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Atom–Atom Ionization Mechanisms in Argon–Xenon Mixtures*

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The atom–atom ionization process occurring in high-purity argon–xenon mixtures has been investigated by means of a conventional shock tube employing a microwave probe to monitor the electron-generation rate. All tests were conducted at approximately atmospheric pressure and at temperatures in the range between 5000° and 9000°K, corresponding to a neutral-particle density of 7.0×10^{17} cm^{-3}. The cross-sectional slope constant for xenon ionized by collision with an argon atom is 1.8×10^{-20} cm^2/eV$\pm$20%, that is, equal to that for xenon ionized by collision with another xenon atom. The data for the reaction of argon ionizing xenon are consistent with an activation energy of 8.315 eV, that is, of the xenon–xenon, atom–atom ionization process. No data were obtained for xenon ionizing argon. Good correlation was obtained between the cross sections for electron elastic momentum exchange derived from the microwave experiment and those obtained from beam experiments.

The argon–xenon ionization cross section implies that, for atom–atom processes in the noble gases at pressures ~1 atm and temperatures $\sim\frac{2}{3}$ eV, the ionization cross section is independent of the electronic structure of the projectile atom.

INTRODUCTION

In a previous paper,[1] the results of an experimental determination of the atom–atom cross section in pure argon, krypton, and xenon are summarized. The aim of the present study, using the same shock-tube and microwave diagnostic techniques, was to determine the effect of controlled amounts of impurity upon the atom–atom ionization process. The impurity will have an excitation level lower than that of the gas under investigation. Of particular interest were the interspecies ionization cross sections. Xenon was chosen as an appropriate impurity to be studied in conjunction with argon. The first excitation level of xenon (8.315 eV) is some 3.233 eV below that of argon (11.548 eV), and the argon–argon and xenon–xenon ionization reactions were well known and could be suitably taken into account.

The details of the shock tube, the microwave diagnostic system, and the data reduction procedure are to be found in Ref. 1. A more elaborate exposition of these details is to be found in Ref. 2. Stringent precautions were taken in order to restrict the level of contamination of the test gas due to the experimental apparatus to less than 1 ppm. All of the argon–xenon mixture tests were conducted using premixed research-grade gases purchased from the Linde Company. These gases had known impurity levels measured in the low parts-per-million range.

Electron Generation Rate from Atom–Atom Interaction

Pure Gas

The preferred mechanism for atom–atom ionization of the noble gases at moderate pressures and temperatures involves two steps; a rate-controlling step in which one of the atoms is excited to the first excited state, and a second step in which the excited atom is ionized. If we define $Q_{ij}(|\bar{v}_i-\bar{v}_j|)$ as the ionization cross section, the ith species in two-body collisions with a member of the jth species, where $\bar{v}_i$ and $\bar{v}_j$ are their respective velocities, we can write the electron-generation rate per unit volume as

$$\frac{N_iN_j}{1+\delta_{ij}}\int_{\bar{v}_i}\int_{\bar{v}_j} f(\bar{v}_i)f(\bar{v}_j)Q_{ij}(|\bar{v}_i-\bar{v}_j|)\,|\bar{v}_i-\bar{v}_j|\,d\bar{v}_id\bar{v}_j. \quad (1)$$

N_i and N_j are the neutral-particle densities of the ith and jth species, respectively, and $f(\ )$ denotes the velocity distribution. Because of the temperatures and pressures encountered in this study and the low levels of ionization attained, it is valid to assume that both species are in thermal equilibrium and that $f(\bar{v}_i)$ and $f(\bar{v}_j)$ are Maxwell–Boltzmann distributions.

Converting to center-of-mass coordinates, denoting the reduced mass $(m_im_j)/(m_i+m_j)$ as μ_{ij} and the relative velocity $\bar{v}_i-\bar{v}_j$ as $\bar{g}$, Eq. (1) can be written as

$$\frac{N_iN_j}{1+\delta_{ij}}4\pi\left(\frac{\mu_{ij}}{2\pi kT}\right)^{3/2}\int_{g_{i^*}}^{\infty}\left[\exp\left(\frac{-\mu_{ij}g}{2kT}\right)\right]Q_{ij}(g)\,g^3dg, \quad (2)$$

where now g_{i^*} is the threshold relative energy at which the reaction begins. The relative interaction energy E is related to the relative center-of-mass velocity g as $E=(\frac{1}{2}\mu_{ij})g^2$ which, for the case of threshold, becomes $E_{i^*}=(\frac{1}{2}\mu_{ij})g_{i^*}^2$. Substitution of a constant-slope ionization cross section,[3] i.e., $Q_{ij}=C_{ij}(E-E_{i^*})$, into (2) results in an expression for the atom–atom electron-generation rate

$$N_e=(N_iN_j/1+\delta_{ij})C_{ij}K_{ij}(1/\beta)^{3/2}(2+\beta E_{i^*})\exp(-\beta E_{i^*}), \quad (3)$$

where $\beta=1/kT$ and $K_{ij}=2(2/\pi\mu_{ij})^{1/2}$.

