is present, the neglect of the requirement that the valence electron wave functions be orthogonal to the ion core functions. It appears, however, that in both cases the qualitative predictions are correct. Other sources of order-dependent energy may, of course, be present in some alloys. Size difference has often been suggested as favoring order, but it is difficult to carry out a good theoretical estimate of the effect or to find clear empirical evidence. Superlattices exist in systems with relatively little lattice distortion and are absent in systems with greater distortion; local order shows no evident correlation with size difference. In alloys of transition metals strong *d*-shell interaction may exist; there is evidence for this in the large number of superlattices occurring in such systems, in the absence of important differences of atomic number or ionic size.

Friedel[20] has discussed a valence effect in solid solutions which includes an order-dependent effect. His prediction is that clustering will occur at low concentrations of the metal with lower valency and short-range order at low concentrations of the metal with higher valency. Unfortunately, no experimental evidence is available for any case in which these predictions are in conflict with those of this paper. Such cases do exist, however, as in the magnesium end of the magnesium-indium system. Until data are available for such a system, it is not possible to say which effect will predominate when both may be present.

[20] J. Friedel, Advances in Phys. 3, 446 (1954).

ACKNOWLEDGMENTS

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Mean Life of the $^3P_2$ Metastable Argon Level*

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Using a previously described light absorption technique, the mean life of the metastable $^3P_2$ level of argon has been measured in pure argon as a function of pressure at 77°K and 300°K, and in mixtures of neon and argon at 300°K. The coefficient of diffusion of metastable argon atoms in the parent gas falls much more rapidly with decreasing temperature than the $T^{\frac{1}{2}}$ dependence predicted using the hard-sphere model. The cross section for the quenching of metastable atoms by two-body collisions with normal atoms changes slightly with temperature, in a manner inconsistent with the assumption of collision-induced transitions to the radiating $^3P_1$ level. As the temperature is reduced from 300°K to 77°K, the frequency of quenching by three-body collisions increases from $13.5p^2$ to $440p^2$ sec^{-1} (mm of Hg)^2. At a given total pressure, the two-body quenching collision cross section is much reduced and the three-body quenching collisions disappear as the ratio of partial pressures of neon to argon is increased.

1. INTRODUCTION

BY definition, an atom that does not emit electric dipole radiation is said to be metastable. The first excited configuration of argon consists of four levels, of which the $^3P_0$ and $^3P_2$ levels are metastable (Fig. 1). In the afterglow of an electrical discharge, atoms leave the metastable levels by the following processes:

1. Diffusion and complete de-excitation at the walls of the container. If the diffusion length of the container is great compared with the mean free path of the metastable atom, the destruction frequency of this process is inversely proportional to the total gas pressure.

2. The emission of forbidden radiation with a destruction frequency independent of the temperature and pressure. Under laboratory conditions, the corresponding destruction frequency is small in comparison with that of the remaining processes.

3. The emission of radiation induced by two-body collsions.

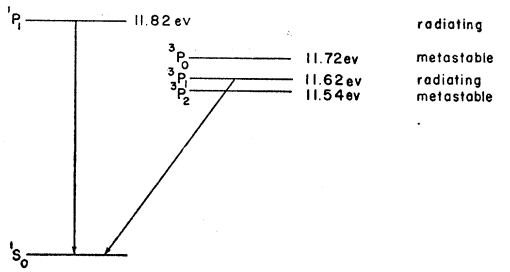

FIG. 1. Energy level diagram of the ground state and of the first excited configuration of argon.

* Supported by the Bureau of Ships.
† Now with E. I. duPont de Nemours and Company, Savannah River, South Carolina.
‡ Now with the National Bureau of Standards, Washington, D. C.

4. Transitions to a radiating level by two-body collisions. The corresponding destruction frequency is proportional to the total gas pressure and increases rapidly with temperature.

5. Ionization of impurities with an ionization potential less than the excitation potential of a metastable atom—the Penning effect.

6. The formation of metastable molecules by three-body collisions.[1,2] The corresponding destruction frequency is proportional to p^2.

