and cooled in nitrogen. The results of Series II are preferred since the salt used in Series I probably contained free bromine. Analysis was effected by comparison with weighed amounts of silver and by weighing the silver bromide formed. Weights are corrected to vacuum.

Neoytterbrium.—Blumenfield and Urbain[1] have purified the nitrate of this element by fractionation, and give its atomic weight as 173.54. This is higher than that of Auer von Welsbach's "aldebaranium," 173.00.

The atomic weights of thorium, cerium, and beryllium have been discussed from the standpoint of transparency to X-rays by Benoist and Copaux,[2] that of nebulium by Bourget, Fabry and Buisson[3] and Nicholson,[4] the relations between the atomic weights by Loring.[5]

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THE DISSOCIATION OF HYDROGEN INTO ATOMS.
[PART II.]
CALCULATION OF THE DEGREE OF DISSOCIATION AND THE HEAT OF FORMATION.

BY IRVING LANGMUIR.

The first part of this paper[6] dealt with experiments on the heat losses from fine tungsten wires in hydrogen at pressures ranging from 0.010 mm. up to atmospheric pressure. The results were given in a series of tables, and form the basis for the present calculation of the degree of dissociation and the heat of formation of molecular hydrogen.

The previous calculations of the dissociation of hydrogen[7] were based on the use of the equation

(3)[8] $$W_D = SDq_1c_1$$

as described in Part I. The equation itself rests on a firm foundation, but the assumptions previously made in applying it to experimental results are open to serious criticism.

In the first place, it was assumed that the diffusion coefficient D could be calculated with sufficient accuracy from some equations of the kinetic

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[1] *Compt. rend.*, **159**, 325 (1914).

[2] *Ibid.*, **158**, 689, 859 (1914).

[3] *Compt. rend.*, **158**, 1017 (1914).

[4] *Ibid.*, **158**, 1322 (1914).

[5] *Chemical News*, **108**, 188, 247, 305; **109**, 169; **110**, 25 (1914).

[6] Langmuir and Mackay, THIS JOURNAL, **36**, 1708 (1914).

[7] *Ibid.*, **34**, 860 (1912). This paper will hereafter be referred to as the "paper of 1912."

[8] For the derivation of this and some of the following equations, see Part I, or the "paper of 1912." The numbers of the equations are the same as those used in Part I.

theory by the rather arbitrary choice of a value for the mean free path of hydrogen atoms through ordinary molecular hydrogen.

Secondly, it was assumed that the shape factor S in the above equation had the same value as that obtained from the data on the convection losses in hydrogen at temperatures below that at which dissociation occurred.

Thirdly, it was assumed that the hydrogen in the immediate vicinity of the tungsten wire was in chemical equilibrium at a temperature corresponding to that of the wire. In other words, c_1 was taken to be the equilibrium concentration at the temperature of the wire.

And finally, the value of q_1 was found by a method which itself involved any error occurring in D.

Each of the four factors in Equation 3 was therefore liable to error. This was realized and pointed out at the time the, calculations were made, but there was then no reason to suspect that any of these sources of error was serious enough to greatly affect the results.

In the present paper we shall endeavor to avoid these arbitrary assumptions and, by a careful analysis of the mechanism of the phenomena occurring in and around the wire, we will attempt to estimate and eliminate the errors which would otherwise occur.

1. Effect of Convection Currents.

In the experiments with hydrogen at atmospheric pressure the effect of convection currents in heating the upper part of the bulb was very noticeable. But in the bulbs with 200 mm. pressure of hydrogen or less, the upper part of the bulb was not as strongly heated as the lower part. It is, in fact, well known that convection currents decrease rapidly in intensity as the pressure is lowered, also that in hydrogen they are very much less pronounced than in other gases. If one considers the cause of convection currents it is evident that the behavior of hydrogen is just what one should expect.

The force producing convection currents is proportional to the difference in the densities of the ascending and descending currents of the gas. Since the density of a gas is equal to pM/RT it is readily seen that the force producing convection is thus proportional to

$$\frac{pM}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \frac{pM}{RT_1}\left(\frac{T_2-T_1}{T_2}\right).$$

This force is directly proportional to the density of the gas and to the fraction $(T_2-T_1)/T_2$. As T_2 becomes large this fraction approaches unity as a limit, so that, at very high temperatures, there is little tendency for convection to increase, and even this is largely counteracted by the increasing viscosity of the gas at high temperatures.

The experimental results themselves, however, furnish us with data by which we can estimate the effect of convection currents.

At temperatures below that at which perceptible dissociation of hydrogen occurs, we have seen that the heat losses from the filament are given fairly accurately by the equation (see Table III, Part I).

(2) $$W_C = S(\varphi_2 - \varphi_1).$$

The shape factor S for concentric cylinders is equal to (*Phys. Rev.*, **34**, 407 (1912))

(7) $$S = \frac{2\pi}{\ln b/d}$$

where b is the diameter of the film of gas around the wire through which conduction takes place and d is the diameter of the wire.

Let us now substitute the experimentally determined values of S from Table III in this equation, together with the known value of d (= 0.00706 cm.) and solve the equation for b. We thus find

p.	S.	b.
750 mm.	1.25	1.08 cm.
200	0.88	9.0
100	0.72	45.0
50	0.56	530.0

At atmospheric pressure the effective diameter of the film of conducting gas around the tungsten wire is about one centimeter, but at 200 mm. pressure the diameter is already 9 cm., which is larger than the diameter of the bulb (7 cm.). This means that the heat loss from the filament is actually less than if there were no convection currents and the ordinary laws of heat conduction could be applied. At lower pressures the heat loss becomes still less, although we know that the true heat conductivity of gases is independent of the pressure.

These considerations lead us to conclude that the effects of convection currents can be neglected even at pressures as high as 200 mm. We shall see that the decrease in the values of S at the lower pressures is due to a temperature discontinuity at the surface of the wire.

2. The Temperature-drop at the Surface of the Wire.

Kundt and Warburg,[1] in a study of the viscosity of gases at low pressures, showed, both experimentally and theoretically, that there is a certain apparent slipping of the gas along the surface. In gases at atmospheric pressure this effect is very small, but it varies inversely proportional to the pressure and thus becomes very important at low pressures. The thickness of the layer in which this slipping occurs is approximately equal to the mean free path of the gas molecules. Kundt and Warburg predicted, from the analogy between viscosity and heat conduction, that a corresponding discontinuity in temperature at the surface of a solid body

[1] *Pogg. Ann.*, **156**, 177 (1875).

would be observed in the case of heat conduction through gases at low pressure.

Over twenty years later Smoluchowski[1] actually observed and studied this temperature drop and developed the theory of it. The temperature drop occurred within a layer about equal in thickness to the free path of the molecules. Smoluchowski found that in some gases, particularly hydrogen, the amount of heat given up to the gas by a solid body was only a fraction of that which should be delivered if each molecule striking the surface reached thermal equilibrium with the solid before leaving it.

Smoluchowski developed the theory of this effect along the lines of two alternative hypotheses, which he denotes by A and B.

Hypothesis A is equivalent to that made more recently by Knudsen.[2] It assumes, when molecules of a temperature T_1 strike a surface at a higher temperature T_2, that the molecules leaving the surface have a temperature T which is intermediate between T_2 and T_1 and that the relation holds

(8) $$T - T_1 = \alpha(T_2 - T_1)$$

where α is a number less than unity and is called by Knudsen the "accommodation coefficient."

Hypothesis B is similar to that originally used by Maxwell[3] in dealing with the slip of gases. It assumes that, of all the molecules striking the surface, a fraction, f, reaches thermal equilibrium with it, while the fraction $1 - f$ is reflected without change of temperature (or rather velocity).

The two methods give analogous, but quantitatively slightly different results. Smoluchowski[4] considers that the accuracy of experimental results has not yet been sufficient to distinguish between them, notwithstanding Knudsen's opinion to the contrary, and that in all probability the truth is intermediate between the two.

The formulas developed by Smoluchowski are only adapted to be applied to small differences of temperature and to heat conduction between surfaces whose radius of curvature is large compared to the mean free path of the molecules. In the present experiments, however, we are dealing with very small wires and with temperature drops of sometimes a thousand degrees or more, and we shall therefore need to derive the equations independently. We shall choose a simpler, although less rigorous method, based upon the same principles as those used by Smoluchowski. In this way we shall gain a clearer insight into the phenomena occurring around the wire and will be in a better position to apply similar principles to the problem of calculating the degree of dissociation of the gas.

[1] *Wied. Ann.*, 64, 101 (1898); *Wien. Sitzungsber.*, 108, 5 (1899); *Phil. Mag.*, 46, 192 (1898).

[2] *Ann. Phys.*, 34, 593 (1911).

[3] *Phil. Trans.*, 170, 231 (1879).

[4] *Ann. Phys.*, 35, 983 (1911).

Theory of Heat Conduction from Small Wires.—Let us consider a small heated wire A (Fig. 1) placed in the axis of a large cylindrical bulb B of diameter b, containing gas at such low pressure that the effects of convection can be neglected. Let T_2 be the temperature of the wire and T_1 that of the bulb. If λ represents the length of the mean free path, then the distance which a molecule leaving the wire travels before colliding with other molecules is approximately λ.[1] On the other hand, the molecules striking the wire come from an average distance λ. Let us draw a circle, C (in Fig. 1), of diameter $d + 2\lambda$, around the wire, whose diameter is d and a similar circle D of diameter $b - 2\lambda$.
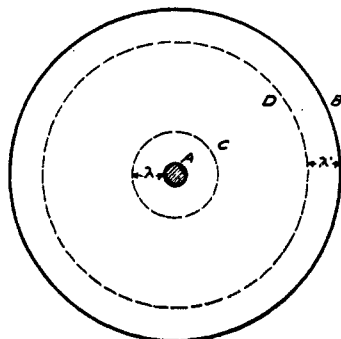

FIG. 1.

We may now look upon the heat conduction from the wire A to the cylinder B as taking place in the following steps:

1. Molecules of gas leave the wire and travel to C, where they are absorbed, and some molecules from C travel to the wire, a certain fraction of these absorbing heat from the wire.

