mobilities at low temperatures, as much ionization is indicated by this conductivity as would be shown by a much higher conductivity at high temperatures.

Summary

Nitric oxide and hydrogen chloride form a molecular complex, probably $[NOH]^+Cl^-$, which exhibits the properties of an "odd" molecule.

The solution has a maximum specific conductivity greater than 10^{-3} mhos between 120° and 130° K.

An apparatus which is convenient for working with gases at low temperature, and a low temperature thermostat are described.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

A STUDY OF THE LUMINOUS DISCHARGE IN IODINE. A DETERMINATION OF THE IONIZATION POTENTIAL OF IODINE

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In a previous article,[1] Gibson and Noyes studied the effect of certain gases and vapors on the emission spectra of metals. Measurements of the sparking potential were also made and it was found that those gases which obliterated the spectra of metals also possessed high sparking potentials. The theory was advanced that heavy negative ions were formed due to the combination of the electronegative gases with electrons and that these ions could not be accelerated sufficiently with the potentials used to produce ionization by collison. In another article,[2] the same authors presented a more quantitative study of the potential necessary to produce luminosity in a gas by measuring the glow potential at low pressures with a heated cathode. It was shown that this potential was a function of the ionization potential of the gas, but both gases studied (hydrogen and mercury) had no appreciable effect on the spectra of metals.

In this article it is desired to present results obtained in studying the glow discharge in one of the typical electronegative gases which have a marked obliterating effect on the spectra of metals. Part I gives a brief theoretical discussion based on the theory presented in the previous article. Part II gives the experimental procedure, while Part III gives the experimental results. Part IV gives a brief discussion of the results together with the most probable value of the ionization potential of iodine as determined in the experiments described.

[1] Gibson and Noyes, THIS JOURNAL, **43**, 1255 (1921).

[2] Gibson and Noyes, *ibid.*, **44**, 2091 (1922).

I. Theoretical Discussion

According to the first assumption made in the previous article[2] the luminous discharge in a gas can be maintained only when positive ions are able to reach the cathode. This is due to the fact that they cause large numbers of electrons to be emitted when they reach the cathode. The exact mechanism of this process is not accurately known. It may be due to a reduction of the space charge in the neighborhood of the cathode or to a sort of spattering action.

If, however, the gas molecules present should combine with all of the electrons emitted, heavy negative ions would be formed which would not be capable of ionizing other molecules by collision. If the assumption is made that all of the current passing through the discharge tube is carried by the electrons,[3] and that this current is 100 milliamperes with a potential of 100 volts (these values are of the order of magnitude of actual conditions), the diameter of the tube 2 cm. and the distance between the electrodes 2 cm., then the average density of electrons would be approximately 10^5 per cu. mm. Even in the neighborhood of the cathode where the number would be largest, the number of electrons per cu. mm. would be only 10^7. In the same volume of gas if the pressure were 0.1 mm., the number of gas molecules would be approximately 10^{12}. If the molecu es of the gas have a strong tendency to combine with electrons, very few of the electrons emitted from the cathode will attain ionizing velocity unless they are moving under the influence of a high potential gradient.

It is possible that all or a large part of the electrons first given off by the filament when the potential is applied combine with the iodine molecules according to the equation,[4] $I_2 + \Theta = I_2^-$. If this were true, then the conductivity of this region of the discharge tube should be much lower than in the case of an electropositive gas. The potential gradient will, therefore, be much greater, and the electrons should attain the ionizing velocity in a much shorter distance. The high potential gradient in the cathode region in the case of iodine has been noted previously.

As the electrons move faster, their chance of attaining ionizing velocity before combining with the molecules of the gas will be greater. There should be a period of induction before the current through the discharge tube attains its maximum value. This has been noticed. Occasionally an arc will strike and 10 or more amperes will pass through the discharge tube. This is probably due to two factors: (1) ionization by multiple

[3] This assumption is made by Sir J. J. Thomson [*Phil. Mag.*, **42**, 981 (1921)] and is undoubtedly especially valid for the case of iodine, since the positive ions would be of relatively large mass and consequently of small mobility.

[4] In the immediate neighborhood of the filament, there should be a fairly high concentration of monatomic iodine due to the high temperature. Monatomic iodine should have an even greater tendency to combine with electrons than the molecules of I_2.

collision; and (2) the large number of electrons liberated when the positive ions strike the cathode.

If the distance through which an electron will move before it attains ionizing velocity is shorter in the case of iodine than in the case of a gas such as hydrogen or mercury, then for the same length of tube one would expect to have a higher multiple of the ionization potential. The same theory will, of course, apply in the region just after ionization is produced since the electrons lose most of their energy on producing ionization. This point is verified by the experiments to be described. For example, in a tube 0.7 cm. long in the case of mercury, the glow potential was equal to the ionization potential, while in the case of iodine with a tube of similar length the glow potential was equal to 5 times the ionization potential.

