3. This formula has been applied to aqueous solutions of potassium chloride, potassium nitrate, and copper sulfate.
4. The value of n seems to approach $^2/_3$.

NOTE.—The manuscript of the above article was read by Dr. W. C. Bray. He has informed me that he and Dr. Kraus have obtained the same formula and that their results were presented at the Washington meeting of the Society and published in *Science*, **35**, 433 (1912). I might mention that the formula occurred to me in August, 1911, but its publication was delayed by various circumstances.

COLLEGE STATION, TEXAS.

THE DISSOCIATION OF HYDROGEN INTO ATOMS.[1]

BY IRVING LANGMUIR.

Received May 4, 1912.

In a previous paper[2] it was shown that at extremely high temperatures the power consumption necessary to maintain a tungsten wire at a given temperature in hydrogen increases abnormally rapidly with the temperature. Let us represent by n the exponent of the power with which the energy consumption varies with the temperature; or, in other words, let us define n by the equation

$$n = \frac{d(\log \mathbf{W})}{d(\log T)},$$

where $\mathbf{W}$ = watts per cm. of length necessary to maintain the wire at the temperature T (absolute).

It was found that n increased with the temperature very rapidly, thus

T.	n.
1000°	1.86
1500	2.08
2000	2.71
2500	4.03
3000	6.90
3400	10.1

An analysis of the mechanism of the convection or conduction of heat failed to suggest any reason why n should ever become greater than 2. The most probable explanation was thought to be that dissociation of the hydrogen molecules into atoms was taking place. This dissociation in the region close to the hot wire would absorb large quantities of energy. The hydrogen atoms would diffuse out into the colder gas some distance from the wire and would there recombine and give up the heat of the reaction, thus causing an abnormally high heat conductivity. Mag-

---

[1] Paper read at the Washington Meeting of the Am. Chem. Soc., Dec., 1911. Abstract appeared in *Science*, **35**, 428 (1912).

[2] *Trans. Am. Electrochem. Soc.*, **20**, 225 (1911).

nanini and Malagnini[1] have actually shown in their study of the heat conductivity of nitrogen peroxide that the partly dissociated gas had a conductivity three times as great as that which was completely dissociated.

Since the publication of the above paper on the heat losses in hydrogen, the author has developed a theory[2] of the convection of heat from hot wires which makes it possible to calculate with considerable accuracy the energy loss from any wire in any gas.

Let us represent by **W** the energy lost per cm. of length of the wire per second by means of convection and conduction through the gas. That is, we deduct from the total watts per cm. lost by the wire, the watts per cm. lost by direct radiation, and we call the difference **W**.

It was shown that the "convection" of heat consists essentially of the *conduction* of heat through a film of relatively stationary gas around the wire. If a is the diameter of the wire and b the outside diameter of the film of gas around the wire, then by the usual laws of heat conduction between two concentric cylinders

$$\mathbf{W} = \frac{2\pi}{\ln b/a}\int_{T_1}^{T_2}\mathbf{k}\,dT \tag{1}$$

where **k** is the heat conductivity (in watts per cm. per degree) of the gas at the temperature T.

T_2 is the temperature of the wire.

T_1 is room temperature which is assumed to be the temperature at the outside surface of the film.

It is further shown that b is related to a as follows:

$$b \ln b/a = 2B \tag{2}$$

where B is independent of the diameter and temperature of the wire, but depends on the nature of the gas, on its pressure and temperature. The quantity B is the thickness that the film would have in the case of free convection from a heated plane surface. For air at room temperature and one atm. pressure B is equal to 0.43 cm. For convenience, let us place

$$\mathbf{s} = \frac{2\pi}{\ln b/a}. \tag{3}$$

We will call **s** the shape factor, since it depends only on the diameter of the wire and that of the film of gas.

Let us also put

$$\begin{aligned} \varphi_2 &= \int_0^{T_2}\mathbf{k}\,dT \\ \varphi_1 &= \int_0^{T_1}\mathbf{k}\,dT \end{aligned}. \tag{4}$$

---

[1] *Nuovo Cim.*, 6, 352 (1897).

[2] *Phys. Rev.*, June, 1912.

Then from (1)

$$\mathbf{W} = \mathbf{s}(\varphi_2 - \varphi_1). \tag{5}$$

Now from (2) and (3) we can eliminate b and thus obtain

$$\frac{a}{B} = \frac{\mathbf{s}}{\pi} \varepsilon^{-2\pi/\mathbf{s}}. \tag{6}$$

From this equation we can plot a curve with $\mathbf{s}$ as abscissa and a/B as ordinate. We can also plot φ as a function of T. In this way the calculation of the energy loss from any wire becomes extremely simple. We need only know the diameter, a, of the wire and the value of B for the particular gas in question. We then look up on the curve the value of s corresponding to the ratio a/B and simply multiply this by $\varphi_2 - \varphi_1$, as found from the curve for φ. According to (5) this product gives us the watts loss per cm. from the wire.

This theory has been thoroughly verified by extensive experiments with platinum wires in air and tungsten wires in hydrogen and mercury vapor. More recent and as yet unpublished results have also confirmed the theory for convection in pure nitrogen and in carbon dioxide.

We are here particularly interested in the experiments with hydrogen. The original results[1] were found to be slightly in error when more careful experiments were made.

The following table gives the results of these later experiments.[2] The watts per cm. have been corrected for the relatively small loss by radiation:

TABLE I.—CONVECTION FROM TUNGSTEN WIRES IN HYDROGEN.

