STUDIES WITH IONIZATION GAUGE

C. G. Found and S. Dushman

II. Relation between Ionization Current at Constant Pressure and Number of Electrons per Molecule

Abstract

Calibration constants for the ionization gauge in various gases.—The relation for the pressure $P=K\times$positive ionization, where K is a constant, was found to hold for Hg vapor (.025 to .21 bar) and for iodine vapor assuming published values of vapor pressures. For H_2, He, Ne, N_2 and CO at pressures around 50 bars, readings were compared with those of a McLeod gauge and the values of K determined. For the same electrical conditions (anode voltage and electron current) $1/K$ is found to be proportional to the total number of electrons per molecule or molar number N, (except for H_2 and He for which KN is half as large). Measuring i_+in microamps and P in bars, the value of the constant KN is 10.4 for an electron current at 0.5 m-amp. and an accelerating voltage of 125 volts. Results for the vapor pressure of water and of HgI_2 also agree with this relation.

Relative ionization due to slow electrons in various gases is, then,p roportional to the pressure and to the molar number (except for H_2 and He). This agrees with results previously obtained for ionization by α and β rays, except that for these H_2 is not abnormal. From the electron current, K and the mean free path, the fraction of the collisions with molecules which produce positive ions can be computed. It comes out ¼ in argon for an accelerating potential of 125 volts.

Vapor pressures of napthalene, —11° to 18°C, and of vacuum oil 0° and 25°C were determined, assuming probable values of K.

IN a previous paper[1] the authors have described the construction of an ionization gauge and a method of calibration using argon. The present paper deals with the calibration of the gauge with other gases and vapors and the relation that these calibrations bear to each other.

Method of Calibration with Mercury Vapor

The calibration of the ionization gauge for a vapor was made by comparing the gauge reading with the known vapor pressures at different temperatures. The arrangement of the apparatus used in the case of mercury is shown in Fig. 1. The ionization gauge was connected through two traps T_1 and T_2 to an exhaust system at P. The exhaust system consisted of a Langmuir condensation pump in series with an oil pump which was backed up by a rough vacuum line. A side tube S containing mercury was attached to the tube T_1. The gauge and trap T_1 were baked

---

[1] Dushman and Found, Phys. Rev., **17**, 7, (1921)

out in an oven at 360°C for an hour at the beginning of the exhaust. The tube S containing the mercury extended below the bottom of the oven and was heated gently by a Bunsen flame during the oven bake-out, in order to drive out all moisture and occluded gases. When the apparatus had cooled down after the oven bake-out, the tube S was immersed in liquid air and the metal parts of the gauge were bombarded as described in the previous paper. The liquid air was then transferred from S to the trap T_1 and the mercury distilled from the former to the latter, after which S was sealed off at C. The gauge was now connected with the inner spiral as cathode, the outer spiral anode (at a positive potential of 250 volts), and the cylinder was made the collecting electrode with a negative potential of 22 volts relative to the negative end of the cathode.

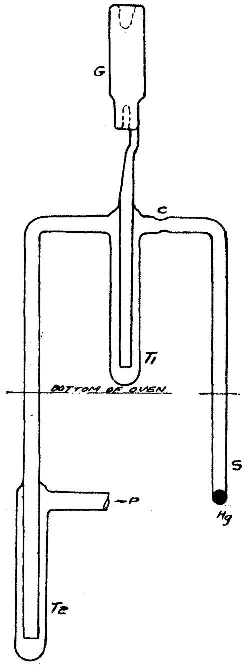

Fig. 1. Apparatus for calibration of ionization gauge with mercury vapor

With an electron current of 20 milliamperes to the anode the measurements of the positive ionization current showed that the pressure when the mercury vapor was condensed by liquid air, was less than .001 bar. The liquid air on T_1 was now replaced by a freezing mixture. The temperature of the mixture was measured and the ionization current was measured at definite intervals of time. These readings showed a gradual change in the amount of ionization which finally reached a steady value. This value is a measure of the ionization in mercury at the pressure corresponding to the temperature of the freezing mixture.

