Ionization by Alpha Particles in Mixtures of Gases*

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The presence of minute impurities greatly increase the ionization produced by Po alpha particles in helium. Systematic studies of this effect show an increase in ionization up to 40 percent for approximately 0.1 percent of argon. Similar results have been obtained with CO_2, Kr, Xe, H_2, N_2, and C_2H_4 as the contaminant. Preliminary experiments with mercury vapor in helium confirm the large effect already reported by others. A similar increase in ionization in pure argon is obtained by the addition of C_2H_2 or C_2H_4. These increases in ionization seem to be caused by the production of ions, when metastable atoms in the parent gas undergo collisions with molecules of the impurity. In mixtures of H_2, N_2, or A with helium, the excess in ionization is observed to decrease by a few percent as the pressure of the gas mixture is increased from 48 to 110 cm of mercury. For no other contaminant gases tested thus far in helium is such a pressure change in ionization observed.

FOR some time experiments have been in progress in this laboratory to study the rather striking changes in alpha-particle ionization in the noble gases produced by the introduction of minute quantities of other gases. Although a complete explanation of all the effects observed cannot be given at the moment, it seems worthwhile at this time to give a more extended description of the phenomena observed than has as yet been published.[1,2]

APPARATUS AND METHOD

Two methods were employed to measure the ionization produced by alpha particles in gaseous mixtures. In the first method[1,3] the ionization produced by single polonium alpha particles was measured by collimating these alpha particles along the axis of a long brass cylindrical ionization chamber (Fig. 1). The effective path was about 20 cm. The ions produced by each alpha particle were collected and fed into a vibrating-reed electrometer connected to a Brown strip chart recorder. The length of jump on the chart produced by each alpha particle was measured and the total of a large number of these averaged. With a knowledge of the voltage sensitivity and electrical capacity of the system one can determine the average number of ion pairs produced per polonium alpha particle. A very small correction for the ions lost within the collimating system was made.

In later determinations of the effect of the pressure of the gas mixture upon the ionization, a more robust chamber was used, in which the energy of alpha particles from Am^{241} was reduced to about 1 Mev by passage through a thin sheet of mica as they entered the chamber. A diagram of the arrangement used has already been given as Fig. 3 in a previous paper.[4] In this arrangement the total integrated current was measured.

Both types of measurement could be compared for any given gas mixture by computing the ratio of the ionization observed for any given impurity concentration to that observed in pure helium.

Elaborate precautions were taken to insure the purity of the gases used. The chamber shown in Fig. 1 was constructed with quartz insulators, to permit baking and pumping for a period of twelve hours at a temperature above 200°C. The gases used were taken from breaker-flasks and were known to be of very high purity. However, variable results in ionization were always obtained with helium and neon unless these gases were further purified by continuous circulation through a purification system consisting of a cocoanut charcoal tube immersed in liquid nitrogen. Such a positive continuous circulation was obtained through the use of a simple metal bellows pump.

When the chamber was filled with presumably pure helium and the circulation started over the purification system, a marked decrease in alpha-particle ionization was always observed within a few minutes after the pump was started. The ionization continued to decrease until a minimum value was reached, beyond which further circulation of the gas produced no effect. This minimum ionization was taken to be characteristic of pure helium, and the attainment of such a minimum was indeed used as a practical measure of the purity of the helium before contaminants were introduced.

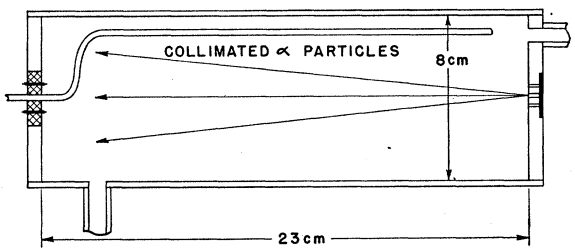

FIG. 1. Schematic diagram of ionization chamber used.

* Work performed under the auspices of the U. S. Atomic Energy Commission

[1] W. P. Jesse and J. Sadauskis, Phy. Rev. **88**, 417 (1952); Phy. Rev. **94**, 764(A) (1954).

[2] W. P. Jesse, Argonne National Laboratory Report No. 4944, 1952 (unpublished).

[3] Jesse, Forstat, and Sadauskis, Phy. Rev. **77**, 782 (1950).

[4] W. P. Jesse and J. Sadauskis, Phy. Rev. **97**, 1668 (1955).

