Ionization of Inert Gases by Positive Alkali Ions

ROBERT N. VARNEY, *University of California, Berkeley*

(Received February 4, 1935)

The ionization potentials of the noble gases under impact of various positive alkali ions have been determined in a new and independent manner which employs the neutralization of an electron space-charge by the newly formed positive ions to show the ionization. The method is extremely sensitive to the positive ions but is not affected by the secondary electrons which are liberated from the walls. The potentials found are different for each combination of gas and alkali ion and range in value from 5 to 20 times the electron ionization potentials. They are lower, by amounts running as high as 45 volts in some cases, than those found by Beeck and Mouzon. No ionization was observed by Li^+ ions, none by Na^+ ions except in Ne gas, or in Ne gas by any ions but Na^+. When the actual energies available for ionization, after conservation of energy and momentum have been taken into account, are calculated, the results are strikingly self-consistent, whereas the unreduced results are not at all so. Certain results published by Beeck and Mouzon, but which could not be checked by the author, fail to show this self-consistency.

THE ionization which results when positive ions strike atoms of various gases has occasioned surprise, on the one hand because the ionizing potentials were so low when compared with those for H^+ and He^{++} collisions, and on the other hand because the same potentials were so high when compared with electron ionization potentials. The argument on the question of whether ions need energies of 10,000 volts or more to ionize by collision or whether they needed only a few times the electron ionization potential of the target atom was settled by Loeb[1] in 1927 when he pointed out the existence of a distinct and different mechanism for ionization by fast ions and by slow ions. It was pointed out that the relatively slow ions might depend on some quantum-mechanical process of interaction to ionize by collision in which the ion and the atom formed a molecule for an instant which had an unstable electron when the ion had sufficient energy. This process has been discussed by Weizel and Beeck[2] in the light of subsequent experiments.

To investigate these low ionization potentials, Sutton,[3] Beeck,[4] Mouzon[5] and others undertook careful investigations of the ionization which occurred when noble gases were bombarded by low energy alkali ions. They found that the efficiency of ionization varied considerably with various combinations of gases and ions and that the greatest efficiency resulted in general when the ion and gas had the most nearly equal atomic weights. Careful investigation of the actual ionization potentials, or minimum speeds necessary for ionization, was completed in 1932 by Beeck and Mouzon,[6] and showed that the potentials ranged in fact from 6 to 20 times the electron ionizing potentials.

The method used to determine the minimum ionizing speeds depended on observing the electrons which were detached from the neutral gas atoms. This method has two serious disadvantages. The first is that the ionization process is inefficient enough to require measuring instruments of the highest possible sensitivity to detect the few ionization electrons. The second disadvantage is that having the instruments of necessary sensitivity, it becomes increasingly difficult to avoid measuring the spurious secondary electrons which are liberated from the walls of the apparatus by radiation, positive ion impact and metastable atom impact.

To eliminate both these difficulties at once, to provide independent checks of the previous results and to investigate whether ionization could be found at energies more nearly equal to the electron ionization potentials, the method of Lawrence and Edlefsen[7] for detecting photo-ionization in vapors was adapted to the problem of positive ion ionization. This method is highly

[1] Loeb, Science **66**, 627 (1927).
[2] Weizel and Beeck, Zeits. f. Physik **76**, 250 (1932).
[3] Sutton, Phys. Rev. **32**, 364 (1929).
[4] Beeck, Ann. d. Physik (5) **6**, 1001 (1930).
[5] Mouzon, Phys. Rev. **35**, 695 (1930).
[6] Beeck and Mouzon, Ann. d. Physik (5) **11**, 737, 858 (1931).
[7] Lawrence and Edlefsen, Phys. Rev. **34**, 233 (1929).

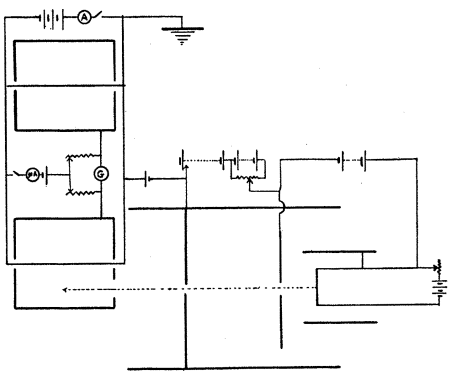

FIG. 1. Diagram of the apparatus showing connections.

sensitive to positive ions and is quite insensitive to electrons, primary or secondary.

