range of concentration of the acid. With acetic acid a maximum increase in hydrogen-ion concentration is obtained which falls off as the concentration of sucrose is increased. With water the thermodynamic concentration of hydrogen ion decreases upon the addition of sucrose.

2. The addition of sucrose to solutions of sodium hydroxide seems to cause an increase in the thermodynamic concentration of hydrogen ion.

3. The thermodynamic concentration of hydrogen ion in the system remains appreciably constant during the course of the inversion process.

4. The velocity of inversion of sucrose by hydrochloric acid is proportional to the thermodynamic concentration of hydrogen ion only for the limited range of concentration of acid which lies between 0.01 and 0.001 mols per liter.

5. The bimolecular velocity coefficients, reduced to unit thermodynamic concentration of hydrogen ion, are constant with changing concentrations of sucrose only for each molecular concentration of hydrochloric acid between 0.01 to 0.3 mols per liter. These constants vary considerably for different concentrations of acid.

6. Evidence has been adduced which shows that for acetic acid, the undissociated molecule is not a positive catalyst in the inversion process; or that there are other factors entering here which have never been considered.

7. With strong acids, the inversion process does not seem to be strictly unimolecular, especially in the early periods of the reaction.

8. Within the limits of the concentrations of the reactants used, no appreciable change in volume was noted when the solutions of hydrochloric acid and sucrose were mixed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A STUDY OF THE LUMINOUS DISCHARGE IN HYDROGEN AND IN MERCURY AND A NEW METHOD OF MEASURING IONIZATION POTENTIALS

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I. Introduction

In a previous article[1] the authors have described some experiments on the obliteration of the characteristic spectra of metals by certain gases. The sparking potentials of these gases relative to air were determined and it was found that the gases which had a marked obliterating effect also had a high sparking potential. The method used for determining the sparking potential was, however, only roughly quantitative and the present

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

investigation was undertaken with the object of obtaining a more precise measure of the voltage required to produce a luminous discharge in a gas. A large amount of work has been done in this field, but the results are in many cases contradictory and no theory has yet been developed which explains satisfactorily the phenomena observed. In the present investigation we have made a fairly systematic study of a number of the factors affecting the luminous discharge and have shown conclusively that there is an intimate connection between the ionization potential of a gas and the potential required to produce luminosity.

In Section II we have developed a theory of the luminous discharge, introducing only such parts of the experimental data as seemed necessary to illustrate the theory. In Section III, the details of the experimental procedure for hydrogen are given, while Section IV contains in detail the results obtained with the various tubes. Section V is devoted to a brief discussion of the most probable value of the ionization potential of hydrogen as obtained from the results presented in the preceding section. Sections VI and VII give the details of the experiments with mercury vapor, together with our most probable value of its ionization potential.

II. Experiments on the Luminous Discharge in Hydrogen

General Conditions for Stability of the Luminous Discharge.—The phenomena in vacuum tubes, furnished with heated platinum or tungsten cathodes, are in many respects similar to those in tubes with cold cathodes, except that the potential required to produce a given kind of discharge is very much less. Thus, in hydrogen we may have a pale blue cathode glow and a positive column which may show striations, or we may have the cathode glow without the positive column, depending upon the pressure of the gas, the dimensions of the tube and the potential difference between anode and cathode. When the luminous discharge is started in such a tube and the potential between anode and cathode is then gradually diminished, the luminosity disappears suddenly at a voltage which can be reproduced with great exactness. The current through the tube is very much greater than the current from the cathode in a vacuum, as long as the luminous discharge persists, but drops to a small value which is of the same order of magnitude as the thermionic current when the glow disappears.

Effect of Varying the Temperature of the Filament.—If the disappearance e.m.f. is measured at various values of the filament current in a tube of given dimensions containing gas at a given pressure, it is found that the disappearance voltage diminishes at first as the filament current is increased but ultimately comes to a constant value. An example of this is given in Fig. 1 in which the filament currents in amperes are plotted as abscissas against the disappearance voltages as ordinates.

The experimental results which are described in this paper may be

explained on the following assumption. (1) *The luminous glow can be obtained only when conditions in the tube are such that the positive ions produced by the impact of electrons on molecules of the gas are able to reach the cathode before combining to form neutral molecules. When positive ions reach the cathode they cause an increase in the number of electrons which escape from it, thus producing the increased current to which the glow is due.*

