The Ionization of Neon, Krypton and Xenon by Bombardment with Accelerated Neutral Argon Atoms*

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A series of experiments on the ionization of noble gases by accelerated noble gas atoms, with an electrometer method, is described. Preliminary measurements by Beeck showing little velocity dependence for ionization of argon by argon atoms between 50 and 100 volts, and showing an ionization of neon by argon atoms in this energy range are shown to be due mostly to secondary effects—principally to argon radiation. Positive evidence is given for the ionization of one noble gas by atoms of another, and onset potentials for ionization are found to be: 55 volts for argon bombarding xenon; 50 volts for argon bombarding krypton, and approximately 130 volts for argon bombarding neon.

CERTAIN of the onset potentials for the ionization of noble gases by neutral noble gas atoms have been measured recently by Varney.[1] By using a balanced space-charge method devised by Lawrence and Edlefsen,[2] and improved by Varney,[3] he was able to measure the onset potentials for ionization of Ne by Ne, A by A, Kr by Kr, and Xe by Xe. Later work with a space-charge detector in conjunction with an apparatus designed to permit different gases to be used for target and projectile gave no measurable results for A in Kr or Xe.[4] The author, after a similar failure with the balanced space-charge method, then undertook to make such measurements using an electrometer method, similar to that employed by Beeck[5] for studying the ionization of noble gases by positive ion bombardment. The space-charge detector possesses many advantages over an electrometer method, since it measures only positive ions, while the latter also measures secondary electrons, which tend to obscure the real effect. Secondaries were found to play a very important role, but it is believed that the evidence for the ionization of Ne, Kr, and Xe by neutral A atoms is definite.

APPARATUS

A diagram of the apparatus is shown in Fig. 1. It is similar in construction to that used by Beeck[6] and the author,[7] except no velocity filter was used, in order to maintain the intensity of the neutral beam for low energies. Positive ions of the gas used as a projectile were formed in chamber I by electron bombardment from a hot tungsten filament. A mixture of ions and unionized gas diffused through slit 1 (slits 1, 2, 3, and 4 were 0.5 mm wide and 5 mm long; slit 1 was 8 mm deep, and the others 5 mm deep). The ions were picked up by an electrostatic field between slits 1 and 2. The ion beam reaching chamber III should be quite homogeneous, since the ions would diffuse from slit 1 with only gas kinetic velocities. The pressure in chamber II was kept low enough (chambers II and IV were evacuated by high speed mercury diffusion pumps) so that there would be few neutralizing collisions between slits 1 and 2. Chamber III was filled with the same gas as chamber I, so that part of the ion beam would be neutralized by charge transfer, a method first employed for this type of work by Beeck.[8] From slit 3 there emerged a mixed beam of ions and neutrals, from which the positives were removed by applying a retarding potential to slit 4. Secondary electrons were deflected out of the beam by the field of a small permanent magnet *m*. The

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[1] R. N. Varney, Phys. Rev. **50**, 159 (1936).

[2] E. O. Lawrence and N. E. Edlefsen, Phys. Rev. **34**, 284 (1929).

[3] R. N. Varney, Phys. Rev. **47**, 483 (1935).

[4] R. N. Varney. Private communication.

[5] O. Beeck, Ann. d. Physik **6**, 1001 (1930).

[6] O. Beeck, Ann. d. Physik **19**, 121 (1934).

[7] O. Beeck and H. Wayland, Ann. d. Physik **19**, 129 (1934).

[8] O. Beeck, Proc. Nat. Acad. Sci. **18**, 311 (1932).