Two hollow, monel metal cylinders, 19 by 20 mm, are mounted with a filament of 5 mil tungsten wire running axially down the center of each. (See Fig. 1.) The ends of the cylinders are closed except for small holes through which the filament connections project and except for a hole through which positive ions may enter one cylinder. A small potential of one or two volts is applied between the cylinders and filaments. When the filaments are heated, a space-charge limited current of electrons flows between the filaments and the cylinders. This electronic current is extremely sensitive to positive ions in the space-charge region. Since the positive ions remain in the region 30,000 to 40,000 times as long as the electrons, each ion is effective in neutralizing the space-charge of 30,000 to 40,000 electrons.

Since a space-charge limited electron current is already flowing in the cylinder, further electrons liberated by positive ions in any manner can have no effect on the electron current. In addition, if they could have an effect, it would only be about 10^{-4} times that of the positive ions. The measuring of the electron current thus provides an excellent means of observing any ionization that may be produced.

Two filament-cylinder units are used instead of one in order to provide means of eliminating small fluctuations in the electron current which would interfere with the measurements. Instead of connecting the two filaments in series as Lawrence and Edlefsen did, they were connected in parallel. This is more satisfactory for the following reason: Aside from geometrical factors, the space-charge limited current depends only on the voltage, $I=kV^{\frac{3}{2}}$. A fluctuation in voltage dV would cause a corresponding change in current $dI=3/2kV^{\frac{1}{2}}dV$. If the geometrical factor k is the same for both cylinders, dI will only be the same in both if V is the same in both (dV will be the same for either series or parallel connection). Because of the voltage drop down the filament, V will not be the same in both cylinders if the filaments are in series, but will be if they are in parallel.

Similarly to Lawrence and Edlefsen's method, the two space-charge units are connected as two arms of a Wheatstone bridge circuit; two variable resistances, about 10,000 ohms each, are used for the other two arms, and a galvanometer of sensitivity 9×10^{-11} amp./mm is used for the bridge.

The positive alkali ions are projected directly into one of the cylinders. The other cylinder is shielded from the ion beam, and so all fluctuations in electron current except those due to the positive ions and the ions they form are balanced out. The ions are obtained directly from a heated platinum filament coated with a Kunsman catalyst[8] containing the salt of the alkali ion desired. The ions are accelerated in two stages through a slit system and then enter the detector. The whole tube is filled with the gas to be ionized at a suitable pressure to insure that ionizing collisions will occur in the cylinder. This pressure ranges from 4×10^{-3} mm to 1.5×10^{-2} mm Hg. The average distance traveled by the alkali ions is about 5 cm. The ions of the beam affect the detector, as is to be expected, but above 10 volts energy, this effect becomes quite independent of speed. It can thus be eliminated by changing the resistances to bring the bridge back to balance.

As the accelerating voltage applied to the beam is raised, the galvanometer deflection is observed to remain constant or nearly so until a critical value of the voltage is reached. Above this voltage the galvanometer deflection increases linearly with the voltage (see Fig. 2). This critical voltage where ionization begins was determined for each of the 5 alkali ions in each of the 5 noble

[8] Kunsman, Science **62**, 269 (1925).

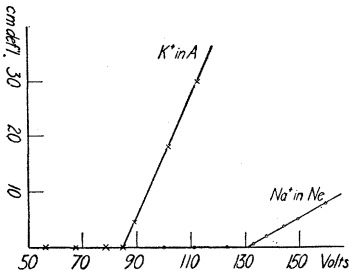

FIG. 2. Plot of galvanometer deflection in cm against alkali ion speed in volts.

gases (He, Ne, A, Kr, Xe). The potentials in volts at which ionization begins in each case are given in Table I.

These results have all been carefully checked. The unknown errors in speed of the ions do not exceed ± 3 volts. Further errors which may exist must tend to give lower rather than higher values, for while it is possible that the ions do not gain the full energy of the applied field, it is quite impossible for them to be moving with greater energies than are actually applied to the tube.

The neon, krypton and xenon gases were purchased from the producers as 100 percent pure, and no further attempts at purification were made. The argon and helium were drawn from commercial tanks, and though they showed no spectroscopic traces of impurities, they were passed over hot copper to remove oxygen and over tubes of calcium chloride, phosphorus pentoxide, and potassium hydroxide to remove water and carbon dioxide. Further, the argon was treated in a calcium arc and the helium was run through a double, liquid-air cooled charcoal trap.

TABLE I.

