in the mixtures. In deriving Eq. (11), Einstein's relation<sup>19</sup> and Blanc's law<sup>20</sup> have been employed. At very low pressures, the second term to the right-hand side of Eq. (11) can be neglected, and

$$D_a \bar{p}(\text{He}) = \frac{T_e}{7.63} \frac{\mu(\text{Kr}^+ \text{ in He})}{1 + [\bar{p}(\text{Kr})/\bar{p}(\text{He})][\mu(\text{Kr}^+ \text{ in He})/\mu(\text{Kr}^+ \text{ in Kr})]}. \quad (11a)$$

$\mu(\text{Kr}^+ \text{ in He})$  and  $\mu(\text{Kr}^+ \text{ in Kr})$  are then determined from the best fit of the measured quantities  $D_a \bar{p}(\text{He})$  and the percentage of Kr (or of Xe in the case of He-Xe mixtures) at a constant temperature according to Eq. (11a). These are shown in Fig. 8. The best fit yields  $\mu(\text{Kr}^+ \text{ in He}) = 20.2 \pm 1.2$  cm<sup>2</sup>/V-sec,  $\mu(\text{Kr}^+ \text{ in Kr}) = 1.01 \pm 0.06$ ,  $\mu(\text{Xe}^+ \text{ in He}) = 18 \pm 1.1$ , and  $\mu(\text{Xe}^+ \text{ in Xe}) = 0.55 \pm 0.03$  at 303°K.

The theoretical calculated mobilities of thermal energy ion relevant to the present experiment, together with the values determined by other authors, are presented in Table I. The theoretical values of  $\mu(\text{Kr}^+ \text{ in He})$

<sup>17</sup> The breakdown voltage pulses are adjusted in strength (keeping the duration fixed at  $\sim 7\mu\text{sec}$  and repeated at 31.2 cps) just enough to maintain a stable, repeatable, pulsed discharge. In this manner, the excitation light is usually very dim. Therefore, the initial concentration of molecular ions formed by HM process is believed to be negligibly small. See Ref. 4 and Sec. IV of the text.

The solution to the electron density for such a decaying plasma is<sup>3,18</sup>

$$n(t) = A \exp(-t/\tau_A) + B \exp(-t/\tau_M), \quad (8)$$

where

$$1/\tau_A = D_{aA}/\Lambda^2 + \nu_{\text{conv}} \quad (9)$$

and

$$1/\tau_M = D_{aM}/\Lambda^2. \quad (10)$$

Here  $n$  is the electron density,  $\Lambda$  is the characteristic diffusion length of the discharge tube,  $D_{aA}$  and  $D_{aM}$  are the ambipolar diffusion coefficients of the atomic and molecular ions in the mixtures, and  $\nu_{\text{conv}} = C_{\text{conv}} \bar{p}_1 \bar{p}_2$  is the atomic to molecular ion conversion frequency.  $A$  and  $B$  are constants related to the initial atomic and molecular ion concentrations and the physical constants just mentioned above. If  $\nu_{\text{conv}}$  is smaller than the molecular ion diffusion rate, and  $B \ll A$  (which is true in our experiment),<sup>17</sup> the electron loss rate in the afterglow is simply described by a single time constant, i.e.,  $\tau_A$ . From Eq. (9) it is easy to show that the product of ambipolar diffusion coefficient  $D_a$  of electrons to the partial pressure of helium in the helium-krypton mixtures, for example, takes the following form:

and  $\mu(\text{Xe}^+ \text{ in He})$  are calculated by the use of Langevin's theory in the polarization limit.<sup>21</sup> The dielectric constant for helium adopted here is that recommended by Maryott and Buckley.<sup>22</sup>

As the total pressure increases while keeping the percentage of krypton in the mixtures fixed, the measured values of  $D_a \bar{p}(\text{He})$  should vary linearly with

<sup>18</sup> Electron decay through electron-ion recombination processes has been neglected in the present treatment for its ineffectiveness under the present experimental conditions. The theoretical treatments of this subject is summarized in the book: *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962).

<sup>19</sup> W. P. Allis, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XXI.