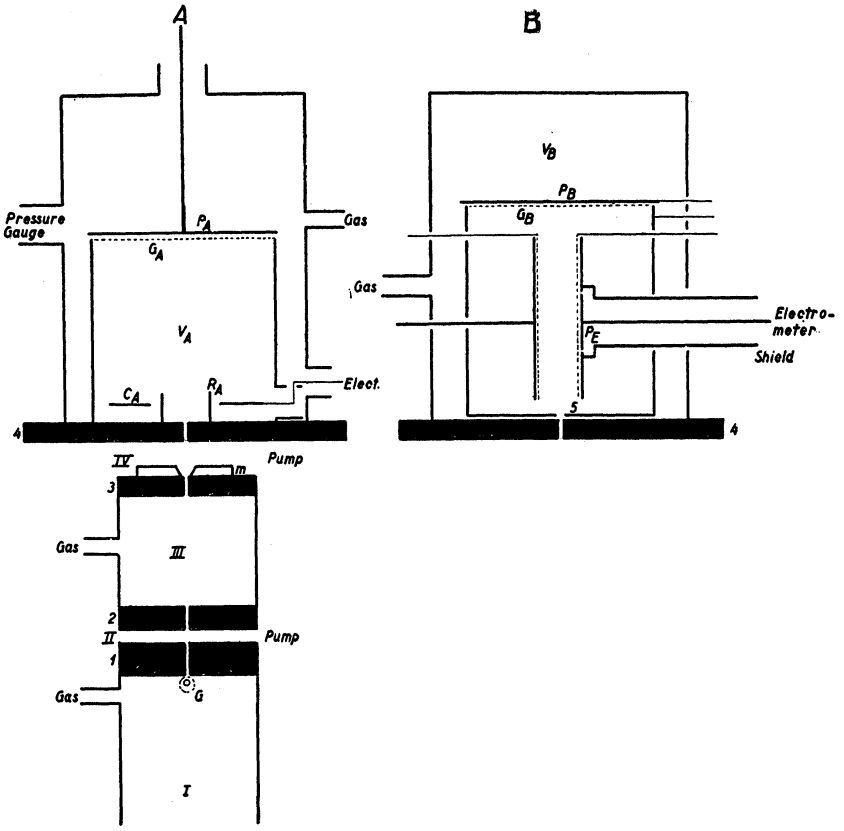

FIG. 1. Diagram of the apparatus.

resulting neutral beam then entered chamber V where its effects on various gases could be measured.

Two different measuring chambers were used for the study of the ionization. The first, V_A Fig. 1, proved to be useful only in determining the origin of the most important secondary effects. This arrangement was a modification of that used by Sutton and Mouzon,[9] and by Beeck[5] in their work on the ionization of gases by positive ion bombardment. A collecting ring C_A, protected by a guard ring R_A from impacts by the atom beam, was made positive with respect to the grid G_A. This field brought any electrons formed in the chamber—both primary and secondary—to the collector.

The actual onset potential measurements were made with arrangement V_B. In this apparatus, a parallel plate guard-ring condenser was used for collecting the electrons, giving a much more uniform collecting field. In addition, the major metal surfaces were protected by grids, which could be adjusted to such potentials as largely to suppress the secondary electron emission. The grids protecting the condenser plates were made of 2-mil Ni wire soldered to narrow brass frames. The wires were mounted 1 mm apart, and the front of the grid was 1 mm from the plate it covered. P_E was the actual collecting plate. The electrometer lead was electrostatically shielded by a brass tube, which also formed the support for the guard ring. The measuring chamber was insulated from the vacuum chamber by a ring of Bakelite BT 61, so that slits 4 and 5 were 1 mm apart. This allowed slit 5 to be made negative with respect to slit 4 in order to hold back secondary electrons formed in slit 4.

All surfaces except the grids and their frames were blackened with benzol soot to cut down

[9] R. M. Sutton and J. C. Mouzon, Phys. Rev. **35**, 694 (1930).

secondary emission, and to avoid reflection of radiation. The grids and grid frames were blackened with Aquadag—colloidal graphite in aqueous solution—since the heat of the sooting flame was sufficient to warp the grids.

The electrometer used for the measurements of the electron current was a Wulff string electrometer with a maximum usable sensitivity of 1000 scale divisions per volt, although it was usually employed at about half this sensitivity.

The gases were admitted to the various chambers through Smythe[10] leaks from 300 cc gasometer bulbs for A and Ne, and 100 cc bulbs for Kr and Xe. The A and Ne were obtained in pure form in liter flasks from the Air Reduction Sales Company. The Kr and Xe were left over from bulbs given to Beeck by the Linde A.G. in Germany. Since these gases had been sealed in only by stopcocks for several years, their purity was checked spectroscopically. The only contamination found was Hg vapor, which the trapping system failed to remove completely from the discharge tube. The A and Ne were passed through a liquid-air trap, and Kr and Xe through a CO_2 trap before being admitted to the apparatus.

The pressures used in chambers I and III were measured by vibration gauges. The readings of the gauges which corresponded to maximum emission were obtained empirically and used in adjusting the leaks, without attempting to measure the absolute values of the pressures. In the measuring chamber the pressure was measured on a McLeod gauge connected to the chamber through a trap cooled with liquid air for A and Ne, and with solid CO_2 and alcohol for Kr and Xe.