2. From C to D the heat is carried according to the ordinary laws of heat conduction.

3. From D to B the energy is transferred by a simple interchange of molecules in a similar way to the transfer from A to C.

Thus we consider a temperature discontinuity from A to C and from D to B, but a continuous variation of temperature from C to D.

Since we are dealing with small wires in relatively large cylinders, we can readily see that the temperature drop from D to B will always be negligible compared to that from A to D. We shall therefore leave it out of consideration.

Let us represent by T_a the temperature of the gas at C. We can now calculate the temperature drop $T_2 - T_a$.[2]

If we let m be the rate at which the gas comes into contact with the

[1] Knudsen, *Ann. Phys.*, 34, 654 (1911), shows that the temperature of the molecules striking a plane surface corresponds to the temperature of the gas at a distance equal to 0.95 times the mean free path of the molecules. Using more recent data than that available to Knudsen, I calculate from his formulas that this coefficient should be about 1.2. Undoubtedly the coefficient would be somewhat different for very small wires from what it is for plane surfaces, but in any case its order of magnitude is close to unity. Fairly large errors in the value of this coefficient make only very slight differences in the results that are to be obtained by its aid.

[2] This is somewhat greater than the temperature drop defined by Smoluchowski, for it includes the *normal* temperature difference between A and C.

wire (in grams per sq. cm. per second), then the heat carried from the wire per second will be (per cm. of length)[1]

$$(9) \qquad W_C = 4.19\, \pi\, d\, (C_v/M)\, \alpha\, (T_2 - T_a)m.$$

Here C_v is the molecular heat at constant volume and the coefficient 4.19 converts calories to watt-seconds. The fraction α is the accommodation coefficient, and d is the diameter of the wire.

In order to calculate $T_2 - T_a$ from Equation 9 we must now substitute in it the value of m as given by Equation 5 of Part I, namely,

$$(5) \qquad m = \sqrt{\frac{M}{2\pi R T_a}}\; p.$$

Here M is the molecular weight of the gas, T_a is the temperature of the gas at a distance λ from the wire (at C in Fig. 1).

In the derivation of this formula Maxwell's distribution law was assumed to hold. Where the temperature discontinuity at the surface is as large as in the present experiments the distribution of velocities among the molecules is undoubtedly very complex. The error involved in using this equation must, however, be relatively small.[2]

Before substituting (5) in (9) let us insert the numerical values of the constants. In (5) we place M = 2, R = 8.32 × 10⁷ ergs/° C. and express p in mm. of mercury and m in grams per sq. cm. per second. We thus obtain

$$(10) \qquad m = \frac{0.0825\, p}{\sqrt{T_a}}.$$

In (9) we place C_v = 5.26 g. cals. per degree (from 300° to 1500° K.)[3] and d = 0.00706 cm. This gives, when we combine with (10)

$$(11) \qquad T_2 - T_a = 49.6\, \frac{W_C \sqrt{T_a}}{\alpha p}.$$

[1] Knudsen shows that this should be multiplied by 4/3, since the average velocity of all the molecules striking any surface is greater than the average velocity of the molecules in the body of the gas. This is due to the fact that the molecules of high velocity have a much greater chance of striking a surface than those of low velocity. On the other hand, for polyatomic gases the exchange of rotational energy is not complete and, therefore, a quantity less than should be substituted in the above equation. According to Smoluchowski, the combined effect of these two corrections would lead to a coefficient of 16/15 in place of the 4/3 mentioned above. For the present purpose this small correction may be neglected.

[2] With large differences of temperature over distances comparable with the free path, another effect, which we may call the radiometer effect, enters to render Equation 5 inaccurate. The rapidly moving molecules leaving the wire tend to drive back the slower incoming molecules and thus to decrease the rate at which the molecules strike the wire. Although this effect would be very important if we were dealing with large flat surfaces, calculation shows that in our present experiments, where only fine wires are employed, this error is always less than 5% and usually much less than this. It has, therefore, been neglected.

[3] The letter K is used to denote temperatures on the absolute scale (Kelvin).

This equation enables us to estimate the difference between the temperature of the wire and that of the gas molecules which strike its surface.

We may also calculate the temperature of the gas molecules striking the wire in another way. Between the surface C (Fig. 1) and the bulb, the ordinary laws of heat conduction must apply at pressures below that at which convection occurs. Thus we may place, according to (2) and (7)

$$(12) \qquad W_C = \frac{2\pi}{\ln b/(d + 2\lambda)} \, (\varphi_a - \varphi_1).$$

If we know the effective diameter of the bulb and the mean free path of the gas molecules, we can calculate from this equation the value of $(\varphi_a - \varphi_1)$, and since φ is a known function of the temperature, this in turn will enable us to determine T_a.

Let us now calculate T_a from our experiments with hydrogen by means of Equations 11 and 12. For this purpose we will choose the data obtained at 1500° K., for at this temperature there is no appreciable dissociation and the temperature measurements are more accurate than at lower temperatures. These data, as taken from Tables I and II of Part I, are given below in Table V in the second column. The figures represent the watts per centimeter carried by the hydrogen from a wire at 1500° K. The first column gives the pressure of hydrogen in mm. of mercury. In the third column are the values of T_a calculated by Equation 11.

TABLE V.—WIRE IN HYDROGEN.

	$T_2 = 1500.$				$\alpha = 0.19.$	
1.	2.	3.	4.	5.	6.	7.
$p.$	$W_C.$	T_a by (11).	λ cm.	$\varphi_a - \varphi_1$	$b.$	T_a by (12).
750	5.50	1428	0.0001	[4.10]	0.78	(1428)
200	3.90	1316	0.0003	[3.53]	1.87	(1316)
100	3.13	1216	0.0006	[3.03]	3.7	(1216)
50	(2.52)	1071	0.0011	2.39	[3.7]	1070
25	1.92	900	0.0020	1.78	[3.7]	920
10	(0.94)	806	0.0037	0.83	[3.7]	660
4.4	0.47	742	0.0063	0.46	[9.0]	520
1.1	0.19	495	0.020	0.16	[9.0]	390
0.207	0.050	341	0.094	0.03	[9.0]	317
0.039	0.009	360	0.5	0.003	[9.0]	302
0.015	0.004	[300]	1.3	0.001	[9.0]	300

The accommodation coefficient α was calculated from the data at the lowest pressure (0.015 mm.) by substituting $T_a = 300$;[1] $T_2 = 1500$; $W_C = 0.004$; and $p = 0.015$ in Equation 11. This gave $\alpha = 0.19$, which, when substituted in (11) gave

$$(13) \qquad T_2 - T_a = 260 \, (W_C/p) \, \sqrt{T_a}.$$

[1] That it is justifiable to place $T_a = 300$ at these lowest pressures is shown by the results obtained below and given in the seventh column.

The values of T_a given in the third column of Table V were obtained by solving these quadratic equations.

The free path of hydrogen molecules at $0°$ C. and 1 mm. pressure is 0.0135 cm., according to O. E. Meyer. The free path varies with the temperature according to Sutherland's formula, but for the present purpose it is accurate enough to assume that it is inversely proportional to the density. The fact that at low pressures the molecules leaving the filament travel through groups of molecules having a much lower temperature, introduces the necessity for a rather special calculation of the free path leading to the formula[1]

$$(14) \qquad \lambda = \frac{49.5 \times 10^{-6}}{p} T_a \sqrt{\frac{2T_2}{T_2 + T_a}}.$$

This equation was used to calculate the free paths given in Col. 4 of Table V.

At the higher pressures the effects of convection currents cannot be neglected, so that Equation 12 would not be expected to hold accurately under these conditions. However, even in the case of convection from small wires in the open air we may profitably look upon the phenomena as consisting essentially in conduction through a film of stationary gas of a certain thickness. If we adopt this view-point, Equation 12 applies even at the higher pressures, but b then no longer represents the diameter of the bulb, but becomes the effective diameter of the film of gas through which conduction occurs. To determine the value of b we need only substitute the values of W_C, d, λ and $\varphi_a - \varphi_1$ in Equation 12 and solve for b. For this purpose the values of $\varphi_a - \varphi_1$ were calculated from T_a, for the pressures of 760 to 100 mm., and are given in Table V (Col. 5) in brackets. These then served to calculate b from (12). At the lower pressures (50–10 mm.) it was then assumed that convection currents were absent and that b was therefore independent of the pressure and equal to the value 3.7 cm., as found at 100 mm. Below 10 mm. b was placed equal to the diameter of the bulb, for in these experiments a straight wire in a cylindrical bulb was used.

The values of $\varphi_a - \varphi_1$ at the lower pressures were obtained from (12) by substituting in it W_C, b, d and λ as given in the table. The results are given in Col. 5 (without brackets) and were used to calculate the corresponding values of T_a given in the seventh column.

By comparison of Cols. 3 and 7, it is seen that there is reasonably good agreement between the values of T_a calculated by these entirely independent methods. The fact that the temperature drop at the surface of the wire $(T_2 - T_a)$ is so large, even at the higher pressures, is the reason

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[1] Derived from the equations given on page 260 of Meyer's "Kinetische Theorie der Gase," German edition of 1899.

for the variation of the shape factor (given in Table III at the heads of the columns).

The accommodation coefficients α is found above to be equal to 0.19. This is considerably lower than the value 0.36 found by Knudsen for hydrogen in contact with polished platinum at approximately room temperature.

The results given in Col. 6 of Table V show that the effective thickness of the layer of "stationary" gas around the wire increases as the pressure decreases from 750 to 100 mm., owing to convection currents. At lower pressures, however, the results indicate that there is no further change in b. If the lamps used in these experiments had contained a long, straight filament in the axis of a cylindrical bulb, then b should be equal to the diameter of the bulb. Actually, however, the filament was a short loop only about 3 cm. long. The resulting divergence of the lines of heat flow would tend to increase the shape factor, which would be equivalent to a decrease in diameter of a cylindrical bulb. Hence the value of 3.7·cm. found above for b is in as close agreement with the actial bulb diameter (7 cm.) as the experimental conditions would seem to warrant.

Nitrogen.—Similar calculations from the data given in Table I, for a filament at a temperature of 2400° in nitrogen yield the results shown in Table VI. The values of T_a in Col. 3 were obtained from a formula similar to (11) in which, however, the coefficient 49.6 was replaced by 166, corresponding to the different molecular weight and specific heat of nitrogen. The columns of Table VI correspond exactly to those of Table V.