Diam. of wire 0.0045 cm.

I. Temp. ° K.[3]	II. $\mathbf{W}$ watts per cm.	III. $\varphi_2 - \varphi_1$.	IV. $\mathbf{W_C}$.	V. $\mathbf{W_D}$.
1100	2.2	2.51	2.8	—0.6
1300	2.9	3.45	3.9	—1.0
1500	3.9	4.51	5.1	—1.2
1700	5.0	5.67	6.4	—1.4
1900	6.9	6.98	7.9	—1.0
2100	8.9	8.38	9.5	—0.6
2300	11.2	9.90	11.2	0.0
2500	16.0	11.54	13.0	+3.0
2700	24.5	13.28	15.0	9.5
2900	39.0	15.26	17.3	21.7
3100	60.2	17.14	19.4	40.8
3300	88.2	19.22	21.8	66.4

The values of φ in column III are taken from the previous paper. They

---

[1] *Trans. Am. Electrochem. Soc., l. c.*

[2] *Phys. Rev., l. c.*

[3] The letter K (Kelvin) is used to denote absolute temperature in accordance with the recommendations of the Association International du Froid. See *Chem. Ztg.*, **35**, 3 (1911).

are based upon the following formula for the heat conductivity of hydrogen

$$\mathbf{k} = 28 \times 10^{-6}\sqrt{T}\frac{1 + 0.0002T}{1 + 77/T} \text{ gram calories per cm. per sec.}$$

The fourth column gives the values of **W** calculated on the assumption that B for hydrogen is 3.05 cm. From this $\mathbf{s} = 1.13$.

The fifth column gives the difference between the observed values and the calculated.

The very rapid increase in conductivity is very strikingly shown by these figures.

Theory of Heat Conduction in a Dissociating Gas.

Let us study the theory of heat conduction in a gas which is partly dissociated. In a straight cylindrical tube of unit cross section the flow of heat along the tube per second, due to the ordinary heat conduction of the gas, will be

$$-\mathbf{k}\frac{dT}{dx}.$$

where **k** is the heat conductivity of the gas (watts per cm.) and dT/dx the temperature gradient in the tube.

Besides the heat carried by conduction, there is a transfer of heat due to the difference of the dissociation product and the recombination of these products in the cooler parts of the tube. Let us take a concrete example and assume that we have hydrogen which is dissociated to a small extent into hydrogen atoms. If $\mathbf{c}_1$ is the concentration of hydrogen atoms (in mols per cm^3.) and **D** is the diffusion coefficient of hydrogen atoms through ordinary hydrogen, then the number of mols of hydrogen that will diffuse per second past any plane P across the tube will be

$$\mathbf{D}\frac{d\mathbf{c}_1}{dx}.$$

Let $\mathbf{q}_1$ be the heat of formation (in Joules) of hydrogen molecules from one mol of hydrogen atoms, *i. e.*, the heat of the reaction

$$H = {}^1/_2H_2.$$

Then every mol of hydrogen atoms diffusing past the plane P represents an amount of heat $\mathbf{q}_1$. Thus the heat carried per second past P by the diffusion is

$$\mathbf{D}\mathbf{q}_1\frac{d\mathbf{c}_1}{dx}.$$

Combining this with that carried by ordinary conduction, we have

$$\left(\mathbf{k} + \mathbf{D}\mathbf{q}_1\frac{d\mathbf{c}_1}{dT}\right)\frac{dT}{dx}$$

for the total heat carried past P per second. In other words, the effect of the dissociation of the hydrogen would be to increase the heat conductivity by the amount

$$\mathbf{D}\mathbf{q}_1\frac{d\mathbf{c}_1}{dT}.$$

To find the energy loss from a wire in partly dissociated hydrogen, we need simply to substitute in equation (1), in place of **k**, the value

$$\mathbf{k} + \mathbf{D}\mathbf{q}_1\frac{d\mathbf{c}_1}{dT};$$

thus combining with (3) we get

$$\mathbf{W} = \mathbf{s}\int_{T_1}^{T_2}\left(\mathbf{k} + \mathbf{D}\mathbf{q}_1\frac{d\mathbf{c}_1}{dT}\right)dT. \tag{7}$$

Hence **W** the total power required to heat the wire, is simply the sum of two terms, thus

$$\mathbf{W} = \mathbf{W_C} + \mathbf{W_D} \tag{8}$$

where

$$\mathbf{W_C} = \mathbf{s}\int_{T_1}^{T_2}\mathbf{k}dT = \mathbf{s}(\varphi_2 - \varphi_1). \tag{9}$$

$$\mathbf{W_D} = \mathbf{s}\int_{T_1}^{T_2}\mathbf{D}\mathbf{q}_1\frac{d\mathbf{c}_1}{dT}dT. \tag{10}$$

Here we have considered **k** and φ to apply only to the ordinary heat conduction. We see, then, that the dissociation simply causes an increase in the power consumption of the wire equal to $\mathbf{W_D}$.