When the gas in the top chamber differed from that used for producing the atom beam, it was impossible to use a sufficiently high pressure in the neutralizing chamber to insure the maximum efficiency of neutralization, since interdiffusion would contaminate the gas being bombarded. Consequently the pressure in the neutralization chamber was adjusted to such a value that the pressure in the upper chamber was at most 2×10^{-4} mm of Hg, when no gas was admitted directly to that chamber. Since the lowest pressure used in the upper chamber was 2×10^{-3} mm of Hg, the contamination was kept to 10 percent or less.

[10] W. R. Smythe, Rev. Sci. Inst. **7**, 435 (1936).

Measurements

Collecting arrangement A.

In this arrangement, only the surface which was struck by the direct atom beam was protected by a grid. Consequently any secondary electrons knocked off the side walls by scattered atoms or radiation would be captured by the collector. For A in A, a very copious emission of electrons existed even for atom beams with energies below the value found by Varney for the onset. This emission also proved to be practically independent of the presence or absence of positive ions in the beam. Brasefield[11] interpreted similar results as indicative of an exceedingly high coefficient of emission of secondary electrons from metal surfaces when bombarded by neutral atoms. Rostagni's measurements,[12] however, showed that Brasefield's value was much too high. Photoelectric effect was believed to be responsible for the difference.

In the present work, the radiation from the filament did not knock off enough photoelectrons to be measurable at the sensitivity used, which allowed a current of about 1×10^{-14} amperes to be measured. However, as soon as the electrons from the filament were accelerated with sufficient energy to ionize, and consequently to excite, the A in the lower chamber, the effect began to show up. A beam consisting only of 60 volt A positives and radiation—chamber III was evacuated—was allowed to bombard the upper chamber. With no gas admitted to V_A, a potential of 20 volts applied to P_A reduced the current to the collector to 16 percent of its value when P_A and G_A were at the same potential. With A at a pressure of 8×10^{-3} mm in V_A, and the same bombarding beam, 20 volts applied to P_A reduced the current collected only to 73 percent of its original value. With Ne in V_A at a pressure of 1.5×10^{-2} mm, a potential of 20 volts on the plate reduced the current collected to 34 percent of its original value. The large amount of ionization apparently coming from the body of the gas in the A-A case

[11] C. J. Brasefield, Phys. Rev. **44**, 1002 (1933).

[12] A. Rostagni, Zeits. f. Physik **88**, 55 (1934) and Nuovo Cimento **11**, 99 (1934).

could not possibly have been due to ionization. Even for a bombarding beam of neutrals, the ionization at 60 volts had been found to be only a small fraction of the background, and in this case the neutral component must have been very small. The positives could have caused no ionization, as the onset for ionization of A by A^+ is about 300 electron volts.[13] * Cutting off the ion beam by a retarding potential made only a small difference, so the principal effect must have been due to scattering of the A radiation formed in the discharge. The A radiation is absorbed by the A in V_A, and reemitted in all directions, knocking secondary electrons off the side walls. Ne would show no such selective effect for A radiation, and consequently would not show so strong an effect, just as observed.

This copious emission of secondaries by the radiation gives experimental evidence for the discrepancy between his and Brasefield's results. It also accounts for the copious "ionization" of both A and Ne by A neutrals with *little velocity dependence* of the intensity of ionization between 50 and 100 volts found by Beeck[8] with an apparatus almost completely unprotected from photoemission. The fact that for A in A he found almost as many positives as negatives is readily explained. If the collecting field is such as to remove the photoelectrons from the plate connected to the electrometer, the string will be charged up positively. Consequently, the only difference between "positives" and negatives will be due to secondary electrons formed elsewhere, and to the small amount of ionization present. In the case of Ne, he would naturally observe fewer positives because the Ne is not so efficient in scattering the A radiation, and the relative importance of secondaries from other parts of the apparatus to those from the condenser plates is much greater.

Collecting Head B

In this apparatus the secondary emission could be suppressed by making the grids covering the major surfaces negative with respect to those surfaces. The effect of varying the collecting potential between the condenser plates, and that of varying the potentials of the grids with respect to the plates are shown in Fig. 2. It is seen from the coincidence of the 6 and 12 volt curves that grid potentials above 6 volts are sufficient to give a minimum of secondaries. Fig. 2 also shows that a collecting potential of 30 volts gives virtual saturation, while one of only 12 volts is sufficient for 90 percent of saturation.