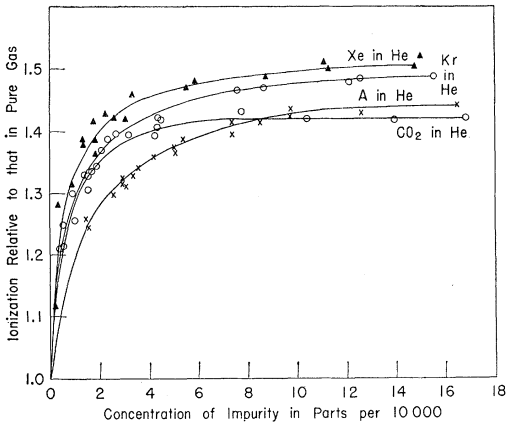

FIG. 2. Relative ionization measured as a function of the impurity concentration in helium.

It may of course be that more effective methods of purification could be devised which would produce a minimum ionization below that observed here. The minimum observed, however, seemed very stable under a wide variety of experimental conditions, and every effort to diminish it by such methods as prolonged gas circulation and periodic rebaking of the charcoal tube proved unavailing. The use of hot calcium as a purifying agent did not seem as effective as the charcoal tube.

The gaseous impurities were introduced into the pure noble gases in accurately measured quantities by means of a system resembling an inverse McLeod gauge. The impurity gas, in general from a breaker flask, was introduced into a small calibrated volume between two stopcocks and its pressure measured. It was then expanded into the accurately calibrated volume associated with the ion chamber and there mixed with a known volume of the noble gas. The composition of the mixture could thus be determined with an error of less than one percent.

EXPERIMENTAL RESULTS

Some of the data on alpha-particle ionization in helium mixtures are shown in Fig. 2. As abscissas are plotted the concentrations of the various impurity gases in parts per 10 000 by volume. As ordinates are plotted the ionization values observed for each impurity concentration relative to the ionization values observed for pure helium. The plotted points include measurements both for polonium and reduced Am^{241} alpha particles without distinction, since these were found in excellent agreement.

In Fig. 2 the ionization relative to that in pure helium increases rapidly at first with increasing impurity concentration, and then more slowly, apparently approaching finally a saturation value. This final saturation value does not seem to be exactly the same for each of the impurities in helium.

The effect of the various impurities can be seen with more exactness from the data in Table I. Here for convenience the ionization data are tabulated as a function of the concentration of the impurity and of the total pressure of the gaseous mixture. Where no pressures are indicated in Table I the ionization values have been shown to be independent of pressure, and those recorded represent a composite of readings taken at several pressures.

The effect of contaminants on the ionization observed in helium is not confined solely to the ionization produced by alpha particles of 5.3 and 1 Mev. Similar experiments for argon in helium mixtures, subjected to radiation from gamma rays from a radium source and also to beta particles from a Ni^{63} source, gave curves very similar to those shown in Fig. 2.

In order to observe the role of the pressure of the gas mixture, extensive measurements were made with the alpha particles of reduced ranges already mentioned. With hydrogen, nitrogen, and argon as contaminants in helium, a change in the ionization relative to that for pure helium was observed as the pressure of the gas mixture was altered between the limits of 45 and 110 cm of mercury. Typical results may be seen in the plotted curves for nitrogen in helium (Fig. 3) at the two pressures indicated, as well as in Table I. At lower pressures the relative ionization was found to be always higher than at the higher pressures. At lower impurity concentrations this change with pressure seems larger and diminishes with increasing concentration until, within the limits of accuracy of measurement, it seems to disappear at the highest concentrations used. Extensive measurements for argon in helium for pressures intermediate between 45 and 100 cm of mercury show an almost linear relation between the change in ionization and pressure. From the discussion which follows, it would seem that this could possibly be represented by an hyperbola of very small curvature, which deviates but little from a straight line within the small range of pressures investigated.

This change in relative ionization with pressure was observed only for the gases hydrogen, argon, and

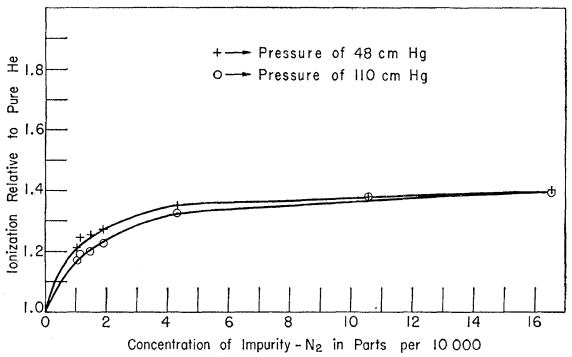

FIG. 3. Ionization curves for N_2 in He, showing the effect of pressure of the gas mixture.

TABLE I. Experimental results for relative ionization as a function of impurity concentration.