Now for our purposes we may consider that $\mathbf{q}_1$ and **D** vary so slowly with the temperature that over the range of temperature in which $\mathbf{c}_1$ is essentially different from zero, we may take them as constant and thus obtain from (10):

$$\mathbf{W_D} = \mathbf{s}\mathbf{D}\mathbf{q}_1(\mathbf{c}_1 - \mathbf{c}_1') \tag{10a}$$

where $\mathbf{c}_1$ is the concentration of hydrogen atoms at the temperature of the filament and $\mathbf{c}_1'$ is the concentration at the temperature T_1(room temperature). Of course in the case of hydrogen we may take $\mathbf{c}_1' = 0$, whence

$$\mathbf{W_D} = \mathbf{s}\mathbf{D}\mathbf{q}_1\mathbf{c}_1. \tag{11}$$

In this equation we should take for **D** a mean value for the range of temperature in which the dissociation is of measurable magnitude.

The quantity $\mathbf{W_D}$ is easily found experimentally as the difference between the observed watts per cm. (corrected for radiation) and watts per cm. calculated on the assumption that there is no dissociation. Column V in Table I gives the values of $\mathbf{W_D}$ found in this way. In any given case we know the value of s and hence from (11) we can calculate the product $\mathbf{D}\mathbf{q}_1\mathbf{c}_1$.

Of course we have no direct experimental data by which we can determin the diffusion coefficient of hydrogen atoms into ordinary hydrogen. But the kinetic theory of gases enables us to calculate its approximate value with a fair degree of accuracy.

Diffusion Coefficient of Hydrogen Atoms.

O. E. Meyer[1] gives for the value of the diffusion coefficient of a small amount of one gas into a large amount of a second gas, the following:

$$\mathbf{D} = \frac{\Omega_1^2}{8N\sigma^2\sqrt{\Omega_1^2 + \Omega_2^2}} \tag{12}$$

but on page 274 he gives

$$N\pi\sigma^2 = \frac{(1/\sqrt{L_1} + 1/\sqrt{L_2})^2}{4\sqrt{2}} \tag{13}$$

and on page 55

$$\Omega = G\sqrt{8/3\pi} = 0.9213\,G \tag{14}$$

and

$$P = \frac{1}{8}\pi\rho\Omega^2 \tag{15}$$

and on page 189 the viscosity **h** is

$$\mathrm{h} = 0.3097\,\rho LG. \tag{16}$$

But from $PV = RT$ we may derive

$$\rho = \frac{PM}{RT} \tag{17}$$

and substituting this in (15) we obtain

$$\Omega = \sqrt{\frac{8RT}{\pi M}} \tag{18}$$

and from (14)

$$G = \sqrt{3RT/M}. \tag{19}$$

Substituting (19) and (17) in (16)

$$L = \frac{1.861}{P}\sqrt{RT/M}\,\mathrm{h}. \tag{20}$$

Finally, by substituting (18) and (13) in (12):

$$\mathbf{D} = \frac{2\sqrt{\pi}\sqrt{RT}}{M_1(1/\sqrt{L_1} + 1/\sqrt{L_2})^2\sqrt{1/M_1 + 1/M_2}}. \tag{21}$$

This last equation enables us to calculate the diffusion coefficient for a small amount of hydrogen atoms diffusing into a large quantity of ordinary hydrogen. In this equation

$M_1 = 1$, the atomic wt. of hydrogen.

$M_2 = 2$, molecular wt. of H_2.

$L_1 =$ length of free path of the hydrogen atom in *completely* dissociated hydrogen at the temperature T and pressure p.

---

[1] *Kinetic Theory of Gases, English Ed.*, p. 267.

$L_2 =$ free path of the hydrogen molecule in ordinary hydrogen.
$R =$ 83.1×10^6.

It is safe to say that L_1 and L_2 will be practically equal. As a matter of fact, the free paths of various gases differ only slightly from each other, even when the molecular weights are quite different. Let us assume $L_1 = L_2$ and substitute this, together with the values of M_1 and M_2 in (21) whence

$$\mathbf{D} = 6600LT^{1/2} \tag{22}$$

The free path L of H_2 is given by (20). At 1 atm. $p = 1{,}013{,}000$ dynes per cm.^{2}, whence

$$L = 0.0118T^{1/2}\text{h}. \tag{23}$$

But for H_2[1]

$$\text{h} = \frac{6.6 \times 10^{-6}T^{1/2}}{1 + 77/T}. \tag{24}$$

And combining this with (23) and (22) we have

$$\mathbf{D} = \frac{0.514 \times 10^{-3}T^{3/2}}{1 + 77/T}. \tag{25}$$

This formula would give for the diffusion coefficient of H into H_2 at room temperature (300° K) a value of 2.14, but at 3100° K it would be 85.

The values of **D** for the temperatures at which it has measurable values have been calculated from equation (25) and are given below.

Table II.—Diffusion Coefficient of Hydrogen Atoms into Hydrogen.

Temp.	D.	Temp.	D.
1500	28.4	2500	62
1700	34.4	2700	70
1900	40.9	2900	77
2100	47.7	3100	85
2300	54	3300	95

It is not expected that these values of **D** are very accurate. An error of 10–50% would not be very improbable. But there is every reason to believe that the order of magnitude would be correct, for none of the assumptions made are likely to be very far from the truth, and furthermore, at very high temperatures the laws of the kinetic theory would probably hold even more accurately than at lower temperatures. In any case, the temperature coefficient of **D** would not be subject to the errors that would affect the absolute value of **D** and should therefore be quite accurate.

Now that we have estimated the approximate value of **D** (and since we know s and $\mathbf{W_D}$), we are in a position to calculate the product $\mathbf{q}_1\mathbf{c}_1$ by equation (11).

---

[1] Fischer, *Phys. Rev.*, 24, 237, 385 (1907).

