of the two and was the one generally employed. In either case the wash-waters were carefully preserved and titrated for the potassium hydroxide.

Potassium chloride was tried in the same manner and very excellent, adherent deposits were quickly obtained.

No.	KCl taken. Gram.	Current. Ampere.	Volts.	Time. Minutes.	Potassium found. Gram.	Potassium present. Gram.	Chlorine found. Gram.	Chlorine present. Gram.
1....	0.0400	0.055–0.07	3.9–3.8	15	0.0207	0.0209	0.0190	0.0191
2....	0.0400	0.08	5	15	0.0208	0.0209	0.0206	0.0191
3....	0.0400	0.08 –0.08	3.8–3.4	10	0.0205	0.0209	0.0187	0.0191
4....	0.0400	0.08 –0.09	3.6	10	0.0205	0.0209	0.0192	0.0191
5....	0.0400	0.08 –0.09	4.2–3.8	10	0.0211	0.0209	0.0189	0.0191
6....	0.0400	0.08 –0.09	5 –4.7	10	0.0198	0.0209	0.0180	0.0191
7....	0.0400	0.08 –0.09	6.3–4.7	10	0.0211	0.0209	0.0187	0.0191

The same conditions were used as in the analysis of potassium iodide with aid of the rotator.

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THE DISSOCIATION OF WATER VAPOR AND CARBON DIOXIDE AT HIGH TEMPERATURES.

BY IRVING LANGMUIR.

THE dissociation of gases at high temperatures has been the subject of many investigations during the past few years. In particular the states of equilibrium in the following reactions have been studied:

$$2HI \rightleftarrows I_2 + H_2.^1$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O.^2$$

$$2SO_3 \rightleftarrows 2SO_2 + O_2.^3$$

$$2NO \rightleftarrows N_2 + O_2.^4$$

$$2CO_2 \rightleftarrows 2CO + O_2.^5$$

$$2H_2O \rightleftarrows 2H_2 + O_2.^5$$

$$2NH_3 \rightleftarrows N_2 + 3H_2.^6$$

[1] Bodenstein: Z. physik. Chem. 29, 295 (1899).

[2] Hahn: Ibid. 44, 513 (1903); 48, 735 (1904).

[3] Knietsch: Ber. 34, 4069 (1901); Bodenstein: Z. Electrochem. 11, 373 (1905).

[4] Nernst: Göttinger Nachr. 1904, Heft 4.

[5] Nernst and v. Wartenberg: Göttinger Nachr. 1905, Heft 1; Löwenstein: Z. physik. Chem. 54, 715.

[6] Haber and van Oordt: Z. anorg. Chem. 44, 341 (1905).

There are two general methods of determining the dissociation constants of gases at high temperatures. First, by the measurement, at the desired temperature, of some property of the gas which varies with the dissociation and which can be measured without disturbing the equilibrium. Such a property is the density. The second method is to heat the gas to the desired temperature and then by rapid cooling or by the removal of some catalytic agent to decrease the velocity of the reaction to a negligible quantity so suddenly that there is no time for a perceptible change to occur in the composition of the gas during the operation.

Each of the above-mentioned investigations except that of Löwenstein depended on the use of the second method. In all these experiments there is necessarily some change in the composition of the gases during the cooling. The important question, and one usually very difficult of solution, is whether this change is so small as to be negligible; the whole value of the results depends upon its being so.

It occurred to Prof. Nernst that around a glowing metallic wire, in a gas capable of dissociating, there would probably be only very slight recombination of the dissociation products, during the short time required for these to diffuse from the surface of the wires out into the comparatively cold layers only a short distance from the wire. Furthermore, if the wire had a sufficiently strong catalytic action there would be equilibrium at the surface of the wire and hence the cold gas some distance from the wire would have the same composition as it would have were the whole gas uniformly heated to the temperature of the wire.

At Prof. Nernst's instigation I undertook a series of experiments in the laboratory of Physical Chemistry of the University of Göttingen to investigate the dissociation of gases around glowing platinum wires in the hope of finding this prediction fulfilled and of so obtaining a new and convenient method for the determination of the dissociation constants of water vapor and carbon dioxide. Prof. Nernst suggested determining the temperatures by means of the change of electric resistance of the wire.

I wish here to express my appreciation of the interest taken in the work by Prof. Nernst and to thank him for many valuable suggestions.

Several investigators have carried out experiments to study the reactions in gases near and on the surface of glowing wires. For example, recently, Haber and van Oordt[1] showed that traces of ammonia are produced when a mixture of hydrogen and nitrogen is passed over an iron wire heated to a bright red heat by an electric current. Emich[2] has shown that nitric oxide is slowly decomposed when brought in contact with white hot platinum wires. v. Hoffman[3] led steam with great velocity over white hot platinum wires and so obtained considerable quantities of hydrogen and oxygen.

All such experiments, however, have given only qualitative results. The reason that no quantitative determinations of the dissociation or association of gases by this method have been made is probably due partly to the difficulty of the determination of the temperature of the glowing wire and partly to the fact that no one foresaw that the degree of dissociation obtained by this method would really correspond to the equilibrium at the temperature of the wire.

Since I began these experiments Prof. Nernst, who has been endeavoring to get several independent ways of determining these very important constants, has published in conjunction with Dr. von Warterberg papers on the dissociation of water vapor and carbon dioxide. The experiments there described were carried out by passing the gases through porcelain tubes, shaped like pipettes, in an electric furnace. The difficulties to be overcome were so great that it seemed that the method of glowing wires would have many advantages.

Another method, also suggested by Nernst, was used in the investigation of Löwenstein who used "semipermeable membranes" of platinum to measure the partial pressure of hydrogen in water vapor heated in an electric furnace.

APPARATUS.