7. Collisions of metastable atoms with ions and electrons early in the afterglow.

8. Collisions between pairs of metastable atoms, and the ionization of one of them, also in the early afterglow.[3]

The fourth process may be complicated by the imprisonment of resonance radiation. The effect appears to be much more pronounced in neon than in argon.

The effect of process (7) may be made negligible by using a sufficiently small excitation current, and that of (5) by the use of pure argon. In this research, no effect due to process (8) was detected. Neglecting higher diffusion modes, the first six processes cause an exponential decay of the metastable atom density with a mean life which may be represented by an equation of the type

$$\frac{1}{\tau}=\frac{D_0}{\Lambda^2 p}+Ap+Bp^2+\nu, \qquad (1)$$

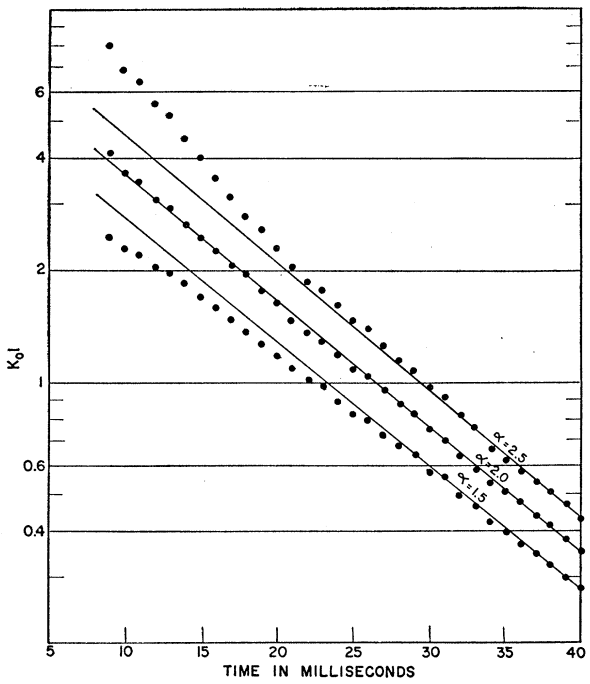

FIG. 2. Decay curves of the $^3P_2$ metastable level of argon illustrating the effect of the choice of effective α. λ7635 A spectral line, pressure 0.90 mm of mercury, tube A, temperature 300°K.

[1] A. V. Phelps and J. P. Molnar, Phys. Rev. **89**, 1202 (1953).
[2] L. Colli, Phys. Rev. **95**, 892 (1954).
[3] R. Schade, Z. Physik **105**, 595 (1937); **108**, 353 (1938); H. Büttner, Z. Physik **111**, 750 (1939).

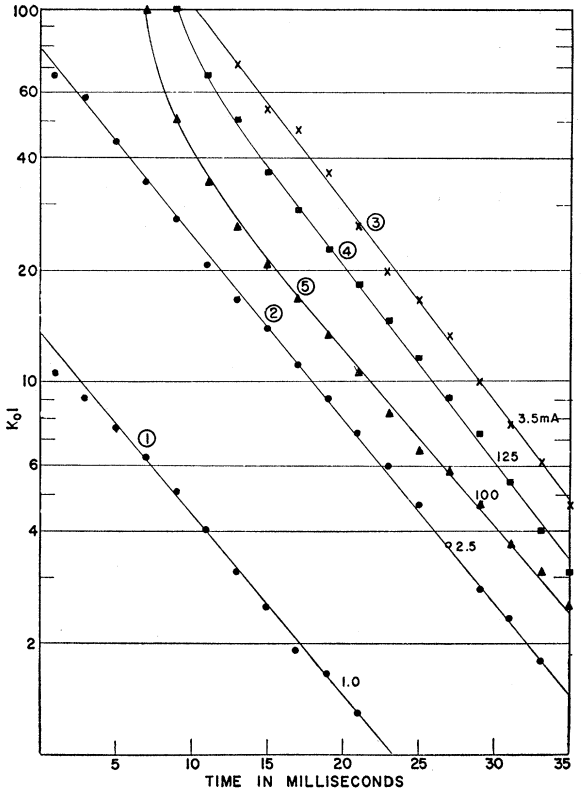

FIG. 3. Decay curves of the $^3P_2$ metastable level of argon illustrating the effect of absorption tube excitation current. λ7635 A spectral line, pressure 0.72 mm of mercury, tube B, temperature 300°K, $\alpha=2.25$, mean life 8.7 milliseconds, pulse duration 1 millisecond.