Let us suppose that conditions in the tube are such that ionization by electron impact occurs at some point midway between cathode and anode. The positive ions produced at this point travel towards the cathode, meeting electrons on the way. Under favorable conditions a positive ion will combine with an electron and, as has been suggested by Sir J. J. Thomson,[2] the region in which this recombination occurs may be very sharply defined if combination occurs only with electrons below a certain limiting speed. If this region falls short of the cathode, the current will exceed the thermionic current in a vacuum by a comparatively small amount, since the positive ions contribute very little to the current. If we increase the temperature of the cathode, the number of ions produced will be increased and this will result in a diminution in the potential gradient in the region between the place where ionization occurs and the place where the positive ions are destroyed by recombination. The place at which ionization occurs will, therefore, move down towards the anode, since the electrons must move through a greater distance in this region of lower potential gradient in order to acquire the ionization speed. The actual potential difference between the place of ionization and the place of recombination will, however, not be greatly affected since the extent of this region will be approximately inversely proportional to the potential gradient. The place at which recombination occurs, however, may be nearly the same as before, for this depends upon the distance through which the electrons have to move from the cathode through the region in which there are few or no positive ions, before their speed exceeds the value which is favorable to recombination. The chance that a positive ion will get through this region without recombination is not affected by the temperature of the filament, since the number of electrons is increased in the same proportion as the number of positive ions which they encounter. The place at which recombination occurs will, however, be moved toward the cathode by an increase in the potential difference between the electrodes, as a

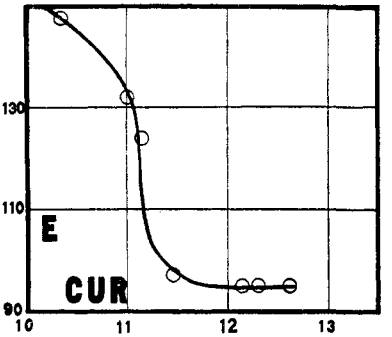

Fig. 1.

[2] Thomson, *Phil. Mag.*, **42**, 981 (1921).

given speed of electron will be found nearer the cathode at the higher voltages. The voltage E, which we have plotted in Fig 1, corresponds to the limiting voltage at which the place of recombination has approached so close to the cathode that positive ions can reach the cathode before recombining. The constancy of the disappearing voltage at the high filament currents is due, on our assumption, to the constancy of the position of recombination, and the constancy of the potential difference between the place of ionization and the place of recombination for the reasons just given. At low filament currents this constancy is not maintained. The disappearance of the luminosity is less sharply defined and the experimental results are less reproducible. In every case, however, the disappearing voltage increased, as shown in Fig. 1, when the filament current was diminished beyond a certain point. At the same time the appearance of the discharge in the tube changed, the cathode glow separating from the glass and in some cases appearing in the form of a narrow stream emanating from a small region on the surface of the cathode. It is probable that this contraction of the discharge is the cause of the increased disappearing voltage, for if the ions and electrons have to travel along a narrower path the chance of recombination will be increased. This assumption is supported by experiments which we shall describe later, in which it is shown that the disappearing voltage is greater in tubes of small diameter. In all subsequent experiments the filament current was maintained at a high value, so that the measured disappearance e.m.f., which we shall call E_d, always corresponds to the constant and reproducible portion of the curves of which Fig. 1 is a type.

The Variation of E_d with Pressure in a Tube of Given Dimensions.— In Fig. 2 the disappearance voltages are plotted as ordinates against the pressure of hydrogen in millimeters of mercury as abscissas. Curve I is for a tube 2.0 cm. in diameter with a distance between electrodes of 26.7 cm. In Curve II the electrode distance was 10.7 cm. and the diameter 1.05 cm. In all, 29 tubes were investigated. With all but the shortest 4 tubes, which we shall discuss separately, the type of curve obtained is of the same general character as those shown in Fig. 2. E_d at first diminishes as the pressure is decreased, coming to a minimum at a pressure which depends on the dimensions of the tube, and then rising rapidly as the pressure is still further diminished. At the higher pressures the discharge showed a positive column, usually striated. As the pressure is diminished the distance between the cathode and the head of the positive column increases, the striations becoming fewer in number, farther apart and less distinct, until at a pressure near the minimum of E_d the positive column is no longer visible. At pressures lower than those corresponding to the minimum of E_d, the blue cathode glow extends through the whole space between the electrodes. On the assumption (1) made above that the glow

disappears when the positive ions just fail to reach the cathode, we may account for these observations as follows. At the higher pressures, where the head of the positive column is at some distance from the anode, the electrons which leave the cathode reach the ionization speed at a point somewhere between the first and second striations. The positive ions produced at this point move towards the cathode. The electrons which they encounter in the first portion of their path have a relatively high speed which, however, at all points in this region must be less than the ionization speed. If a positive ion captures one of these relatively fast electrons, the light emitted will probably correspond to a fall to one of the outer "Bohr" orbits. The first striation is probably produced in this man-

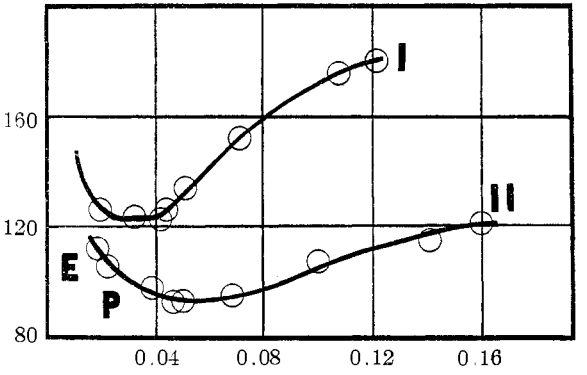

Fig. 2.—I, Tube 8; —II, Tube 6.