For this purpose, however, we should not take the value of **D** corresponding to the temperature T_2, of the wire, but rather a mean value of **D** for the range of temperature in which the conductivity of the hydrogen is due largely to its dissociation. By a few rough calculations, it was estimated that if **D** was taken at a temperature 200° below that of the wire, it would correspond closely with such a mean. So in Table III the value of **D** tabulated in Column 3 is that corresponding to a temperature equal to T_2 —200°.

From these data, assuming $\mathbf{s}$ equal to 1.13, the values of $\mathbf{q}_1\mathbf{c}_1$ were calculated and are tabulated in column 4 of Table III.

Calculation of the Heat of Dissociation and Degree of Dissociation of Hydrogen.

The heat of the reaction $H = {}^1/_2H_2$ which we call $\mathbf{q}_1$ will have only a very small temperature coefficient, so that the temperature coefficient of $\mathbf{q}_1\mathbf{c}_1$ will be due entirely to $\mathbf{c}_1$. Now van't Hoff's equation

$$\mathbf{q} = RT^2\frac{d\ln\mathbf{K}}{dT} \tag{26}$$

gives us a means of calculating $\mathbf{q}_1$ if we know the temperature coefficient of $\mathbf{c}_1$. Applying the law of mass action to the reaction $2H = H_2$, we have

$$\mathbf{K} = \mathbf{c}_1^2/\mathbf{c}_2 \tag{27}$$

where $\mathbf{c}_2$ is the concentration of H_2. As a *first* approximation, we may assume that $\mathbf{c}_1$ is small compared to $\mathbf{c}_2$ and hence the temperature coefficient of $\mathbf{c}_2$ is negligible, compared to that of $\mathbf{c}_1$. This gives

$$\frac{d\ln\mathbf{K}}{dT} = 2\frac{d\ln\mathbf{c}_1}{dT} = 2\frac{d\ln\mathbf{q}_1\mathbf{c}_1}{dT}$$

whence, approximately

$$\mathbf{q}_2 = 2RT^2\frac{d\ln\mathbf{q}_1\mathbf{c}_1}{dT}. \tag{28}$$

Here $\mathbf{q}_2$ is the heat of the reaction $2H = H_2$, so that $\mathbf{q}_2 = 2\mathbf{q}_1$.

From this relation (taking $R = 8.31$ joules per degree), an approximate value of $\mathbf{q}_2$ was calculated. This is given in Column 5, Table III.

At low temperatures the assumption that $\mathbf{c}_1$ is small compared to $\mathbf{c}_2$ will be more accurately fulfilled than at high temperatures, but on the other hand, small errors in $\mathbf{W}_\mathbf{D}$ have a much greater effect on $\mathbf{q}$. Bearing this in mind, the value

$$\mathbf{q}_2 = 550{,}000, \text{ or } \mathbf{q}_1 = 275{,}000 \text{ joules}$$

was taken as the most probable value, and from this, and the figures for $\mathbf{q}_1\mathbf{c}_1$ the values of $\mathbf{c}_1$ were calculated, and are tabulated in Column 2, Table IV.

At atmospheric pressure the sum of the concentrations $\mathbf{c}_1 + \mathbf{c}_2$ must be equal to

$$\frac{1}{22400} \cdot \frac{273}{T} = \frac{0.0122}{T}. \tag{29}$$

From this $\mathbf{c}_2$ was calculated, and from $\mathbf{c}_1$ and $\mathbf{c}_2$ the dissociation constant **K** was found. The values of **K** at various temperatures are given in Column 5, Table IV.

We have now the data by which $\mathbf{q}_2$ can be accurately calculated by equation (11), using the above values of **K**. The results so obtained are given in Column 6, Table IV.

It will be seen that $\mathbf{q}_2$ is now much more nearly constant than before. This constancy of $\mathbf{q}_2$ is strong evidence that the values of **D** are approximately correct. An analysis of the sources of error in this method of calculating **q** and **c** is, however, very desirable.

TABLE III.

Temp. T_2. °K.	$\mathbf{W_D}$.	**D**.	$\mathbf{q}_1\mathbf{c}_1$.	$\mathbf{q}_2$ joules. 1st approximation.
2500°	3.0	54	0.049	570,000
2700	9.5	62	0.135	462,000
2900	21.7	70	0.275	398,000
3100	40.8	77	0.468	334,000
3300	66.4	85	0.691	

TABLE IV.

Temp. T_2. °K.	$\mathbf{C}_1 \times 10^6$. Atoms.	$\mathbf{C}_2 \times 10^6$. Molecules.	Degree of dissociation, per cent.	$10^6\mathbf{K}$.	$\mathbf{q}_2$.
2500	0.178	4.70	3.7	0.0067	610,000
2700	0.49	4.02	10.8	0.0595	540,000
2900	1.00	3.20	23.8	0.312	530,000
3100	1.70	2.24	43.0	1.29	600,000
3300	2.51	1.19	68.0	5.30	

Sources of Error.

The experiments by which **W** was found were performed by heating a tungsten wire in hydrogen in a glass tube of about 5 cm. diameter. The values of $\mathbf{W_C}$ (see Table I) are greater than the observed values of **W** up to 2100°. This is probably due to the prevention of free convection by the walls of the tube. Previous results have indicated that at high temperatures the effect of the tube becomes less marked, therefore it was thought best to use $\mathbf{W_C}$ as calculated, rather than to choose a value of **s** that would give good agreement at the lower temperatures. It will be of interest, however, to see what would have been the result if we had calculated **s** from the data at temperatures up to 2100°.