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[1] A. J. Kelly, J. Chem. Phys. 45, 1723 (1966), preceding paper.
[2] A. J. Kelly, "Atom–Atom Ionization Mechanisms and Cross Sections in Noble Gases and Noble Gas Mixtures," Ph.D. thesis, California Institute of Technology, 1965.
[3] Cf. Ref. 2 regarding the validity of constant-slope, approximation for energy dependence of atom–atom ionization cross section.

Binary Gas Mixture

When a binary gas mixture undergoes atom–atom ionization, there are four electron-generation processes occurring simultaneously, two between like particles and two between unlike particles. The electron-generation rate for binary mixtures is therefore:

$$\dot{N}_e=\tfrac{1}{2}N_1^2C_{11}K_{11}(1/\beta)^{3/2}(2+\beta E_{*1})\exp(-\beta E_{*1}) \quad \text{Species 1 ionized by Species 1,} \tag{4a}$$

$$+N_1N_2C_{12}K_{12}(1/\beta)^{3/2}(2+\beta E_{*1})\exp(-\beta E_{*1}) \quad \text{Species 1 ionized by Species 2,} \tag{4b}$$

$$+N_2N_1C_{21}K_{21}(1/\beta)^{3/2}(2+\beta E_{*2})\exp(-\beta E_{*2}) \quad \text{Species 2 ionized by Species 1,} \tag{4c}$$

$$+\tfrac{1}{2}N_2^2C_{22}K_{22}(1/\beta)^{3/2}(2+\beta E_{*2})\exp(-\beta E_{*2}) \quad \text{Species 2 ionized by Species 2.} \tag{4d}$$

It is assumed that the pure-gas cross-sectional slope constants (C_{11}, C_{22}) and the threshold energies E_{*1} and E_{*2} are known. For interactions between unlike particles [Eqs. (4b) and (4c)] it is assumed that the threshold energies for the reaction are determined by the characteristics of the particle undergoing reaction and are independent of the particle causing the excitation. Thus, the threshold energy for an argon atom exciting a xenon atom is 8.315 eV, the value observed for an argon atom exciting a xenon atom is 8.315 eV, the value observed for a xenon atom exciting another xenon atom. This assumption appears to be substantiated by experiment. Under these assumptions, there are two unknowns, C_{12} and C_{21}. In argon–xenon mixtures for temperatures appropriate to this experiment, the difference between the threshold energies of argon and xenon is sufficiently large so that the exponential factors differ by as much as two orders of magnitude. Since the interspecies cross sections probably do not differ by more than an order of magnitude, the reaction with the lowest threshold energy is dominant. This is actually observed in the Arrhenius plots of the data for argon–xenon mixtures, the slopes indicating a threshold energy the same as that for pure xenon. As a consequence of these considerations, we are required experimentally to determine only the interspecies cross section corresponding to the ionization of the species possessing the lower threshold energy. Although it is theoretically possible to determine both C_{12} and C_{21} by conductlng two independent experiments, this did not prove possible because the influence of the slower reaction was obscured by data scatter.

EXPERIMENTAL RESULTS

Ionization Cross Section

Four different argon–xenon mixtures were studied; 0.1% (i.e., 1000 ppm xenon in argon) 0.48%, 5%, and 20% xenon in argon. Because the results from the testing of the 0.1% and 0.48% mixtures were not substantially different from those obtained when testing pure argon, they have not been presented. The Arrhenius plots for the 5% and 20% mixture ratios are presented in Figs. 1 and 2, respectively. All these data were obtained at a nominal preshock pressure of 5 torr, corresponding to a postshock neutral-particle density of 7.0×10^{17} cm^{-3}. No attempt was made to investigate pressure dependence.

The best fit to the data for both the 5% and 20% mixtures was obtained by letting C_{21} equal $C_{22}=1.8\times10^{-20}$ cm^2/eV and, for consistency, C_{12} equal $C_{11}=1.2\times10^{-19}$ cm^2/eV, with $E_{*1}=11.548$ eV and $E_{*2}=8.315$ eV, corresponding to the first excitation energy levels of argon and xenon, respectively. As was the case with the pure noble-gas ionization data,[1] diffraction effects associated with electron-density gradients lateral to the direction of the microwave beam have apparently shifted the low β ($\beta\lesssim1.6$) data below their true position. No correction has been applied in the data reduction procedure to compensate for this effect. The extent to which uncertainties associated with the known slope constants C_{11} and C_{22} and with the unknown slope constant C_{12} would affect the determination of C_{21} can be judged from the relative contribution each reaction makes to the total electron-generation rate. Denoting the reactions by their cross-sectional slope constants, the fractional contribution that each makes to the electron population in shown in Table I for temperatures representing the extremes of the range studied.