ner. The remaining positive ions which escape neutralization in this portion of the tube move on toward the cathode and if the voltage in the tube is less than E_d they will finally be neutralized by low-speed electrons at some point short of the cathode. If the voltage is greater than E_d and the conditions in the tube are those of the luminous discharge, the point at which the positive ions are finally neutralized is on or very close to the cathode and cause, on our assumption, the increase in electron emission to which the glow is due. The manner in which the positive ions increase the electron emission is immaterial to the present argument. We may suggest diminution in the negative space charge, photo-electric effect, or expulsion by impact on the cathode as possible mechanisms. If the pressure in the tube is increased, the mobility of the positive ions will be diminished owing to the increased number of collisions with neutral molecules. The chance of recombination is thereby increased, so that a greater potential difference is necessary to enable them to reach the cathode. In other words E_d increases as the pressure is increased. This state of affairs is illustrated by the curves in Fig. 2. At the higher pressures dE/dp is always positive.

The Minimum Value of E_d is an Integral Multiple of the Ionization Potential.—In the two curves shown in Fig. 2 the minimum values of E_d are 123 and 92 volts, respectively. It will be noticed that these values are very close to 4 and 3 times 30.9 volts which, within the limits of error of previous determinations, is the potential necessary for the complete ionization of hydrogen. Twenty-three of the hydrogen tubes investigated gave minimum values of E_d which, within the limits of error, were simple multiples of this value. The data are given in detail in Section V. As a general rule, we may say that the integer by which the minimum value of E_d must be divided in order to obtain the ionization potential, 30.9 volts, is greater the longer the tube. E_{dmin} will remain constant at a certain multiple throughout a considerable range of length and will then rise to the next higher multiple, remaining constant at this value for a further range of lengths after which there will be another abrupt rise of 30.9 volts and so on. The length, however, does not alone determine the multiple of 30.9 volts which will be obtained. Thus, the wider tubes, on the whole, give lower multiples than the narrower. It is possible that other factors have some effect. Thus Tube 1, which was 27 cm. long and 1.1 cm. in diameter, gave a minimum of 96 volts, while Tube 3, which was 20.7 cm. long and also 1.1 cm. wide, gave 128 volts at the minimum. In Tube 1, however, the cathode was oxide-coated platinum, while in Tube 3 the cathode was of tungsten. In every case, however, E_d was within the limits of error, an integral multiple of 30.9 volts. In order to account for this phenomenon we make the following assumptions. (2) *The potential gradient in the portion of the tube between the cathode and the place where ionization first occurs, diminishes as the pressure is diminished until at the minimum of E_d the total potential drop in this region has fallen to a very low value, not more than a few tenths of a volt in the shorter tubes nor more than about a volt in the longest tubes measured.* (3) *At the higher pressures, ionization occurs at regions intermediate in position between the anode and cathode. As the pressure is diminished these regions recede from the cathode until at the minimum of E_d, the ionization occurs only in the immediate neighborhood of the anode.*

Consider a tube through which the luminous discharge is passing, corresponding to a point at the minimum on one of the curves of the type shown in Fig. 2. Suppose now that we gradually increase the distance between anode and cathode, keeping the pressure at the value corresponding to the value of E_d. From what we have said above, the glow can persist as long as the positive ions can reach the cathode. Let us suppose that the voltage at the minimum was 123 volts, as in Curve I of Fig. 2. The positive ions which enter the region of low potential gradient between the cathode and the first ionization will have speeds corresponding to 30.9, 61.8, 92.4 and 123.6 volts, according as they have come from the first,

second, third or fourth ionization position, respectively. As we lengthen the distance between anode and cathode, the 30.9 volt ions will be the first to fail to reach the cathode. As the length of the tube is further increased, the 61.8 volt ions will be the next removed by recombination until finally the only ions which reach the cathode are those which originally had a speed of 123.6 volts. If the length of the tube is increased sufficiently, these also will fail to reach the cathode and the glow will disappear. The potential at this point is very close to 123.6 volts on account of Assumption 2, namely, that the potential difference between the cathode and the ionization region near the anode is negligible.

We may point out here that the experiments of van der Pol[3] on the conductivity at various parts of the striated discharge in hydrogen are in complete accord with the present theory. In Fig. 6 of his paper, van der Pol has plotted his experimental values for the absorption (which varies inversely as the conductivity) against the distance from the anode. From his figure we infer that the conductivity is a maximum on the anode side of each striation, a minimum at about the point where the light reaches its maximum intensity in each striation, and that the conductivity increases steadily as we go towards the cathode in the region between the cathode and the first striation. The conductivity which van der Pol measures must be very nearly proportional to the concentration of electrons at each point in the tube since the large and much less mobile positive ions can carry very little of the current. According to our hypothesis, the main source of electrons in the tube is the cathode itself, and we may say that the number of electrons passing through each cross section of the tube per second is approximately constant, since the current through the tube is determined mainly by this quantity. The concentration of the electrons at any point must, therefore, be inversely proportional to their speed. The speed of the electrons must be smallest near the cathode, and this is the region in which van der Pol finds the greatest conductivity. The electrons acquire their greatest speed just before each ionization position in the gas, that is, somewhere in the regions between striations, and it is in these regions that van der Pol finds the minima of conductivity.