In Table V the value of **s** is calculated by dividing **W** by the corresponding value of $\varphi_2 - \varphi_1$ (Table I). From the results obtained up to 1700° it would seem that the value of **s** is 0.88 and if we then use this value to calculate $\mathbf{W_C}$ we get the results in the fourth column. $\mathbf{W_D}$ is obtained by subtracting $\mathbf{W_C}$ from **W**. From these values of $\mathbf{W_D}$ taking $\mathbf{s} = 0.88$ we may then calculate $\mathbf{q_1c_1}$ as before from (11). If we now calculate from these the values of $\mathbf{q_2}$ we get results ranging from 160,000 up to 370,000 joules. Taking 350,000 as being the most probable, and calculating $\mathbf{c_1}$, we get the results given in Column 7, and then by comparing this with the greatest possible concentration as given by (29) we calculate the percentage dissociation. This leads us to the absurd result that the dissociation is 148% at 3300°. Furthermore, if the values of **K** are calculated, and from these the values of $\mathbf{q_2}$ are obtained, the latter are found to be very far from constant, and to increase rapidly up to an infinit value.

TABLE V.

I. *T*.	II. **W**.	III. **s**.	IV. $\mathbf{W_C}$.	V. $\mathbf{W_D}$.	VI. $\mathbf{q_1c_1}$.	VII. $10^6\mathbf{c_1}$.	VIII. $10^6\mathbf{c_2}$.	IX. Dissociation. Per cent.
1100	2.2	0.88	2.2	0.0				
1300	2.9	0.84	3.0	0.1				
1500	3.9	0.86	4.0	0.1				
1700	5.0	0.88	5.0	0.0				
1900	6.9	0.99	6.1	0.8	0.026	0.15	6.26	2.3
2100	8.9	1.06	7.4	1.5	0.042	0.24	5.57	4.1
2300	11.2	1.13	8.7	2.5	0.060	0.34	4.96	6.4
2500	16.0	1.39	10.2	5.8	0.122	0.70	4.18	14.2
2700	24.5	1.84	11.7	12.8	0.234	1.34	3.17	29.7
2900	39.0	2.[illegible]5	13.4	25.6	0.415	2.39	1.81	56.8
3100	60.2	3.53	15.1	45.1	0.664	3.81	0.13	96.5
3300	88.2	4.60	16.9	71.3	0.952	5.47	—1.77	148.0

We might help ourselves out of this difficulty by assuming that the diffusion coefficient of hydrogen atoms is about twice as great as we have calculated, and that $\mathbf{q_2}$ has the value 440,000 joules. The percentage dissociation is then found to be 39% of the values given in Table V. These agree fairly well with the results of Table IV, as will be seen from the following comparison:

TABLE VI.

Temp.	$10^6\ \mathbf{c_1}$. Recalculated from Table V.	$10^6\ \mathbf{c_1}$. From Table IV.
2500	0.27	0.18
2700	0.52	0.49
2900	0.92	1.00
3100	1.46	1.70
3300	2.10	2.51

In the derivation of equation (11) it has been assumed that the film thickness is not influenced by the dissociation of the gas. It seems probable that this is approximately true. But even if the film thickness, B, should be proportional to the total heat lost by the wire, that is, if the dissociation of the hydrogen should cause a four-fold increase in B, the effect on $\mathrm{W_C}$ would amount to only 18% and this only at the very highest temperature.

Another factor that would cause some error at very high temperatures is that the heat conductivity of the dissociated hydrogen would be somewhat greater than that of the ordinary hydrogen from which it is formed. This would tend to make the calculated values of $\mathbf{W}_C$ too low.

On the whole, however, the results on the dissociation seem to be accurate within perhaps 20–30%, and when one considers that a temperature elevation of about 50° will cause an increase in the dissociation of about that amount it is considered that the accuracy is satisfactory for this type of reaction.

Experiments at Low Pressures.

A tungsten wire 0.0069 cm. in diameter was heated in hydrogen at two different pressures: 760 mm. and 50 mm. The results (corrected for radiation) were:

TABLE VII.

	Watts per cm.		
Temp.	760 mm.	50 mm.	Ratio $\frac{\text{at 50 mm.}}{\text{at 760 mm.}}$
1500° K	4.9	2.6	0.53
1700	6.8	3.4	0.50
1900	8.7	4.2	0.48
2100	10.9	5.8	0.53
2300	13.9	8.2	0.59
2500	17.1	13.2	0.77
2700	23.7	21.0	0.89
2900	33.8	36.3	1.08
3100	51.8	58.0	1.12

These results are very strong evidence that we are dealing here with a *dissociation*, not an association of molecules, for the heat conductivity at low pressures increases much more rapidly with the temperature than it does at high pressures. In other words, a reaction takes place which is favored by low pressure, hence must be one in which the volume of the products is greater than that of the original gas. Since hydrogen gas can only increase in volume (under standard conditions) by dissociating into atoms, we have nearly conclusive evidence that this is what actually occurs. Whether or not the atoms are electrically charged will be considered shortly.

Another experiment on the heat loss from wires in hydrogen at various pressures was made in the following way: A tungsten wire lamp with a filament of only two loops was connected to a Töpler pump and McLeod gage. The characteristics of the lamp with a good vacuum (pressure less than 0.0001 mm.) were measured with the filament at two different temperatures, 1770 and 2270° K. Then various pressures of hydrogen were admitted and the characteristics were again determined at the same temperatures (*i. e.*, resistance of the filament kept constant). The results are given in Table VIII.

