THE EFFICIENCIES OF IONIZATION AND IONIZATION POTENTIALS OF VARIOUS GASES UNDER ELECTRON IMPACT

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Abstract

The efficiencies of ionization of N_2, CO, O_2, NO, H_2 and C_2H_2 by electron impact have been measured. The curves are similar to those of He, Ne, A and Hg vapor. The ionization potentials of the molecules were found to be: N_2, 15.7; CO, 14.1; O_2, 12.5 and 16.1; NO, 9.5; H_2, 15.6; and C_2H_2, 11.6. The probable error in each case is about a tenth of a volt. Negative ions were formed by electron impact in NO, CO, O_2 and C_2H_2. None were observed in H_2 or N_2.

AN ELECTRON having sufficient energy may, at impact with an atom or molecule, cause one or more electrons to be ejected. This ionization process is of prime importance in the study of all electrical discharges in gases. The present paper is a continuation of a systematic study begun some time ago in this laboratory of the probabilities of ionization, by electron impact, of various atoms and molecules.

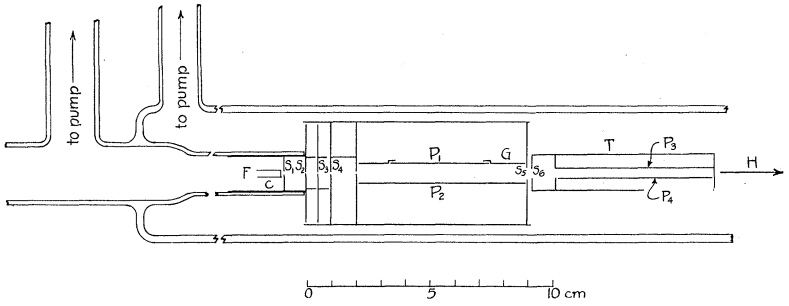

Fig. 1. Diagram of apparatus.

The results for helium, neon, argon and mercury vapor have already been reported.[1] In the present paper the results for nitrogen, carbon monoxide, oxygen, nitric oxide, hydrogen and acetylene are presented. The method used is essentially the same as that previously described although the apparatus was so modified as to permit the measurements to be extended to gases which are dissociated by the hot filament.

The essential features of the modified apparatus are shown in Fig. 1. The tube is divided into two compartments each of which is connected to a separate pump. The tantalum cylinder C is sealed into a Pyrex tube. A number of holes were drilled through the disk immediately in front of the filament F so

[1] P. T. Smith, Phys. Rev. **36**, 1293 (1930); Phys. Rev. **37**, 808 (1931).

that the region between the diaphragms S_1 and S_2 could be pumped out quickly. S_2 is about 0.035 cm in diameter and is the only opening connecting the two compartments. With this arrangement the products of the dissociation of the gas by the filament are pumped away and do not diffuse back into the main part of the tube.

Constant differences of potential are maintained between the filament and S_1 and between S_2 and S_3 while a variable accelerating potential V is applied between S_3 and S_4. With this arrangement of fields the electron current to the trap T is quite independent of V. One can conclude from this fact that any voltage correction due to space charge is not a function of V.

The electron current is confined to a fine beam by means of the magnetic field H from a solenoid surrounding the tube. With liquid oxygen on the mercury traps and with no gas in the tube a galvanometer capable of detecting a current of 10^{-11} amperes remained at zero when connected to all of the apparatus excepting the cylinder C and the electron trap T, while a current of 10^{-6} amperes was passing down the tube. With a gas in the tube at the pressures used in this work an electron current less than 0.5 percent of the total electron current was recorded by the galvanometer.

A sufficiently high field is maintained between the two parallel plates P_1 and P_2 in the ionization chamber to draw out all of the ions formed. The ions from a 4 cm length of path are measured by a galvanometer or electrometer connected with P_1. The plates P_2 and G are connected together by means of a high resistance the midpoint of which is connected to the slit S_5, so that the speed of the electrons is not appreciably altered by the transverse electric field after they enter the ionization chamber.

Procedure

The gas under consideration was allowed to leak into the tube through a small capillary and was pumped out at the other end. By using the apparatus as a pressure gauge, a constant check was kept on the pressure during a run to be sure that it was constant. Curves were obtained in this manner which showed the relative values of the efficiency of ionization as a function of the speed of the electrons. To obtain the absolute values of the ordinates the accelerating potential was set at the maximum of the curve and the flow of the gas was slowed down sufficiently so that a suitable pressure could be maintained with the pumps cut off the main compartment of the tube, the gas being pumped through the slit S_2. The pressure in the tube was then measured with a McLeod gauge. The ionization of argon and neon measured by this method differed by less than a percent from that previously determined by a static method.