The Variation of E_d with the Diameter of the Tube.—Although our experiments do not give us directly the variation of E_d with diameter at constant length and pressure, it is possible by graphical methods to calculate for any desired length and pressure, the values of E_d at various diameters. We have performed this calculation for 6 lengths, varying from 5 to 30 cm., and for pressures of 0.08 mm. and 0.13 mm. In every case the value of E_d increases markedly as the diameter is diminished. There are some apparent exceptions to this rule in the shorter tubes, but these are certainly due to failure to correct for the widening of the tube in

[3] van der Pol, *Phil. Mag.*, **38**, 361 (1919).

the neighborhood of the cathode (see Fig. 5). We have not thought it worth while to make this correction. This regularity is also readily explained by our theory. In the narrower tubes the chance of recombination is greater and it would be necessary to impart a greater speed to the ions in order to enable them to reach the cathode.

The Variation of E_d with Pressure at Pressures Below the Minimum.—In the region corresponding to the descending branch of a curve of the type shown in Fig. 2, that is, at pressures below the minimum of E_d, we find that the disappearance voltage is much less reproducible, although in every case E_d increases very rapidly as the pressure is diminished. At the same time the appearance of the discharge alters and we have again the marked tendency of the discharge to contract in the neighborhood of the cathode, which we have already noticed in the case of small filament currents. Often the discharge would seem to emanate from a very small region on the cathode. This effect can be counteracted, to a certain extent, by an increase in the temperature of the filament. The explanation of these phenomena follows readily from our theory. If the pressure is diminished beyond a certain point, the number of positive ions produced will be also diminished. If we suppose that the liberation of electrons from the cathode is due, in part at least, to a local heating produced by the impact of the positive ions, it would be necessary to concentrate the stream of ions on a small region of the cathode if their number is insufficient to raise the temperature of the whole surface. Whenever, by chance, such a hot spot on the cathode has formed, all other positive ions will be forced into the narrow stream of discharge which emanates from it, for the narrow track of conducting gas will absorb into itself most of the lines of force which emanate from the cathode, so that there will be very little fall of potential in parts of the tube through which the discharge is not passing. The effect of concentrating the discharge in this manner must be similar to that of diminishing the diameter of the tube. The chance of recombination becomes much greater and a greater potential will have to be applied to enable the positive ions to reach the cathode. It seems probable that the high cathode fall of potential in tubes with cold cathodes is due to the same phenomenon.

III. Experimental Procedure for Hydrogen

It has often been pointed out[4] that small amounts of impurity in hydrogen produce a large difference in the character of the luminous discharge produced in it. The hydrogen used in these experiments was produced by the electrolysis of sodium hydroxide. In the early experiments it was first passed over heated platinized asbestos which had previously been heated for several hours in a vacuum, dried by passing through two

[4] See, for example, Research Staff of the General Electric Co., Ltd., *Phil. Mag.*, **40**, 585 (1920).

long phosphorus pentoxide tubes and finally passed through a trap immersed in liquid air which removed the last traces of water vapor, as well as any other impurities such as stopcock grease and mercury vapor. Nitrogen and oxygen both react with hydrogen in the luminous discharge, to form ammonia and water, respectively. Since both of these gases are completely condensed at liquid-air temperatures, it was deemed unnecessary to used the platinized asbestos and the phosphorus pentoxide tubes and these were not used in the later experiments. Since the character of the discharge was very sensitive to impurities, their presence would have been easily detected.

The pressures were measured with a McLeod gage, capable of reading pressures of 0.0001 mm. with accuracy. The discharge tubes were always made of Pyrex glass. Since it is impossible to make a vacuum-tight seal of platinum through Pyrex, the device shown in Fig. 3 was used to make the apparatus vacuum tight.

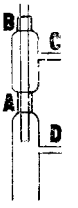

Fig. 3.

The wires are sealed through the glass at A and at B. These seals are sufficiently tight to prevent any appreciable diffusion of the gas at low pressures. C was attached to a separate vacuum pump through a trap immersed in liquid air, so that the pressure in the space between the two seals was always maintained at approximately 0.0001 mm. D is connected to the hydrogen generator, main vacuum pump, etc.

With this arrangement, the pressure inside to the tube could be maintained constant over long periods of time. In the later experiments tungsten electrodes were used and these could be sealed through a special glass which in turn, could be sealed directly to Pyrex.

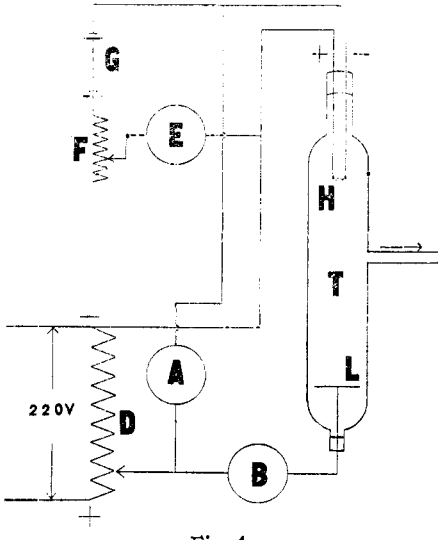

Fig. 4.