II. Experimental Procedure

Fig. 1 shows a diagram of the connections used. The procedure for obtaining the values of E_d was analagous to that used by Gibson and Noyes.[2]

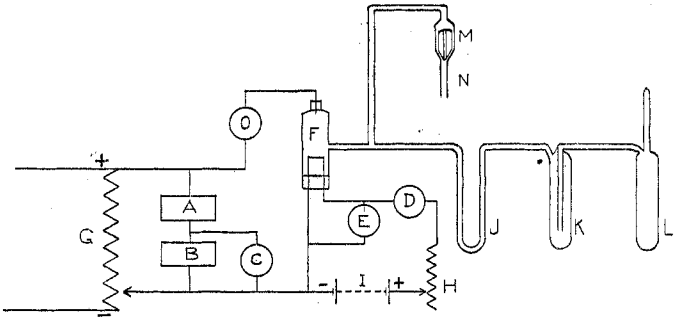

Fig. 1.

G is a 750-ohm resistance shunted across a 220-volt line. I is a 16-volt storage battery for heating the filament, H being a resistance in series, D an ammeter and E a voltmeter. F is the discharge tube, the electrodes being of tungsten and the glass Pyrex. In the early experiments a tungsten spiral was used as an anode, but the heavy currents which passed through the tube at times melted the tungsten. It was decided, therefore, to reduce the area of the anode and use a single straight tungsten wire. A and B are standard box-resistances and C is a voltmeter.

To avoid the use of stopcocks in the high-vacuum part of the system, the device shown at M was used. It consists of a plunger containing an iron rod. The plunger was ground into the lower part of the outside tube so that when down it made a fairly tight seal. A solenoid was placed around the whole, and by passing a current through the solenoid the plunger could be raised. This device would not, of course, hold a high vacuum, but it prevented the rapid diffusion of the iodine into the liquid-air trap.

The iodine was purified by sublimation. Some of the U. S. P. material was placed in L and the latter surrounded by a freezing mixture. The plunger in M was raised and the whole system evacuated to a pressure below 10^{-6} mm. (the limit of estimation of the McLeod gage used). After evacuation of the system for several hours in this manner, the freezing mixture was removed from L and placed around K and the system evacuated again for several hours with the filament hot. Finally, most of the iodine

was sublimed into the U-tube J by a similar procedure. While making readings the plunger in M was allowed to fall and the U-tube J was immersed in a bath which gave the desired vapor pressure of iodine. A U-tube beyond N was immersed in liquid air, which prevented the entrance of any mercury vapor into the system.

Small traces of air make an enormous difference in the values of E_d. For example in one case when the air pressure was approximately 10^{-4} mm. the value of E_d was 190.8 volts. Upon further evacuation to a pressure well below 10^{-6} mm. the value of E_d fell to 70.00 volts. For this reason after a point was taken the plunger in M was raised and the system evacuated for 15 minutes or more before taking another reading. By varying the resistances A and B, the readings of the voltmeter could be made near the end of the scale, the percentage error being much less.

III. Results

Table I gives a typical series of results obtained with one tube. Each voltage is the average of several readings.

TABLE I

TYPICAL RESULTS WITH ONE TUBE

Diameter of tube, 2.1 cm.; distance between electrodes, 3.1 cm.; electrodes of tungsten; resistance of voltmeter C, 298.3 ohms.

Resistance A	Resistance B	Voltmeter (C)	Current (D)	Voltage (E)	E_d (calc.)	Temp. °C.	$V.p.$ I_2 Mm.
10700	300	0.965	3.3	7.3	70.00 ± 0.20	0	0.030
		1.379	3.4	7.4	100.25	22	0.232
		0.689	3.4	7.8	50.00	−2	0.022
		1.24	3.4	7.7	89.94	18	0.172
		0.964	3.4	7.6	69.92	15	0.131

Table II gives a general summary of the data. The number of readings taken in each case is given in the fifth column.

TABLE II

SUMMARY OF DATA

Distances between electrodes: Tube 1, 3.1 cm.; Tube 2, 1.7 cm.; Tube 3, 0.65 cm.; Tube 4, 0.25 cm.

Temperature °C.	E_d Volts	$V.p.$ I_2 Mm.	Tube No.	Number of readings	Temperature °C.	E_d Volts	$V.p.$ I_2 Mm.	Tube No.	Number of readings
−4	60.57	0.018	1	1	17.5	40.25	0.164		3
−2	50.01	0.022		4	27	49.89	0.371		2
0	70.00	0.030		5	−3	29.83	0.020	4	2
15	69.88	0.131		3	0	30.04	0.030		2
18	89.70	0.172		3	13	30.04	0.111		3
0	59.48	0.030	2	2	..	40.17	...		2
24	69.63	0.273		3	24	30.04	0.273		5
−0.5	59.30	0.027	3	2	26.5	50.05	0.355		2
0	49.63	0.030		3	29	30.03	0.371		3

IV. Discussion of Results

The values of the vapor pressure of iodine are taken from a curve made from the results of Baxter, Hickey and Holmes[5] and Naumann.[6] It will

[5] Baxter, Hickey and Holmes, THIS JOURNAL, 29, 127 (1907).