The gases were prepared from chemically pure reagents and the necessary precautions observed to insure their purity. Nitrogen was obtained from the interaction of bromine, water and ammonium hydroxide, carbon monoxide from formic and sulphuric acids, oxygen from manganese dioxide, and nitric oxide from ferrous sulfate and nitric acid. The hydrogen was introduced into the tube through a heated paladium tube in an atmosphere of commercial

hydrogen. The acetylene was obtained from the Chemistry Department through the courtesy of Mr. J. L. Wilson who also purified it by repeated distillation.

Results

The results are shown in Fig. 2. The ordinate ϵ represents the number of positive charges per electron per cm path per mm pressure at 0°C. The data are also shown in tabular form in Table I. All of these gases show the same form of curve as do He, Ne, A, and Hg vapor.[1] It is of interest to note that N_2

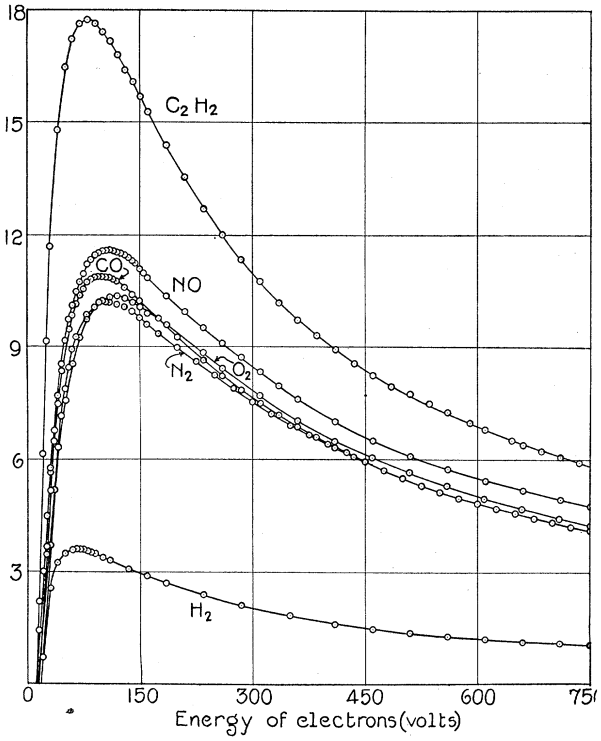

Fig. 2. The efficiency of ionization of N_2, CO, O_2, NO, H_2 and C_2H_2. The ordinate represents the number of positive charges per electron per cm path at 1 mm pressure and 0°C.

and CO share the same values for ϵ beyond about 400 volts. Bleakney[2] determined the efficiency of ionization of H_2 in arbitrary units. If the maxima of the curve shown here and his curve are made to fit, the rest of the ordinates agree almost exactly.

The ionization potentials of the gases were determined by introducing a second gas, whose ionization potential is known, into the tube for calibrating the voltage scale. A typical set of curves are shown in Fig. 3. Only the essential parts of the curves are shown. The voltages on the arrows indicate the differences between the ionization potentials of the two gases in the tube at

[2] W. Bleakney, Phys. Rev. **35**, 1180 (1930).

TABLE I. *ϵ represents the number of positive charges per electron per cm path per mm pressure at 0°C. V_a is the velocity of the impacting electron in volts and has been corrected for contact potentials and space charge.*