The apparatus used (see Fig. 1) for my experiments consisted of a difficultly fusible (Durax) glass tube of 0.9 cm. internal diameter, in the center of which a fine platinum wire was stretched. A little above the lower end was a bulb to give room for the electric connections. In order to measure the resistance of the wire accurately it was necessary to determine the ratio of "drop" to current between two points on the uniformly glowing wire.

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[1] Loc. cit.

[2] Monatsh. 13, 78 (1893).

[3] Ber. 23, 2, 3314 (1890).

There were four platinum wires, A, B, C and D (0.3 mm. diameter) sealed into the glass. The wires A and B were used for supplying the current and C and D to measure the voltage between the two points P and P′. To avoid errors due to poor contacts one

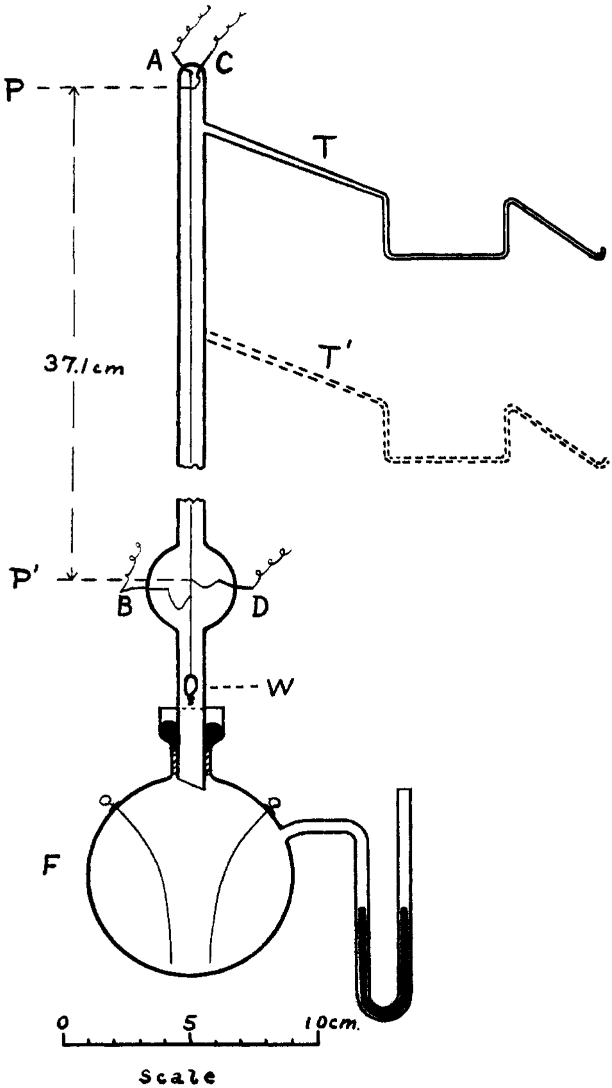

Fig. 1.

end of the main wire was fastened to C with silver solder and the other end similarly fastened to D. To A was soldered a short piece of wire, of the same kind as the main wire, and the other end of this was twisted around the main wire near its end so that the twisted part came between P and C. At P′ a short piece of wire was twisted with the main wire so the twisted part was between P′ and D. The other end of this piece had a small weight, W, of heavy platinum wire (about 2 grams) fastened to it to keep the main wire straight. A short distance below P′ a piece of wire was twisted around the wire P′W with the twisted part down and the end of this short piece was soldered to B. All the twisted parts were carefully welded. The wire in the path of the current was thus made of the same diameter everywhere from A to B and glowed uniformly when heated by the current. The portion PA was made shorter than PC so that the tension of the wire insured good contact at P.

In the bulb the connections BP′ and DP′ were made sufficiently long to allow for the expansion (about 4 mm.) of the wire when heated. The connection BP′ was made rather long, 1.5 cm., so that the gas upon entering the bulb would be rapidly heated to the temperature prevailing in the tube above, notwithstanding the cooling effect of the relatively large surface of the bulb.

When the wire was made to glow by an electric current, the temperature, to judge by the intensity of the emitted light, seemed to be perfectly uniform from A to B except within a distance of about 0.5 mm. from P and P′. But even at these joints themselves the wire would show a bright red heat when the rest of the wire was white hot.

The main wire was of the purest platinum that could be obtained from Heraeus. It had a diameter of 0.06 mm.

At the upper end of the tube a side tube, T, was attached. The internal diameter of this tube varied from about 2 mm. where it joined the main tube to about 0.6 mm. in the bent part. The object of bending it into the shape shown in the figure was to allow it to dip under the surface of the water in a beaker so that the water vapor passing through the apparatus would be condensed and could be collected over mercury together with any oxygen and hydrogen produced. The condensation occurred only after the first bend, that is, where the tube dipped under the water. The high velocity of the gases and the length of the straight part of the tube prevented any hydrogen and oxygen diffusing back into the main tube.

The side tube T was joined to the main tube about 3 cm. below the end of the latter to avoid a possible change in the composition of the gases, due to the recombination of the dissociation products on the cooler platinum surfaces at the top of the tube. To be certain that this length of 3 cm. was sufficient to avoid error, one apparatus was made in which there were two side tubes, T and T′, but it was found that the gases from each had the same composition.

In the experiments the apparatus was set up with the main tube vertical; the connections A and C were bent by means of a long glass rod so that the wire was exactly in the middle of the tube.

EXPERIMENTS WITH WATER VAPOR.