It is seen by the variation of b that the effect of convection is much more marked than with hydrogen and persists at pressures even as low as 50 mm.

TABLE VI.—WIRE IN NITROGEN.

$T_2 = 2400.$					$\alpha = 0.60.$	
1.	2.	3.	4.	5.	6.	7.
p.	W_C.	T_a.	λ cm.	$\varphi_a - \varphi_1$.	b.	T_a by (12).
750	2.46	2356	0.0001	[1.68]	0.54	(2356)
200	2.06	2264	0.0003	[1.56]	0.89	(2264)
100	1.87	2160	0.0006	[1.44]	1.01	(2160)
50	1.34	2064	0.0011	[1.32]	4.4	(2064)
10	0.75	1580	0.0046	0.74	[8]	1530
1	0.16	1000	0.031	0.12	[8]	650

The accommodation coefficient is much larger than that of hydrogen, but is again less than that given by Knudsen (for air) at room temperature.

The agreement between the values of T_a calculated by the two independent methods, in both Tables V and VI, is sufficiently good to show that the general theory of heat conduction and convection used in making the calculations can safely be applied to the case of fine tungsten wires in hydrogen and nitrogen at all pressures. Evidently the heat conductivities

of these gases, within the ranges of temperature considered above, vary with the temperature in the way that is to be expected from their behavior at ordinary temperatures.

3. Concentration Drop at the Surface of the Wire.

We have seen that the temperature of the layer of gas next to the wire may be very much lower than that of the wire itself. To assume that these two temperatures are equal, which amounts to assuming temperature equilibrium at the surface of the wire, would lead to entirely erroneous results.

The diffusion of one gas through another is a phenomenon closely related to heat conduction. In the case of the evaporation of a solid surrounded by a gas, where the vapor must diffuse outward through the gas, the partial pressure of the vapor at the surface of the solid will be less than that of the saturated vapor. In other words, there will be a "concentration-drop" at the surface, just as there is a "temperature drop" in the analogous case of heat conduction, and a "slip" in gases where viscosity effects are involved. Analogy suggests that this concentration drop will be inversely proportional to the pressure.

In the previous calculations of the' dissociation of hydrogen it was assumed that the concentration of the hydrogen atoms close to the wire, was that corresponding to equilibrium at the temperature of the wire. As the experiments underlying these calculations were made at atmospheric pressure, this assumption involved no serious error, but at the low pressures which we are now to consider, such an assumption would render the results worthless.

In analyzing the effect of the surface concentration drop in our present experiments, we may follow methods entirely analogous to those which we adopted in estimating the temperature drop.

Let us consider the mechanism of the phenomena occurring on and around a tungsten wire surrounded by hydrogen, and heated to such a high temperature that the hydrogen is partly dissociated. The hydrogen molecules striking the surface come from an average distance of approximately λ (the mean free path). A certain proportion of these molecules leave the surface without change (reflected) and another portion is absorbed by the wire and may thus be dissociated. Similarly, hydrogen atoms striking the filament may be absorbed or reflected. The hydrogen which is absorbed probably reaches chemical equilibrium within the wire and the atoms and molecules in certain proportions diffuse out and away from the wire. We assume that the hydrogen not absorbed undergoes no chemical change.

Let m_2 represent the rate at which hydrogen molecules strike the surface of the filament (in grams per sq. cm. per second) and m_1 be the corresponding rate for the hydrogen atoms. Let $\alpha_1 m_1$ be the rate at which the hydrogen atoms are absorbed by the wire and $\alpha_2 m_2$ be the rate at which the

molecules are absorbed. Now in a stationary condition the total amount of hydrogen escaping from within the wire must be equal to the rate at which it is absorbed. We may look upon the surface of the wire as the boundary of a space containing hydrogen in equilibrium. The rate at which the hydrogen atoms in the metal reach the surface (from within) we shall call n_1, and the corresponding rate for the molecules n_2. Similarly, we shall let $\beta_1 n_1$ be the rate at which atoms escape from the metal and $\beta_2 n_2$ the rate at which molecules escape. Then in a stationary state we have

$$(15) \qquad \beta_1 n_1 + \beta_2 n_2 = \alpha_1 m_1 + \alpha_2 m_2.$$

We assume that the coefficients α and β are constant; that is, that they are independent of m and n, although they may vary with the temperature.

The energy (watts) carried away from the wire (per cm.) because of the dissociation, we have called W_D. If q_1 be the heat (calories) necessary to dissociate 1 g. of hydrogen, then we have

$$(16) \qquad W_D = 4.19\, \pi\, d\, q_1\, (\alpha_2 m_2 - \beta_2 n_2).$$

Here d is the diameter of the wire. The quantity in parenthesis is the difference between the rates at which hydrogen molecules are absorbed and are given up by the wire and therefore is equal to the rate at which hydrogen is dissociated.

If we place

$$(17) \qquad \omega = W\, /(4.19\, \pi\, d\, q_1)$$

then (16) becomes

$$(18) \qquad \omega = \alpha_2 m_2 - \beta_2 n_2$$

Combining this with (15), we obtain

$$(19) \qquad \omega = \beta_1 n_1 - \alpha_1 m_1$$

whence

$$(20) \qquad \begin{cases} \beta_1 n_1 = \alpha_1 m_1 + \omega \\ \beta_2 n_2 = \alpha_2 m_2 - \omega \end{cases}$$

Now we have assumed that equilibrium exists between the hydrogen atoms and molecules absorbed by the wire. According to the law of mass action, the concentration of the hydrogen molecules in the metal is proportional to the square of the concentration of the atoms. But n_2 and n_1 must be proportional to these concentrations. From Equation 20 we thus obtain

$$(21) \qquad (\alpha_1 m_1 + \omega)^2 = A(\alpha_2 m_2 - \omega).$$

Here A is a constant which is proportional to the dissociation constant of hydrogen dissolved in the metal. We may now obtain a relation between this quantity A and the true dissociation constant K of gaseous hydrogen (outside the wire).

We have

$$(22) \qquad K = (p_1')^2 / p_2'$$

where p_1' and p_2' are, respectively, the partial pressures of hydrogen atoms and molecules corresponding to equilibrium in the gaseous phase.

By Equation 5 (Part I) we have from (22) by placing $M_1 = 1$ and $M_2 = 2$

$$(23) \qquad\qquad K = \sqrt{4\pi RT_2}\,(m_1')^2/m_2'$$

where T_2 is the temperature of the filament.

On the other hand, if we place $\omega = 0$ in (21), we obtain the condition for equilibrium. In this case (21) becomes

$$(24) \qquad\qquad A = (\alpha_1^2/\alpha_2)\cdot(m_1')^2/m_2'$$

and by combining this with (23) we find the desired relation between A and K

$$(25) \qquad\qquad K = \sqrt{4\pi RT_2}\,(\alpha_2/\alpha_1^2)\,A.$$

If we now substitute in (21) the values of m_1 and m_2 from Equation 5 and then combine with (25), we obtain

$$(26) \qquad\qquad K = \sqrt{T_2/T_a}\;\frac{(p_1 + \omega\sqrt{2\pi RT_a}/\alpha_1)^2}{p_2 - \omega\sqrt{2\pi RT_a}/\alpha_2\sqrt{2}}.$$

Here T_a is the temperature of the gas around the wire at a distance λ from it (corresponding to circle C of Fig. 1). When $\omega = 0$ and $T_a = T_2$ this equation reduces to the ordinary form of the law of mass action. The "drop in concentration" corresponding to the drop in temperature previously considered is equivalent to $\omega\sqrt{2\pi RT_a}/\alpha_1$.[1]

In the above equation p_1 and p_2 are the partial pressures of hydrogen atoms and molecules at a distance λ from the wire.

Let us substitute the numerical values of the constants involved in (26). If we express p in mm. of mercury, then the factor $\sqrt{2\pi R}$ is 17.15. If we place $d = 0.00706$ cm. (the diameter of the wire) in (17) we find $\omega = 10.8\,W_D/q_1$. Substituting these in (26), we obtain

$$(27) \qquad\qquad K = \sqrt{T_2/T_a}\;\frac{(p_1 + 185.W_D\sqrt{T_a}/\alpha_1 q_1)^2}{p_2 - 131\,W_D\sqrt{T_a}/\alpha_2 q_1}.$$

Here p is expressed in mm., W_D in watts per cm., and q_1 in calories per gram.

4. Diffusion of Atomic Hydrogen away from the Wire.

In the calculation of the temperature drop around a wire in hydrogen, we used two methods which led to Equations 11 and 12, respectively. Similarly, in the calculation of the concentration drop, two methods may be used. The method adopted above in obtaining Equation 27 is analogous to that used in deriving (11), whereas the following method corresponds to that employed in obtaining (12).

In the "paper of 1912" it was shown that

$$(3) \qquad\qquad W_D = SDq_1c_1$$

[1] Expressed as partial pressure instead of concentration.

Here c_1 is to be expressed in mols per cc., and is equal to

(28) $$c_1 = p_1/RT.$$

The diffusion coefficient varies with the temperature according to Sutherland's formula, but at the high temperatures we are dealing with, this becomes equivalent to stating that the diffusion coefficient varies with the 3/2 power of the temperature. We will assume that the diffusion coefficient of hydrogen atoms through molecular hydrogen varies in this way with the temperature, although we shall avoid assumptions as to its actual magnitude. Since the diffusion coefficient is inversely proportional to the pressure, we may thus place:

(29) $$D = D_0 (T_a/273)^{3/2}.(760/P)$$

where D_0 is the diffusion coefficient at $0°$ and 760 mm. pressure, and T_a is the temperature of the gas around the wire (*i. e.*, at the distance λ from it).

Combining (29), (28), and (3) we obtain, after substituting the numerical value for R.

(30) $$W_D = 11.3 \times 10^{-6} Sq_1D_0 \sqrt{T_a}\, p_1/P.$$

This equation gives us the desired relation between p_1, the partial pressure of hydrogen atoms around the wire, and W_D. It enables us to calculate the degree of dissociation if we know S, q_1 and D_0.