CO		NO		O_2		N_2		H_2		C_2H_2	
V_a	ϵ	V_a	ϵ	V_a	ϵ	V_a	ϵ	V_a	ϵ	V_a	ϵ
16	0.40	9.9	0.098	13	0.049	20	0.71	16.3	0.02	12.6	0.421
20	1.47	10.9	0.253	18	0.907	25	2.18	21.3	1.082	14.6	2.20
25	3.47	14.9	1.645	28	3.64	30	3.71	31.3	2.565	19.6	6.15
30	5.18	19.9	2.99	38	6.31	40	6.27	41.3	3.220	24.6	9.18
40	7.50	24.9	4.47	48	7.57	50	7.88	51.3	3.490	29.6	11.73
50	9.02	35	6.78	58	8.56	60	8.95	61.3	3.575	35	14.00
60	9.87	45	8.53	68	9.27	70	9.48	66.3	3.605	45	15.75
70	10.42	55	9.74	78	9.74	80	9.93	71.3	3.600	55	16.90
80	10.75	65	10.47	88	10.07	90	10.15	76.3	3.580	65	17.50
90	10.88	75	10.97	98	10.28	95	10.20	81.3	3.550	75	17.72
100	10.90	85	11.35	105	10.31	100	10.25	86.3	3.520	80	17.75
105	10.90	95	11.56	115	10.34	105	10.23	91.3	3.480	85	17.73
110	10.88	105	11.61	120	10.36	110	10.21	101.3	3.390	95	17.55
120	10.75	115	11.58	135	10.26	120	10.15	125	3.14	105	17.33
130	10.60	125	11.52	145	10.14	130	10.09	150	2.94	115	17.02
140	10.42	135	11.43	155	10.02	140	9.97	200	2.58	125	16.63
150	10.25	145	11.27	185	9.60	150	9.81	225	2.43	150	15.70
175	9.79	155	11.07	200	9.40	175	9.38	250	2.28	175	14.75
200	9.28	185	10.34	225	9.00	200	9.00	300	2.03	300	13.88
225	8.92	200	10.13	250	8.60	225	8.63	350	1.86	225	13.04
250	8.40	250	9.27	300	7.82	250	8.26	400	1.65	250	12.26
300	7.65	300	8.50	350	7.14	300	7.55	450	1.50	300	10.95
350	7.01	350	7.76	400	6.58	350	6.93	500	1.40	350	9.90
400	6.43	400	7.13	450	6.12	400	6.43	550	1.30	400	9.08
450	5.96	450	6.60	500	5.73	450	5.95	600	1.21	450	8.38
500	5.52	500	6.14	550	5.37	500	5.53	650	1.12	500	7.85
550	5.16	550	5.80	600	5.03	550	5.15	700	1.09	550	7.36
600	4.84	600	5.50	650	4.73	600	4.84	750	1.04	600	6.90
650	4.57	650	5.23	700	4.46	650	4.57			650	6.47
700	4.34	700	5.00	750	4.27	700	4.35			700	6.12
750	4.16	750	4.78			750	4.15			750	5.84

one time. The arrows also indicate how the curves were interpreted. Consistent values were obtained with other combinations of gases than those shown in Fig. 3.

Nitrogen

Both N_2+Ne and N_2+Hg show the ionization potential of N_2 to be 15.7 volts. This is somewhat lower than the generally accepted value of 16.9 volts, but it agrees with that given by Vaughan,[3] Samson and Turner,[4] Boucher,[5] and Found,[6] namely, 15.8. The data obtained by the writers indicate that 15.8 is an upper limit and that it is quite probable that the true value may be even lower than 15.7. Work is now in progress in this laboratory which will make it possible to compare the ionization potentials of argon and nitrogen.

Carbon monoxide

Combination of CO+Hg, CO+A, and CO+Ne lead to 14.1 ± 0.1 volt as the ionization potential of CO. Vaughan[3] gave 13.9 but a further consideration of his data gives 14.0, 14.1 agrees with Mackay's[7] value, while Hogness and Harkness[8] give 13.9, Foote and Mohler[9] 14.3, and Found 15.1. Birge[10] has calculated it to be 14.2 volts.

[3] A. Vaughan, Phys. Rev. **38,** 1687 (1931).
[4] L. A. Turner and E. W. Samson, Phys. Rev. **34,** 747 (1929).
[5] P. E. Boucher, Phys. Rev. **19,** 189 (1922).
[6] C. G. Found, Phys. Rev. **16,** 41 (1920).
[7] C. A. Mackay, Phys. Rev. **24,** 319 (1924).
[8] T. R. Hogness and R. W. Harkness, Phys. Rev. **32,** 936 (1928).
[9] Foote and Mohler, Phys. Rev. **17,** 394 (1921).
[10] R. T. Birge, Nature 117, 229 (1926).

Oxygen

Ionization potentials were observed at 12.5 and 16.1 volts in O_2. These agree with the values given by Mackay.[7] Smyth[11] and Foote and Mohler[12] give 15.5, while Boucher[13] gives 14.0. In the present study the work was repeated with oxygen prepared from manganese dioxide as well as from the electrolysis of dilute sulphuric acid.