The steam was generated from a flask connected by a mercury seal directly below the main tube of the apparatus. In the flask were two electrodes of platinum wire to produce hydrogen and oxygen, if desired, along with the steam. In this way the equilibrium could be reached from both sides. The water in the flask contained a little sodium hydroxide to give it sufficient conductivity. The rate of boiling was regulated by a small flame, and the flask enclosed in an asbestos box. The heat given off by the wire prevented any condensation of the steam until it had passed under the water around the tube T. The water and the dissociation products were collected in a calibrated eudiometer which contained 3 cc. and which was subdivided to 0.02 cc.

The volume of gas and water was read off, then the gas exploded and a reading again taken. Then a little air was added and usually there was another explosion when sparks were passed. In this way the amount of hydrogen, oxygen and other gases could be determined. These results were corrected for temperature and pressure and solubility of the gases in water. As there was often a considerable excess of hydrogen it was necessary in some cases to consider the partial pressures of each gas in making the correction for solubility. As an example of this calculation let us take the data of one experiment (No. 67) and calculate the dissociation.

2.761 cc. water and 0.182 cc. gas were collected over mercury. The mercury and water column below the gas were equivalent to 2.8 cm. mercury. After the first explosion the gas volume was 0.096 over a column equivalent to 3.3 cm. mercury. Air was now added until the volume was 0.420 (over 1.6 cm. mercury). Finally, after another explosion the volume was 0.318 (over 2.1 cm. mercury).

The barometer read 74.1 cm. and the temperature was 28°. The vapor-pressure of water at this temperature is 2.8 cm. mercury. The pressures of the dry gases for each of the four readings of volumes were 68.5, 68.0, 69.7 and 69.2 cm.

The volumes reduced to 0° and 76 cm. and the dry condition and calculated to the basis of 1 cc. of water are: Before first explosion, 0.054; after first explosion, 0.028; before second explosion, 0.125; after second explosion, 0.095.

Thus the decrease of volume (V_1) on the first explosion was 0.026 and on the second (V_2) 0.030.

The absorption coefficients in water are for O_2, 0.031;[1] for H_2, 0.018.

The pressure in the eudiometer was on the average 70 cm.; the volume of dissolved gases (at 0° 0.76 cm.) per cubic centimeter of water is then for H_2

$$\frac{70}{76}\,\frac{\frac{2}{3}(V_1+V_2)}{V_0}\times 0.018 = 0.011\,\frac{V_1+V_2}{V_0};$$

for O_2

$$\frac{70}{76}\,\frac{\frac{1}{3}V_1}{V_0}\times 0.031 = 0.0095\,\frac{V_1}{V_0}.$$

V° is the volume before the first explosion. In our example the dissolved gases amounted to 0.011 cc. of H_2 and 0.0046 cc. of O_2 per cubic centimeter of water.

Altogether then there was $\frac{2}{3}(V_1+V_2)+0.011$ cc. hydrogen and $\frac{1}{3}V_1+0.0046$ cc. oxygen or 0.040 cubic centimeter of oxygen and hydrogen in the proportion to form water and an excess of 0.022 cc. of hydrogen.

The excess of hydrogen was rarely as large as in the above example and was observed only in the first few experiments after filling the flask F with water, or in the experiments in which the water was electrolyzed. The excess of hydrogen is due to the presence of traces of ammonia in the water or to the separation of peroxide of lead at the anode by the electrolysis of lead salts formed by the action of the sodium hydroxide on the glass.

The volume of other gases (nitrogen from the air or from the decomposition of ammonia) is found to be

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[1] Landolt-Börnstein's tables.

$$V_0—V_1—\tfrac{2}{3}V_2;$$

in our example 0.008 cc. per cubic centimeter of water.

The excess of hydrogen drives back the dissociation of the water vapor. We want in each case to know what the dissociation would be for equivalent amounts of hydrogen and oxygen. According to the law of mass action:

$$K=[H_2]^2[O_2];$$

since the concentration of the steam may be considered constant, now $[H_2]$ is proportional to $\tfrac{2}{3}G+E$ where G is the amount of gas of equivalent proportions and E is the excess of hydrogen. Similarly, $[O_2]$ is proportional to $\tfrac{1}{3}G$. If K′ is a new constant, we have

$$K'=G(G+\tfrac{3}{2}E)^2=G_0{}^3$$

where G_0 is the amount of oxygen and hydrogen which would be found if there were no excess of hydrogen. Solving for G_0 and expanding in a series we get

$$G_0=G+E(1—\tfrac{1}{4}E/G+\ldots\ldots\ldots).$$

In most cases it is sufficiently accurate to write

$$G_0=G+E.$$

If x is the degree of dissociation when there is no excess of hydrogen then, $x=\tfrac{2}{3}\ \dfrac{G_0}{1246}=0.000535\times G_0$. 1246 is the volume in cubic centimeters which 1 gram of steam would occupy at 0° and 76 cm. if the gas laws held down to 0°.

Returning to our example we have

$$G=0.040 \qquad E=0.022$$

$$\frac{1}{4}\ \frac{E^2}{G}=0.003 \qquad G_0=0.059$$

and $100\ x=0.0032$.

EXPERIMENTS WITH CARBON DIOXIDE.

In the experiments with carbon dioxide this gas was prepared from marble and 50 per cent. chemically pure nitric acid in a Kipp's apparatus. The marble was boiled several times in weakly acidulated water to free it from air and the acid was freed from air by a stream of carbon dioxide. The gas was purified by passing through a saturated sodium bicarbonate solution then through concentrated sulphuric acid and finally through a long tube containing phosphorus pentoxide. This tube had a bulb at one end with two platinum wires sealed in it between which sparks from a powerful induction coil were passed. In this way

8 per cent. of carbon monoxide could be produced and in these experiments, too, the equilibrium could be reached from both sides.

The carbon dioxide apparatus was connected to the dissociation apparatus by means of a mercury seal.