By varying the temperature of the freezing mixture a series of ionization current readings corresponding to different temperatures were obtained. Since the ionization gauge was attached to the inner part of the trap T_1, the pressure of mercury vapor in G was the pressure corresponding to the temperature of the freezing mixture.

While the measurements were being taken the exhaust system was connected to the gauge. This took out any reaction products which might be produced by the action of the hot cathode on the vapor, and also took care of residual gases which might happen to be liberated.

Table I gives the results obtained for mercury vapor. The pressures were extrapolated from data and from an extrapolation formula given in Kaye and Laby's Tables.

TABLE I

Readings in mercury vapor

Temperature of mixture	Pressure of mercury p	Positive ionization i	$K=P/i$
°C	.21 bar	57 $(10)^{-6}$ amp.	.0037
− 4	.13	38.5	.0034
− 8	.095	23.5	.0040
−10.9	.061	17.8	.0034
−12.7	.052	13.2	.0039
−13.9	.045	11.6	.0039
−16.7	.033	7.3	.0045
−18.9	.025	6.2	.0040
		Average value of $K=$	.0038

A plot of these results is shown in Fig. 2. From the slope of the line it is found that $K=.0038$.

MEASUREMENTS WITH OTHER GASES

The value of K obtained for argon[1] with the same electrical connection was .0132. Such a large variation in the relative ionization for the two gases suggested measurements with other gases.

It was shown in the previous paper[1] that the linear relation ($P=Ki$) between pressure and ionization current is valid up to pressures as high as 50 bars when the electron current is reduced to 0.5 milliamperes and the anode voltage to 125 volts. By working under these conditions, we were able to compare the ionization gauge readings for non-condensible gases, with pressures measured by a McLeod gauge. The use of these relatively higher pressures also reduced the effect of any impurity which might come from the glass walls, although precautions were taken to reduce this as much as possible. The ionization gauge was baked out in an oven at 360°C for one hour and was washed out several times with the gas to be used before the measurements were taken. The ionization currents were then measured for different pressures.

Measurements were made with iodine using an arrangement similar to that employed for mercury. The vapor pressure data were taken from the published results of Haber and Kirschbaum.[2]

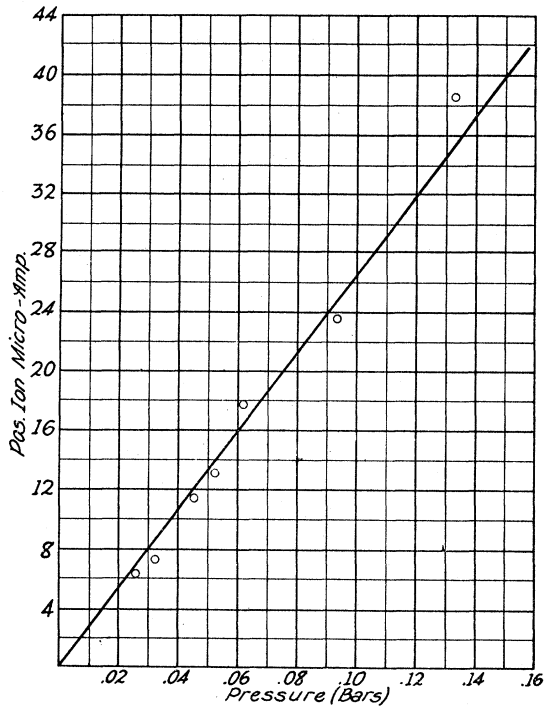

Fig. 2. Calibration of ionization gauge with mercury vapor. Anode voltage 250; collector voltage −22; current 22 milli-amp.

Table II gives the results obtained for the different gases.

TABLE II

Results for various gases

Gas	$K=P/i$	$1/K$	N	KN
Helium	2.74	.36	2	5.5
Neon	1.08	.92	10	10.8*
Argon	.58	1.72	18	10.6
Nitrogen	.67	1.51	14	9.4
Carbon monoxide	.72	1.39	14	10.1
Mercury	.13	7.6	80	10.5
Iodine	.10	9.8	106	10.6

---

[2] Haber and Kirschbaum, Zeit. f. Elektrochem. **20,** 296 (1914)

* We are indebted to Dr. K. H. Kingdon for the measurements with neon.