	Ne	A	Kr	Xe
Li^+	*307*	*100*	*420?*	*250*
	—	—	—	—
Na^+	*175*	*105*	*400?*	*360?*
	130	—	—	—
K^+	*320*	*95*	*80*	*120*
	—	82	69	114
Rb^+	*423*	*180*	*100*	*145*
	—	135	$97\frac{1}{2}$	150
Cs^+	*437*	*365*	*243*	*105*
	—	338	200	77

Italics, Beeck and Mouzon results.
Ordinary figures, Varney results.

Before taking readings the tube was thoroughly baked out at about 400°C, the test of the thoroughness being that when the tube was cut off from the pumps with less than 10^{-6} mm Hg pressure, the pressure would not show any signs of starting up when all the filaments were heated to their maximum temperatures for half an hour. The time necessary for a complete set of readings with one ion source in one gas did not exceed this period. The pressure was measured on a large McLeod gauge. A liquid-air trap was connected to the tube at all times when readings were taken to remove Hg vapor and any last traces of water or grease vapors which might be present.

All the catalysts emitted only the ion desired with the exception of the Rb^+ source and the spodumene Li^+ source. The Rb^+ showed all the other alkali ions, and all the curves using the Rb^+ source had two or three break points corresponding to ionization by the "impurity" ions as well as the Rb^+ ions (see Fig. 3). Because of the great efficiency of K^+ in A and Kr, and of Cs^+ in Xe, the effect of one or another of these impurities was almost as great as the effect of the Rb^+. The voltage obtained as the ionization potential for any ion in a gas was of course the same whether the ion came directly from a pure source or as an impurity in some other source. The only possible doubt of the possibility of interference of an impurity with the results on the ion desired is that the values for Rb^+ in Kr and in Xe seem a little high. The spodumene used as a Li^+ source showed considerable quantities of K^+ which interfered with the use of the source in anything but He and Ne. No ionization was observed with the Li^+ nor with Na^+ in any gas except Ne. Likewise, no ionization was observed in He or in Ne (except for Na^+ in Ne). H_2, N_2 and CH_4 were also tried with several ion sources (Na, K, Rb, Cs) and although ionization by Na^+ and K^+ was originally reported in N_2,[9] the results could not be repeated, even under conditions of greater sensitivity, so it was necessary to conclude that it did not occur at all. It is possible that since the degassing of the tube was not so carefully done at first, traces of argon from previous readings gave wrong results. No ionization was observed at all in the other two gases.

It is believed that the sensitivity of the

[9] Varney, Phys. Rev. **46**, 235 (1934).

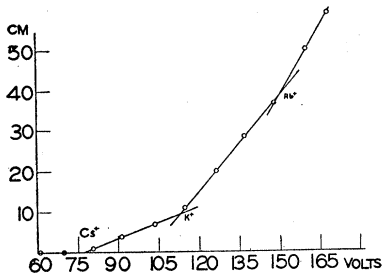

FIG. 3. Plot of galvanometer deflection in cm against alkali ion speed in volts when the Rb^+ ion catalyst containing impurities was used in Xe gas.

apparatus was sufficient to enable less ionization to be observed than Beeck and Mouzon reported, but this point is hard to establish because it is only possible to make qualitative comparisons of relative ionizing efficiencies.

When energy and momentum are conserved in an inelastic collision of the type above, it can easily be shown that only a fraction of the energy of the incident ion is available for changing the internal energies. This fraction has a maximum value for direct impact and is equal to $m_aE/(m_i+m_a)$, where m_a is the mass of the gas atom, m_i is the mass of the alkali ion and E is the incident energy of the alkali ion. When this factor is applied to the results, they assume a much more significant form. (Table II.)

Attention is called to the following features of Table II. First, in certain cases, the same electronic configuration is involved in two different collisions. For example, K^+ and A are identical in structure except for a difference of one proton in the nucleus, and the same is true for Rb^+ and Kr. Consequently, collisions of Rb^+ and A involve the same electron structures as K^+ in Kr, the only difference lying in which is the colliding ion and which is the atom ionized. Similarly, Cs^+ ions in A and K^+ in Xe involve collisions of identical groups of electrons, and likewise Cs^+ ions in Kr, and Rb^+ in Xe. Now the table of reduced results shows corresponding

TABLE II.

	Ne	A	Kr	Xe
Na^+	61			
K^+		41	47	83
Rb^+		43	48	90½
Cs^+		78	77	38

TABLE III.

	Reduced	Unreduced
Rb^+ in A	43	135
K^+ in Kr	47	69
Difference	− 4	66
Cs^+ in A	78	338
K^+ in Xe	83	114
Difference	− 5	224
Cs^+ in Kr	77	200
Rb^+ in Xe	90½	150
Difference	−13½	50

similarities in ionization potentials which do not appear in the unreduced results. (Table III.) This improvement in correlation of results in corresponding cases is decidedly striking.