TABLE VIII.

Pressure.		Filament at 1770° K. $\varphi_2 - \varphi_1 = 6.13$. $D = 30.5$.					Filament at 2270°. $\varphi_2 - \varphi_1 = 9.67$. $D = 47$.					Ratio 1770 : 2270.	
Mm. of Hg.	P atmos.	Total watts.	$W_C + W_D$.	Degree of diss. p_1/P.	$\frac{W_C + W_D}{W_C}$.	W_C.	Total watts.	$W_C + W_D$.	Degree of diss. p_1/P.	$\frac{W_C + W_D}{W_C}$.	W_C.	$W_C + W_D$.	W_C.
760	1.00	44.4	42.8	0.00014	1.001	42.8	109	103	0.0098	1.07	96	0.42	0.45
100	0.132	37.8	36.2	0.00038	1.004	36.2	105	99	0.0268	1.19	83	0.37	0.44
10	0.0132	11.4	9.8	0.0012	1.012	9.8	46.5	40.4	0.082	1.59	25.5	0.24	0.39
2.7	0.0036	5.34	3.7	0.0023	1.023	3.6	25.6	19.5	0.15	2.08	9.4	0.19	0.38
0.1	0.00013	1.96	0.36	0.012	1.12	0.32	8.28	2.21	0.57	5.10	0.43	0.16	0.75
0.0	0.0	1.60	0.0	..	...	...	6.07	..	..	..	...	...	..

In this table, under the heading total watts, are given the watts actually measured by the voltmeter and ammeter. The voltage was varied so as to give the resistance, which corresponded to the given temperatures. By subtracting the watts observed in a good vacuum from that at other pressures, the total energy carried by the gas, *i. e.*, $\mathbf{W_C} + \mathbf{W_D}$, was found. From the formula given later in this paper, equation (32), it was calculated that at 1 atm. the dissociation of hydrogen would be 0.014% at 1770° K, and 0.98% at 2270° K. From these and from the law of mass action:

$$\frac{p_1}{\sqrt{P - p_1}} = \text{constant at any temperature}$$

the degree of dissociation at the various pressures was calculated and is given in the fifth and tenth columns.

By dividing equation (11) by (9) we obtain

$$\frac{\mathbf{W_D}}{\mathbf{W_C}} = \frac{\mathbf{D}\mathbf{q}_1\mathbf{c}_1}{\varphi_2 - \varphi_1}. \tag{30}$$

But the diffusion coefficient **D** is inversely proportional to the pressure, so that if $\mathbf{D}_1$ is the diffusion coefficient at 1 atm., then

$$\mathbf{D} = \frac{\mathbf{D}_1}{P}.$$

From (29)

$$\mathbf{c}_1 = \frac{0.0122 p_1}{T}.$$

If we take $\mathbf{q}_1 = 275{,}000$, we then have, by substituting in (30):

$$\frac{\mathbf{W_D}}{\mathbf{W_C}} = \frac{3350}{T} \frac{\mathbf{D}_1}{\varphi_2 - \varphi_1} \frac{p_1}{P}. \tag{31}$$

From this relation the ratio $\frac{\mathbf{W_C} + \mathbf{W_D}}{\mathbf{W_C}}$ was calculated and is tabulated in Table VIII. By dividing this latter into $\mathbf{W_C} + \mathbf{W_D}$ the value of $\mathbf{W_C}$ was found and tabulated.

In next to the last column in Table VIII is given the ratio of the total conducted watts ($\mathbf{W_C} + \mathbf{W_D}$) at the two temperatures. If there were no dissociation of the hydrogen this ratio should remain constant at all pressures, but actually it decreases to not much over one-third its original value, as the pressure decreases. On the other hand, the ratios between the values of $\mathbf{W}'_\mathbf{C}$, the watts corrected for the dissociation, are very nearly constant. In fact, the slight trend downwards is not greater than might be caused by the errors in estimating the temperatures of the filament by the resistance. For example, if the filament temperature were 2330° instead of 2270°, this trend would entirely disappear. The cooling effects of the leads and anchors, which have not been allowed for in this calculation, would produce an error in this direction. The last figure in the last column is probably not reliable, as it is based on the ratio between small differences and is hence very sensitive to experimental error.

This experiment affords conclusive quantitative proof that we are dealing with a dissociation and not an association of molecules.

Experiments with Other Gases.

Mercury Vapor.—In the previous paper[1] it was shown that the heat loss from a tungsten wire in mercury vapor increased regularly and slowly with the temperature up to 2700°. Above that the experiments showed an increase in the energy loss which was explained by the diffusion of hydrogen down into the mercury vapor. By equation (21) and (20) we can calculate roughly the diffusion coefficient of hydrogen atoms into mercury vapor and find that it is one-half as great as into hydrogen. Then from (11), assuming that the hydrogen is completely dissociated at the very high temperatures and low partial pressures, we can calculate the effect of traces of hydrogen in mercury vapor on its heat conductivity and obtain the striking result that about 0.2% of hydrogen would double the heat conductivity of mercury vapor at 3000°.