in which τ is the mean life of the level, D_0 the diffusion coefficient of the metastable atoms at a gas pressure of 1 millimeter of mercury, Λ the diffusion length of the container, p the gas pressure in millimeters of mercury, and ν the destruction frequency of a metastable atom resulting from the emission of "forbidden" radiation. The terms Ap and Bp^2 are respectively the frequency of two- and three-body quenching collisions of a metastable atom with normal atoms. For a cylindrical discharge tube $1/\Lambda^2=(5.81/a^2)+(\pi^2/L^2)$, where a and L are respectively the radius and the length of the container.

2. OPTICAL ABSORPTION TECHNIQUE

Light from the "emission tube" traverses the "absorption tube" and then a monochromator, which rejects all but one argon spectral line. The light flux is measured by a photomultiplier tube and the output displayed on a cathode-ray tube screen as a function of time. The type of electronic circuit used, and the method of synchronization have been described elsewhere.[4] The relative absorption of the light beam is a measure of the population of the corresponding excited level in the absorption tube.

[4] F. A. Grant and A. D. Krumbein, Phys. Rev. **90**, 59 (1953).

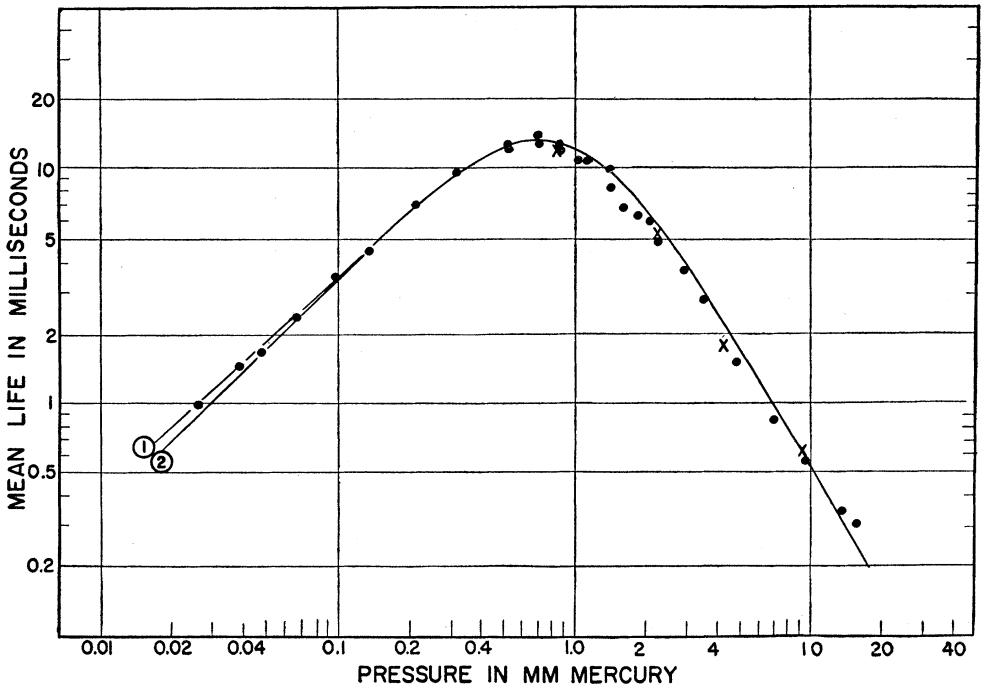

FIG. 4. Mean life *vs* pressure, $^3P_2$ metastable level of argon. Solid circles—λ7635 A spectral line, crosses—λ8115 A spectral line, tube *A*, $\Lambda_0^2=1.81$ cm², temperature 300°K. Solid curve (1) calculated using the equation $1/\tau=(54/p\Lambda^2(p))+37.5p+13.5p^2$; curve (2) calculated from the equation $1/\tau=(54/p\Lambda_0^2)+37.5p+13.5p^2$.