[6] Naumann, *Dissertation*, Berlin, 1907.

be noticed that all of the values of E_d are approximately multiples of 10 volts. Table III gives a summary of all of the readings.

TABLE III

AVERAGE VALUES OF E_d

No. Readings	E_d	No. Readings	E_d
11	30.00	9	69.91
5	40.20	3	89.82
8	50.03	4	99.98
7	59.79	..	...

According to the theory outlined here, the ionization potential of iodine should be approximately 10 volts. The more exact value may be obtained in one of two ways: (1) by subtracting each value from the following one, or by subtracting the values in this way and dividing by the proper integer; (2) by dividing the values by the proper integer. The first method puts any error in the reading directly into the value of the ionization potential, while the second method introduces an error due to the velocity of thermal emission of the electrons. Krüger[7] and Bloch and Bloch[8] give this correction as approximately 1 volt, while Becker[9] gives a slightly lower value. It will, of course, depend upon the temperature of the filament.

By the first method, the following values for the ionization potential are found: 10.20, 9.83, 9.76, 10.12, 9.96, 10.16, 10.02, 9.93, 9.98, 9.97, 10.00, 9.80, 9.87, 9.99, 10.01, 10.05, 10.04. The average of all of these values for the ionization potential of iodine is 9.98 with a maximum deviation of 0.22 volt and an average deviation of 0.09 volt.

By the second method, assuming the initial velocity of the electrons to be 1 volt, the following values are obtained: 10.33, 10.25, 10.21, 10.13, 10.13, 10.09, 10.10. It will be noticed that the values increase with decreasing multiple of the ionization potential. This would seem to indicate that the correction for thermal emission does not enter into the values obtained by this method or is not as large as supposed. The most probable value of the ionization potential of iodine as obtained by this method is 10.0 ± 0.2 volts.

Mohler and Foote[10] found 10.1 for the ionization potential of iodine, while Compton and Smyth[11] for ordinary iodine found 9.4 for the molecule and 8.0 for the atom. Found[12] reports an ionization potential of 8.5 volts. The heat of dissociation of iodine as calculated by Lewis and Randall[13]

[7] Krüger, *Ann. Physik*, **64**, 288 (1921).

[8] Bloch and Bloch, *Compt. rend.*, **170**, 1380 (1920).

[9] Becker, *Ann. Physik*, **60**, 30 (1919).

[10] Mohler and Foote, *Phys. Rev.*, **15**, 321 (1920).

[11] Compton and Smyth, *ibid.*, **16**, 501 (1920).

[12] Found, *ibid.*, **16**, 41 (1920).

[13] Lewis and Randall, THIS JOURNAL, **36**, 2259 (1914).

from the data of Starck and Bodenstein[14] is 36,860 calories, which corresponds to 1.59 volts. If the ionization potential corresponds to the reaction $I_2 = I^+ + I + \Theta$, then the ionization potential of the atom should be 10.0 − 1.6 = 8.4 volts, which agrees well with the value of Found, but is slightly higher than that of Compton and Smyth. Series relations for the spectrum of iodine are not known, so that it is impossible to calculate a theoretical value; 8.4 volts would correspond to a wave length of 1472 Å. In view of the relatively low heat of dissociation of iodine, the above equation probably corresponds to the principal ionization potential of iodine.

Summary

1. The theory of the luminous discharge proposed by Gibson and Noyes is discussed with reference to its applicability to the luminous discharge in an electronegative gas such as iodine.

2. The most probable value of the ionization potential of iodine as determined in the experiments described is 10.0 ± 0.2 volts. This gives 8.4 volts as the ionization potential of the atom, which would correspond to a wave length of 1472 Å. It is impossible to verify this from the spectroscopic data now available.

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THE DISSOCIATION PRESSURES OF CERTAIN SALT HYDRATES BY THE GAS-CURRENT SATURATION METHOD

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Numerous methods, both direct and indirect, have been devised for the measurement of the dissociation pressures of salt hydrates. Some of these are more ingenious than accurate; others involve apparatus so elaborate that few experimenters would be inclined to adopt them, if other, less troublesome methods could be found to serve the same purpose.

The static methods, involving the use of the tensimeter, require the greatest care in the elimination of sources of error—in particular, the removal of adsorbed moisture from the walls of the instrument, and in the elimination of parallax in determining the difference in level in the two arms of the tensimeter while it is immersed in a thermostat. Furthermore, in the case of those salts which are slow to reach equilibrium with the gaseous phase, a determination by such a method is very time-consuming. Likewise, the dew-point method, originated by Lescoeur,[1]

[14] Starck and Bodenstein, *Z. Elektrochem.*, **16**, 961 (1910).

[1] Lescoeur, *Ann. chim. phys.*, [6] **16**, 394 (1889).