Gas mixture	Gas press. cm	Impurity concentration in parts per 10 000 by volume 0.25	0.50	1.00	1.50	2.0	3.0	4.0	5.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0	25.0	30.0
A in He	87.5	1.068	1.122	1.195	1.246	1.280	1.323	1.353	1.374	1.390	1.414	1.429	1.435	1.439	1.440			
Kr in He	···	1.169	1.226	1.296	1.337	1.365	1.401	1.422	1.439	1.451	1.466	1.473	1.480	1.484	1.484			
CO_2 in He	···	1.114	1.190	1.277	1.320	1.347	1.379	1.398	1.408	1.414	1.418	1.418	1.418	1.419	1.419			
Xe in He	···	1.170	1.252	1.331	1.369	1.398	1.436	1.455	1.468	1.477	1.488	1.495	1.502	1.503	1.504			
N_2 in He	48	1.080	1.13	1.206	1.246	1.273	1.317	1.347	1.357	1.360	1.370	1.380	1.390	1.400	1.402			
N_2 in He	110	1.049	1.097	1.166	1.207	1.236	1.283	1.316	1.330	1.338	1.350	1.364	1.375	1.390	1.400			
C_2H_4 in He	···	1.105	1.173	1.250	1.302	1.330	1.357	1.360	1.366	1.370	1.376	1.380	1.382	1.385	1.388	1.391		
H_2 in He	87.5	1.036	1.066	1.110	1.141	1.162	1.208	1.237	1.254	1.268	1.290	1.316	1.342	1.370	1.390	1.393	1.420	
H_2 in Ne	87.5	1.035	1.065	1.109	1.143	1.167	1.201	1.223	1.234	1.243	1.258	1.274	1.290	1.306	1.322	1.338		1.355
A in Ne	87.5	1.040	1.073	1.130	1.173	1.207	1.266	1.308	1.339	1.362	1.389	1.402	1.416	1.429				
Xe in Ne	87.5	1.170	1.240	1.303	1.343	1.371	1.407	1.430	1.444	1.453	1.460	1.460	1.460	1.461	1.462			
C_2H_2 in A	22.0	1.023	1.047	1.086	1.118	1.143	1.181	1.205	1.221	1.232	1.239	1.242	1.247	1.251	1.254	1.258		
C_2H_4 in A	22.0	1.012	1.023	1.041	1.055	1.067	1.084	1.093	1.099	1.102	1.107	1.110						

nitrogen as contaminants in helium. For no other gases was this change with pressure found, although similar measurements were made with CO_2, Kr, Xe, and C_2H_4. For the last four gases the ionization change between the limits of pressure indicated, if it exists at all, cannot be more than ten percent of that found for hydrogen, nitrogen, and argon. This represents the estimated limit of accuracy of the measurements.

COLLISION CROSS SECTIONS FOR METASTABLE ATOMS

A plausible explanation of the increase in alpha-particle ionization described in the last section is that this increase results from a transfer of energy from the metastable states in helium,[5] when an excited atom of helium encounters an impurity atom—let us say an argon atom. In the process the argon is ionized and a pair of ions collected in the chamber. Thus for argon in helium we have

$$He^*+A \rightarrow He+A^++e^-. \quad (1)$$

Any additional energy imparted by the metastable helium atom He* to the argon atom A above that energy to produce an ion pair is carried off as kinetic energy in the ejected electron e^-. The above reaction has already been studied under quite different experimental conditions in connection with metastable atoms.[6,7]

According to this explanation the two metastable states, 2^1S and 2^3S occurring in helium, of energy respectively 20.6 and 19.8 ev, should be able to ionize any impurity gas whose ionization potential is lower than these energies. However, neon, whose ionization potential is 21.6 ev, should not be ionized when added as an impurity. This is in accord with experiment, where no significant increase in ionization is observed when neon is added to helium.

With argon it is not easy to find a contaminant ionizable by its metastable states, since the energy available is low—about 11.6 ev. However, benzene vapor (ionization potential 9.2 ev) was found to give a marked effect. Similar effects were found for acetylene and ethylene as impurities in argon (Table I). The ionization potentials of these two gases are 11.4 and 10.5 ev, respectively.

The maximum increase in ionization produced by the various contaminants seemed to vary much more in the case where argon was the parent gas than for either helium or neon. Thus, the increase in ionization produced by acetylene in argon is almost double that produced by ethylene, Table I. Furthermore, an increase in ionization of about one percent was found when five percent of CO_2 or CH_4 were added to pure argon. Such an effect has already been noted.[8,9] Since the ionization potentials of both these gases are well above the energy available in the metastable states of argon, it would seem possible that the discharge of higher excited states in argon accounts for this ionization increase. Thus, in general, our own results confirm those already cited[9] to indicate that in argon mixtures the metastable states may not play as dominant a role in ionizing the impurity atoms as do the metastable states in helium and neon.