The transformation of measured absorption into relative values of the metastable atom concentration depends somewhat on the relative line widths of the emission and absorption lines. When all except Doppler-type broadening may be neglected, the absorption is related to the concentration of absorbing atoms by the equation[5]:

$$A_\alpha=\frac{k_0 l}{(1+\alpha^2)^{\frac{1}{2}}}-\frac{(k_0 l)^2}{2\,!(1+2\alpha^2)^{\frac{1}{2}}}+\cdots. \qquad (2)$$

l is the length of the absorbing path, and k_0 is the absorption coefficient. Provided that the population of the upper (final) level involved in the absorption transition is negligible in comparison with that of the lower (initial) level, k_0 is proportional to the concentration of the absorbing atoms. The quantity α is defined by the equation

$$\alpha\equiv\frac{\text{emission line breadth}}{\text{absorption line breadth}}.$$

For pure Doppler broadening, the value of α is determined by the temperature of the gas in the emission and absorption tubes. The gas was excited by electrical pulses short in comparison with the time intervals between them, thereby reducing considerably the average power supplied to the discharge tubes. The average temperature of the gas was practically that of the walls of the container, but during the excitation pulse and early afterglow, it could be somewhat greater. Since measurements were made in the afterglow of the absorption tube, the emission line breadth corresponded to a higher temperature than that of the absorption line. The value of α was therefore always greater than unity.

At gas pressures used in the present research, pressure broadening is small in comparison with Doppler-type broadening.[6] In order to permit the experimental determination of α, it was assumed that the effects of self-absorption[7] and other types of broadening were also sufficiently small to permit the line shapes to be described adequately in terms of "equivalent Doppler line widths."

It was further assumed that at sufficiently small small excitation currents the decay was an exponential function of time. The "effective α" for a given temperature and pressure was then taken to be that value which resulted in a straight line over the greatest time interval in the later afterglow, when the relative metastable atom density was plotted against time on semilogarithmic graph paper.

Experimental Determination of the "Effective α"

The decay curves of Fig. 2 were obtained when the transformation from absorption to relative metastable

[5] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, Cambridge, 1934), p. 323.

[6] K. Lang, Acta Phys. Austriaca **5**, 376 (1952); Sitzber. Österr. Akad. Wiss., Math.-naturu. Kl. **161**, 65 (1952), has measured the half-width of a number of neon spectral lines as a function of pressure using a Fabry-Perot interferometer. His emission tube had an inside diameter of 1 mm, the same as that used in the present research.

[7] To reduce the effect of self-absorption, small bore tubing, 1 mm inside diameter, was used in the construction of the emission tube.