5. Equations Involved in Calculating the Dissociation Constant, etc.

Equation 27 has given us a means of calculating the dissociation constant from the partial pressures of hydrogen atoms and molecules around the wire. These partial pressures may be expressed in terms of the diffusion constant by means of Equation 30. By combining these two equations it is possible to obtain a general solution of the problem in the following form:

(31) $$K = \sqrt{T_2/T_a} \frac{W^2{}_D(BP + E)^2}{P - W_D(BP + C)}$$

where

(32) $$B = 88500/(SD_0 q_1\sqrt{T_a})\ \text{cm. per watt}$$

(33) $$C = 131\sqrt{T_a}/(\alpha_2 q_1)\ \text{mm. of Hg per watt/cm.}$$

(34) $$E = 185\sqrt{T_a}/(\alpha_1 q_1)\ \text{mm. of Hg per watt/cm.}$$

The dissociation constant K increases rapidly with the temperature, while B, C and E depend only to a small degree on the temperature, and therefore we see by (31) that at low temperatures W_D will increase approximately proportional to $\sqrt{K}$. At high temperatures, however, the two terms in the denominator must tend to become equal, so that W_D would approach a limiting value. From Equation 31 we can readily derive simple equations for these limiting cases.

At low temperatures the second term of the denominator is negligible, so that

(35) $$K = \sqrt{T_2/T_a} \; W_D{}^2(BP + E)^2/P.$$

At low pressures this gives:

(36) $$W_D = \sqrt[4]{\frac{T_a}{T_2}} \sqrt{\frac{PK}{E}}.$$

At high pressures (here $T_a = T_2$).

(37) $$W_D = \sqrt{K/P}/B.$$

At intermediate pressures W_D increases to a maximum. Differentiating (35) with respect to P and placing $dW_D/dP = 0$ leads to following maximum value of W_D (here $T_a = T_2$):

(38) $$W_{max.} = \sqrt{K/4BE}.$$

The pressure at which this maximum occurs is

(39) $$P' = E/B.$$

At high temperatures W_D increases so that ultimately $W_D(BP + C)$ becomes nearly equal to P. Beyond this value it cannot go. Therefore, at high temperatures W_D must gradually approach a limiting value. This limit is

at low pressures

(40) $$W_D = P/C$$

at high pressures

(41) $$W_D = 1/B.$$

The higher the pressure the higher is the temperature at which W_D approaches its limiting value.

We shall see that the case where $C = E$, is of special importance. If we make this substitution in (31) and place

(42) $$F = BP + E$$

we obtain the very simple equation

(43) $$K = \sqrt{T_2/T_a} \; \frac{F^2W^2{}_D}{P - FW_D}.$$

At higher pressures T_a becomes practically equal to T_2, so the equation is still further simplified.

(43a) $$K = F^2W^2{}_D/(P - FW_D).$$

Comparing this with (22), we see that FW_D is equal to the partial pressure of hydrogen atoms corresponding to equilibrium at the temperature of the filament. The degree of dissociation of the hydrogen in equilibrium is therefore FW_D/P.

At low temperatures we have already found expressions for the maximum value of W_D and the pressure at which this occurs. On the assumption that $C = E$ we may now find more general expressions applicable even

at high temperatures. Differentiating (42) and (43a) with respect to P, placing $dW_D/dP = 0$ and solving the resulting equation together with (31), we obtain

(44) $$W_{max.} = 1/(B + \sqrt{4BE/K}).$$

(45) $$P' = (E/B) + \sqrt{EK/B}.$$

6. Calculation of Results from Experimental Data.

The equations that have been derived in the preceding section give us means of calculating the coefficients B, C and E, and in this way of determining the dissociation constant K. Thus from the experiments at low pressures and at low temperatures it should be possible by (36) to find the ratio $\sqrt{K}$: E. Experiments at high pressures give by (37) $\sqrt{K}$: B, while those at high temperatures and low pressures give C according to (40). At high pressures and high temperatures we should then obtain B by (41). By combining these results it would thus be possible to find the actual values of B, C, E and K, separately. In practice, however, this method gives difficulty, because the experiments do not cover a sufficiently wide range of pressures or temperatures to allow these limiting equations to hold accurately. Furthermore, the values of W_D obtained under the extremes of temperature or pressure are often subject to unusually large experimental error, and it is unwise to use such data exclusively for the determination of the coefficients. A third difficulty is that Equations 36, 37, 40 and 41 all involve to some extent T_a, the temperature of the gas around the wire, which is not accurately known.

The method finally adopted to determine the coefficients B, C and F has been chosen because of its relative freedom from these difficulties,

1. **The Value of C.**—According to our theory, at very low pressures, W_D does not increase indefinitely with rising temperature, but approaches a limiting value equal to P/C (Equation 40). If we examine the experimental data of Table III we see, in fact, that W_D at the three lower pressures, 0.015, 0.039 and 207 mm., becomes constant at temperatures over 2700°. This is also readily seen from Fig. 2, in which log W_D has been plotted against $1/T$. The limiting value of W_D at high temperatures for each of these pressures is given in the following table, along with the ratio P/W_D, which, according to (40), is equal to C:

TABLE VII.

P.	W_D.	C = P/W_D.	T_a.
0.015	0.18	0.0835	300
0.039	0.47	0.083	300
0.207	1.85	0.112	545

The constancy of C at the lower pressures and its increase at the higher pressure, is in full accord with Equation 33, which states that C is proportional to $\sqrt{T_a}$. At very low pressures T_a must be equal to the tempera-

ture of the bulb (300° K.), just as it was at lower filament temperatures (see Table V). At higher pressures, however, where the hydrogen atoms recombine long before reaching the surface of the bulb, the heat evolved raises the temperature of the gas considerably. At the lower pressures, however, we may safely place $T_a = 300$, and we then find, by comparing Table VII with Equation 33:

$$(46) \qquad\qquad C = 0.0048 \sqrt{\overline{T_a}}$$

$$(47) \qquad\qquad \alpha_2 q_1 = 27300$$

This indicates, since by definition α_2 cannot exceed unity, that q_1 must be greater than 27300, or the heat of formation of 2 g. of hydrogen molecules, must be greater than 54600 calories.

If we compare (46) with the value $C = 0.112$ obtained for $P = 0.207$, we find $T_a = 545$. This is, as we shall see later, an entirely reasonable value.

2. Calculation of an Approximate Value of q_1.—If we can determine q_1, then by (47) we can calculate α_2. This will, in a certain measure, give us a check on our theory, for we know that α_2 cannot exceed unity.

To calculate q_1, we may make use of van't Hoff's equation

$$(48) \qquad\qquad d \ln K/dT = q/RT^2.$$

Here q is the heat of reaction at constant pressure since K is expressed in terms of partial pressures. The relation between q and q_1 is

$$(49) \qquad\qquad q = 2q_1 + RT.$$

If we use ordinary logarithms in place of naperian and substitute $R = 1.98$ calories, we may write Equation 48 as follows:

$$(50) \qquad\qquad d \log K/d(1/T) = - q/4.57$$

Since q varies so little with the temperature, we should, according to (50), obtain practically a straight line if we plot log K against $1/T$. The slope of the line would then be $q/4.57$, from which, by (49), we could calculate q_1. The slope of this line, however, would be the same if we plot the logarithm of any quantity proportional to K, instead of the logarithm of K itself. If we could assume that $T_a = T_2$ and that B and E were independent of the temperature, then we see from (35) that W'_D should be proportional to K. The values of q_1 that we might thus obtain by plotting log W^2_D would not be very accurate, because the above assumptions are not strictly correct. However, by using Equation 38, which gives us a relation between K and $W_{max.}$ we avoid these difficulties. By (32) and (34) we see that the factor BE is independent of T_a and T_2, so that K is strictly proportional to $W_{max.}$. Another important advantage in using this equation in determining q is that it does not involve a knowledge of the pressure within the bulb. It should be remembered that in the experiments at pressures of 10 mm., and above, the pressures

of the hydrogen as given in Table III were not measured while the filaments were heated, but were the pressures at which the bulbs were sealed at room temperature. The actual pressures in the bulbs during the experiment must have been considerably higher.[1]

It is clear, however, that this uncertainty in the pressure does not affect $W_{max.}$ nor the accuracy of K calculated from it by (38).

By examining Table III we see, as the pressure increases, that W_D increases to a maximum and then decreases. In the following table are the maximum values of W_D corresponding to various temperatures as given in Table III:

TABLE VIII.

T.	$W_{max.} = \sqrt{K/4BE}$.	T.	$W_{max.} = \sqrt{K/4BE}$.
2000	1.3	2500	12.5
2100	2.4	2600	16.7
2200	4.0	2700	22.7
2300	6.1	2800	30.0
2400	8.9		

By plotting 2 log $W_{max.}$ against 1/T we obtain in fact an almost perfectly straight line. From the slope of this line we calculate by (50) that $q = 85500$ calories. If we take $T_2 = 2400$ (the center of the range of temperatures in the experiments), we then find by (49)

$$(51) \qquad q_1 = 40300 \text{ calories.}$$

3. Calculation of α_2 and Lower Limit for E.—Substituting (51) in (47), we obtain

$$(52) \qquad \alpha_2 = 0.68.$$

This means that 68% of all the hydrogen molecules which strike the filament at high temperatures are absorbed by the filament.

If we substitute (51) in (34), we obtain

$$(53) \qquad E = 0.0046 \sqrt{T_a}/\alpha_1.$$

Since α_1 cannot exceed unity, E must be greater than $0.0046 \sqrt{T_a}$.

The coefficient α_1 gives the fraction of the hydrogen atoms striking the filament which dissolve in it or are absorbed by it. There is a strong probability that this fraction should be very close to unity, for there is every reason to think that hydrogen atoms would be absorbed by a metal surface much more readily than the molecules, and we have just seen that 68% of the latter are absorbed. We shall see, however, that there is another way of estimating the value of α_1.