The cathodes in the earlier experiments were coated with a mixture of barium and calcium oxides. This procedure was later abandoned because the oxide coating never adhered satisfactorily to the electrode. The cathode was ordinarily a simple straight wire, and the anode either a small platinum plate or tungsten spiral.

Fig. 4 shows the connections that were used.

G is a 20-volt storage battery used for heating the filament, and F is a resistance in series for varying the temperature of the filament. T is the discharge tube, H being the cathode and L the anode. B is a milliammeter connected so as to measure the current flowing through the tube and A is a voltmeter for the purpose of reading the voltage

between anode and cathode. D is a 259-ohm resistance shunted across a 220-volt source of potential, so arranged that the potential between the anode and cathode could be varied by moving the sliding contact. The positive pole of the filament battery was connected to the negative end of the 220-volt line and the voltmeter arranged so as to read the entire potential drop between the negative end of the filament and the anode. The potential drop across the filament was from 1 to 3 volts.

Before any measurements were made, the apparatus was evacuated with the filament hot and with continual flaming until the pressure was too low to be read on the McLeod gage (below 10^{-6} mm.). The apparatus was then filled with hydrogen and evacuated to a similar pressure several times. Finally, before actually beginning a run the apparatus was filled with hydrogen to a pressure of 0.2 mm. to 0.5 mm. and the luminous discharge started and allowed to run for at least half an hour.

During the preliminary runs in each case a large amount of gas was "cleaned up" which did not reappear on allowing the tube to remain for a time without the luminous discharge, but this effect grew decidedly less with continued use of the tube and was not noticeable after the tube had been used continuously for several hours.

The procedure in each case was to increase the potential across the tube until the discharge took place, using a spark coil as a means of excitation when necessary, and then to decrease the voltage between the anode and cathode until the glow disappeared. Several such points were taken with various filament currents until the range over which E_d remained constant (See Fig. 1) was determined. The disappearance of the glow was always accompanied by a great decrease in the current as indicated by the milliammeter, and in the short tubes where it was hard to see the glow due to the brightness of the filament, this method was used to ascertain the value of E_d.

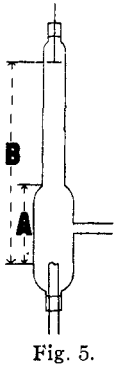

Fig. 5.

Twenty-nine tubes were tried in all, of different sizes and shapes. In the case of the narrow tubes the cathode portion was enlarged, and the diameter of this portion is given in the tables as well as that of the main part (see Fig. 5). A great number of points were obtained in each case. Frequently the first points obtained were erratic, due probably to the fact that gas was still being liberated from the glass walls and from the electrodes. More weight is given, therefore, to the later runs in each case. Two or more runs which checked accurately were obtained with each tube. The figures given in the tables are generally those obtained during the last run made on a given tube.

IV. Results for Hydrogen

In Table I, the first row is the number of the tube, the second and third rows are the diameters of portions A and B (see Fig. 5) and the fourth and fifth rows are the lengths of these portions.

TABLE I

DIMENSIONS OF THE HYDROGEN TUBES

Tube	No.	1	2	3	4	5	6	7	8	9	10	11	12
Diam.	A	2.9	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.0	2.0
(cm.)	B	1.1	1.1	1.1	1.1	1.1	1.1	1.1	2.0	2.0	2.0	2.0	2.0
Length	A	1.5	4.5	4.0	4.0	4.0	4.5	4.5	4.0	4.0	4.0	0.0	0.0
(cm.)	B	27.0	22.2	20.7	18.3	15.0	10.7	5.7	26.7	21.3	17.3	9.3	4.1

Tube	No.	13	14	15	16	17	18	19	20	21	22	23	24
Diam.	A	3.9	3.9	3.9	3.9	3.9	3.9	1.4	1.5	1.5	1.5	1.5	1.5
(cm.)	B	3.9	3.9	3.9	3.9	3.9	3.9	1.5	1.5	1.5	1.5	1.0	1.0
Length	A	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	3.0
(cm.)	B	35.3	30.4	20.3	10.8	4.9	2.8	4.4	3.1	2.5	1.8	22.9	12.9

Tube	No.	25	26	27	28[a]	29[a]
Diam.	A	1.5	1.5	2.9	..	..
(cm.)	B	1.0	1.0	2.9	15.2	14.5
Length	A	3.0	3.0	0.0	..	..
(cm.)	B	8.7	5.2	6.0	8.3	2.4

[a] Tubes 28 and 29 were spherical.

In Table II the tube numbers correspond to those in Table I. Each pair of rows gives respectively the value of E_d in volts and of the pressure p in mm. The minimum value of E_d is given in parenthesis at the end of each row.