Nitrogen.—A couple of careful experiments have been made in very pure atmospheric nitrogen. Very great precautions were taken to guard against traces of moisture or oxygen. The tube (6 cm. in diameter) was first exhausted to a pressure of a few thousandths of a millimeter and heated several minutes to a temperature of about 300° to drive out all moisture into a U tube immersed in liquid air. All joints were sealed glass. The nitrogen was admitted through the liquid air U tube and then through two tungsten lamps with the filaments heated to brilliant incandescence, to remove the last traces of oxygen. The following tables give the results of these two experiments.

The temperatures were determined as in the case of the experiments in hydrogen by measurement of both the candle power and the resistance. The agreement between the two methods was nearly perfect up to about 2300°, and then slight differences were observed, caused probably by minute traces of moisture attacking the filament.

In the second column φ was calculated from the following equation for the heat conductivity of nitrogen:

$$\mathbf{k} = 4.75 \times 10^{-6}\sqrt{T}\,\frac{1 + 0.0002\,T}{1 + 110.4/T} \text{ gram cal. per cm. per degree per sec.}$$

φ_1 is the value of φ at 300° K.

It will be seen from the table that the energy carried by the nitrogen does not show, as in the case of hydrogen, any abnormal increase at high temperatures. This is shown particularly by the nearly constant values

---

[1] *Phys. Rev.*, June, 1912.

of s in the case of nitrogen. On the other hand, in hydrogen (see Table V) s remains constant only up to 1700° and then increases to over five times its original value.

TABLE IX.—CONVECTION FROM TUNGSTEN WIRES IN NITROGEN.

		Wire 0.0127 cm. diam.				Wire 0.0045 cm. diam.			
T Temp. ° K.	$\varphi_2 - \varphi_1$.	Total watts per cm.	Radiation: watts per cm.	Convection: watts per cm.	$s = \frac{W}{\varphi_2 - \varphi_1}$.	Total watts per cm.	Radiation: watts per cm.	Convection: watts per cm.	$s = \frac{W}{\varphi_2 - \varphi_1}$.
1100	0.403	0.68	0.05	0.63	1.56	0.54	0.02	0.52	1.29
1300	0.556	0.89	0.12	0.77	1.37	0.73	0.04	0.69	1.25
1500	0.729	.26	0.25	1.01	1.39	0.98	0.09	0.89	1.22
1700	0.920	1.82	0.48	1.34	1.46	1.27	0.17	1.10	1.20
1900	1.130	2.57	0.84	1.73	1.53	1. 2	0.30	1.32	1.17
2100	1.359	3.57	1.40	2.17	.60	2.05	0.50	1.55	1.14
2300	1.607	4.86	2.21	2.65	1.65	2.58	0.78	1.80	1.12
2500	1.876	6.41	3.26	3.15	1.68	3.21	1.16	2.05	1.09
2700	2.160	8.29	4.68	3.61	1.67	3.96	1.66	2.30	1.06
2900	2.469	10.55	6.44	4.11	1.66	4.82	2.28	2.54	1.03
3100	2.792	13.14	8.56	4.58	1.64	..	..	..	..
3300	3.134	16.18	11.14	5.04	1.61	..	..	..	..
3500	3.498	19.68	14.14	5.54	1.58	..	..	..	..

This method of detecting dissociation should be just as sensitive in the case of nitrogen as in the case of hydrogen, as can be seen from equation (7). It would seem that a dissociation of 5% at 3500° could be detected with certainty. It is a safe conclusion from this experiment that nitrogen at 3500° K is not dissociated to over 5%.

Oxygen.—Some previous work of the author[1] led him some years ago to conclude that the energy loss by convection from a Nernst filament in air increased with nearly the 6th power of the temperature. Since nitrogen does not produce this effect, we have here a clear indication that in the neighborhood of 2400° K, oxygen is very largely dissociated into atoms or associated into ozone. Experiments at various pressures would easily show to what extent each of these two reactions occurred.

Nature of the Dissociation Products.

The experiments at low pressures have shown that the volume of the dissociation products is approximately twice that of the original hydrogen.

It remains to determin whether these atoms are electrically charged or not. The writer is convinced that they are not, or at least that any ionization of the gas is entirely secondary and is not related to the abnormal heat conductivity observed. The reasons for this conviction are very numerous and are partly theoretical and partly experimental. Only a few of these reasons will be mentioned here.

---

[1] *Trans. Am. Electrochem. Soc.*, **20**, 225 (1911).

1. The good agreement between the two methods of measuring temperature (*i. e.*, by resistance and by candle power) prove that the amount of current carried by the heated gas near the wire is entirely negligible compared to that in the wire, although as much as 20 volts per cm. was sometimes used.

2. Nitrogen, and especially mercury vapor, conduct electricity at low pressures very much better than hydrogen, and yet do not show these abnormal effects.

3. It can be readily shown that if a gas were dissociated to any large percentage such as 10% into ions its conductivity would be better than that of copper.

Final Results for the Dissociation of Hydrogen.

The results given in Table IV are considered the most reliable.

Van't Hoff's equation (26) enables us to derive an equation which will allow us to calculate the degree of dissociation at any temperature.

The temperature coefficient of q_2 is equal to the difference of the heat capacities of the hydrogen molecules and hydrogen atoms. The specific heat of the latter would be 2.98 gram calories per mol. per degree or 5.96 for two mols. For hydrogen molecules the molecular specific heat is $4.454 + 0.0009\,T$.