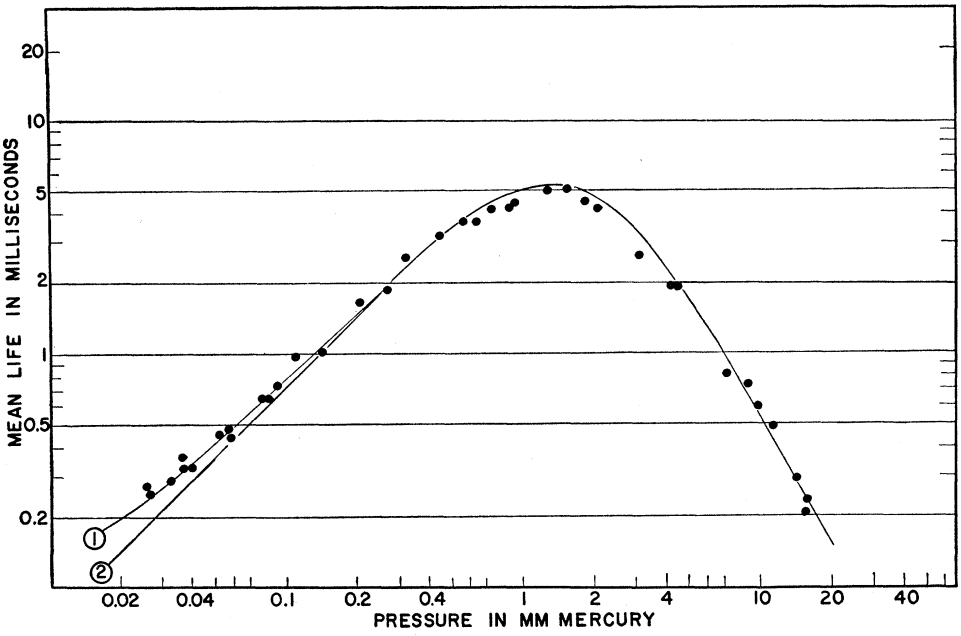

FIG. 5. Mean life *vs* pressure, $^3P_2$ metastable level of argon. λ7635 A spectral line, tube *C*, $\Lambda_0^2=0.337$ cm,^{2} temperature 300°K. Solid curve (1) calculated from the equation $1/\tau=(48/p\Lambda^2(p))+42p+13.5p^2$; curve (2) calculated using the equation $1/\tau=(48/p\Lambda_0^2)+42p+13.5p^2$.

atom density was based on choices of 1.5, 2.0, and 2.5 for the equivalent α. The value of 2.0 satisfied the foregoing criteria.

3. MEAN LIFE OF THE $^3P_2$ METASTABLE LEVEL OF ARGON AT 300°K

Effect of the Amplitude of the Absorption Tube Current Pulse

As the amplitude of the absorption tube current pulse was increased, the decay curves remained exponential in character, and the initial metastable atom density increased until the current exceeded about four milliamperes. Thereafter the initial metastable atom density decreased and the decay became increasingly nonexponential in the early afterglow. At a fixed time in the late afterglow, it is seen that the metastable atom density increases to a maximum and then decreases as the excitation current increases. Late in the afterglow there appears to be no significant difference in the rates of decay (Fig. 3).

We believe these effects to be due to the higher electron and ion density in the early afterglow, when the excitation current pulse is large. Under these conditions the decay may be further complicated by the relaxation of the gas temperature in the absorption tube after the cessation of the excitation.

Mean Life as a Function of Pressure

Tube A

Using an absorption tube having an inside diameter of 6.5 cm, the mean life of the $^3P_2$ metastable level of argon was measured as a function of the gas pressure. The results obtained by the use of the 7635-A and 8115-A spectral lines are in good agreement (Fig. 4).

The solid curve (2) of Fig. 4 represents an attempt to fit an expression of the type of Eq. (1) to the experimental data. The agreement is improved at low pressures [curve (1)] when allowance is made for the finite mean free path on the boundary conditions.[8]

Tube C

To accentuate the effect of the finite mean free path at lower pressures, the measurements were repeated, using an absorption tube having an inside diameter of 2.8 cm. The corresponding data and curves are plotted in Fig. 5.

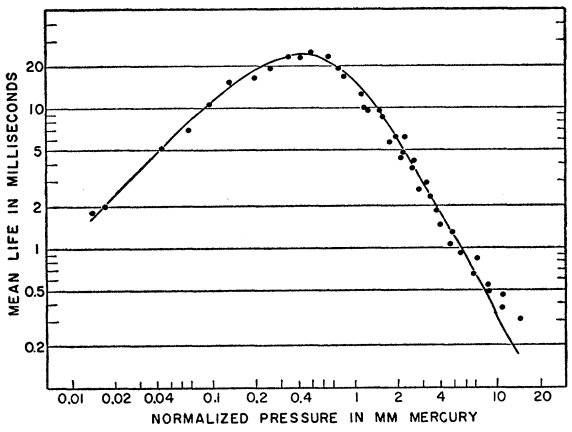

FIG. 6. Mean life *vs* normalized pressure $^3P_2$ metastable level of argon. λ7635 A spectral line, tube *B*, $\Lambda_0^2=0.95$ cm^2, temperature 77°K, solid curve calculated using the equation $1/\tau=(8.12/p\Lambda_0^2)+10+16p+29p^2$.