Methods of Calculation of Cross Sections

It is possible from the experimental results given in Fig. 1 and Table I to make an estimate of the relative cross sections for the reactions of metastable helium atoms with the various impurity atoms, as indicated by Eq. (1). In very pure helium this reaction does not take place at all, whereas for high impurity concentrations, we shall assume that almost all of the metastable helium atoms are destroyed by this process.

It is evident that in addition to the process above, where metastable helium atoms are destroyed with the production of ions, there must also be another process of destruction of metastable atoms without the production of ions, where the energy is lost perhaps by radiative processes. Such a process would be the dominant one in pure helium and would continue to compete with the ionization process in the presence of an impurity. In the present experiment these two

[5] The writers are indebted to Dr. Roland Meyerott who first suggested to them this explanation of the above phenomena.
[6] M. A. Biondi, Phy. Rev. **88**, 660 (1952).
[7] A. V. Phelps and J. P. Molnar, Phy. Rev. **89**, 1202 (1953).
[8] J. Sharpe, Proc. Phys. Soc. (London) **A65**, 859 (1952).
[9] Melton, Hurst, and Bortner, Phy. Rev. **96**, 643 (1954).

TABLE II. Calculation of cross sections for metastable atoms.

Gas	Direct method conc.	K_i/K_d-reciprocal of last column	K_i/K_d Stern-Volmer	Mean K_i/K_d	σ_i/σ_d	σ_i cm²
A in He	1.23×10^{-4}	8.1×10^{3}	5.7×10^{3}	6.9×10^{3}	9.3×10^{3}	Biondi (9.7×10^{-17})
H_2 in He	3.4×10^{-4}	2.9×10^{3}	3.0×10^{3}	3.0×10^{3}	2.4×10^{3}	2.5×10^{-17}
N_2 in He			6.5×10^{3}	6.5×10^{3}	8.6×10^{3}	9×10^{-17}
CO_2 in He	0.58×10^{-4}	17.2×10^{3}	13.0×10^{3}	15.1×10^{3}	20.4×10^{3}	21.3×10^{-17}
Kr in He	0.60×10^{-4}	16.7×10^{3}	17.1×10^{3}	16.9×10^{3}	23.3×10^{3}	24.4×10^{-17}
Xe in He	0.30×10^{-4}	20×10^{3}	20.9×10^{3}	20.5×10^{3}	28.5×10^{3}	29.7×10^{-17}
C_2H_4 in He	0.63×10^{-4}	15.9×10^{3}	12.2×10^{3}	14.0×10^{3}	18.5×10^{3}	19.4×10^{-17}
Hg in He	0.015×10^{-4}	670×10^{3}		670×10^{3}	950×10^{3}	1×10^{-14}
A in Ne	2.3×10^{4}	4.4×10^{3}	4.0×10^{3}	4.2×10^{3}	4.8×10^{3}	Biondi (2.6×10^{-16})
Xe in Ne	0.45×10^{-4}	22.2×10^{3}	23.7×10^{3}	23.0×10^{3}	30.4×10^{3}	16.4×10^{-16}
H_2 in Ne	2.3×10^{-4}	4.4×10^{3}	4.6×10^{3}	4.5×10^{3}	1.9×10^{3}	1.0×10^{-16}

competing processes would be the major sources of destruction of metastable helium atoms. The discharge of such atoms by diffusion to the walls of the chamber, while very important in small chambers at a few millimeters gas pressure, is negligible for the large chamber volume and gas pressures used here. Likewise the interaction of one metastable atom upon another with the production of an ion pair and a neutral atom must be assumed negligible here because of the relatively low density of metastable atoms.

In the two competing processes we may assume that the probability of a collision producing an ion pair is given by $\sigma_i N_i V_i$ and the probability of a collision producing the destruction of a metastable atom without ion formation by $\sigma_d N_{\mathrm{He}} V_d$. Here N_{He} and N_i are the number of atoms per cc of helium and of the impurity gas respectively, and σ_i and σ_d are the cross sections for the two reactions. V_i and V_d are the relative velocities of approach of the particles in the two cases.

At the impurity concentration where the probabilities of the two reactions are equal, we have the relation

$$\frac{\sigma_i V_i}{\sigma_d V_d} \equiv \frac{K_i}{K_d} = \frac{N_{\mathrm{He}}}{N_i} = \frac{1}{C},$$

where C is the concentration of the impurity in helium for this particular set of conditions. For convenience we shall henceforth represent the product terms $\sigma_i V_i$ and $\sigma_d V_d$ by the symbols K_i and K_d.