At worst, the $\pm15\%$ uncertainty in C_{11} (cf. Ref. 1)

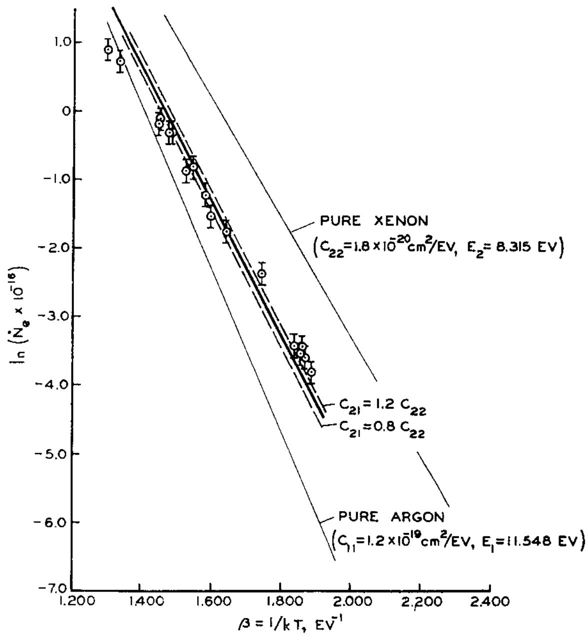

FIG. 1. Arrhenius plot for ionization of argon+5% xenon. ⊙, 5 torr, $N=6.96\times10^{17}$ cm^{-3}. Calculated using $C_{11}=C_{12}=1.2\times10^{-19}$ cm^2/eV; $C_{21}=C_{22}=1.8\times10^{-20}$ cm^2/eV, $E_1=11.548$ eV, and $E_2=8.315$ eV.

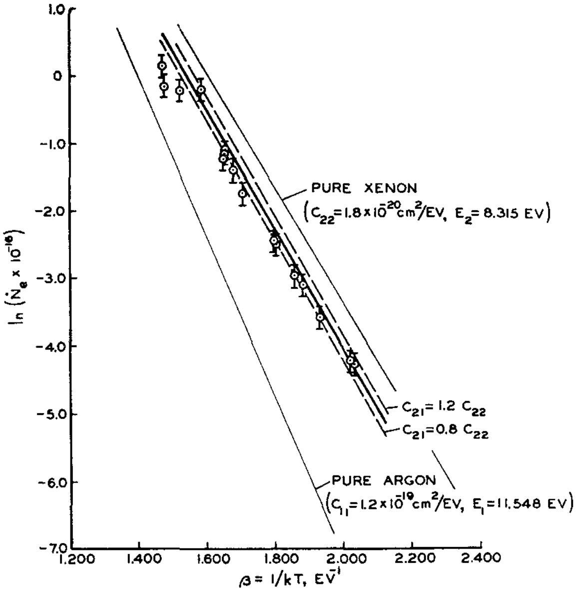

FIG. 2. Arrhenius plot for ionization of argon+20% xenon. ⊙, 5 torr, $N=6.96\times10^{17}$ cm^{-3}. Calculated using $C_{11}=C_{12}=1.2\times10^{-19}$ cm^2/eV, $C_{21}=C_{22}=1.8\times10^{-20}$ cm^2/eV, $E_1=11.548$ eV, and $E_2=8.315$ eV.

contributes ~8% uncertainty to C_{21}. Similarly, the error in C_{21} due to the uncertainty in C_{22} could at most amount to about 1%. Finally, it is clear that even if the assumed value of C_{12} were in error by 100%, the resulting value of C_{21} would be affected by only 10% for the extreme case, low β, 5% xenon in argon. No reasonable estimate of the slope constant C_{12} can be made on the basis of this experimental work; the majority of the generated electrons, for the mixtures studied and the test conditions encountered, arise from argon ionizing xenon.

TABLE I. Relative reaction rates.

Mixture	Reaction				
	β	C_{11}	C_{12}	C_{21}	C_{22}
5% xenon in argon	1.4	0.501	0.042	0.449	0.008
	1.8	0.230	0.020	0.737	0.013
20% xenon in argon	1.6	0.098	0.040	0.794	0.068
	2.0	0.032	0.013	0.881	0.075

The mixture data have associated with them error brackets which are equivalent to those for pure gases. The uncertainty introduced by possible variations from the specified mixture ratio is included in the brackets shown in the figures. Also shown in these figures are dashed lines representing the calculated composite atom–atom ionization behavior for a variation of ±20% in the slope constant C_{21} from its most probable value, 1.8×10^{-20} cm^2/eV. This uncertainty is judged to be a reasonable estimate of the error with which this cross section is determined. For comparison, the pure argon and pure xenon results of Ref. 1 are included on these figures.