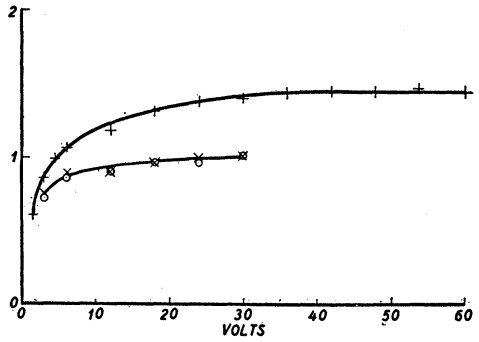

Fig. 2. Collecting potential required for saturation. Abscissae: collecting potential on condenser in volts. Ordinates: electron current to arbitrary scale. Legend: + grids at 0 volts; ○ grids at −6 volts; × grids at −12 volts.

The secondary electrons emitted from P_B could be held to a minimum by making it $22\frac{1}{2}$ volts positive with respect to G_B. Below G_B an attempt was made to keep the various potential differences low enough that electrons accelerated by them would not have sufficient energy to ionize the gas in the chamber, although actual measurements showed that the position of an inset was not affected by varying the collecting potential or the grid potentials. Slit 5 was made negative with respect to slit 4, 45 volts giving a minimum of secondaries.

In spite of all these precautions, secondary electrons formed a fair percentage of the total effect measured, but it was possible to get effects which seem attributable only to ionization of the gas by atom collision. Actual measurements were made collecting negatives, but in all cases except Ne in Ne a check run was made collecting positives to be sure that they were present. Since a collecting potential of 60 volts was required even to approach saturation for positives, it was deemed advisable not to attempt to collect them for an actual determination of the

[13] F. Wolf, Zeits. f. Physik **74**, 575 (1932).

* *Note added in proof:* Recent work by F. Wolf (Ann. d. Physik **29**, 33 (1937)) indicates that the onset of ionization of A by A^+ may occur below 100 volts. The efficiency indicated in his experiments is so low as not to affect the validity of the arguments presented here.

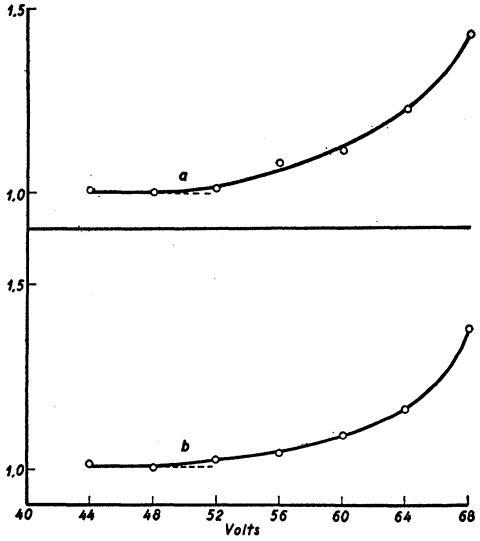

FIG. 3. Ionization of A by A neutrals. Abscissae: atom accelerating potential in volts. Ordinates: ionization current collected, reduced to background as unity.

onset, since both primary and secondary electrons would have enough energy to ionize the gas. Using low enough collecting potentials to be sure of no ionization by the electrons gave such small currents that no good determination of the onset could be made.

Runs were made as quickly as possible to avoid pressure changes, and warping of the filament as the supports became heated. The data taken under different conditions could not be reduced to a common basis by any method of correction that presented itself, so data were plotted run for run, and the onset potential obtained from comparing various runs. A point below the onset was taken as a standard, and a measurement of the current to the collecting plate was taken for this accelerating potential. The accelerating potential was then changed, and the current measured again. The acceleration was then returned to the standard value, and if the current collected had not changed appreciably, the run was continued. If the current collected at the standard points drifted slowly downward, as would be expected from decreasing pressures, the run was used. If, however, the standard was erratic, or drifted very rapidly, so that interpolation was dangerous, the run was thrown out. Data were generally plotted in relation to the background as unity, as this gives a good idea of the reliability, and absolute values are unnecessary for the location of the onset potentials.

ARGON IN ARGON

A in A gave not only the largest ionization currents of any of the combinations tried, but it also gave the largest absolute value of the background. Many runs were taken with A in A in learning to manipulate the apparatus, but very few data were taken under the conditions required for a "usable" run. The practice runs gave an indication that ionization set in in the neighborhood of 50 volts. The two runs which fulfilled the required conditions for steadiness are given in Fig. 3. It will be seen that the check with Varney's value of 48 volts ± 2 volts is excellent—so good that no further work with A in A was deemed necessary.