The gases passing out through the tube T were collected in 33 per cent. potassium hydroxide solution contained in an apparatus described by Nernst.[1] The mixture of carbon monoxide and oxygen were measured in a eudiometer which formed the upper part of the apparatus; the amount of carbon dioxide was found from the increase in the weight of the whole apparatus. Then the gas was exploded and the contraction noted. The only corrections needed were for temperature and pressure.

No excess of carbon monoxide could be detected in any case. In order to avoid solubility of the gases in the caustic potash, this was first shaken with a mixture of carbon monoxide and air. The eudiometer was calibrated and contained 5 cc.

After the carbon dioxide apparatus was freed from air the gas was very pure; only one part in 10,000 to 20,000 by volume was not absorbed in the caustic potash.

The degree of dissociation was calculated from the formula

$$x = \tfrac{2}{3}\,G \times \frac{1.96}{1000} = 0.00131\ G.$$

G is the contraction on explosion (reduced to 0° and 76 cm.) per gram of carbon dioxide and 1.96 is the weight of a liter of this gas under standard conditions.

RESISTANCE OF THE WIRE.

In order to measure the temperature of the wire the resistance of the hot wire had to be measured and compared to the resistance at some lower temperature, 100° and room temperature being chosen. Thus the resistance had to be determined first with a current of 1 to 1.5 amperes flowing through it, and then with a current so small as to not perceptibly warm it. The Wheatstone bridge method could not well be used. The following method gave very satisfactory results and had the advantage that the resistance could be determined easily once every minute during the whole course of the experiment.

A constant resistance (N, Fig. 2) of 1.174 ohms was made of very thick constantan wire wound upon a large glass tube and the whole immersed in oil. A current of 1.5 amperes did not per-

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[1] Nernst and v. Wartenberg: Göttingen Nach. 1905, Heft 1.

ceptibly warm this resistance. This known resistance and the wire in the dissociation apparatus were connected, by means of the wires A and B, in series, together with the variable resistance *r*.

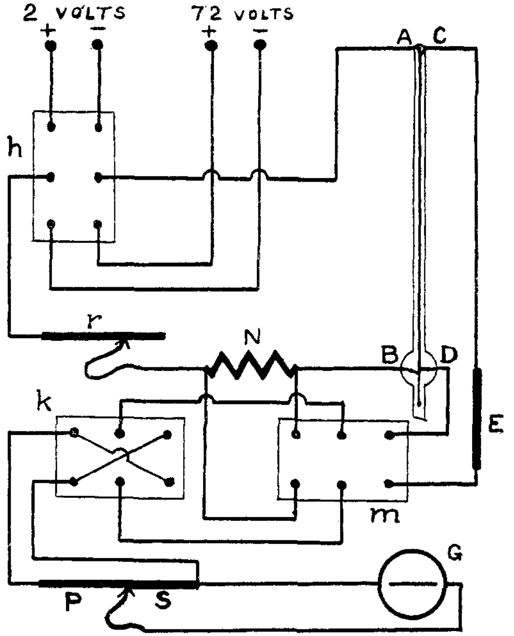

Fig. 2.

The two-way double switch *h* allowed either 2 or 72 volts to be used from a large storage battery, which gave a very constant current. The potential differences between C and D and between the two ends of N were then compared by means of the deflections obtained with a Deprez-d'Arsonval galvanometer, G. The resistances E, P and S were so chosen that the deflections were nearly equal for both potential measurements. *k* in the figure is a commutator and *m* a two-way double switch.

For measurements of the resistance at the various temperatures the following values of P S and E (in ohms) were used.

	P.	S.	E.
At room temperature...........	2000	500	20,000
At 100°......................	2400	500	30,000
At a red to white heat..........	2000	2	90,000

The resistance of the wire in the apparatus varied from 11 to

55 ohms, according to the temperature. The resistance of the galvanometer was 1077 ohms.

All resistances were carefully calibrated and the resistance of all connections measured and taken into account wherever these were not negligible. Although the system of wiring is rather complicated and a calculation of the resistance seems at first troublesome, it may be easily calculated from the formula

$$R = K - K\frac{\Delta e}{e_N}.$$

Here K is a constant to be determined once for all from the formulas

$$K = N\frac{E+P+S'}{P+S'}$$

$$S' = \frac{S}{1+\frac{S}{G}}.$$

e_N is the deflection of the galvanometer when connected with N.

Δe is the difference between e_N and the deflection when connection is made with C and D.

The possible sources of error such as thermocurrents, elastic lag in the galvanometer, lack of proportionality between the deflection and the current in the galvanometer, imperfect insulation, etc., were considered and by commutation, reading the galvanometer at regular intervals, and by a careful arrangement of the wiring such errors were avoided or eliminated as far as possible.

With these precautions the resistances are probably always accurate to one part in 1,000 and usually to one part in 4,000.

The resistance at 100° was determined by boiling the water in the flask until all the air was driven out of the apparatus. The pressure of the steam was observed on the manometer on the side of the flask. A simple calculation shows that the conductivity of the water layer on the wire and on the walls of the tube can be entirely neglected.

STUDY OF THE ACCURACY OF THE METHOD.

Before proceeding with the determination of the temperature coefficient of the resistance, without which the temperature could not be accurately known, it seemed best to find out whether this method for determining dissociations was capable of giving uniform and accurate results. For this purpose a series of about forty preliminary experiments were made.

Through an oversight of Heraeus a wire containing 10 per cent. rhodium was furnished in place of the pure platinum ordered, and only after the apparatus was constructed and several experiments had been made was it noticed that the temperature coefficient of the wire was much lower than that of platinum (only 44 per cent. as great). Since the temperature determination was not important for the preliminary experiments these were continued with the platinum-rhodium wire. The final series of experiments were made with platinum wire of exceptional purity as was proved by the high value of the temperature coefficient of the electric resistance (0.003909). This is a higher value than any that could be found in the literature except a practically identical value given by Holborn.[1]

Before each experiment the resistance of the wire at room temperature and at 100° was determined and then the resistance of the glowing wire measured several times in the course of the experiment.