4. Upper Limit for B.—According to (41), the limit which W_D approaches at high temperatures does not increase indefinitely with the pressure,

[1] In some of the experiments at a pressure of 100 mm. of hydrogen, the bulbs became so hot at the higher filament temperatures that the glass softened and sucked in slightly. In another experiment the bulb was immersed in water to keep it cool. This cooling did not have any perceptible effect on the value of W_D.

but ultimately becomes equal to $1/B$. By examining the results given in Table III for the higher pressures we see that W_D does not become constant even at the highest temperatures. This merely indicates that $1/B$ must be considerably greater than 117, the highest value of W_D observed. Or in other words, B must be less and probably much less than $1/117$, or 0.008.

5. Estimation of Ratio $E : B$.—According to (39) at low filament temperatures the fraction E/B should be equal to the pressure at which the maximum values of W_D occur. By referring to Table III we see that the highest values of W_D are observed at 50 mm. pressure. At the lower temperatures there is evidence that the maximum should lie at a pressure rather lower than 50 mm., although above 25 mm. The lack of experimental data at intermediate pressures makes it impossible to determine this pressure with much accuracy, but, making allowance for the heating of the gases in the bulb, it is probable that the true pressure at which the maximum W_D would occur is approximately 50 mm. From this we may conclude that $E/B = 50$.

6. Most Probable Values of E and α_1.—Since B must be considerably less than 0.008 and E/B is equal to 50, we may conclude that E must be considerably smaller than 50×0.008 or 0.40. We have already seen that E must be greater than $0.0046\ \sqrt{T_a}$. If we take $T_a = 2500$, E would have to be greater than 0.23. Therefore, E must lie between the comparatively narrow limits 0.23 and 0.40. There is, however, no reason for thinking that E must be greater than the lower limit, whereas there is evidence that it is considerably less than the upper limit. The most probable value of E is therefore obtained by placing $\alpha_1 = 1$ in (53). The value thus obtained is, however, almost identical with the value of C given by (46). We have seen from (43) that the mathematical treatment is much simplified if $C = E$. The small difference between 0.0048 and 0.0046 is well within the experimental error, so that for convenience we may place

$$(54) \qquad\qquad C = E = 0.0048\sqrt{T_a}.$$

7. Calculation of K from Low Pressure Data.

By the aid of these values of C and E we may calculate K from (43). We have seen that at high temperatures B is less than 0.008. Taking Equation 32 into consideration, we may thus conclude that B must always be less than $0.47/\sqrt{T_a}$. At very low pressures $T_a = 300$, so that under these conditions B might be as large as 0.027. At similarly low pressures $E = 0.083$. At a pressure $P = 0.207$ the term BP in (42) is less than 0.005 and may be neglected as compared to E in calculating F. We may thus calculate K from (43) without knowing the value of B, provided we use the data at pressures of 0.207 mm. and lower.

Table IX gives the results of such calculations from the data at the

lowest pressures. The values of K were calculated from the corresponding values of W_D by Equation 43, placing F = E. At 0.015 and 0.039 mm. pressure, T_a was placed equal to 300°, but at 0.207 mm. the values of T_a used in the calculation were those given in the next to the last column of the table.

TABLE IX.—DISSOCIATION CONSTANT OF HYDROGEN FROM LOW PRESSURE DATA.

	P = 0.015 mm.		P = 0.039 mm.		P = 0.207 mm.		
T.	W_D.	K.	W_D.	K.	W_D.	T_a.	K.
1800	0.007	58×10^{-6}	0.019	165×10^{-6}	0.068	317	501×10^{-6}
1900	0.013	210×10^{-6}	0.05	1.2×10^{-3}	0.15	329	2.1×10^{-3}
2000	0.025	870×10^{-6}	0.09	4.6×10^{-3}	0.27	347	7.5×10^{-3}
2100	0.048	3.9×10^{-3}	0.14	13×10^{-3}	0.45	372	25×10^{-3}
2200	0.085	17×10^{-3}	0.20	34×10^{-3}	0.65	400	64×10^{-3}
2300	0.112	42×10^{-3}	0.27	85×10^{-3}	0.90	430	160×10^{-3}
2400	0.139	112×10^{-3}	0.35	250×10^{-3}	1.17	460	380×10^{-3}
2500	0.169	......	0.40	1.07	1.48	500	1.17
2600	0.179	......	0.45	2.5	1.71	520	2.6
2700	0.180	......	0.47	......	1.84	540	......
2800	0.180	......	0.47	......	1.85	540	......
2900	0.180	......	0.47	......	1.85	540	......

The choice of $T_a = 300$, at the lowest pressures and the tabulated values at 0.207 mm., was based upon calculations similar to those previously employed in obtaining the temperature drop around a wire at low pressures. Thus we may calculate $\varphi_a - \varphi_1$ according to (12), substituting, however, $W_C + W_D$ in place of W_C. The data for the calculation, together with the results, are given in Table X. The values of $W_C + W_D$ were

TABLE X.

P.	λ.	S.	$W_C + W_D$ at 2800.	$\varphi_a - \varphi_1$.	b = 9 cm. T_a.
0.015	1.3 cm.	5.0	0.19	0.038	321
0.039	0.5	2.8	0.50	0.18	400
0.207	0.1	1.7	1,98	1.19	760
1.1	0.018	1.2	....	.....	...
4.4	0.004	1.0	....	.....	...

taken directly from Table II. In this calculation it is assumed that the hydrogen atoms leaving the filament all recombine to form molecules within a distance λ from the filament and that the heat thus liberated is carried to the bulb by ordinary heat conduction. This assumption, of course, cannot correspond exactly with the facts, but would lead to too high a value for T_a. It is therefore not surprising that the value $T_a = 760$ found at 0.207 mm. should be higher than the value $T_a = 545$ previously calculated by Equation 46 from the data of Table VII. Taking the value $T_a = 545$ as being correct and making a proportionate change in the corresponding values of $\varphi_a - \varphi_1$, we obtain the values of T_a given in Table IX. At the lower pressures the values of T_a are so close to 300° that it

is not worth while to take into account the departures from this temperature.

Before discussing the values of K of Table IX, we shall first attempt to calculate K from the data at pressures of 1.1 and 4.4 mm.

At these higher pressures there is more uncertainty as to the value that should be assigned to T_a. We may, however, adopt a method similar to that we employed to calculate T_a at a pressure of 0.207 mm. In the latter case at very high temperatures W_D became independent of T showing that the denominator in Equation 31 was practically zero. This led to Equation 40, from which we determined C and then by (33) we solved for T_a. At the pressures above 0.207 mm., however, W_D does not reach a constant value at the highest temperatures, although it shows a distinct tendency to do so. This is readily seen from Fig. 2, where log W_D has been plotted against 1/T for the data at pressures up to 4.4 mm. At the three lower pressures the curve becomes horizontal at the highest temperatures, but at 1.1 mm. the temperatures reached were not high enough to give the maximum value of W_D. From the degree of curvature or the change of slope, we may, however, estimate the value of C and in this way find T_a.

By substituting the value of K from (43) in the modified form of van't Hoff's Equation 50 and carrying out the indicated operations, we obtain (considering F as constant and $T_a = T_2$)

$$(55) \qquad \frac{2d \ln W_D}{d(1/T)} + \frac{F \, dW_D/d(1/T)}{P - FW_D} = -\frac{q}{R}.$$

If we let — U be the slope of the curve obtained by plotting log W_D against 1/T, then the first term of this equation becomes equal to -2×2.30 U and in the second term we find $dW_D/d(1/T) = -2.30$ U W_D. Substituting these values in the equation and solving for U we find (since R = 1.98)

$$(56) \qquad U = \frac{q}{4.57} \left(\frac{P - FW_D}{2P - FW_D} \right)$$

At lower temperatures FW_D becomes negligibly small compared to P, so that U approaches a definite limit U_o which is equal to 0.109 q. From this relation we can eliminate q from (56) and then solve for F, with the result:

$$(57) \qquad F = \frac{P}{W_D} \cdot \frac{U_o - U}{U_o - \frac{1}{2}U}$$

From the curve of Fig. 2 we find the slope of the curve at 2700° (1/T = 0.000370) to be 3760. We have already calculated that q is approximately 85000 and from this we obtain $U_o = 0.109$, q = 9300. Substituting these in (57), together with W_D(at 2700°) = 5.7 and P = 1.1, we obtain

$$F = 0.145.$$

According to (42) $F = BP + E$. The term BP is very small compared to E. We shall see that $B = 0.23/\sqrt{T_a}$ and have already found $E = 0.0048\ \sqrt{T_a}$. Substituting these values of B, E and F in (42) and solving for T_a, we find $T_a = 810$. From this we may now calculate T_a at all other filament temperatures, as we did at the lower pressures. Thus, taking $S = 1.2$ from Table X, we calculate $\varphi_a - \varphi_1$ from the corresponding values of W in Table II. If we use these values of $\varphi_a - \varphi_1$ we obtain temperatures for T_a that are much too high. However, by empirically taking $0.26\ (\varphi_a - \varphi_1)$ we find, at a filament temperature of $2700°$, the value $T_a = 810$ in agreement with the calculation above. The values of T_a for other filament temperatures are obtained from the corresponding values of $0.26\ (\varphi_a - \varphi_1)$. The results are recorded in Table XI.

Having thus determined T_a, it is easy to find F at other temperatures by Equations 42, 54 and the relation $B = 0.23/\sqrt{T_a}$. These results are given in the fourth column of Table XI. The values of K given in the fifth column were obtained from F and W_D by (43).

The results shown in Table XII were obtained by exactly similar methods from the data of the experiments at a pressure of 4.4 mm.

TABLE XI.

Pressure 1.1 mm.

T_1.	W_D.	T_a.	F.	K.
1800	0.11	350	0.106	0.28×10^{-3}
1900	0.24	360	0.107	1.45×10^{-3}
2000	0.54	390	0.110	7.8×10^{-3}
2100	0.94	430	0.113	25×10^{-3}
2200	1.45	490	0.119	68×10^{-3}
2300	2.22	560	0.125	0.19
2400	3.13	630	0.131	0.47
2500	4.19	720	0.137	1.18
2600	5.00	760	0.141	2.35
2700	5.7	810	0.145	4.7
2800	6.4	840	0.147	10.2
2900	7.0	870	0.149	33.0

TABLE XII.

Pressure 4.4 mm.