NEON IN NEON

The efficiency of ionization of Ne by Ne is very small, and in addition it is very difficult to get an intense neutral beam. In the only curve obtained for this case, Fig. 4, it is seen that the rise above

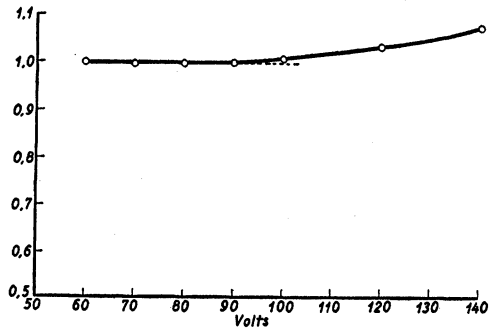

FIG. 4. Ionization of Ne by Ne neutrals. Abscissae: atom accelerating potentials in volts. Ordinates: ionization current collected, reduced to background as unity.

the background is small. The likelihood of obtaining a measurement for the onset which could be compared in precision with Varney's was deemed to be so small that further work with Ne as a bombarding agent was abandoned.

ARGON IN NEON

From a beam of A neutrals, with Ne in the ionizing chamber, curves *b*, *c*, *d*, and *e*, Fig. 5, were obtained. Curves *b*, *c*, and *d* gave promise

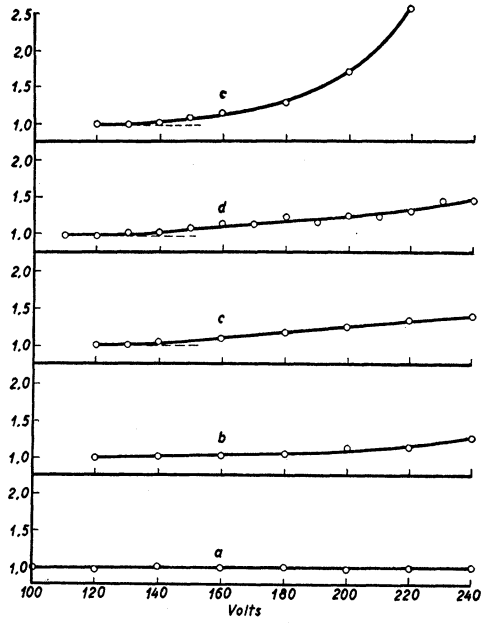

FIG. 5. Ionization of Ne by A neutrals. Abscissae: atom accelerating potentials in volts. Ordinates: ionization current collected, reduced to background as unity. Collecting potential 30 volts; grids 12 volts. Neon pressures: 4.5×10^{-3} mm Hg for *b*, 9.5×10^{-3} for *c*, 4.5×10^{-3} for *d*, and 1.6×10^{-2} for *e*.

that Ne really was ionized by A neutrals, and curve *e*, taken at a considerably higher pressure, gives definite evidence of ionization, and indicates the region of onset. Preliminary experiments showed no measurable rise in the curve below 120 volts. In order to ascertain the effect due to the residual A in the upper chamber, a run was taken over this energy range with the Ne shut off. This is shown in Fig. 5*a*, the flatness of which indicates that the effect in Ne is real, with ionization occurring above 130 volts.

ARGON IN XENON

Fig. 6 shows the results obtained for A bombarding Xe. Curves *a* and *b* gave the region of onset, using Xe pressures of about 4×10^{-3} mm of Hg. For the other measurements, the McLeod was out of order, so the pressure was not known accurately, but was estimated from a vibration gauge to be higher than for the first run. Two runs were attempted, the data for the first being given in curve *c*. The warping of the filament, with a resulting drop in the intensity of the atom beam, prevented the successful completion of the second run. Both runs, however, gave evidence of a definite break in the curve between 55 and 60 volts, as shown so clearly in curve *c*. Sufficient gas was not at hand to make further runs.