The impurity concentration corresponding to equal probabilities for the two methods of destruction of metastable atoms is easily determined from the corresponding plot of Fig. 1. At zero impurity concentration, that is, for pure helium, no metastables produce ions, while at the estimated maximum of the curve all the metastables produce ion pairs. The difference in these two ordinate values is proportional to the total number of metastables produced and one half the difference represents the case where half the metastables produce ions. The corresponding impurity concentration may easily be read from the curve for this particular set of conditions.

Thus for argon in helium the maximum ordinate of the curve is estimated to be 1.44, and the value for pure helium is unity by definition. The concentration corresponding to the mean of the two values is read on the curve to be 1.23×10^{-4}. Hence, $K_i/K_d = 1/C = 8100$. The K_i value for collisions producing ionization is hence some 8100 times larger than the K_d value for de-excitation without ionization. The ratios K_i/K_d thus determined are shown in column 3 of Table II.

It should be pointed out that in this somewhat naive method of determining K_i/K_d, no attempt has been made to correct the results for the ionization produced by "subexcitation electrons," which have been postulated by Platzman[10] to account for the differences in maximum value attained by the curves for the various impurity gases in helium. According to such a postulate, from each of these maximum values there should be subtracted a correction corresponding to the ionization produced by subexcitation electrons, and this adjusted maximum should be used in the calculations above. Since no precise estimates of the corrections involved are at present available, no such correction has been made here.

A more precise mathematical method for the computation of the ratio K_i/K_d may be employed.[11] It follows in general a relation first formulated by Stern and Volmer[12] in experiments dealing with the decay of fluorescent radiation.

Here virtually the same assumptions are made as were made above. Thus the metastable helium atom may be destroyed either by impact with an impurity atom resulting in an ion pair or by impact with one or more helium atoms resulting in de-excitation with ionization.

A simple mathematical derivation[2] results in the equation

$$\frac{1}{N_p - N_0} = \left(\frac{K_d}{K_i}\frac{1}{\alpha_0}\right)\frac{1}{C} + \frac{1}{\alpha_0}. \qquad (2)$$

[10] R. L. Platzman, Radiation Research 2, 1 (1955).

[11] The authors are indebted to Professor Robert Platzman who first called this useful method of representation of the data to their attention.

[12] O. Stern and M. Volmer, Physik Z. 20, 183 (1919).

Here N_0 is the total number of ion pairs collected per alpha particle in pure helium, and N_p is the total number of ion pairs collected in helium in the presence of an impurity at a partial pressure p. α_0 is the initial number of metastable helium atoms produced by one alpha particle. This equals the maximum value of (N_p-N_0) for high-impurity concentrations, if we ignore the correction for subexcitation electrons; C is the concentration of the impurity in helium; K_i and K_d are the constants as previously defined.

If, following the equation above, one plots on the ordinate axis the variable $1/(N_p-N_0)$ from the experimental data against $1/C$ on the abscissa axis, one should get a linear relation. The slope of the resulting straight line is equal to $(K_d/K_i)(1/\alpha_0)$ and the intercept on the ordinate axis is equal to $1/\alpha_0$, the reciprocal of the initial number of metastable atoms produced per alpha particle.

The Stern-Volmer plots derived from the data of Table I are shown in Fig. 4. For the data for H_2 and A as impurities, where some variation of ionization with the pressure of the gas mixture has been found, the data corresponding to a pressure of 87.5 cm of mercury were used in the plots. The implications of the variation with pressure will be discussed later.

It will be seen in Fig. 4 that the plotted points derived from the He data of Table I lie reasonably well on straight lines as is predicted by the Stern-Volmer equation. The heavier gas impurities have smaller slopes for their straight lines, corresponding to smaller values of $(K_d/K_i)(1/\alpha_0)$, and hydrogen has a much larger value for the slope. All the lines, with the possible exception of that for H_2, seem to meet at a common ordinate intercept indicating a constant value of $1/\alpha_0$. This is what would be expected if the effect of ionization by subexcitation electrons is assumed negligible, i.e., that the maximum ordinate of all the curves in Fig. 1 is the same. The data in Table I, however, show small but definite differences in these values at high-impurity concentrations. These small differences are apparently not readily distinguishable in the relatively small value of the reciprocal $1/\alpha_0$. Perhaps, on the whole, the chief deficiency of the Stern-Volmer relation is the difficulty in determining from the plots an accurate value of the ordinate intercept $1/\alpha_0$, since this intercept value is at times very sensitive to the exact manner in which the straight line is drawn through the plotted points—as in the plot for H_2 above.