The variation in the value of K shown in the second column of the above table suggested that this constant is connected with the molecular structure of the gas.

In Fig. 3 we have plotted the values of $1/K$ against the number of electrons per molecule (this will be called molar number). It will be observed that, at constant electron current, the ionization per bar is proportional to the molar number. While this relation has not been subjected to extremely accurate measurements, the present results show that this is at least approximately true for the gases mentioned in Table II and is valid over a range from $N=10$ to $N=106$. The last column of Table II gives the product KN, which is approximately constant.

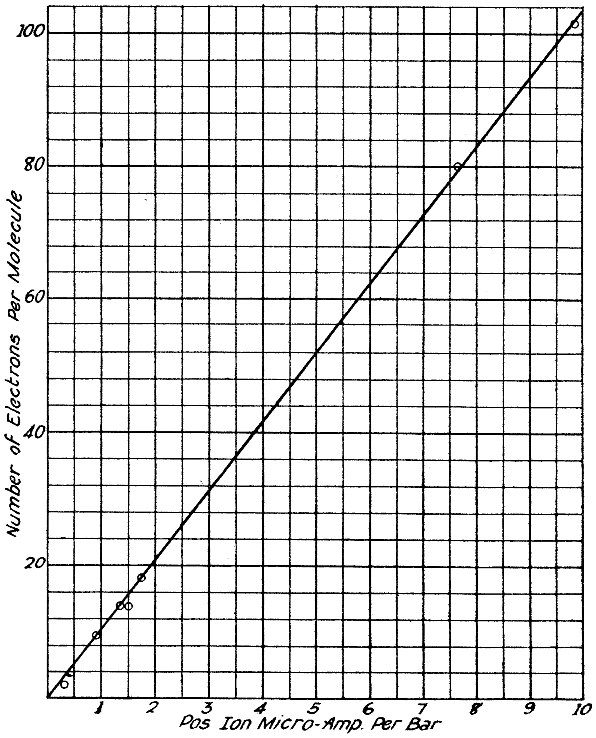

Fig. 3. Variation of the relative ionization of low velocity electrons with the numbe of electrons per molecule.
Anode voltage 125; collector voltage 22; current 0.5 milli-amp.

It will be observed that the values of K for argon and mercury as obtained with an electron current of 20 milliamperes are 0.0132 and 0.0038 respectively while the values obtained with 0.5 milliampere are 0.58 and 0.13 respectively. The ratio of the values of K is 3.5 in the first case and 4.4 in the latter. Since the measurements with 0.5 milliampere were carried out at higher pressures, the ratio 4.4 has been considered as much more reliable. However, it is also essential to point out that owing to traces of other gases and other conditions under which the observations were taken, the accuracy of the values of K given in Table II is probably not greater than 10 per cent. This would account for the difference between the values obtained for nitrogen and carbon monoxide which, if the conclusion reached in the present investigation is valid, ought to be identical.

While the actual values of K were found to vary with the anode voltages such variations were only slight when voltages over 250 were used with 20 milliampere electron current, and for voltages over 125 with 0.5 milliampere. Furthermore the relative values of K for different gases were found to vary only slightly with varying anode voltages.

Hydrogen and helium both show consistently higher values of ionization than would be expected from the above relation between ionization and molar number. Measurements with these gases are extremely difficult since small amounts of other gases affect the ionization to a relatively greater extent, although in the present case extreme precautions were taken to eliminate impurities as much as possible. Moreover, in the case of hydrogen it is difficult to maintain constant pressure on account of the rapid cleanup by the hot cathode. However, all the results are consistent in indicating much smaller values of KN. This is in agreement with results of other observers. Kossel[3] found that the total ionization was proportional to the molecular weight for electrons having velocities equivalent to 100 volts except in the case of hydrogen which gave double that expected from density relation. Lenard[4] and Strutt[5] obtained the same results for cathode rays and β rays respectively.