T_1.	W_D.	T_a.	F.	K.
1800	0.22	370	0.155	0.59×10^{-3}
1900	0.43	390	0.156	2.3×10^{-3}
2000	0.71	420	0.157	6.3×10^{-3}
2100	1.26	460	0.158	20×10^{-3}
2200	2.10	520	0.162	59×10^{-3}
2300	3.42	600	0.166	0.163
2400	4.95	690	0.172	0.38
2500	7.10	790	0.177	0.90
2600	9.80	900	0.183	2.10

8. Final Results for the Dissociation Constant K, and the Heat of Formation q_2.

From the experiments at low pressures we have been able to calculate the numerical value of C and E and obtain preliminary estimates of B and q. From the experiments at each of the pressures up to 4.4 mm. we have calculated the dissociation constant K at temperatures from 1800 to 2900° and have collected the results in Tables IX, XI and XII.

We are now in a position to test out the correctness of the theory which has been developed in this paper. The conditions which should be fulfilled by the values of K are

1. K should be independent of the pressure.

2. K should vary with the temperature according to van't Hoff's equation; that is, log K plotted against 1/T should give a straight line. The slope of this line determines the value of q.

3. The value of q thus found should agree with that obtained at higher pressures.

We see by examination of the tables that the values of K, found at the three higher pressures 0.207, 1.1 and 4.4 mm. are in excellent agreement. At 0.039 mm. the agreement is also good at the higher temperatures, but poorer at the lower temperatures. The results at 0.015 mm. are considerably lower than the others. On the whole, however, considering that these experiments extend over a range of pressures of nearly 300-fold, the agreement between the different values of K is surprisingly good.
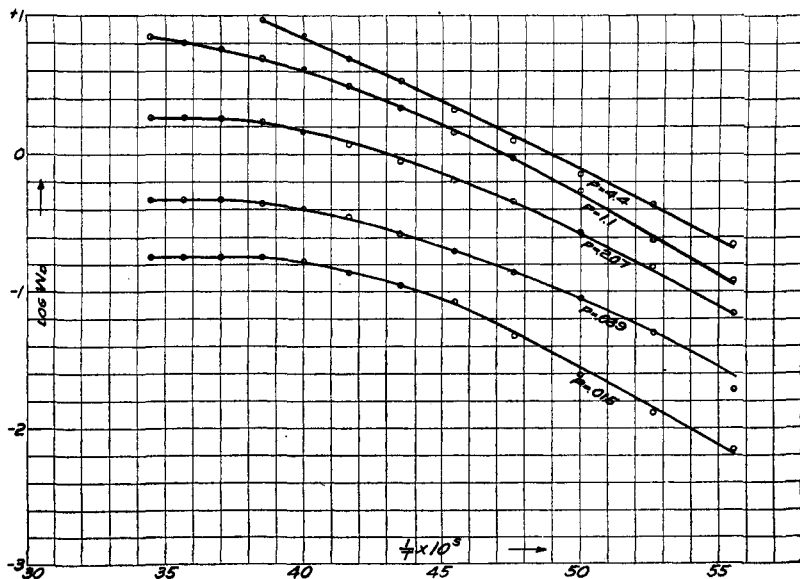

FIG. 2
EXPERIMENTS AT LOW PRESSURES

At the lowest pressures the correction for radiation from the filament is so large that errors from this cause, particularly at the lower temperatures, may perhaps account for the observed variation in K.

In Fig. 3 the values of log K have been plotted against $1/T$. In order to prevent the curves from overlapping, the successive curves have been displaced vertically by one unit; thus log K is plotted for P = 0.015 mm., while $(1 + \log K)$ has been plotted for P = 0.039 and $(2 + \log K)$ for

FIG. 3.
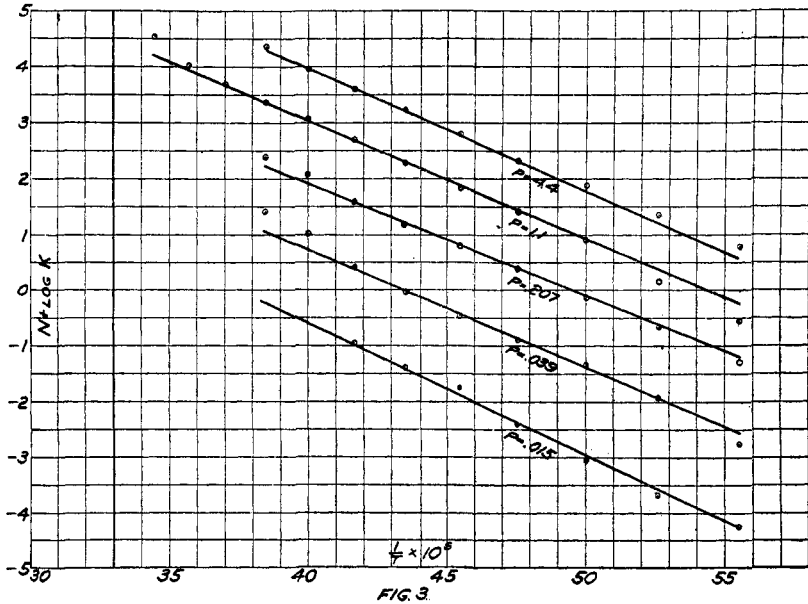
P = 0.207, etc. The curves should be parallel and equidistant straight lines. The fact that they are actually so very nearly straight and parallel is excellent evidence of the correctness of the theory, especially so, since the curves obtained by plotting W_D in a similar way (see Fig. 2) are by no means straight.

Before proceeding further we will now examine the data and choose the most probable values of q to be used in subsequent calculations.

The slope of the lines in Fig. 3 enables us to calculate q by Equation 50. The results thus obtained are given in Table XIII.

TABLE XIII.
q = Heat of Formation of Hydrogen at Constant Pressure.

Pressure.......	0.015	0.039	0.207	1.1	4.4
q............	108,000	96,000	91,500	100,000	97,000

We may also determine q from the experiments at higher pressures. For this purpose we may combine Equations 50 and 43. The difficulty arises that F is not strictly independent of the temperature, but varies

with it slightly and to an extent that depends on the relative magnitude of BP and E (see Equation 42). Since the variation of F with the temperature is small compared with that of W_D, we may proceed as follows in calculating q:

At the higher pressures now being considered, we may safely place $\sqrt{T/T_1} = 1$ in Equation 43. We shall also see that under the conditions of our experiments at higher pressures the term FW_D in the denominator of (43) can be neglected in comparison with P.

Equation 43 thus simplifies to

$$(58) \qquad\qquad K = F^2W^2{}_D/P.$$

If we substitute this value of K in (50) and carry out the indicated operations, we obtain

$$(59) \qquad \frac{2d \log W_D}{d(1/T)} + \frac{2d \log F}{d(1/T)} = -\frac{q}{4.57}$$

Now it can be readily shown by taking into account Equations 42, 32 and 34 that

$$(60) \qquad \frac{2d \log F}{d(1/T)} = \frac{T}{2.30} \frac{PB - E}{PB + E}.$$

This term is in the nature of a correction term. The first term of (59) is obtained directly by plotting $\log W_D$ against $1/T$. To calculate q we may therefore transform (59) to the following:

$$(61) \qquad q = -9.14 \frac{d \log W_D}{d(1/T)} - 1.98\, T \frac{PB - E}{PB + E}.$$

It is seen that the correction term can never exceed $1.98\ T$.

Curves were prepared from the data of Table III by plotting $\log W_D$ against $1/T$. At the higher pressures these curves were very nearly straight lines. The slopes of these lines, multiplied by 9.14, gives the quantities represented by the first term of the second number of Equation 61. The values thus found are given in the second column of Table XIV.

TABLE XIV.

Pressure.	—9.14 × slope.	$-1.98T\dfrac{PB - E}{PB + E}.$	$q.$
10	+79400	+4000	83400
25	80200	+2000	82200
50	81000	0	81000
100	96200	—2000	94200
200	107600	—3600	104000
750	91400	—5200	86200

To calculate the correction term, the relative values of B and E must be known. We shall see that B is equal to $0.23/\sqrt{T_a}$. If we consider that $T_a = T_2$ and thus calculate B for a mean temperature of 3000, we obtain $B = 0.005$. Similarly, we find from (54) $E = 0.26$. With these values

we may calculate the correction term corresponding to the second term of the second member of (61). The results are shown in the third column of Table XIV.

The resulting values for the heat of formation are given in the fourth column. When these are compared with the values obtained at low pressures (given in Table XIII), it is seen that the agreement is reasonably good.

Averaging all the results gives $q = 93000$. It is felt, however, that a properly weighted mean is closer to 90000. We shall therefore adopt for our final value of q.

$$(62) \qquad q = 90000 \text{ calories.}$$

This is the heat of formation of 2 grams of hydrogen molecules from atoms at constant pressure and at 3000° K. At constant volume we obtain (at 3000° K.)

$$(63) \qquad q_2 = 84000 \text{ calories.}$$

Substituting the above value for q in (50) and integrating, neglecting the small variation of q with the temperature, we find

$$(64) \qquad \log K = a - \frac{90000}{4.57T} = a - \frac{19700}{T}.$$

To determine the coefficient a we need to know the value of K at some one temperature. Let us choose 2300° as the temperature at which the low pressure results for K are most nearly free from experimental error. At higher temperatures the term FW_D in the denominator of (43) introduces some uncertainty, whereas at lower temperatures W_D becomes too small compared with W_C (see Tables II and III). By referring to Tables IX, XI, XII, we thus obtain for $T_2 = 2300$:

Pressure	0.015	0.039	0.207	1.1	4.4
K	0.042	0.085	0.160	0.193	0.163

The mean of these is $K = 0.12$, but since the results at the lowest pressures are more subject to error a more probable value is thought to be

$$K = 0.16 \text{ at } T_2 = 2300.$$

Substituting this in (64), we find

$$a = 7.77.$$

Our final equation for the dissociation constant of hydrogen is

$$(65) \qquad \log K = 7.77 - 19700/T.$$

The values of K corresponding to various values of T as calculated from this equation, are given in the second column of Table XV. From these, the corresponding degree of dissociation at atmospheric pressure and at 1 mm. pressure were calculated by solving the equation:

$$(66) \qquad x^2/(1 - x) = K/P$$

where x is the degree of dissociation and is equal to

(67) $x = p_1/\mathrm{P}$.