Therefore, it is concluded that, within a probable error of about ±20%, the cross section for argon ionizing xenon is equal to the cross section for xenon–xenon ionization, as reported in Ref. 1.

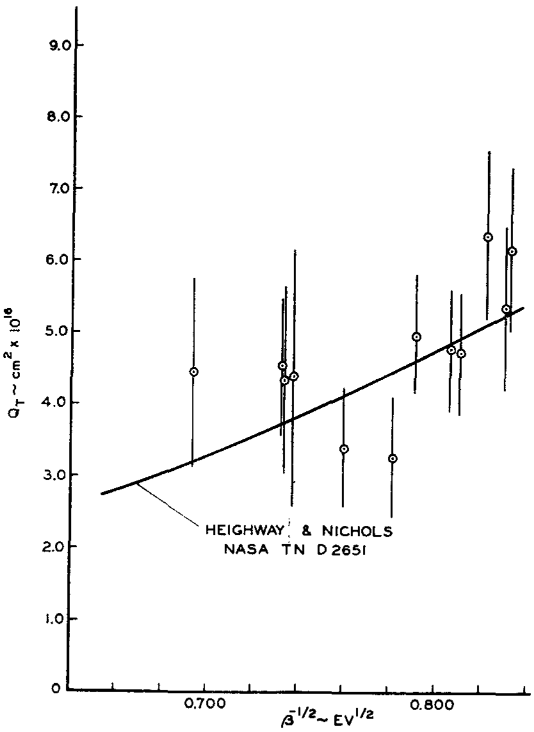

FIG. 3. Q_T versus $\beta^{-\frac{1}{2}}$ for argon+5% xenon. ⊙, 5-torr data. Electron and atom temperature assumed equal.

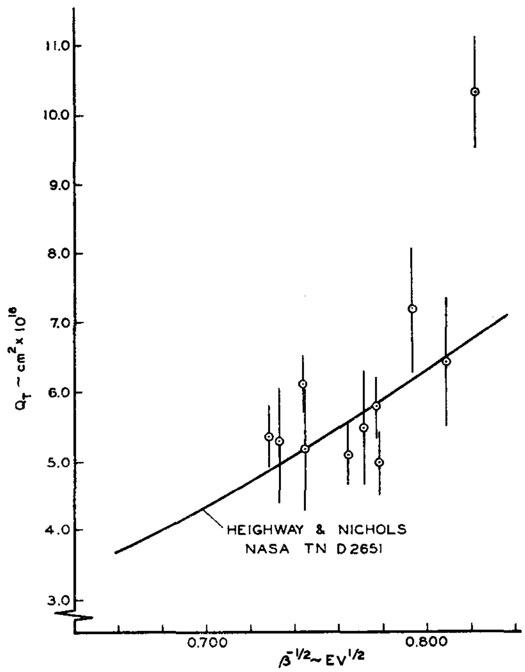

FIG. 4. Q_T versus $\beta^{-\frac{1}{2}}$ for argon+20% xenon. ⊙, 5-torr data. Electron and atom temperature assumed equal.

Electron–Atom Elastic Cross Sections

The transverse 24-GHz microwave probe,[4] in addition to sensing electron density, provided data on the electron collision frequency and consequently permitted an electron-heavy component cross section to be calculated. Because of the low level of ionization ($<10^{-4}$) present during microwave interaction, it was possible to discount electron–ion and inelastic electron–atom collisions and to identify the collision frequency as that due to electron–atom elastic momentum-exchange encounters. Assuming that the electron gas has a Maxwellian velocity distribution, the cross section obtained from these data is the Maxwell-averaged electron–atom elastic momentum-exchange cross section. The electron–atom elastic momentum cross section determined from the data is denoted Q_T and is shown plotted as a function of $\beta^{-1/2}$ in Figs. 3 and 4, assuming that the electron and atom temperatures were equal. Figure 3 presents results for 5% xenon in argon, and Fig. 4 for 20% xenon in argon. Electron–argon and electron–xenon cross sections for elastic momentum exchange, based on beam experiments, Ref. 5, are shown for comparison. In making this comparison, these results have been weighted in accordance to the relative proportions of the two gases present in the mixtures. The correspondence between the microwave and the beam results is good.

[4] R. G. Jahn, Phys. Fluids 5, 678 (1962).

[5] J. E. Heighway and L. D. Nichols, "Brayton Cycle MHD Power Generation with Non-Equilibrium Conductivity," Natl. Aeron. Space Admin. Tech. Note D-2651 (1965).