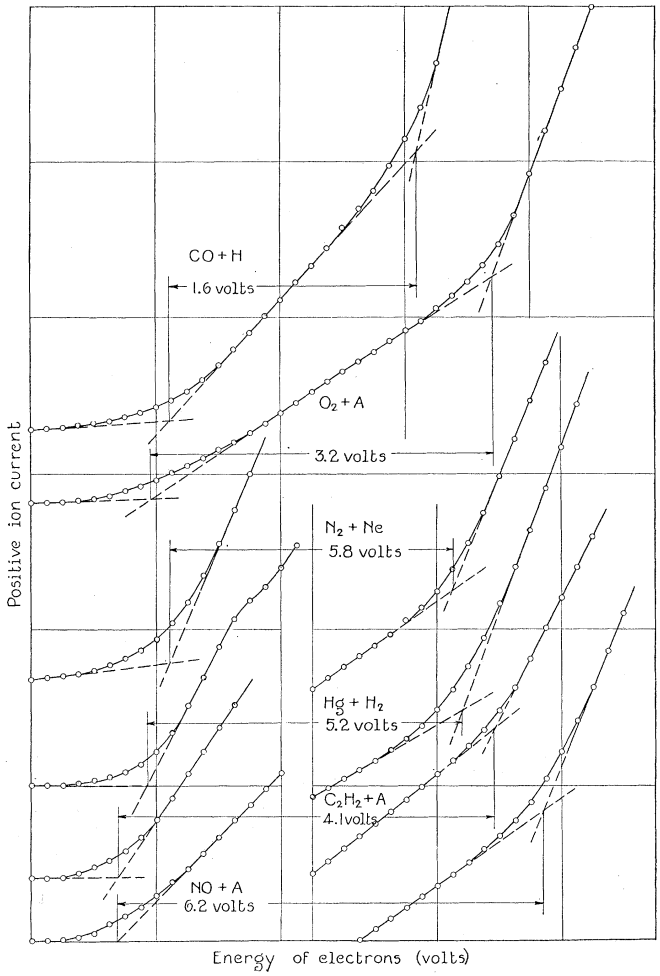

Fig. 3. Curves obtained with various mixtures of gases to ascertain the ionization potentials.

Hydrogen

H_2+Hg gave 15.6 as the ionization potential of H_2. H_2+A curves could

[11] H. D. Smyth, Proc. Roy. Soc. **A105**, 116 (1923).
[12] P. D. Foote and F. L. Mohler, Bur. Stan. Jour. Res. paper No. 400 (1920).
[13] P. E. Boucher, Phys. Rev. **19**, 189 (1922).

not be resolved. Bleakney[2] gave 15.4 whereas the previously accepted value was 15.9.

Nitric oxide

9.5 ± 0.1 is to be compared with Mackay's value of 9.4 and Hughes' and Dixon's value of 9.3.

Acetylene

Morris[14] gave 12.3 whereas the value given here is 11.6 ± 0.10 volts. $C_2H_2 + Hg$ curves were difficult to interpret because of the point of inflexion in the Hg curve at about 11.8 volts, (see Fig. 3), but they do show that the ionization potential of acetylene is less than 12 volts.

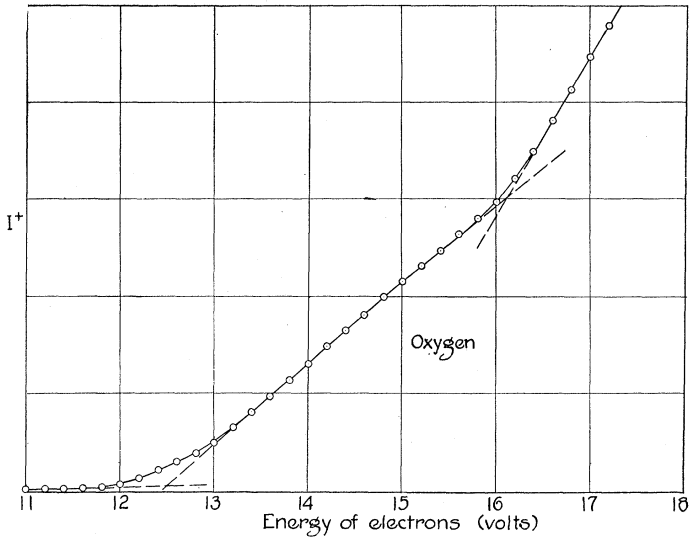

Fig. 4. Showing the second ionization potential in O_2 at 16.1 volts.