The results of these calculations are given in the third and fourth columns of Table XV.

TABLE XV.

Dissociation Constant K (mm. pressure) and Degree of Dissociation x.

T.	K.	x. P = 760 mm.	P = 1 mm.	T.	K.	x. P = 760 mm.	P = 1 mm.
1200	0.0023 × 10⁻⁸	0.000002	0.00005	2500	0.78	0.0315	0.575
1300	0.042 × 10⁻⁸	0.000007	0.0002	2600	1.55	0.044	0.692
1400	0.48 × 10⁻⁸	0.000025	0.0007	2700	3.0	0.061	0.79
1500	4.3 × 10⁻⁸	0.000075	0.0021	2800	5.4	0.081	0.86
1600	30.0 × 10⁻⁸	0.00020	0.0055	2900	9.3	0.105	0.91
1700	0.00015		0.00044	0.012	3000	16.2	0.13	0.94
1800	0.00066	0.00093	0.025	3100	26.0	0.17	0.96
1900	0.0025	0.0018	0.049	3200	42.0	0.21	0.98
2000	0.0083	0.0033	0.087	3300	63.0	0.25	0.985
2100	0.024	0.0056	0.143	3400	93.0	0.29	0.989
2200	0.065	0.0092	0.224	3500	138	0.34	0.993
2300	0.16	0.0145	0.328	4000	710	0.61	0.999
2400	0.36	0.0216	0.447				

9. Test of the Theory.

By examining Equations 31 to 34, we see that, by a knowledge of the values of K, q, T_a, B, C, and E, we should be able to calculate W_D for any temperature and pressure. By comparing the results of these calculations with the observations (Table III), we are enabled to test the validity of the assumptions made.

Before making such calculations it is necessary to determine the numerical value of the coefficient B. We have already seen that the maximum value of W_D which we have denoted by $W_{max.}$ is not subject to error through the uncertainty in the actual pressures within the bulb. Equation 44 is therefore particularly well adapted for the calculation of B.

By substituting the values of $W_{max.}$ from Table VIII in Equation 44, together with the corresponding values of K and E and solving the resulting equations for B, the average result is found to be

(68) $B = 0.23/\sqrt{T_a}$.

As a test of the theory from which (44) was derived, we may now employ this value of B to calculate $W_{max.}$ and by Equation 45 to calculate P′, using the values of K from Table XV and the values of E given by (54). For these calculations T_a was taken equal to T_2, since the pressures at which W_D reaches a maximum are so high that this must be approximately true. Moreover, the value of $W_{max.}$ is only dependent on T_a to a very slight degree.

TABLE XVI.

T.	W_{max}.		P'.	
	Calculated.	Observed.	Calculated.	Observed.
2000	1.36	1.4	43	25
2200	3.85	4.0	48	50
2400	8.62	8.9	54	50
2600	17.6	16.7	63	50
2800	30.4	30.0	76	50
3000	48.3	48.0	94	50
3200	69.4	75.0	120	100
3400	92.5	117.0	152	100

The calculated values of W_{max}. and P' thus obtained are placed in Table XVI side by side with the experimentally found figures.

The agreement in the values of W_{max}. is surprisingly good, especially when it is remembered that the values of K and E, which were used in the calculation, were obtained solely from the experiments at low pressures. The closeness of the agreement over such a wide range of temperature is strong evidence of the correctness of the value of q that was adopted in calculating K.

The discrepancy at the highest temperatures may be explained, I think, as being due to experimental errors caused by electrical leakage through the gas. This effect was noticed strongly at the highest temperatures in the experiment at 4.4 mm. pressure. In this case the discharge through the gas entirely prevented measurements above about 2800°, since the voltage actually decreased as the current was raised. Since the resistance was observed in all cases it was possible to show that this effect was not very serious in the other experiments. It is possible, however, that this effect in an incipient stage may have slightly increased the values of W_D at the highest temperatures, at pressures below 200 mm.

In future experiments this effect could be avoided by using wires of larger diameter so that the potential drop along the wire would be insufficient to ionize the gas.

The agreement between the calculated and observed values of P' in Table XVI is also satisfactory. The calculated gradual increase in P' with increasing temperature is in full accord with the observations.

It must be remembered that the observed pressures were those at which the bulbs were sealed off and that the actual pressures in the bulbs while the filaments were heated must have been much higher. The fact that the calculated values are larger than the observed therefore adds support to the theory.

The value of B obtained above, (68), enables us to calculate the diffusion coefficient D by Equation 32. The shape factor S which is involved in this equation may be calculated from (7), taking $d = 0.00706$ cm. and $b = 3.7$ cm. (see Table V). This gives S = 1.01. By substituting this

in (32), together with $q_1 = 42000$ and the value of B from (68), we find

(69) $D_o = 9.6$ cm^2. per sec.

This is the value of the diffusion coefficient at $0°$ C. as obtained by extrapolation downwards from high temperatures by Equation 29. At higher temperatures and at atmospheric pressure, we thus obtain from the same equation, together with (69):

(70) $D = 2.14 \times 10^{-3} \, T^{3/2}$

In the "paper of 1912" D was calculated to be equal to

(71) $D = \dfrac{0.514 \times 10^{-3} \, T^{3/2}}{1 + 77/T}$.

This result was obtained, according to the kinetic theory, on the assumption that the free path of hydrogen atoms and hydrogen molecules are the same. At high temperatures the second term in the denominator of (71) becomes negligible and we thus see that the present results show that the diffusion coefficient of hydrogen atoms through molecular hydrogen is 4.2 times as great as had been previously calculated.

A very thorough test of the theory is afforded by a comparison of the values of W_D calculated according to the theory, with those determined experimentally. In Tables XVII and XVIII the observed and calculated

TABLE XVII.

Comparison of Observed and Calculated Values of W_D.

Low Pressures.

T_1.	P = 0.015 mm. W_D.		P = 0.039 mm. W_D.		P = 0.207 mm. W_D.		P = 1.1 mm. W_D.		P = 4.4 mm. W_D.	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
1800	0.007	0.022	0.019	0.037	0.068	0.083	0.11	0.17	0.22	0.24
2000	0.025	0.066	0.09	0.116	0.27	0.27	0.54	0.58	0.71	0.85
2200	0.085	0.124	0.20	0.25	0.65	0.64	1.45	1.44	2.10	2.31
2400	0.139	0.162	0.35	0.38	1.17	1.12	3.13	2.82	4.95	4.95
2600	0.179	0.176	0.45	0.44	1.71	1.49	5.00	4.4	9.8	9.0
2800	0.180	0.179	0.47	0.46	1.85	1.69	6.4	5.8	....	....

TABLE XVIII.

Comparison of Observed and Calculated Values of W_D.

Higher Pressures.

T_1.	P = 10 mm.		P = 25.		P = 50.		P = 100.		P = 200.		P = 750.	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
1800	...	0.31	0.41	0.38	...	0.38	0.33	0.35	0.23	0.28	0.19	0.17
2000	1.0	1.02	1.3	1.3	...	1.35	1.1	1.3	0.67	1.04	0.64	0.62
2200	2.7	2.8	3.2	3.6	4.0	3.8	2.8	3.5	1.70	2.98	1.8	1.8
2400	5.8	6.1	7.1	8.1	8.9	8.7	6.5	8.2	4.0	7.1	4.2	4.4
2600	10.8	11.2	13.5	15.4	16.7	17.2	12.5	16.7	9.0	14.6	8.8	9.2
2800	19.3	17.2	24.0	25.2	30.0	29.7	25.0	30.0	20.0	27.0	17.0	17.3
3000	30.0	23.0	38.6	37.0	48.0	45.5	45.0	48.5	40.0	44.9	29.0	30.0
3200	46.0	26.5	58.0	47.2	74.0	62.0	75.0	69.3	68.0	67.0	47	47.5
3400	....	29.0	.....	54.0	107	75.5	117	90.3	97.0	91.0	69	70.7

values have been placed side by side. The "observed" values are taken directly from Table III of Part I. The calculated values were obtained by solving Equation 43 for W_D after substituting it in the numerical values of K, F, T_a and T_2.

For this purpose the values of K were taken from Table XV, which was obtained directly from Equation 65. At 0.015 and 0.039 mm. pressure T_a was taken to be 300° K., whereas at pressures from 0.207 to 4.4 mm. the values of T_a used in the calculations were those given in Tables IX, XI and XII. At pressures of 10 mm. and more, T_a was taken equal to T_2. The coefficient F was calculated for each temperature and pressure by substituting the values of B and E from (68) and (54) into Equation 42.

The values of W_D have thus been calculated directly from the dissociation constant, the diffusion coefficient, and the coefficients α_1 and α_2. An examination of Tables XVII and XVIII shows that the agreement is on the whole excellent; so good, in fact, that it would seem to show not only that we are dealing with a real dissociation of hydrogen into atoms, but that our theory of the mechanism of the process is substantially correct.

10. General Discussion.

The theory which has been used in the present paper was only developed after several attempts had been made to calculate the degree of dissociation by other methods. Each of these other methods, however, seemed to lead to conclusions which could only be reconciled with the experimental data by making many improbable and arbitrary assumptions. These difficulties disappear, however, when we adopt the present theory of the mechanism of the reaction. A brief discussion of the unsuccessful hypotheses will enable us to see that they are untenable.

In attempting to analyze the probable mechanism of the reaction, three possibilities suggest themselves:

1. The dissociation occurs in the heated gas around the wire.

2. The dissociation occurs *on the surface* of the wire by the impact of the molecules and atoms against the surface.

3. The dissociation occurs in the wire or in a surface layer where equilibrium prevails.

The first hypothesis assumes that the tungsten does not act catalytically on the reaction, and is therefore in itself very improbable. Moreover, it leads to conclusions irreconcilable with the experiments at low pressures, where, in a sense, there is no heated gas around the wire.

The second hypothesis seemed at first sight to have much in its favor, and by its aid it was possible to estimate an upper and lower limit to the degree of dissociation.