IONIZATION BY OTHER MEANS

Kleeman[6] has summarized the work on relative ionization for α, β and x-rays. The results obtained by him for the ionization by α and β rays are analogous to those obtained in the present investigations, i. e., the relative ionization is proportional to the molar number. The relative ionization for x-rays in many cases is much higher than that given by the molar number relation. This is very probably due to the ionization from secondary radiation. Table III, based on Kleeman's paper,

---

[3] Kossel, Ann. der Phys. **37**, 393 (1912)

[4] Lenard, Ann. der Phys. **56**, 255 (1895)

[5] Strutt, Phil. Trans. **195**. 507 (1901)

[6] Kleeman, Proc. Roy. Soc. **79**, 220 (1907)

gives the relative ionization $1/K$, with air taken as unity. The molar number N is given in the second column, while the last column gives the product KN. These results are plotted in Fig. 4. While there is a considerable departure from the linear relation for several of the values, it is evident that for the case of these ionizing agents the relative ionization is also approximately proportional to the number of electrons per molecule.

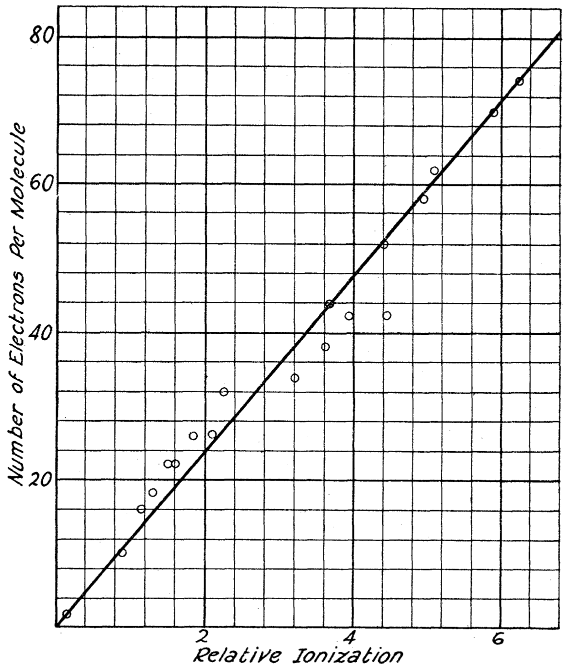

Fig. 4. Kleeman's results for the relative ionization by β-rays in various gases as a function of the number of electrons per molecule.

VAPOR PRESSURE MEASUREMENTS WITH THE IONIZATION GAUGE

Measurements of the vapor pressure of vacuum oils at different temperatures have been made by Mr. Huthsteiner, of this laboratory. Assuming a composition corresponding to the formula $C_{12}H_{26}$ ($N=98$) which seems reasonable from the observed boiling and freezing points of the oil, vapor pressures were calculated from ionization gauge readings. The values obtained ranged from .01 to 0.1 bar at 0°C and from 0.2 to 2.0 bars at 25°C.

Measurements of the vapor pressure of napthalene ($C_{10}H_8$), $N=68$, obtained by Mrs. McLane are given in Table IV and are in fair agreement with the published data of Barker[7] and Allen.[8]

---

[7] Barker, Zeit. Phys. Chem. **71**, 235 (1910)

[8] Allen, Journ. Chem. Soc. **77**, 412 (1900)

TABLE III

Relative ionization due to β-rays in various gases (after Kleeman).

Gas	*N*	*1/K*	*NK*
H_2	2	0.16	12.5
NH_3	10	0.89	11.2
Air	(14)	1.00	14.0
O_2	16	1.17	13.6
CO_2	22	1.60	13.8
C_2N_2	26	1.86	14.0
N_2O	30	1.55	19.3
SO_2	32	2.25	14.2
CS_2	38	3.62	10.5
Methyl Alcohol	18	1.69	10.6
Ethyl Aldehyde	32	2.12	15.0
Ethyl Chloride	34	3.24	10.0
Ethyl Ether	42	4.39	9.6
Pentane	42	4.55	9.2
Benzene	42	3.95	10.6
Methyl Bromide	44	3.73	11.2
Ethyl Bromide	52	4.41	11.8
Chloroform	58	4.94	11.8
Methyl Iodide	62	5.11	12.1
Ethyl Iodide	70	5.90	11.9
$C\,Cl_4$	74	6.28	11.8