[8] A. O. McCoubrey, Phys. Rev. **93**, 1257 (1954).

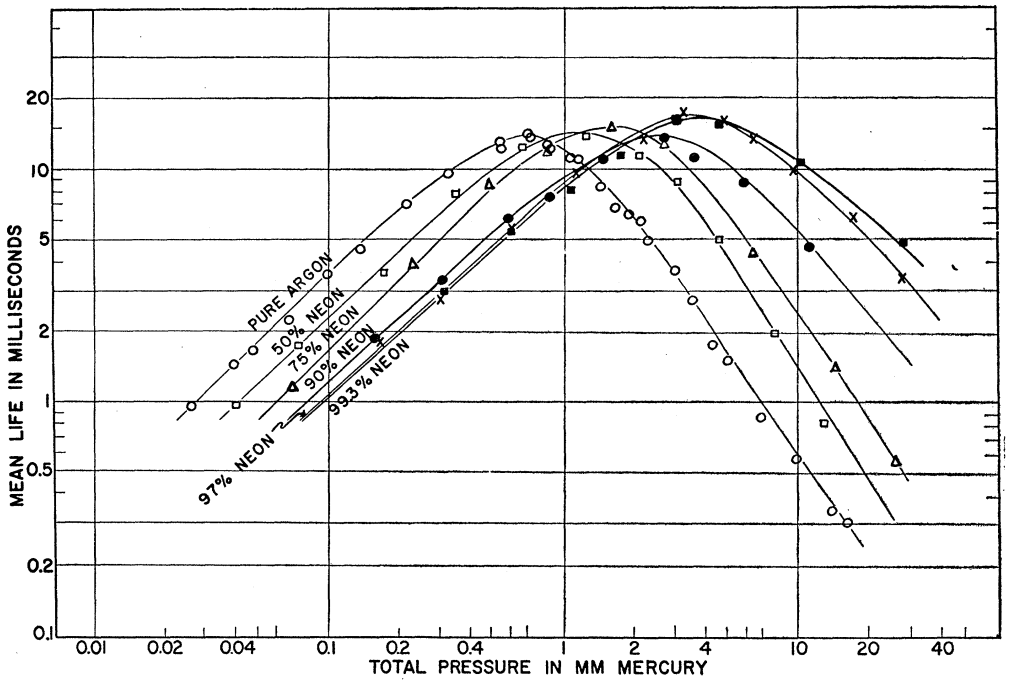

FIG. 7. Mean life of the $^3P_2$ argon level *vs* total gas pressure in mixtures of neon and argon. λ7635 A spectral line, tube *A*, $\Lambda_0^2 = 1.81$ cm², temperature 300°K.

Volume Destruction

Only the diffusion term in Eq. (1) is expected to depend upon the dimensions of the absorption tube (except when imprisonment of resonance radiation is important). The coefficient of the two-body collision term evaluated from the measurements obtained using the absorption tube of smaller inside diameter (2.8 cm) is ten percent greater than that obtained using the tube of larger inside diameter (6.5 cm). However, the variation is within the limits of the experimental error.

4. MEAN LIFE OF THE $^3P_2$ METASTABLE LEVEL OF ARGON AT 77°K

In order to fit a curve to the experimental results obtained at 77°K (Fig. 6), it was found necessary to include the constant term in Eq. (1). This constant term could possibly represent the effect of the decay of the level by the emission of "forbidden radiation," with a radiative transition probability of 10 per second. It is uncertain whether the disagreement between the solid curve and the experimental points at pressures greater than 10 mm is significant. These short mean lives could not be measured with the same accuracy as was obtained at lower pressures.

TABLE I. Diffusion coefficients and cross sections of the $^3P_2$ metastable argon atom in argon at 77°K and 300°K and in neon at 300°K.

	Discharge tube	Inside diameter cm	Diffusion length cm	Temp. °K	Diffusion coefficient at 1 mm Hg (cm² sec⁻¹)	Q_d cm²
A^* in A	*A*	6.5	1.81	300	54 ±6	95×10^{16}
A^* in A	*C*	2.8	0.34	300	48 ±6	107
A^* in A	*B*	4.7	0.95	77	2.1±0.4[a]	321
A^* in Ne	*A*	6.5	1.81	300	171 ±16	37

[a] For true (not normalized) pressure of 1 mm of mercury.