The second feature of the reduced table is that with the exception of Rb^+ in Kr the voltages along the main diagonal of the table are less than any other values in the same row and column. (The deviation in the case of Rb^+ in Kr is, however, within the probable error claimed for the results.) This fits in with the expectation that the lowest potentials should be obtained for the ions most nearly alike in electronic configuration. Previous attempts to correlate results showed K^+ in Kr much lower than either K^+ in A or Rb^+ in Kr and by amounts well beyond the experimental error.

The results obtained in this experiment are with a single exception (Rb^+ in Xe) lower than those obtained by Beeck and Mouzon. The maximum difference amounts to 45 volts in a few cases. The results are, however, substantially in agreement with those obtained by Beeck and Mouzon. Nordmeyer[10] has obtained 75 volts for K^+ in A by using a method similar in principle but not in detail to that of Beeck and Mouzon. (Beeck had 95 volts, the author had 82 volts for K^+ in A.)

The greatest disagreement is in the results with Li^+ and Na^+ ions and in Ne gas. With the exception of Na^+ in Ne, no ionization has been observed by the space-charge method in these cases. The application of the reduction factor given above to the results in these cases obtained by Beeck and Mouzon are given in Table IV.

[10] Nordmeyer, Ann. d. Physik (5) **16**, 706 (1933).

TABLE IV.

	Ne	A	Kr	Xe
Li^+	228	85	385	237
Na^+	82	67	314	306
K^+	109			
Rb^+	81			
Cs^+	58			

Correlation similar to that found in other cases does not appear here.

K^+ in Ne	109	Rb^+ in Ne	81	Cs^+ in Ne	58
Na^+ in A	67	Na^+ in Kr	314	Na^+ in Xe	306
Difference	42		−233		−248

The potentials do not even drop off uniformly in one direction as might be anticipated. The difficulties of avoiding secondary electrons becomes increasingly great with ions of higher speeds, and this interference of secondaries may possibly explain the results of Beeck and Mouzon. It is to be noted that the ionization potentials they observed are in most cases up in the range of 300 to 400 volts. Oliphant[11] and others have shown that the emission of secondary electrons when positive ions strike metal surfaces increases strongly with increasing energy. Nordmeyer[10] has also discussed in detail the strong likelihood of certain disagreements between his results and Beeck's being due to secondary electrons.

Finally, it may be pointed out that the investigation was carried out on the ionization at energies from 5 volts up. Although the behavior of the ion detector is difficult to analyze when such slow ions are used in the beam, it was concluded that no ionization occurred at energies below those given in the table of results.

The writer is particularly indebted to Professor L. B. Loeb and Professor E. O. Lawrence who suggested the application of the space-charge method to this problem, and to the helpful direction of Professor Loeb. Doctor C. H. Kunsman, Chief of the Fertilizer Investigations of the U. S. Bureau of Chemistry and Soils, very kindly furnished the catalysts used as ion sources. The writer is also indebted to Doctor O. Beeck for numerous discussions of the problem.

[11] Oliphant, Proc. Roy. Soc. **A127**, 373 (1930).

MARCH 15, 1935 PHYSICAL REVIEW VOLUME 47

The Rotational Energy of Polyatomic Molecules

J. H. VAN VLECK, *Harvard University*

(Received February 5, 1935)

It is shown that the quantized energy of a polyatomic molecule is approximately separable into the internal electronic and vibrational energy plus the rotational energy with the latter determined by solving the conventional problem of the rigid asymmetrical top. Because of the large oscillating terms in the Hamiltonian function due to interaction between vibration and rotation, this conclusion is not as obvious as it sounds, and seemed, if anything, to be contradicted by Eckart's recent investigation on the choice of a reference frame. The discrepancy, however, disappears when a second order perturbation calculation is made with Eckart's coordinates.

IT has commonly been supposed in the literature that the rotational energy of a polyatomic molecule is very approximately the same as that of a rigid body with three unequal moments of inertia I_1, I_2, I_3. In other words, it is assumed that the total energy can be obtained by computing first the internal electronic and the vibrational energy, and then adding an eigenvalue of the "asymmetrical top" problem, whose Hamiltonian function is

$$H_{\text{rot}}=\sum_{i=1,\ 2,\ 3}(P_i-\zeta_i)^2/2I_i, \qquad (1)$$

where P_1, P_2, P_3 are the components of total angular momentum relative to the three principal