Negative ions

While working with an apparatus which contained water vapor, Lozier[15] observed two groups of negative ions which were formed only in a small range of electron velocities. Bleakney and later Mueller and Smyth[16] found them to be H^- ions. A similar group of ions was also found by Lozier[15] in CO, which Vaughan[3] showed to be O^- ions.

The writers have found that the same process exists in NO, O_2, and C_2H_2. The data are shown in Fig. 5. The ordinates are given in aribtrary units since a quantitative measure of the number of these ions found per electron was not made. In all of the gases studied the maxima of the curves represent currents

[14] J. C. Morris, Jr., Phys. Rev. **32,** 456 (1928).
[15] W. W. Lozier, Phys. Rev. **36,** 1417 (1930).
[16] H. D. Smyth, Rev. Mod. Phys. **3,** 385 (1931).

which are only a fraction of a percent of the positive ion currents at their maxima.

That these ions are atomic was indicated by the fact that they possess as much as two volts of kinetic energy which results from the dissociation of the molecule. By analogy with CO one is lead to believe that the ions in NO are O^-.

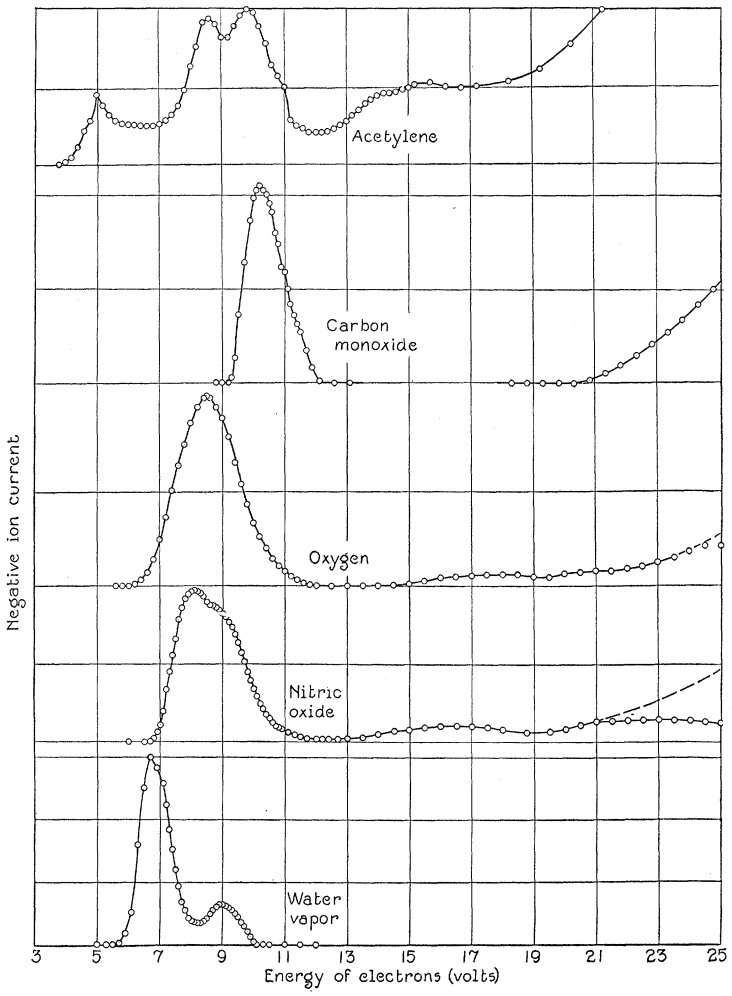

Fig. 5. Negative ions in H_2O, NO, O_2, CO and C_2H_2.

Beyond 21 volts none of the curves has the proper form since above 30 volts the electrometer in all cases showed a positive current due to the formation of positive ions having sufficient kinetic energy to be able to go through a retarding potential of several volts. A notion of the true curves is given by the broken lines.

Nothing can be said at present about the nature of the negative ions in acetylene except that they are not $C_2H_2^-$ since they possess some kinetic energy. A more detailed discussion of these ions will be given in the near future after work which is now in progress has been completed.

No negative ions could be detected in H_2[15].

The writers take this opportunity to thank the graduate school for a grant which made the continuation of this study possible.