The ratio of the resistances of the hot and cold wire served as a sort of temperature scale whose absolute value was not known. For the sake of convenience, however, let us speak of the temperature of the wire not as it is given in this scale, but as it was afterward found to be in the absolute scale, by comparison of experiments made with the two kinds of wires.

The results of the preliminary experiments and also a few facts about the usefulness of the method which were found from the experiments with pure platinum can be summarized as follows:

(1) The observed degree of dissociation x was the same whether the water was electrolyzed or not or whether sparks were passed through the carbon dioxide or not. This was true even when the temperature was as low as 1050° absolute and the current of gas as rapid as 0.6 gram H_2O or 0.3 gram CO_2 per minute.

(2) Within wide limits x was independent of the velocity (S) of the gas (in grams per minute).

In a series of experiments with steam the current was maintained constant and S was gradually increased from 0.09 to 0.6. The temperature of the wire and also x remained, however, en-

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[1] Drude's Ann. 6, 242 (1901).

tirely unchanged. When S was increased still more, the temperature decreased somewhat because of the cooling effect of the cold gas; x also decreased. For example while S grew from 0.6 to 1.10 the average temperature of the wire fell 20° and x decreased 42 per cent. The temperature difference of 20°, however, corresponds to a decrease of x of 24 per cent.; that is, the error in x was 18 per cent. With this strong current of steam, one could easily see that the wire directly opposite the opening to the tube T (Fig. 1) glowed less brightly than the rest. The whole decrease of x was probably due to the recombination of the hydrogen and oxygen on this short (3 mm.) length of cooler wire.

From these experiments it appears that the equilibrium around the wire is reached with extraordinary rapidity. A value of $S=1.10$ corresponds to 33 cc. of steam at 125° per second or a linear velocity of 52 cm. per second. When one considers that the surface of the wire is only 0.7 sq. cm. it seems remarkable that 33 cc. can reach equilibrium in one second.

In another paper I will attempt to show theoretically that from this rapid rate of formation and by application of certain formulas which I have developed,[1] the observed value of x cannot differ from the value corresponding to the true equilibrium by more than 10^{-12}; that is, the observed dissociation must be identical with the equilibrium value.

(3) The resistance of the wire decreases about 2 per cent., while the temperature coefficient between 20° and 100° increases somewhat upon heating the wire for the first time. Upon further heating the wire changes very little if heated only in steam. In all the experiments the platinum-rhodium wire was heated altogether about twenty hours at temperatures between 1200 and 1600° (abs.). During the first five hours the resistance increased about 1 per cent., but in the remaining fifteen hours remained constant within the experimental error.

In the experiments with pure platinum wire the resistance increased slowly but steadily (about 1 per cent. in a long series of experiments). The wire had, however, become somewhat elongated. If one assumes the density of the platinum remained unchanged then the following relation should hold between the change of resistance ΔR and the change of length ΔL.

$$\frac{\Delta R}{R} = 2\frac{\Delta L}{L}.$$

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[1] Dissertation Göttingen, 1906.

During cleven experiments a wire of 37.1 cm. length stretched 1.1 mm. The calculated increase of resistance is 0.60 per cent. Actually, the resistance at 20° increased 0.59 per cent. and at 100° 0.70 per cent.; that is, nearly within the experimental error.

Naturally, such lengthening of the wire introduces no error if the temperature coefficient remains unchanged.

In the preliminary experiments it was found that the value of x that was obtained depended solely upon the value of the ratio of the resistances of the hot and cold wire. The length of time the wire had been in use made no difference in this result.

Thus, eight preliminary experiments made at a temperature of 1440° (abs.) and distributed among all the preliminary experiments showed only irregular differences with a probable error of 2.9 per cent. in x for a single observation which corresponds to a temperature error of 3.0°.

The pure platinum wire, however, showed a tendency to give slightly increasing values for x as it was used even though the ratio of the resistances was kept constant. It seems then that the temperature coefficient of the resistance of platinum-rhodium remains constant but that of pure platinum decreases very slightly with continued heating.

(4) The lowest temperature at which the dissociation can be measured is about 1270° (abs.) as the gas formed then dissolves nearly completely in the water. Perhaps by determining the dissolved oxygen by chemical means it would be possible to work at much lower temperatures. The upper limit is set by the disintegration of the platinum, and it appears that a measurement of the dissociation is a very sensitive method of detecting disintegration ("Zerstäubung") of the platinum. When once the platinum-rhodium wire had been heated to 1650° (abs.) all further experiments gave too small values for x. For instance, after the wire was heated twenty-five minutes at 1670° (abs.) an experiment at 1460° (abs.) gave a value of x only 67 per cent. of what had previously been obtained at the same temperature. The explanation of this is that very finely divided platinum is deposited on the walls of the glass tube and that recombination of the gases occurs by catalysis. No deposit could be seen on the tube, but it was found that if the walls of the tube were rinsed out with aqua regia the original results could again be obtained.

With pure platinum wires no disintegration was observed either in steam or in carbon dioxide up to temperatures of 1550° (abs.). Hulett and Berger[1] showed that in air disintegration occurs even at 1073° (abs.). It is therefore very important in these experiments never to heat the wire when air is in the apparatus. As was found later, heating in air also changes the temperature coefficient of the resistance.

By application of the law of mass action the effect of pressure on the degree of dissociation may be calculated. It was found that the variations of the barometric pressure from the normal had so small an effect on the dissociation that it could be safely neglected.