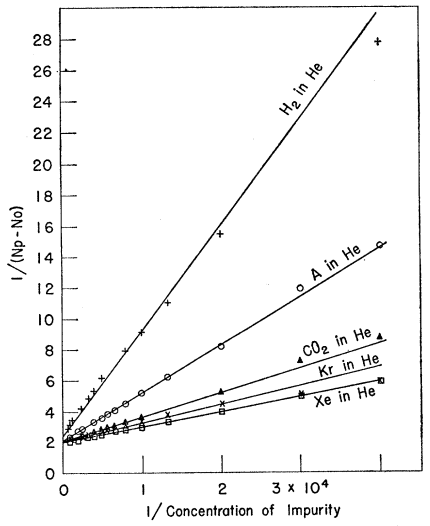

FIG. 4. Stern-Volmer plots for contaminants in helium.

Since the slopes of the Stern-Volmer lines are equal to $(K_d/K_i)(1/\alpha_0)$, one can determine values of the cross-section ratios K_i/K_d from values of the slopes and intercepts $1/\alpha_0$ in Fig. 4. These values are given in column 4 of Table II for comparison with the ratios obtained by the simpler method. The agreement between the two methods is satisfactory.

EFFECT OF PRESSURE OF THE GASEOUS MIXTURE

In order to interpret the observed change in ionization with the pressure of the gas mixture in the cases of H_2, N_2, and A, it is necessary to consider the mechanism by which a metastable atom may be de-excited in pure helium (see references 6 and 11). Such a de-excitation may occur through the following mechanisms:

(1) A two-body collision with a neutral helium atom. The possibility of raising by collision the electron from the metastable state to a higher state from which it can radiate would seem ruled out in helium because of the large energy required. It is possible, however, by a suspension of the selection rules for the electron to fall to a lower state during the collision and thus radiate energy. The probability for collision in any such two-body problem would increase directly with the number of helium atoms per unit volume and hence with the pressure of the mixture.

(2) A second possibility of de-excitation is a three-body collision of the metastable atom with two neutral helium atoms. An excited helium molecule is formed, which radiates energy and then immediately dissociates. Such a possibility has already been suggested by Burhop[13] from a consideration of preliminary data from our experiment. Thus

$$\mathrm{He^*+He+He\rightarrow He_2^{excited}+He}$$
$$\rightarrow \mathrm{He_2^{ground}+He+h\nu\rightarrow He+He+He+}h\nu.$$

The probability of such a three-body collision, being a compound probability, would be proportional to the square of the gas pressure. Thus,

$$\text{Collision probability}=Kp^2=(Kp)p.$$

For convenience the collision cross section may be considered to be (Kp), which is itself a function of pressure, and this quantity identified with the K_d

[13] E. H. S. Burhop, Proc. Phys. Soc. (London) A67, 276 (1954).

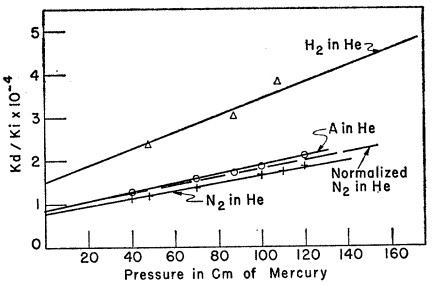

FIG. 5. Dependence of K_d/K_i upon pressure for H_2, N_2, and A in He.

above, with the understanding that K_d is now itself a function of pressure wherever this three-body collision is involved.

In Fig. 5 we have plotted for H_2, N_2, and A mixtures the values of K_d/K_i, the reciprocal of the quantity previously computed, against the corresponding pressure of the gas mixture. The plotted values of K_d/K_i are obtained by the following process. From a series of measurements at different impurity concentrations the approximate straight line relation between relative ionization and pressure is established for each value of impurity concentration. Ionization values for a series of interpolated pressures are then read from each plot. A Stern-Volmer plot for each interpolated pressure may then be constructed, relating the reciprocals of ionization values to those of impurity concentrations. From these straight lines the values of K_d/K_i may be computed by the method above. These values are plotted in Fig. 5 against the corresponding interpolated pressures. In the case of hydrogen, values of K_d/K_i, taken directly from three curves similar to those of Fig. 3, at 87.5, 108, and 48 cm pressure, were used in the plot.

All three plots in Fig. 5 for mixtures of helium with A, N_2, and H_2 show a linear increase of K_d/K_i with pressure, but each line has a definite intercept on the ordinate axis instead of passing through the origin. The latter might be expected if the three-body interaction is the only reaction involved. It would thus seem that $K_d/K_i=Kp+$constant, indicating a cross section directly proportional to pressure combined with a cross section which is independent of pressure—the latter probably a two-body interaction. For each of the mixtures the two component cross sections become equal when the pressure is approximately 80 to 90 cm of mercury.

If the hypothesis of Burhop is correct, the variation of K_d/K_i with pressure is caused by a variation in K_d rather than the alternative variation in K_i with pressure. In this case, since the variation in K_d is common to the three mixtures, the three plots in Fig. 5 should be identical except for the ordinate scale.