TABLE IV

Vapor pressure of napthalene

Temperature	Vapor pressure Ionization gauge	Barker and Allen
18°C	85 bars	106 bars
14	68	76
11	52	57
5	36.5	33
0	20	18.5
− 2.5	15.6	14
− 6	12.0	10
− 7	10.2	9.3
− 9.5	7.6	6.6
−10.5	7.3	6.0
−11	6.4	5.3

More recently, determinations of the vapor pressure of napthalene, at a temperature of about 30°C, have been made by Mrs. Mary Andrews. The method employed was similar to that used by Knudsen[9] for mercury. The results indicate that the above measurements, obtained by the ionization gauge, are a little high. This will be discussed more fully in a paper which Mrs. Andrews will publish in the near future.

---

[9] Knudsen, Ann. der Phys. **29**, 179 (1909)

We have measured the vapor pressure of water at temperatures ranging from $-50°C$ to $-78°C$. Scheele and Heuse[10] measured the vapor tension of water to a temperature as low as $-60°C$. If their values of $\log P$ are plotted against $1/T$, a straight line is obtained from which values of P may be extrapolated for lower values of T. The results obtained with the ionization gauge were found to agree with these values, if we assume $N=10$.

Similarly, our observations with mercuric iodide, HgI_2 agree with values obtained from published data by plotting $\log P$ against $1/T$ and extrapolating to the temperatures at which our measurements were obtained.

EFFICIENCY OF IONIZATION AND COLLISION FREQUENCY

According to the results of the measurements given above, the number of ions formed per unit volume, with a definite electron current, is proportional to the *total number* of electrons in the gas molecules per unit volume. Furthermore, for small electron currents, the number of ions at constant gas pressure, is proportional to the electron current. A simple interpretation of these observations would be that the collisions occur between electrons emitted from the cathode and electrons in the gas molecules. Assuming that every collision results in the formation of an ion, it is possible to calculate values of the mean free path of the electrons in different gases.

If L is the mean free path, then in traveling the distance d, the number of collisions is d/L. If i denotes the ionization current, and I the electron current,

$$d/L=i/I \qquad \text{or} \qquad L=dI/i.$$

In order to obtain measurements under conditions in which d would be definitely known, the outer grid of the gauge was made cathode, the cylinder anode, and the inner grid, the collecting electrode. For this arrangement $d=4$ mm. The value of the constant K for argon as given in the previous paper is $P/i=K=0.032$ when $I=20$ milliamperes. Hence $i/I=P/640$. That is, at 1 bar pressure, $d/L=i/I=1/640$. Hence $L=640\times d=256$ cm.

This, therefore, is the free path for argon at 1 bar pressure. On the other hand, the value of L at 25°C as calculated from considerations based on the kinetic theory of gases is $4\sqrt{2}\times 10.6=60$ cm (approx.) which is only about 24 per cent of the value derived from the measurement of the ionization current. This would lead to the conclusion that only

---

[10] Scheele and Heuse, Ann. der Phys. **29**, 723 (1909)

about 24 per cent of the collisions with molecules are effective in producing ionization.

The most interesting result of this investigation is the observation that under similar conditions of accelerating voltage, and electron current, and for the same arrangement of electrodes, the number of ions produced per unit electron current is (in most gases) approximately proportional to the total number of electrons per unit volume. We might conclude therefore that the probability of ionization on collision is proportional to the total number of electrons in the atom. The voltages used in the present investigation are obviously too low to enable the incident electrons to cause emission of electrons from the *K* or *L* ring of such an atom as that of mercury. This would lead to the view that the energy of collision is transmitted unaltered from the inner electron which has been stimulated to an external electron which is then ejected.

The experiments described in the present paper were performed about two years ago, but publication was delayed in the hope that further experiments could be carried out in order to interpret the significance of the observations described above. Such experiments are now under way, but it has been considered that there is sufficient interest in the results obtained so far to make them worth publishing even before the underlying explanation is fully understood.

RESEARCH LABORATORY OF THE
GENERAL ELECTRIC COMPANY,
SCHENECTADY, NEW YORK,
November 14, 1923.