TABLE II

VARIATION OF E_d WITH PRESSURE IN TUBES FILLED WITH HYDROGEN

1	E_d	178	150	118	111	96	(96)				
	p	0.085	0.058	0.021	0.020	0.012					
2	E_d	178	145	141	119	103	99	105	232	(95)	
	p	0.095	0.056	0.051	0.031	0.019	0.019	0.015	0.013		
3	E_d	178	140	136	132	130	128	134	160	180	(128)
	p	0.017	0.055	0.052	0.044	0.036	0.029	0.025	0.017	0.006	
4	E_d	173	164	147	141	125	125	180	(125)		
	p	0.135	0.129	0.087	0.085	0.048	0.046	0.017			
5	E_d	137	120	115	98	98	141	182	(98)		
	p	0.106	0.103	0.084	0.057	0.049	0.013	0.011			
6	E_d	140	121	108	95	93	92	99	110	(92)	
	p	0.252	0.160	0.100	0.068	0.050	0.046	0.039	0.019		
7	E_d	79	66	62	62	62	73	198	(62)		
	p	0.316	0.126	0.099	0.065	0.063	0.027	0.016			
8	E_d	180	152	126	123	124	126	(123)			
	p	0.122	0.071	0.044	0.044	0.033	0.019				
9	E_d	142	105	97	92	93	94	230	(92)		
	p	0.119	0.053	0.043	0.040	0.024	0.022	0.012			
10	E_d	122	102	95	93	94	93	104	230	(93)	
	p	0.105	0.061	0.054	0.049	0.048	0.044	0.037	0.027		
11	E_d	86	76	69	63	64	65	(63)			
	p	0.163	0.099	0.072	0.051	0.044	0.041				
12	E_d	52	43	36	32	31	31	(31)			
	p	0.316	0.188	0.130	0.088	0.078	0.059				

TABLE II (*Continued*)

13	E_d	165	148	130	125	121	163	197	(121)		
	p	0.068	0.048	0.029	0.027	0.019	0.018	0.004			
14	E_d	206	132	111	100	92	94	108	142	(92)	
	p	0.197	0.075	0.054	0.034	0.032	0.029	0.012	0.004		
15	E_d	120	112	103	100	93	93	236	(93)		
	p	0.134	0.106	0.070	0.065	0.053	0.037	0.019			
16	E_d	86	70	64	63	65	136	(63)			
	p	0.156	0.075	0.066	0.045	0.041	0.031				
17	E_d	48	48	48	48	52	76	(48)			
	p	0.416	0.149	0.080	0.072	0.056	0.007				
18	E_d	31	31	34	47	48	48	52	(31)		
	p	0.456	0.188	0.160	0.060	0.048	0.038	0.016			
19	E_d	78	62	62	60	61	63	116	248	(60)	
	p	0.360	0.184	0.159	0.135	0.039	0.022	0.007	0.004		
20	E_d	48	48	48	52	61	72	(48)			
	p	0.186	0.135	0.126	0.114	0.034	0.014				
21	E_d	48	48	48	42	42	42	(42)	main glow		(48)
	p	0.279	0.200	0.183	0.143	0.085	0.027				
22	E_d	36	33	32	33	32	32	43	(32)		
	p	0.214	0.187	0.143	0.135	0.121	0.088	0.016			
23	E_d	164	158	132	124	123	131	(123)			
	p	0.092	0.070	0.044	0.013	0.007	0.006				
24	E_d	140	132	125	122	121	124	152	(121)		
	p	0.128	0.097	0.073	0.054	0.053	0.034	0.028			
25	E_d	116	102	99	93	93	139	(93)			
	p	0.158	0.129	0.098	0.063	0.049	0.019				
26	E_d	75	72	62	62	72	91	(62)			
	p	0.127	0.100	0.068	0.084	0.059	0.013				
27	E_d	105	95	75	63	63	88	(63)			
	p	0.442	0.292	0.141	0.054	0.024	0.005				
28	E_d	50	52	48	64	63	75	91	91	91	(91 and 48)
	p	0.456	0.252	0.075	0.055	0.040	0.031	0.025	0.009	0.003	
29[a]	E_d	38	47	53	78	91	104	118			
	p	0.015	0.012	0.006	0.003	0.001	0.0007	0.0004			

[a] In Tube 29 the following values were obtained at higher pressures; the glow did not always disappear at these values, but they were frequently noticed as transition points; 25.6 ± 0.2; 30.5 ± 0.5; 27.7 ± 0.2; 22.9 ± 0.5; 29.0 ± 0.3 (rare); 26.3 ± 0.5 (rare); 17.3 ± 1.0; 39.5 ± 0.5. Once or twice indications in the neighborhood of 13.5 volts were obtained.

V. Discussion of Results for Hydrogen

There are 6 tubes which show a minimum approximately equal to 4 times the highest ionization potential of hydrogen, the average being 123.5 volts. Neglecting the first, Tube 3, which was one of the early ones tried, the average is 122.6 volts. Dividing this by 4 would give 30.7 ± 0.5 volts as the potential necessary to dissociate the hydrogen molecule and ionize both atoms.