<sup>20</sup> L. B. Loeb, *Basic Processes in Gaseous Electronics* (University of California Press, Berkeley, 1955), Chap. 1; M. A. Biondi and L. M. Chanin, *Phys. Rev.* **122**, 843 (1961).

<sup>21</sup> P. Langevin, *Ann. Chim. Phys.* **5**, 245 (1905).

<sup>22</sup> A. A. Maryott and F. Buckley, *Natl. Bur. Std. (U. S.), Circ.* **537** (1953).

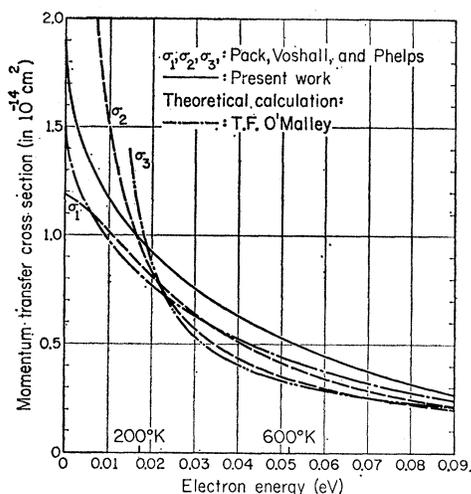


FIG. 6. Momentum transfer cross section of electrons with krypton atoms. The result of the present experiment is compared with those found by PVP and the theoretical calculations by O'Malley.

TABLE I. Comparison of experimental and theoretical values of  $\text{Kr}^+$  and  $\text{Xe}^+$  mobilities (in  $\text{cm}^2/\text{V}\cdot\text{sec}$ ).

Gas \ Ion	$\text{Kr}^+$		$\text{Xe}^+$	
	Experiment	Theory	Experiment	Theory
He	$20.2 \pm 1.2^a$	17.0	$18 \pm 1.1^a$	16.8
Kr	$0.9\text{--}0.95^b$	$1.0^d$	...	
	$0.90^c$	$0.9^e$		
Xe	$0.01 \pm 0.06^a$		$0.6\text{--}0.65^b$	$0.66^d$
	...		$0.58^c$	$0.60^e$
			$0.55 \pm 0.03^a$	

<sup>a</sup> Present data.

<sup>b</sup> R. N. Varney, Phys. Rev. **88**, 362 (1952).

<sup>c</sup> M. A. Biondi and L. M. Chanin, Phys. Rev. **94**, 910 (1954).

<sup>d</sup> I. B. Bernstein (unpublished).

<sup>e</sup> A. Dalgarno, Phil. Trans. Roy. Soc. London **A250**, 426 (1958).

$p^2(\text{He})p(\text{Kr})$  should there be the three-body molecular ion formation process. The slope of  $D_a p(\text{He})$  versus  $p^2(\text{He})p(\text{Kr})$  yields the value of  $C_{\text{conv}}\Lambda^2$ , and should be

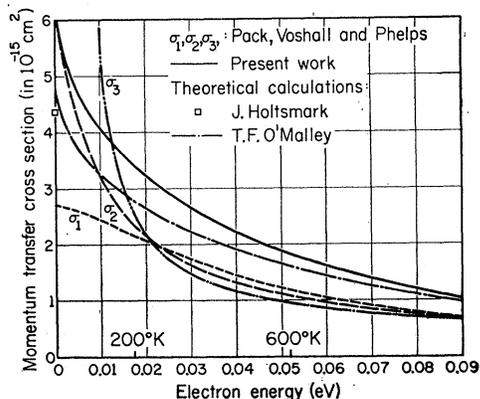


FIG. 7. Momentum transfer cross section of electrons with xenon atoms. The result of the present experiment is compared with those found by PVP and the theoretical calculations by O'Malley.