TEMPERATURE COEFFICIENT OF THE RESISTANCE.

According to Callendar[2] and Heycock and Neville[3] and particularly Harker,[4] one should be able to measure temperatures up to 1000° with great accuracy from the resistance if this is known for the three temperatures 0° and 100° and 440°. If R_t is the resistance at the temperature t then the following should hold

$$t - \theta = \delta \left\{ \left(\frac{t}{100}\right)^2 - \frac{t}{100} \right\}$$

where

$$\theta = \frac{R_t - R_0}{R_{100} - R_0} 100,$$

and δ is a constant depending only on the purity of the platinum.

Holborn and Wien[5] measured the resistance of platinum wires up to 1600°. Unfortunately, the platinum they used was not very pure, since the temperature coefficient was only 90 per cent. of that which one gets from the wire that Heraeus now furnishes. Holborn and Wien found that above 1000° the resistance was a linear function of the temperature.

The resistance of the wire used in our dissociation experiments was determined at 0°, at 100°, and at the temperature of boiling sulphur. However, different values of δ were obtained for different treatments of the wire. The wire was first heated to a red heat in air to anneal it. The followng table shows the results of the tests on three wires.

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[1] This Journal, 26, 1512 (1904).

[2] Phil. Mag. 5, 48, 519 (1899).

[3] Jour. Chem. Soc. Trans. 67, 160 (1895).

[4] Proc. Royal Soc. 73, 217 (1904).

[5] Wied. Ann. 56, 360 (1895).

Wire No.	First heated to	During the time. Minutes.	R_0.	R_{100}/R_0.	$R_{444.5}/R_0$.	R_{1710}/R_0.	δ.
1........	1640° (abs.)	15	1.0028	1.3909	2.6335	....	1.74
2........	1640° "	10	1.0202	1.3884	2.6338	6.20	1.57
3........	1470° "	16	1.0029	1.3902	2.6350	....	1.66
3........	1470° "	10	1.0022	1.3896	2.6387	....	1.56
3........	1820° "	4	1.0226	1.3880	2.6404	6.27	1.41

The resistances are accurate to 2 or 3 units in the fourth decimal place. R_{1710} is the resistance measured at the moment at which the wire melted when heated by a strong current. Since the temperature of the wire was not uniform (as the piece used was only 4 cm. long) the resistance measured must be considered only as a lower limit to the true resistance at 1710°, the melting-point of platinum.

The table shows that glowing the wire in air decreases the temperature coefficient between 0° and 100°, but increases it between 100° and 440°.

A comparatively large change in δ corresponds to a small error in the temperature determination. Thus if δ changes from 1.50 to 1.55 the calculated temperature at 1000° changes but 4°.

According to the table, when δ is large R_{100}/R_0 is also large and it thus happens that at high temperatures it makes very little difference which pair of values of δ and R_{100}/R_0 are chosen for the calculation of the temperature from R_T.

The final values chosen for a wire which had been in use a long time were

$$R_{100}/R_0 = 1.3900.$$
$$\delta = 1.55.$$

This method of determining the temperature of the wire by extrapolating from 440° is rather unsatisfactory and it was therefore used only as a control on the other method adopted. The results, however, may have an interest in themselves.

The final arrangement was to measure the resistance of the wire directly while it was being heated in an electric furnace. In order to avoid the errors due to the action of the air on the wire and to have conditions as nearly like those in the experiments as possible, a current of steam was passed through the furnace during the time of heating. The furnace consisted of a very thin-walled porcelain tube wound with platinum wire.

The wire which had been used in apparatus No. 5 was used for these measurements. After the last experiment (No. 86) had been made the apparatus was broken and the wire removed, care being taken not to bend or stretch it.

The resistance of one piece of this wire was determined at 0°, 100° and 440°. Another piece about 3 cm. long was wound around a small porcelain tube of 3 mm. diameter such as are used for thermo-elements. The turns were about 5 mm. apart. In this tube was brought the junction of a thermo-element near the middle of the coiled wire. To each end of the wire wound on the tube two platinum wires were welded; these, insulated in porcelain tubes, led out of the furnace. This bundle of porcelain tubes and wires was then placed in the electric furnace. The porcelain tube of the furnace was then connected with a brass tube for preheating the steam, a gas-tight joint being made by means of asbestos paper and water glass. After the furnace was heated to about 200° the superheated steam was passed in a gentle stream through the furnace. The resistance was then measured with the same apparatus that was used for all the other experiments. Two series of measurements were made. The thermo-couple was calibrated at the melting-point of antimony 630.6° and then, before and after each series of resistance determinations the reading of the thermo-couple was taken at the melting-point (1064°) of a short piece of pure gold wire placed about 3 mm. from the junction of the thermo-couple.

By moving the thermo-element back and forth in the tube it was found that the temperature over the whole length of the coiled wire was uniform.

The resistance at 0° (calculated from the resistance at room temperature and the temperature coefficient) was not just the same before and after the heating but it increased about 0.6 per cent. in each series. If this change is distributed over the observations at various temperatures the values for R_0 are obtained that appear in the following table which gives the results of the experiments with the electric furnace.

V.	R_0.	R_T.	R.	T (abs.). Degrees.
7.513	1.638	6.495	3.965	1130
9.390	1.639	7.321	4.467	1298
10.63	1.642	7.816	4.760	1406
7.377	1.645	6.438	3.914	1117
9.391	1.646	7.390	4.490	1298
11.48	1.650	8.204	4.972	1477
9.33	1.654	7.375	4.459	1293

V is the voltage of the thermo-couple multiplied by 1000. The cold junction was at 0°. For the melting-point of gold V was found to be 9.83.

R is equal to R_T/R_0.