There are 10 tubes which show a minimum E_d approximately equal to 3 times the highest ionization potential of hydrogen. The average is

93.5 volts or, neglecting the first 3 values which were preliminary, the average is 92.3. Dividing this by 3 gives 30.8 ± 0.5 volts as the highest ionization potential of hydrogen.

There are 6 tubes which show points approximately twice the ionization potential of hydrogen. The average is 62.2 volts and dividing this by 2 gives 31.1 ± 1 volt as the ionization potential of hydrogen.

There are 5 tubes which show points in the neighborhood of 31 volts and the average value obtained from them is 30.8 ± 1 volt.

The average of all 23 of the values for the ionization potential gives 30.9 volts, with a maximum deviation of 1.1 volts and an average deviation of 0.4 volt. In addition, 5 tubes show points at 48 ± 1 volt. Subtracting 30.9 from this value gives 17.1 volts, which is the voltage given by Krüger[5] as that necessary to dissociate the hydrogen molecule and ionize one of its atoms. This value is somewhat higher than that calculated by Bohr[6] in his articles on the structure of the hydrogen molecule. Recently, Foote and Mohler[7] and later Duffenback[8] found experimentally a value which agrees well with Bohr's theoretical value. They find, however, 13.5 volts as the ionization potential of the atom, and this added to the potential required for dissociation (3.6 volts as calculated from Langmuir's value of the heat of dissociation[9]) would give 17.1 volts. The heat of dissociation of hydrogen as calculated by Bohr (60,000 calories) is probably too low.

Most, or all, of the points can be accounted for as sums of various ionization and resonance potentials, but since several explanations are possible in each case, the subject will not be treated in further detail.

In a great many cases the distance between striations was measured. In general this distance agrees very well with that calculated from a for-

TABLE III

VARIATION OF STRIATION DISTANCE WITH PRESSURE AND TUBE DIAMETER

Tube	Pressure	Dist. betw. str. obs.	Dist. calc. from $l=\frac{2r^{1-m}}{p^m}$ ($m=0.53$)
	Mm.	Cm.	Cm.
3	0.122	1.35	1.35
3	0.224	1.15	1.00
3	0.17	1.4	1.3
4	0.169	1.4	1.42
2	0.095	1.6	1.55
9	0.190	1.7	1.8
13	0.167	5.4	6.0

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

[6] Bohr, *Phil. Mag.*, **29**, 332 (1915), and earlier articles.

[7] Foote and Mohler, *Bur. Standards, Sci. Papers*, 400, 700 (1920).

[8] Duffenback, *Science*, **55**, 210 (1922).

[9] Langmuir, THIS JOURNAL, **37**, 417 (1915).

mula given by Wehner.[10] This point is illustrated by the preceding table.

VI. Experimental Procedure for Mercury

Fig. 6 shows the apparatus used for the experiments on mercury vapor. The mercury was washed with nitric acid and then distilled, and gave no residue on evaporation. The discharge tube and mercury container were immersed in a vapor-bath which gave constant temperatures within a few tenths of a degree.

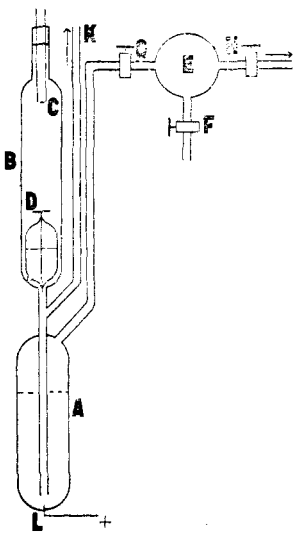

Fig. 6.

The procedure in each case was to heat the vapor-bath for a considerable length of time to make sure that the whole apparatus had attained a uniform temperature, while the apparatus was evacuated with the filament hot. H was attached to a vacuum pump capable of giving a few millimeters' pressure and was used only to withdraw the mercury from the discharge tube. The stopcocks G and H were then closed and air admitted to the flask E, by means of the stopcock F. By turning the stopcock G, the mercury was forced up into the discharge tube, the float D, rising up towards the cathode, thereby varying the distance between the electrodes. Contact with the anode was made through the mercury. The discharge was now started as for hydrogen and the values of E_d obtained in the same manner for various distances between the electrodes. After taking each point the mercury was withdrawn from the discharge tube by opening stopcocks G and H and closing the stopcock F, and the apparatus evacuated to a pressure below 10^{-6} mm. in order to remove any traces of air which might have been liberated from the electrodes or from the glass.

VII. Results for Mercury Vapor

Measurements were made at 6 different temperatures ranging from 34° (boiling ether) to 136° (boiling xylene). With the size of tube chosen (diam. 2.2. cm.) the variation with temperature and hence with pressure was very slight. It seems likely that with narrower tubes the marked pressure variation observed in hydrogen could also be obtained in mercury.

In Table IV a typical run is given in detail. Fig. 7 is a typical graph of such a run.

[10] Wehner, *Ann. Physik*, **32**, 49 (1910).