5. MEAN LIFE OF THE $^3P_2$ METASTABLE LEVEL OF ARGON IN MIXTURES OF ARGON AND NEON AT 300°K

Measurements of the mean life of the $^3P_2$ metastable level of argon in mixtures of neon and argon were made at 300°K. At pressures below about 0.5 mm of mercury the diffusion process is dominant. The results plotted in Fig. 7 show that at a given total pressure, the diffusion coefficient of metastable argon atoms increases with increasing neon admixture, and reaches a limiting value as the ratio of partial pressures of neon to argon is increased indefinitely. In the limiting case, the metastable argon atom is in effect diffusing through neon gas.

At higher pressures, the decrease in slope with increasing neon argon ratio indicates the decreasing importance of three-body quenching collisions.

6. DIFFUSION COEFFICIENTS AND CROSS SECTIONS

In Table I are listed the diffusion coefficients and diffusion cross sections calculated from the data of Figs. 4 to 7. Two points are worthy of notice. First, the large cross section for diffusion at 77°K reflects the effect of long-range forces and departure from the hard-sphere model. Secondly, the diffusion cross section for argon metastables in pure argon is much larger than for diffusion in neon.

TABLE II. Two-body quenching collision cross sections of the $^3P_2$ metastable argon atom for collisions with normal argon atoms at 77°K and 300°K and with normal neon atoms at 300°K.

	Discharge tube	Inside diameter cm	Diffusion length cm	Temperature °K	Frequency of two-body quenching in collisions at 1 mm Hg sec^{-1}	Density of normal atoms at 1 mm Hg cm^{-1}	Mean relative velocity cm sec^{-1}	Effective cross section Q_{eff} cm^2	$\frac{Q_d}{Q_{eff}}$
A^* in A	A	6.5	1.81	300	37 ±5	3.22×10^{16}	5.62×10^4	2.04×10^{-20}	476 000
A^* in A	C	2.8	0.337	300	42 ±5	3.22	5.63	2.32	462 000
A^* in A	B	4.7	0.95	77	62 ±10[a]	12.5	2.84	1.73	1 850 000
A^* in Ne	A	6.5	1.81	300	8.1±1	3.22	6.88	0.37	1 010 000

[a] For true (not normalized) pressure of 1 mm of mercury.

7. TWO-BODY QUENCHING COLLISIONS

In Table II have been listed the two-body collision coefficients, and the corresponding effective cross sections, Q_{eff}. The ratio Q_{eff}/Q_d is a measure of the probability per collision that an inelastic collision will take place. The value of this ratio increases by a factor of approximately four as the temperature is increased from 77°K to 300°K. Since transitions from the $^3P_2$ metastable level to the $^3P_1$ radiating level would increase more rapidly with temperature, this process is ruled out as the dominant two-body quenching mechanism.

8. THREE-BODY QUENCHING COLLISIONS

The three-body quenching collisions referred to a pressure of 1 mm of mercury have been listed in Table III. Also included is an estimate of the frequency of three-body collisions based on the assumption that the ratio of the two-body to the three-body collision frequency is approximately equal to the ratio of the mean free path to the sum of the radii of the metastable and normal atoms. This sum has been calculated from the measured diffusion coefficients.

TABLE III. Frequency of three-body quenching collisions of the $^3P_2$ metastable argon atom with two normal argon atoms at 77°K and 300°K.

	Discharge tube	Inside diameter cm	Temperature °K	Frequency of three-body quenching collisions at 1 mm Hg sec^{-1}	Mean free path from measured diffusion coefficient cm	Estimated frequency of three-body collisions at 1 mm Hg sec^{-1}
A^* in A	A	6.5	300	13.5	29×10^{-4}	100
A^* in A	C	2.8	300	13.5	26	100
A^* in A	B	4.7	77	440.	2.2	4500