In Fig. 5 the dotted lines represent the plots for N_2 and H_2 after they are normalized to agree in intercept value with the argon value. This is done by multiplying each ordinate value by an appropriate constant. The normalized line for N_2 falls just below the argon line. The normalized H_2 line falls almost exactly on the argon plot—so close in fact that no additional line has been drawn. It should be noted, however, that the almost exact agreement between A and H_2 is somewhat subject to question, since the three experimental points in the original H_2 plot do not uniquely determine any straight line drawn through them.

The reasonably good agreement found here would seem to indicate the general correctness of the hypothesis of Burhop, that de-excitation of the metastable helium atoms takes place at least in part by a process of formation of excited molecules. There is, however, in addition another process of de-excitation of the metastable helium atoms the cross section for which is independent of pressure, probably representing an additional two-body interaction.

Perhaps the most puzzling part of the present experiment is the fact that for mixtures of helium with H_2, N_2, and A the pressure effect described above is observed, while mixtures with Xe, Kr, CO_2, and C_2H_4 give no detectable pressure change. A clue to the situation, however, seems to be furnished by a grouping of these gases in the order of their ionization potentials as in Table III. Here it seems that the pressure effect is observed with gaseous impurities whose ionization potential exceeds about 15 ev, while it is not observed in gases whose ionization potential falls below this approximate value. The widely diverse physical and chemical properties of the gases comprised in each group would serve to argue against any other criterion for classification than the value of the ionization potential.

No entirely satisfactory explanation of these facts is at once apparent. Perhaps the most plausible is that which assumes that the net energy available for transfer in the excited state of the helium molecule is about 15 ev. This net energy is the energy in the first vibrational level of the excited molecular state minus the energy of repulsion of two normal helium atoms at the same internuclear separation.

To explain the presence or absence of pressure effects let us first consider an idealized case, where the helium metastable atoms in pure helium are assumed to be de-excited solely by two-body collisions. When an impurity is added, one has then a competition be-

TABLE III. The presence or absence of a pressure effect in helium as it depends upon the gaseous contaminant.

Contaminant	Pressure effect	Ionization potential of contaminant gas (ev)
A	+	15.76
N_2	+	15.51
H_2	+	15.43
Kr	0	14.0
CO_2	0	13.73
Xe	0	12.127
C_2H_4	0	10.5

tween two processes the cross section of each of which is independent of pressure. Hence, K_d/K_i is not pressure-dependent.

Now let us assume that in the mixture helium metastable atoms may also in part be de-excited by the formation of helium molecules as described above. Provided the ionization potential of the impurity molecules is above the energy available in the excited molecule, a helium excited molecule cannot produce ions directly and must lose its energy only by radiative processes. Thus the competitive balance between the two processes is altered and K_d/K_i, following the law of formation of helium molecules, becomes pressure-dependent.

If, on the other hand, the ionization potential of the impurity molecules is below the energy available in the helium molecule, it might be expected that a direct energy transfer would take place on collision, resulting in the production of an ion pair. Thus the competition between the processes of radiation and direct ionization is again restored and the pressure effect would tend to be diminished.

In favor of the tentative hypothesis advanced above is the fact that independent measurements would seem to give a value for the available energy in the excited helium molecule in the neighborhood of 15 ev. Meyerott,[14] from optical spectra measurements, has argued for a potential energy curve for the helium molecule somewhat above that of Slater, and has established two points on the new curve. In Fig. 1 of Meyerott's paper the energy difference from the extreme limit of vibrational energy to his potential energy curve, somewhat extrapolated, is consistent with the value of 15 ev indicated by the results above.

Perhaps at present the most serious objection to the above hypothesis rests in the fact that we make the tacit assumption that for impurities of lower ionization potential the excited molecule may either produce directly a pair of ions on collision with an impurity, or radiate its energy on collision with a neutral helium atom. This assumes essentially that the excited helium molecule is in a metastable state.

Platzman has made calculations[15] to show that for the ionization by alpha particles in the present experiment more than 90 percent of the helium metastable atoms formed are in the singlet rather than the triplet state. Such singlet metastable atoms produce singlet helium molecules, while triplet metastable atoms produce triplet helium molecules. Only the latter molecules are metastable. The singlet molecules are in excited states and radiate with a comparatively short half-life. If the hypothesis above really depends on the assumption that the reacting helium molecules are metastable, it is difficult to see how one can obtain them in sufficient quantity by alpha-particle ionization processes which result, according to Platzman, mainly in singlet metastable atoms.

[14] R. Meyerott, Phy. Rev. **70**, 671 (1946).

[15] The authors are indebted to Professor Platzman for a private communication giving them the results of such calculations.