TABLE IV

VARIATION OF E_d WITH DISTANCE BETWEEN ELECTRODES IN MERCURY

Temp. 111° (boiling toluene); vap. pressure of Hg, 0.489 mm.

Distance between electrodes, cm.	22.8	17.5	13.3	8.5	7.8	4.2	1.8	0.7
E_d (volts)	32.0	31.0	21.9	21.0	15.6	10.9	10.5	10.5

Davis and Goucher[11] give 10.4 volts as the ionization potential of mercury; Franck and Einsporn[12] give 10.38 volts and Stead and Gossling[13] 10.8 volts. In all, 68 values were obtained which were approximately 4 times these values. The average is 42.12 volts, and dividing this by 4 gives 10.53 volts as the ionization potential of mercury vapor.

In all, 86 values of E_d were obtained which were nearly 3 times the ionization potential, and the average value is 32.08 volts. Dividing this by 3 gives 10.69 as the ionization potential of mercury vapor.

51 values were obtained in the neighborhood of 22 volts, the average being 21.6, and dividing this by 2 gives 10.8 volts. 13 values were obtained in the neighborhood of the ionization potential, and their average is 10.71 volts.

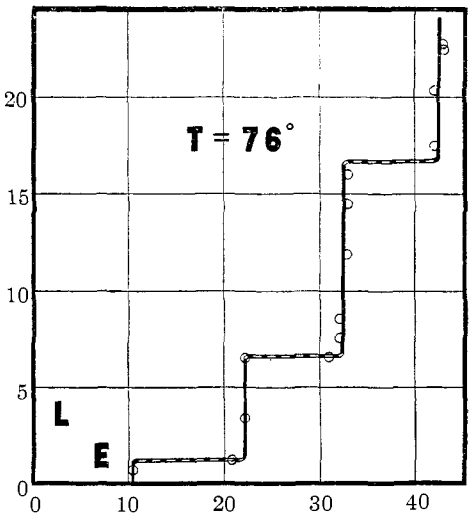

Fig. 7.

The average of the 218 determinations of the ionization potential is 10.7, with a maximum deviation of 0.7 volt and an average deviation of 0.4 volt. The agreement with the values referred to above is excellent.

Certain intermediate points were obtained, particularly in the shorter tubes and at the lower pressures. One of these points is 15.6 ± 0.3 volts; 10.7 subtracted from this gives 4.9 volts, which is the resonance potential of mercury as reported by Davis and Goucher[11] and by Franck Hertz.[14] Another such point is 26.4 ± 0.5 volts, which, minus 2 times the ionization potential, 10.7 volts, gives 5 volts, within the experimental error of the resonance potential.

The point at which the jump occurred from one multiple of the ionization potential to another is not definite, but for a small range of lengths first one and then the other multiple may be obtained.

[11] Davis and Goucher, *Phys. Rev.*, **10**, 101 (1917).

[12] Franck and Einsporn, *Z. Physik.*, **2**, 18 (1920).

[13] Stead and Gossling, *Phys. Rev.*, **15**, 413 (1920).

[14] Franck and Hertz, *Verh. deut. phys. Ges.*, 11, 512 (1914).

In conclusion, the authors wish to express their gratitude to Mr. R. M. McManigal who aided in the performance of many of the experiments herein described.

Summary

1. The voltage at which the luminous discharge in hydrogen disappears in tubes furnished with heated tungsten cathodes, is a function of the pressure for a given tube, passing through a minimum value which is usually a simple multiple of the ionization potential, 30.9 ± 0.4 volts.

2. In mercury vapor the disappearance voltage of the luminous discharge is a simple integral multiple of the ionization potential, 10.7 ± 0.4 volts.

3. A simple hypothesis is advanced to account for these facts.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

REACTION BETWEEN POTASSIUM TRINITRIDE AND IODINE IN THE PRESENCE OF CARBON DISULFIDE[1]

BY A. W. BROWNE AND A. B. HOEL

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During the course of an investigation of the solubility of iodine in aqueous solutions of potassium trinitride, to be recorded in a later article, the deeply colored solutions obtained were shaken with various non-aqueous liquids in a test-tube for the purpose of ascertaining qualitatively the manner in which partition of the iodine between the two liquid layers might take place.

When carbon disulfide was brought into contact at room temperature with a solution of iodine in aqueous potassium trinitride, the color of the solution was quickly discharged, as a result of rapid reduction of the iodine, with copious evolution of gas. A similar result was obtained when solutions of potassium trinitride were treated with a solution of iodine in carbon disulfide, or were at first treated with carbon disulfide alone, and then, either in presence or in absence of the excess of carbon disulfide remaining as a second liquid layer, were brought into contact either with a solution of iodine in aqueous potassium iodide, or with crystals of iodine. As each crystal of iodine was introduced, it was vigorously attacked, so long as the solution contained undecomposed potassium trinitride, with the result that reduction of the iodine, accompanied by a brisk evolution of gas, was promptly effected. The gas was subsequently shown by analysis to consist of pure nitrogen.

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