By plotting R and T one finds that up to $T = 1400$ the points lie in a smooth curve which does not differ very much from that obtained from the Heycock and Neville formula by using the values $\delta = 1.55$ and $R_{100} = 1.390$. At $T = 1300°$ the difference is about 20°.

If the curve be drawn through the points at $T = 1406°$ and 1477° it appears that the curvature at about $T = 1350°$ is greater than at lower temperatures, whereas from Holborn and Wien's paper it ought to be practically a straight line at this temperature. It seems probable that the cause of this is a slight conductivity at this high temperature of the porcelain on which the wire was wound and that therefore the results for R are slightly too low. The curve was drawn through the points at 1200° and carried to higher temperatures with approximately the same curvature that it has from 1100° to 1300°. The distance of the points at 1400° and 1477° from the curve then corresponds to 8° and 10° respectively. The curve was so nearly straight between 1300° and 1550° that it could be represented by the following formula without appreciable error.

$$T = 344.4\,R - 247.$$

FINAL EXPERIMENTS WITH STEAM AND CARBON DIOXIDE.

With apparatus No. 4 a series of experiments were made to get the ratio of the dissociations of steam and carbon dioxide at different temperatures. Since this ratio varies very little with the temperature, it was not necessary to get the temperature accurately for these experiments. With apparatus No. 5 the object was to determine as accurately as possible the relation between the temperature and the degree of dissociation of water vapor, hence the wire of apparatus No. 5 was used for the determination of the temperature coefficient. The water was not electrolyzed and sparks were not passed through the carbon dioxide in these experiments for the preliminary work had shown such a treatment to be without material influence.

The results of these experiments are given in the following table. R is the ratio of the resistance of the hot wire to that at 0°. T is the absolute temperature. It was assumed that the temperature coefficient of the wire in apparatus No. 4 was the same as that in apparatus No. 5.

EXPERIMENTS WITH APPARATUS NO. 4.

Pure Platinum Wire.

Experiment. Number.	S. g. gas per min.	R.	T (abs.). Degrees.	100 x.	A.	Average. A.	Remarks.
30	0.14	5.00	1474	0.0140	3.746	3.7420	H_2O
31	0.30	5.00	1474	0.0132	3.720		
33	0.25	5.15	1526	0.0225	3.753		
35	0.13	5.02	1481	0.0281	5.05	5.05	CO_2
36	0.18	5.26	1565	0.0642	5.05		
37	0.43	5.00	1474	0.0135	3.730	3.728	H_2O
38	0.48	5.00	1474	0.0134	3.727		
49	0.64	4.935	1451	0.0136	3.826	3.823	H_2O
50	0.35	5.165	1531	0.0270	3.812		
51	0.45	4.94	1453	0.0139	3.829		
52	0.42	4.64	1351	0.0050	3.825		
53	0.12	4.77	1395	0.0140	5.168	5.181	CO_2
55	0.18	4.77	1395	0.0144	5.176		
57	0.22	4.91	1443	0.0250	5.179		
58	0.20	5.07	1498	0.0471	5.201		
60	0.50	4.95	1457	0.0144	3.828	3.817	H_2O
61	0.46	5.18	1537	0.0270	3.792		
62	0.47	4.96	1460	0.0150	3.831		

EXPERIMENTS WITH WATER-VAPOR WITH APPARATUS NO. 5.

Pure Platinum Wire.

Experiment No.	S. g. gas. per min.	R.	T (abs).	100 x.	A.	Average. A.
67	0.30	4.559	1324	0.0032	3.755	3.753
68	0.27	4.670	1360	0.0045	3.733	
69	0.25	4.781	1399	0.0067	3.731	
70	0.26	4.870	1429	0.0100	3.780	
71	0.28	4.991	1471	0.0143	3.767	
77	0.32	5.007	1476	0.0150	3.769	3.778
78	0.43	5.232	1555	0.0292	3.762	
79	0.30	5.206	1545	0.0282	3.780	
80	0.33	5.000	1474	0.0149	3.761	
81	0.33	4.893	1437	0.0106	3.775	
82	0.35	4.770	1395	0.0072	3.783	
83	0.32	4.651	1354	0.0051	3.818	
84	0.31	4.564	1325	0.0033	3.765	
85	0.61	4.744	1386	0.0067	3.789	

Under A is a number obtained as follows: Nernst and v.

Wartenberg[1] give for the dissociation of steam at atmospheric pressure:

$$\log_{10}\frac{2(100\,x)^3}{(2+x)(1-x)^2} = [11.51] - \frac{25030}{T} + 2.65\log_{10}\frac{T}{1000} - 0.00055(T-1000)$$

and for carbon dioxide

$$\log_{10}\frac{2(100\,x)^3}{(2+x)(1-x)^2} = [9.54] - \frac{29560}{T} + 2.97\log_{10}\frac{T}{1000} - 0.00074(T-1000).$$

The numerical coefficients except those in brackets are all determined thermodynamically and do not depend in any way on the results of the experiments on the dissociation. Hence, for my experiments the same coefficients should apply if only new values are substituted for the quantities in the brackets. But it is more convenient to first simplify the expression. By neglecting x compared to 1 and by division by 3 we obtain for steam

$$\log_{10} x = A_{H_2O} - \frac{8343}{T} + 0.88\log_{10}\frac{T}{1000} - 0.00018(T-1000) \quad (1)$$

for carbon dioxide

$$\log_{10} x = A_{CO_2} - \frac{9853}{T} + 0.99\log_{10}\frac{T}{1000} - 0.00025(T-1000) \quad (2)$$

A_{H_2O} and A_{CO_2} are then to be found from the experiments; the same values should be obtained no matter at what temperature the experiments were made. From Nernst's experiments the values are

$$A_{H_2O} = 3.83.$$
$$A_{CO_2} = 5.18.$$

A change in A of 0.01 corresponds to a change in x of 2.3 per cent. A small error ΔT in the temperature measurement makes a corresponding error in the value of A (ΔA) which for temperatures not too far from $T = 1400°$ is given by

for steam

$$\Delta T = -109\left(\frac{T}{1000}\right)^2 \Delta A, \quad (3)$$

for carbon dioxide

$$\Delta T = -93\left(\frac{T}{1000}\right)^2 \Delta A. \quad (4)$$

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[1] Göttingen Nachrichten.