independent of the krypton percentage. Figure 9 presents the results in He-Kr mixtures for four different krypton percentages; i.e., 1.7, 4.3, 5.97, and 14%. The slopes are fairly well the same, and  $C_{\text{conv}}$  so determined is  $(76 \pm 4) \text{ mm Hg}^{-2}\text{-sec}^{-1}$ , i.e.,

$$\nu_{\text{conv}} = (76 \pm 4) p(\text{He})p(\text{Kr}). \quad (12)$$

Similar studies are also made for  $\text{Xe}^+$  to  $\text{Xe}_2^+$  conversion. Typical results are shown in Fig. 10. In this case,  $C_{\text{conv}} = (140 \pm 9) \text{ mm Hg}^{-2}\text{-sec}^{-1}$ , and

$$\nu_{\text{conv}} = (140 \pm 9) p(\text{He})p(\text{Xe}). \quad (13)$$

Similar to the gas-kinetic conditions<sup>23</sup> in two-body charge or excitation transfer collisions, it is reasonable to believe that the lesser the amount of energy carried away by the third body in reaction (7), the higher the probability of molecular ion formation. Then the larger

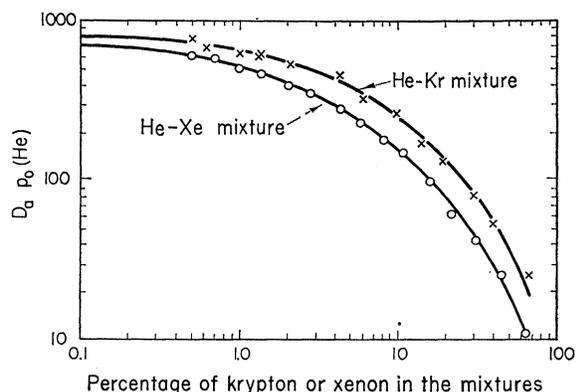
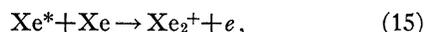
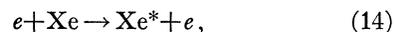


FIG. 8.  $D_a p(\text{He})$  versus percentage of krypton or xenon in helium-krypton or helium-xenon mixtures. The solid curves are the best fits according to the functional form of Eq. (11a). From these, it is determined that  $\mu(\text{Kr}^+ \text{ in He}) = 20.2 \pm 1.2 \text{ cm}^2/\text{V}\cdot\text{sec}$ ,  $\mu(\text{Kr}^+ \text{ in Kr}) = 1.01 \pm 0.06$ ,  $\mu(\text{Xe}^+ \text{ in He}) = 18 \pm 1.1$ , and  $\mu(\text{Xe}^+ \text{ in Xe}) = 0.55 \pm 0.03$ .

value of  $C_{\text{conv}}$ , which is proportional to the formation probability, for  $\text{Xe}^+$  to  $\text{Xe}_2^+$  than  $\text{Kr}^+$  to  $\text{Kr}_2^+$  indicates that the amount of energy carried away by He is smaller in the former than in the latter case. Should this be so, the binding energy of  $\text{Xe}_2^+$  would be smaller than that of  $\text{Kr}_2^+$ . This has to await a further study of the appearance potentials in these gases to confirm it. Nevertheless, observations by HM<sup>4</sup> seemed to suggest the same explanation. They noticed, in their mass-spectrometry studies of molecular ions formed by electron bombardment in noble gases, that the current peaks of  $\text{Xe}^+$  to  $\text{Xe}_2^+$  is  $4 \times 10^4$  to 1 while  $\text{Kr}^+$  to  $\text{Kr}_2^+$  is  $2 \times 10^4$  to 1. The apparent greater difficulty in  $\text{Xe}_2^+$  formation than  $\text{Kr}_2^+$  through (taking xenon as an example)



<sup>23</sup> H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, England, 1952).

could be explained as that  $\text{Xe}^*$  (stands for xenon atom in a high-lying, short-lived excited state) required for the reaction must be very close to the ionization limit if the binding energy of  $\text{Xe}_2^+$  were very small. The excitation cross section is known to drop off rapidly, in general, as the total quantum number increases.<sup>23</sup> Therefore, their finding seems to be in harmony with  $C_{\text{conv}}$  determined here.