ARGON IN KRYPTON

The results for A in Kr are shown in Fig. 7. Curves *a* and *b* were taken quickly to establish the general region of onset, using low pressures to conserve gas. The pressure was then raised and curve *c* taken at 5 volt intervals. The flatness of the curve below 50 volts indicated that the onset must occur at that point or above, so curve *d* was taken with 2 volt intervals. The pressure was beginning to fall rapidly, so no further curves were taken. Although the major differences in background are due to the different pressures used, the intensity of the A beam may very well have dropped during the sequence of runs. Immediately after the last run, all of the gas was turned off, and the system allowed to pump down to a pressure of about 10^{-5} mm. Then the stopcocks leading from the leaks to chambers I and III were reopened, and the system allowed to come to equilibrium. The A pressure in the upper chamber was found to be 2×10^{-4} mm. The filament was then turned on, and a background set of readings was taken, Fig. 7*e*. It is apparent

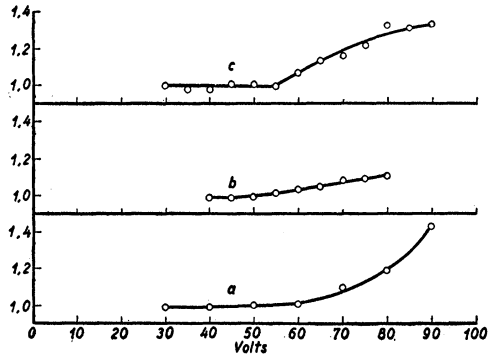

FIG. 6. Ionization of Xe by A neutrals. Abscissae: atom accelerating potentials in volts. Ordinates: ionization current collected, reduced to background as unity. Collecting potential 30 volts; grid potentials 12 volts.

from this that the onset for ionization of Kr by A in the neighborhood of 50 volts is real. The shape of the background curve also leaves little doubt as to the reality of the effect in xenon.

Discussion of Results

The conclusions to be drawn from the work with chamber V_A have already been discussed. Chamber V_B afforded the possibility of measuring the onset potentials for ionization of A, Ne, Kr, and Xe by A neutrals. The check with Varney's value for A in A makes this work directly romparable with his in studying the variation of onset potential with change of target atom. His cesults are given in parentheses in Table I, while those of this work are given without parentheses. It is interesting to note that the onset potential rises as we progress from the diagonal, as predicted by the simple theory of Zwicky.[14] The actual value for the onset in the case of A in Ne cannot be taken too seriously, as the rise of the curve is so slow. The value for A in Xe is considerably better, although it is true that curve *b* suggests that there may be some effect below the 55 volts assigned to the onset. This may have been due to the A background, as the total rise is not great in this case. The case for A in Kr is certainly the most clean cut. Here there can be no question that a marked effect sets in just above 50 volts.

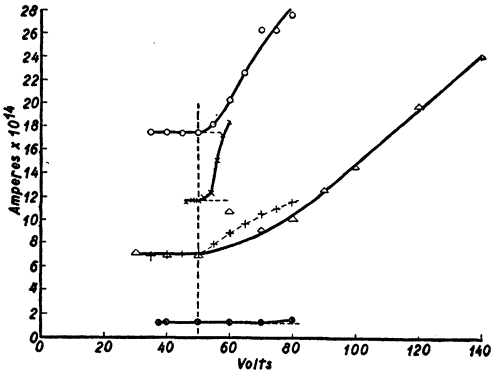

Fig. 7. Ionization of Kr by A neutrals. Abscissae: atom accelerating potential in volts. Ordinates: ionization current collected, in amperes $\times 10^{14}$. Legend: △ curve *a*; + curve *b*; ○ curve *c*; × curve *d*; ⊕ curve *e*. Collecting potential 30 volts; grids 12 volts. Krypton pressures: 3.3×10^{-3} mm Hg for *a* and *b*; 9×10^{-3} for *c*, and 7×10^{-3} for *d*.

[14] F. Zwicky, Proc. Nat. Acad. Sci. **18**, 313 (1932).

Table I. *Ionization potentials (in electron volts) for ionization of gases by bombardment with noble gas atoms. Varney's results in parentheses.*

Bombarding Atoms	Target Atoms			
	Ne	A	Kr	Xe
Ne	(74)			
A	130?	48 (48)	50	55
Kr			(40)	
Xe				(35)

All of the curves, with the possible exception of those for A in Kr, tend to indicate that the onset for ionization by atom bombardment is not sharp. For the A-Kr case, if we were to take curve *c*, Fig. 7, we would be tempted to extrapolate back to 52 volts as a sharp inset. However, when a 52-volt point was taken, curve *d*, it is seen to make the curve swing into the background instead of cutting it sharply. The probability of ionization must rise sharply between 50 and 55 volts, but there may still be some ionization even at much lower potentials.

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