DISCUSSION OF THE RESULTS.

The values of A in general seem to be independent of the temperature and the velocity of the gas current S. Experiments in which the temperature is below 1400° (abs.) often give values of A which differ considerably from the mean, but these differences are so irregular that they are probably due simply to the relatively inaccurate determination of the very small quantities of gas appearing at these low temperatures.

The longer the wire has been in use, the larger the values of A become. As was mentioned before this change does not occur to an appreciable extent with platinum-rhodium wire. During the determination of the temperature coefficient the same change was undoubtedly going on. The value of A which corresponds to the temperature measurements is then somewhat larger than in Expts. 77–85. As the most probable value we may take

$$A_{H_2O}=3.79.$$

From Expts. 30–38 we get

$$A_{H_2O}=3.734 \qquad A_{CO_2}=5.050,$$

and from Expts. 49–62

$$A_{H_2O}=3.820 \qquad A_{CO_2}=5.181.$$

The deviation of A_{H_2O} from the value 3.79 can only be caused by errors in the temperature measurement ($\varDelta T$). This error must naturally be the same for the experiments with carbon dioxide as for those with steam. Thus in equation (3) and (4) the values of $\varDelta T$ are equal and we have

$$\frac{\varDelta A_{CO_2}}{\varDelta A_{H_2O}}=\frac{109}{93}.$$

For Expts. 30–38

$$\varDelta A_{H_2O} \text{ is } 0.056;$$

therefore

$$\varDelta A_{CO_2}=0.066;$$

hence

$$A_{CO_2}=5.116.$$

Similarly, Expts. 49–62 give

$$A_{CO_2}=5.147.$$

Expts. 47–64 were much more carefully made than Expts. 30–38, and since too low results can occur much more easily than too high results the most probable value seems

$$A_{CO_2}=5.15.$$

From these results for A_{H_2O} and A_{CO_2} with the help of (1) and (2) we can calculate the dissociation at all temperatures at atmospheric pressure. At exceedingly high temperatures one must substitute

$$\frac{x}{\sqrt[3]{\left(1+\frac{x}{2}\right)\left(1-x\right)^2}} \text{ in place of } x.$$

The following table gives the dissociations as calculated for various temperatures.

T (abs.).	100 x for H_2O.	100 x for CO_2.
1000	0.000028	0.000020
1200	0.000745	0.00093
1300	0.00266	0.00407
1400	0.00787	0.0146
1500	0.0197	0.0436
1600	0.0446	0.110
1700	0.0920	0.260
1800	0.170	0.546
1900	0.302	1.04
2000	0.504	1.84
2200	1.21	5.00
2500	3.38	15.6
3000	11.1	48.5

These values for the dissociation are 9.5 per cent., in the case of steam, and 7 per cent., in the case of carbon dioxide, lower than those of Nernst. These differences however correspond to temperature differences of only 8° and 6° respectively.

The possible sources of error in this method lie almost entirely in the measurement of the temperature. It seems probable that the error in the temperature determination is not over 5° and almost certainly not over 10°.

SUMMARY AND CONCLUSIONS.

First. It is shown that when water vapor or carbon dioxide is passed through a tube containing a glowing platinum wire, amounts of dissociation products are obtained which correspond to the dissociation equilibrium at the temperature of the wire.

Second. The degree of dissociation of water vapor and carbon dioxide were determined by this method and results were obtained which for water vapor were 9.5 and for carbon dioxide 7 per cent. lower than those previously obtained by Nernst by another method.

Third. In determining the temperature of the wire the temperature-coefficient of the electric resistance of pure platinum up to 1200° was measured.

Fourth. It was found that platinum and platinum-rhodium wires do not disintegrate perceptibly in steam or in carbon dioxide up to 1300°. At 1400° platinum-rhodium begins to disintegrate in steam.

The method of determining the dissociation of water vapor and carbon dioxide by means of glowing wires has many advantages. The apparatus is simple and the experiments are quickly made.

The great rapidity of cooling of the gases insures accurate results for every reaction where the substance of the wire has a strong catalytic action.

The only serious difficulty lies in the determination of the temperature of the wire. A modification of the method by which instead of a wire a platinum tube or other surface of platinum is used might be very useful in some cases. The outer surface of the tube should be exposed to the dissociating gas. The temperature could then be determined either by a thermo-element inside the tube or by optical methods.

For the determination of the dissociation under high pressures the method would present great advantages. It would be a difficult task to make a tube which could withstand very high pressure at 1300° or 1400°, but to heat a wire to that temperature in a tube containing gas at a very high pressure is a comparatively easy matter. Such an arrangement would be well adapted for the study of the formation of ammonia from the elements since not only the velocity of the reaction, but also the amount of ammonia corresponding to the equilibrium would be much increased by high pressure. A few rough experiments have been made with ammonia and it seems the method would be capable of giving good results.

Another case in which this method may be of use is in determining the temperature of platinum wires or other platinum bodies. As v. Wartenberg has shown, temperatures may be accurately determined by means of the dissociation of steam. If the object is platinum, it need only be surrounded by steam and some of the steam withdrawn and analyzed in order to determine the temperature accurately.