We thus obtain

$$\frac{dq_2}{dT} = 1.51 - 0.0009\,T.$$

Hence at 1700° the temperature coefficient is zero. Between 3500° K and 1700° the heat of reaction q_2 *increases* only 1500 calories, or 6250 joules. From 1700° down to 300° it would *decrease* about 3600 joules. This is, however, only 1% of the total heat of reaction and may be considered negligible.

We will take, therefore, at all temperatures

$$q_2 = 550{,}000 \text{ joules}.$$

By integrating van't Hoff's equation and substituting the above value of q_2 and also placing $P - p_1$ in place of p_2 we obtain:

$$\log\frac{p_1}{\sqrt{P - p_1}} = A - \frac{14\,400}{T} + \log\sqrt{T}. \qquad (32)$$

The constant of integration, A, is found from the data in Table IV.

TABLE X.

T.	p_1 "obs."	A.	p_1 calc.
2500	0.037	2.637	0.039
2700	0.108	2.677	0.105
2900	0.238	2.668	0.236
3100	0.430	2.660	0.435
3300	0.680	2.684	0.650
		Mean, 2.665	

In Table X, p_1 "obs.," is taken from Table IV. In the third column A is calculated by equation (32) and p_1 cal. in the fourth column is calculated from this same equation by taking A = 2.665.

Summary and Conclusions.

1. The energy loss from heated wires in various gases can be readily calculated by simple equations.

2. For nitrogen and mercury vapor the results calculated in this way agree well with experimental results up to temperatures as high as 3500° K.

3. With air and carbon dioxide similar agreement was obtained up to the melting point of platinum.

4. In the case of hydrogen, however, there is agreement only up to about 2100° K. Above that the energy loss increases extremely rapidly so that at 3300° it is four or five times the calculated value.

5. This is explained by assuming that hydrogen at very high temperatures is dissociated into atoms.

6. The theory of the heat conductivity of a dissociating gas was developed.

7. The heat of the reaction and the degree of dissociation at various temperatures was thus calculated and was found to agree well with van't Hoff's equation.

8. Experiments at low pressures prove that the phenomenon is a true dissociation, which follows the law of mass action and that the volume of the dissociation products is approximately twice the volume of the original hydrogen. That is, the dissociation takes place according to the equation

$$H_2 = 2H.$$

9. There is much evidence that the dissociation is *not* electrolytic.

10. Nitrogen, even at 3500° K, is not perceptibly dissociated at atmospheric pressure. That is, its dissociation does not exceed 5%, at 3500° K.

11. The following quantitative results have been obtained. The heat of reaction at constant volume for

$$2H = H_2$$

is 550,000 joules, or 130,000 calories. At constant pressure it would be approximately 575,000 joules, or 136,000 calories at 3000° K.

The degree of dissociation at any temperature, T, is given by the equation

$$\log \frac{p_1}{\sqrt{P-p_1}} = 2.665 - \frac{14400}{T} + \frac{1}{2}\log T.$$

Here p_1 is the partial pressure of the hydrogen atoms (in atm.), and P is the total pressures (in atm.).

From this equation the free energy of formation of hydrogen molecules from atoms can be calculated.

The following table gives the degree of dissociation (p_1) of hydrogen at 1 atm. pressure at various (absolute) temperatures.

Table XI.

Degree of Dissociation of Hydrogen at Atmospheric Pressure.

$T.$ °K.	p_1 atm.	$T.$ °K.	p_1 atm.
293° (20° C.)	5.4×10^{-46}	2900°	0.236
		3100	0.441
500	1.7×10^{-25}	3300	0.666
1000	5.8×10^{-11}	3500	0.840
1500	4.49×10^{-6}	3700	0.933
2000	1.30×10^{-3}	3900	0.973
2300	0.0121	4100	0.988
2500	0.0394	4500	0.9962
2700	0.106	5000	0.99981

I wish here to acknowledge the valuable assistance of Mr. E. Q. Adams, Mr. S. P. Sweetser, Mr. H. Huthsteiner, and Mr. G. S. Meikle, who have carried out most of the experimental work involved in this investigation.

Research Laboratory,
General Electric Company,
April 23, 1912.

THE DISSOCIATION PRESSURES OF PHOSPHONIUM BROMIDE AND IODIDE.

By F. M. G. Johnson.

Received April 27, 1912.

The dissociation pressures of phosphonium chloride have been investigated by Tammann,[1] but for the bromide and iodide only the temperatures at which the dissociation pressures are one atmosphere appear to have been determined.[2] These two substances have therefore been made the subject of this investigation.

The salts were prepared by passing PH_3 into tubes containing the liquefied acid cooled by CO_2 and ether. The PH_3 was obtained by the action of KOH solution on PH_4I. The gas was bubbled through KOH solution and then passed through a U tube surrounded by solid CO_2. The halogen acids were prepared by the method used by McIntosh and Steele,[3] but were not dried by P_2O_5. Both salts appeared as white powders which in time changed to large colorless crystals.

The method employed for the measurement of the pressures was similar in principle to that used in former work of this nature.[4] The apparatus,

---

[1] *Arch. néerl.*, 244 (1901). *Z. Elektrochem.*, **8**, 158 (1902).

[2] Abegg, *Handbuch*, **3**, III, 398.

[3] *Phil. Trans. Roy. Soc.*, (*A*), **205**, 99. *Z. physik. Chem.*, **55**, 129 (1906).

[4] *Z. physik. Chem.*, 61, 457 (1908); 65, 36 (1908). This Journal, **31**, 1138 (1909); **33**, 777 (1911).