COMPARISON WITH OTHER EXPERIMENTS

Any valid comparison of the above results with the work of others is extremely difficult in that in the above work one determines only a ratio of cross sections σ_i/σ_d. Any absolute determination of either depends upon an assumed absolute value of the other. To obtain such an absolute value from the work of others is again difficult, since it is not at all certain that the same cross sections are being measured in the various experiments.

Absolute measurements of σ_d and σ_i for pure helium and for argon in helium have been made both by Biondi[6] and by Phelps and Molnar.[7] The former used a microwave technique to measure the ionization produced by metastable atoms in the afterglow of a pulsed discharge, while the latter made similar measurements using an optical absorption method. The measurements of both were made at gas pressures of a few millimeters of mercury. It seems apparent[16] that both of the above experiments dealt with interactions of metastable helium atoms mainly in the triplet state, while in our own case, according to the calculations of Platzman, the singlet state greatly predominated. Thus the expected cross sections in our own experiment should differ somewhat from the other two.

Although no exact agreement can be expected, it is possible to compare the three experiments solely as to order of magnitude of the results. If, so far as order of magnitude is concerned, Biondi's absolute measured value of 9.7×10^{-17} cm^2 for σ_i for argon in helium is identified with our own σ_i, then from our corrected ratio one can solve and obtain a value of $\sigma_d=9.8\times10^{-21}$ cm^2, which is in excellent agreement with Biondi's direct measurement of 9.6×10^{-21} cm^2. The exact agreement is somewhat illusory, since at least part of our cross section σ_d is a variable with pressure. Since the total cross section at 87.5 cm pressure is made up of almost equal parts of pressure dependent and pressure independent quantities, to correspond with the pressures of a few millimeters used by Biondi our own σ_d value should be reduced to about half the above value, or 4.9×10^{-21} cm^2.

Phelps and Molnar have found for the interaction of triplet state metastable atoms with neutral helium atoms a variation of the cross section σ_d with pressure according to the relation $\sigma_d=0.3\times10^{-23}p$ cm^2. Here p is the pressure in millimeters of mercury in experiments ranging from 20 to 100 millimeters. They apparently found no pressure independent cross section term as in the present experiment. For a pressure of 875 mm, corresponding to our own experiment, the Phelps and Molnar relation gives an extrapolated value for σ_d of 26×10^{-21} cm^2. This should correspond to the variable portion of our own cross section of σ_d, which at 875 mm

[16] A. V. Phelps, Phy. Rev. **91**, 436(A) (1953).

is about half the total of 9.8×10^{-21} cm^2 or 4.9×10^{21} cm^2. This is about five times smaller than that computed from the Phelps and Molnar relation.

While it may be possible that the fivefold discrepancy in cross section results from a difference in behavior between triplet and singlet metastable atoms, this divergence would seem somewhat excessive. It may also be that the large extrapolation with pressure in the calculation from the Phelps and Molnar relation is not justified.

For the sake of completeness, estimated values of σ_i for the various impurity gases are assembled in the last column of Table II. It should be pointed out again that at best these can only indicate order of magnitude. The values of σ_i were obtained by the following procedure.

The values of the cross section ratios σ_i/σ_d in column 6 were obtained from the K_i/K_d ratios in the preceding column by correcting for the relative velocities of approach of the particles in the two cases. This involves multiplying by

$$V_d/V_i=\left[\left(\frac{1}{m}+\frac{1}{m}\right)\Big/\left(\frac{1}{M}+\frac{1}{m}\right)\right]^{\frac{1}{2}}.$$

Here V_d and V_i represent, respectively, the relative velocities of approach for the interaction of a helium metastable atom with a neutral helium atom and for a helium metastable atom in its interaction with an impurity atom. The quantities M and m represent the mass numbers for the impurity atom and the helium atom respectively.

The relative velocity correction for a two-body interaction has been used here throughout, although for great accuracy the more complicated relation for a three-body interaction should in part probably be used. The final accuracy of the results, however, would hardly seem to warrant this added refinement.

The values of σ_i listed in the last column of Table II are obtained by again assuming σ_i for argon in He to be equal in order of magnitude to the Biondi value of 9.7×10^{-17} cm^2. The values of σ_i for the other gaseous impurities are computed on this basis from the relative ratios of σ_i/σ_d in the preceding column. This essentially assumes the constancy of σ_d in column 6. Similarly for the values where neon is the parent gas, the Biondi value of 2.6×10^{-16} cm^2 was adopted and other values calculated from this.

The values of σ_i in the last column are, as might be expected, of the same order of molecular cross sections as are computed by kinetic theory considerations. The variation in collision cross section does not seem very large with the exception of that for mercury, which is of the order of a hundred times greater than the others. This is in agreement with the findings of Biondi.

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