We have also studied qualitatively the molecular ion formation processes proposed by HM [see Eqs. (14) and (15)]. We observe that the characteristic time constant of the electron density decay is a strong function of the excitation light in the active discharge, while keeping  $p_i$  and the relative concentration of Kr (or Xe) unchanged. Qualitatively, the brighter the excitation light, the smaller the characteristic ambipolar diffusion time constant. Since electrons have already relaxed back to the gas temperature at times in the afterglow the measurements were made and high-order modes of diffusion are believed not to exist at such late times (2 to 12 msec) in the afterglow. The only feasible explanation offered to such phenomenon is the formation of molecular ions through processes (14) and (15).  $\text{Xe}_2^+$  or  $\text{Kr}_2^+$

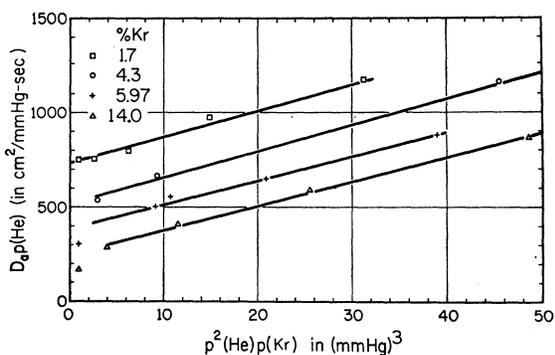


FIG. 9.  $D_a\phi(\text{He})$  versus  $p^2(\text{He})p(\text{Kr})$ . The slope is proportional to the conversion frequency of reaction (7).

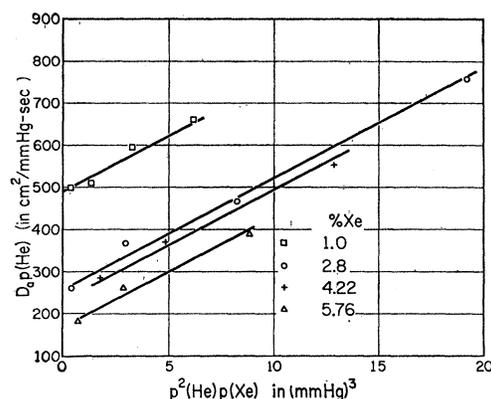


FIG. 10.  $D_a\phi(\text{He})$  versus  $p^2(\text{He})p(\text{Xe})$ . The slope is proportional to the conversion frequency of reaction (7).

ions are known to have a higher mobility than  $\text{Xe}^+$  or  $\text{Kr}^+$  in their parent gases due principally to lack of charge exchange.<sup>24</sup> The light intensity in the active discharge is interpreted as an indirect measure of  $\text{Xe}^*$  or  $\text{Kr}^*$  concentrations. No detailed correlations between the distribution of line intensities and the molecular ion concentrations are pursued at the present time. Further mass- and optical-spectrometry studies are necessary.

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<sup>24</sup> R. N. Varney, Phys. Rev. 88, 362 (1952); M. A. Biondi and L. M. Chanin, *ibid.* 94, 910 (1954).

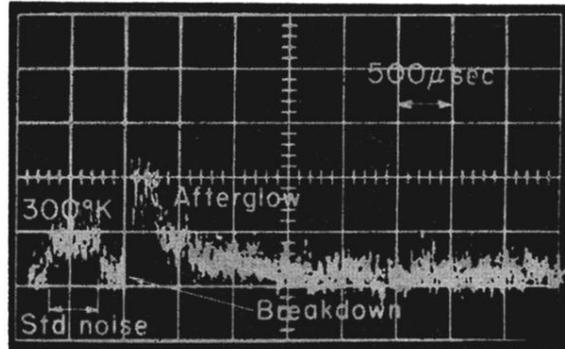


FIG. 2. A direct comparison of the noise emitted by the decaying plasma, created in He-Xe mixture of 54.6% Xe and a total gas pressure of 4.83 mm Hg, with that from a standard noise source of 300°K. The absorptivity of the plasma is checked with a  $\sim 2 \mu\text{W}$ , 8.53 kMc/sec coherent radiation and is found to be 1 up to 450  $\mu\text{sec}$  in the afterglow. The photograph shows that the electrons relax back to the gas temperature approximately 300  $\mu\text{sec}$  after termination of the pulse.