Whatever the mechanism of the reaction on, or in, the wire, it was possible to analyze the process as follows:

Let ϵ_2 represent, out of all the hydrogen molecules which strike the

wire, that fraction which becomes dissociated into atoms. Similarly, ϵ_1 represents, out of all the atoms that strike the wire, that fraction which recombines to form molecules. We may consider that the reaction actually observed is simply the difference between these opposite reactions. It is clear that neither ϵ_1 nor ϵ_2 can ever exceed unity.

For further progress, it is necessary to make some assumptions regarding these coefficients. It is evident that either ϵ_1 or ϵ_2 or both must vary with the temperature. The simplest assumption is that they are independent of the pressure. By applying Equation 5 we then readily find that the condition for equilibrium is

$$p_1' = \sqrt{2} \ (\epsilon_2/\epsilon_1) \ p_2'.$$

Since ϵ_1 cannot exceed unity, this gives us a lower limit for the degree of dissociation, provided we can estimate ϵ_2. By assuming a value for the heat of reaction it is possible to calculate ϵ_2 from W_D by an equation similar to (16). In this way it was concluded that the degree of dissociation at 3200° K. and atmospheric pressure must *exceed* 5%.[1]

In order, however, to account for the manner in which W_D had been observed to vary with temperature and pressure, it was necessary that ϵ_2 should increase with the temperature up to a limiting value of 0.68, but at the same time should decrease in a complicated way as the pressure increased. Similarly, ϵ_1 would have to increase with the pressure and decrease with increasing temperature. This theory gave no clue as to the cause of the variations of ϵ_1 and ϵ_2.

The fact that ϵ_1 and ϵ_2 were found to be such complicated functions of both temperature and pressure suggested the third hypothesis; namely, that the reaction does not occur at the surface, but that there is an actual equilibrium in the wire which determines the velocity of the reaction. This view was strengthened by the fact that ϵ_1 and ϵ_2 varied with the temperature and pressure in the way that would be expected of the partial pressures of two gases in equilibrium.

On the basis of the third hypothesis, the coefficients ϵ_1 and ϵ_2 lose their fundamental significance, while the coefficients α_1 and α_2 take their place. The fact that the latter coefficients prove to be constant and practically equal to unity over such wide ranges of temperature and pressure is excellent evidence that, in the present theory, we are dealing with the factors that fundamentally determine the velocity of the reaction.

By means of our present theory we are enabled to calculate ϵ_1 and ϵ_2 at any temperature and pressure.

Let us consider the case that hydrogen molecules at pressure p_2 strike the wire, but that the hydrogen atoms formed do not again return to the wire. Then $\epsilon_2 m_2$ represents the rate of formation of atomic hydrogen.

[1] Table XV gives 21%.

This, however, is equal to the quantity we have called ω (see Equation 17): thus,

$$(72) \qquad \omega_2 = \epsilon_2 m_2.$$

Substituting this, together with the value of m_2 (by Equation 5) in (26), we obtain, after placing $\alpha_1 = \sqrt{2}\alpha_2 = 1$

$$(73) \qquad K = \sqrt{\frac{T_2}{T_a}} \frac{2 p_2 \epsilon_2^2}{1 - \sqrt{2}\ \epsilon_2}$$

This equation shows clearly that at low temperatures, where K is small, ϵ_2 is inversely proportional to $\sqrt{p_2}$, whereas at higher temperatures it approaches a limiting value of 0.71. Thus the variation of ϵ_2 with the temperature and pressure which it was necessary to assume when working with the second hypothesis, receives a complete explanation by the third hypothesis.

In a similar way, the value of ϵ_1 may be calculated for the case that the wire is surrounded by atomic hydrogen, while the partial pressure of molecular hydrogen is zero. In this case

$$(74) \qquad \omega_1 = -\ \epsilon_1 m_1$$

and we thus find, from (26)

$$(75) \qquad K = \sqrt{\frac{T_2}{T_a}} \frac{(1 - \epsilon_1)^2 p_1}{\epsilon_1}.$$

This shows that at low temperatures ϵ_1 must be constant and equal to unity, whereas at high temperatures it decreases and becomes proportional to the pressure. Thus again, the third hypothesis offers a simple explanation of the difficulty encountered in applying the second hypothesis.

It is evident that ϵ_1 and ϵ_2 completely lose their significance when both hydrogen molecules and atoms are present around the wire. We cannot profitably look upon the reaction as being the difference between two opposing reactions taking place *upon the surface*.

In fact, the velocity of the reaction does not follow Gulberg and Waage's Mass Law in the ordinary sense. Neither do diffusion phenomena (at least at low pressures) seem to have any effect on the reaction velocity. The velocity is determined simply by the rate at which the molecules and atoms strike the surface of the wire and the *equilibrium concentrations* of atomic and molecular hydrogen within the wire.

Effect of Bulb Temperature.—In studying chemical reactions at low pressures it has been pointed out[1] that the temperature of the filament and that of the gas molecules striking it can be varied independently of one another. By changing the bulb temperature, the velocity (and internal energy) of the hydrogen molecules striking the filament can be varied over a wide range. If the reaction takes place entirely on the surface in accordance with the second hypothesis, we should expect that the

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[1] Langmuir, THIS JOURNAL, **35**, 105 (1913).

relative velocities of the hydrogen molecules and the tungsten atoms with which they collide, would determine the velocity of the reaction. Because of the small mass of the hydrogen molecules it happens that the average velocity of hydrogen molecules at room temperature or even liquid air temperatures, is much greater than that of tungsten atoms at 3500°. Therefore, the amount of impact between the hydrogen molecules and tungsten atoms depends vastly more on the bulb temperature than it does on the temperature of the filament. In case the impact determines the reaction velocity, we see that the latter should be greatly affected by bulb temperature.

On the other hand, if the reaction takes place in the metal in accord with the third hypothesis, we should not expect the bulb temperature to materially affect the velocity of the reaction. It is to be expected, however, that the bulb temperature might have a slight effect on the coefficient α_2 and thus slightly change the velocity of the reaction.

Some experiments were undertaken to determine whether cooling the bulb in liquid air had any effect on the values of W_D obtained at low pressures (from 0.01 to 0.1 mm.). The results showed conclusively that the bulb temperature was without material effect on the velocity of the reaction. This fact affords additional evidence that the velocity depends primarily on some equilibrium condition within the surface of the wire.

Specific Heat of Hydrogen at High Temperatures.—When hydrogen is heated to a temperature at which appreciable dissociation occurs, the heat absorbed by the reaction may be very large compared with that which would be required if there were no dissociation. We should therefore expect a very large increase in the apparent specific heat of hydrogen at very high temperatures. In Part I we have already briefly discussed Pier and Bjerrum's experiments on the specific heat of hydrogen by the explosion method. We saw that the earlier calculations of the dissociation of hydrogen (paper of 1912) led to apparent specific heats too high to reconcile with the results of the explosion method, unless we assumed that equilibrium was not reached during the short period of the explosion.

In order to compare our present results with the data of the explosion method, we shall calculate the increase in apparent specific heat caused by the dissociation as given in Table XV.

If we heat a gram molecule of hydrogen from 0° K. to T, the number of gram molecules of hydrogen dissociated will be $x/(2-x)$ where x is the degree of dissociation at the temperature T, x being expressed in terms of partial pressures according to (67).

The heat absorbed by this dissociation will be

$$q_2 \; x/(2-x).$$

In comparison with this we may neglect the increase in specific heat

due to the difference in the specific heat of the molecular hydrogen and that of the atomic hydrogen formed (2 × 2.98).

Pier[1] gives for the *mean* specific heat of hydrogen from room temperature up to $t°$ C.

$$C_v = 4.70 + 0.00045t$$

or in absolute temperatures

$$C_v = 4.578 + 0.00045T$$

The dissociation at higher temperatures would cause an increase in this mean specific heat amounting to

$$\frac{q_2}{T - 273} \cdot \frac{x}{(2 - x)}.$$

In Table XIX are given the mean specific heats for a few temperatures, as calculated from Pier's formula, together with those calculated by taking into account the increase due to dissociation. For this calculation the values of x were taken from Table XV and q_2 was taken to be 84000 calories.

TABLE XIX.

T.	C_v. Pier.	Apparent C_v (considering dissociation).	Ratio.
1600	5.30	5.306	1.0012
1800	5.39	5.41	1.0047
2000	5.48	5.56	1.015
2200	5.57	5.77	1.036
2400	5.66	6.09	1.078
2600	5.75	6.56	1.14
2800	5.84	7.25	1.24
3000	5.93	8.09	1.36
3200	6.02	9.40	1.56

Siegel, in a recent paper,[2] discusses in detail the errors of the explosion method. He points out that, owing to a faulty method of calculation, the temperatures given by Bjerrum are considerably too high, in some cases as much as 400°. He then shows that Bjerrum's experiments exhibit certain discrepancies which could be readily explained by assuming a dissociation of the hydrogen. He then says (pages 649–50):

"In order to reconcile Langmuir's results with those of the explosion method, one must assume that in the calculations thus far, the capacity of the system (in the explosion chamber), that is, $C_{H_2O} + MC_{H_2}$, has been taken about 30% too high.

"Such an assumption......is impossible. However, if we take for the heat of dissociation of hydrogen, the value 140000 calories instead of the 131000 calories given by Langmuir, we then find by the Nernst approximation formula:

$$\log K = Q/4.57 T + \Sigma\nu . 1.75 \log T + \Sigma\nu C$$

that at 2850° and atmospheric pressure the dissociation is about 11%, which is the value given by Langmuir for 2700°. With this assumption it can be shown that the heat

[1] *Z. Elektrochem.*, **15**, 536 (1909).
[2] *Z. phys. Chem.*, **87**, 641 (1914).

capacity of the system at 2850° would be 13% less than previously taken. This result is no longer irreconcilable with the other results of the explosion method. However, I am of the opinion that the heat of dissociation of hydrogen should be at least 150000 calories. On the other hand, it should be emphasized that from my experiments it is not possible to determine with certainty whether or not hydrogen is dissociated at all. And—what is here very significant—by the assumption of such a dissociation, the observed anomalies in the heat losses do not find a sufficient explanation, for the anomalies also occur even at temperatures as low as 2300–2400°, where surely the dissociation of hydrogen can play no part."

Thus, according to Siegel, a dissociation as large as 11% at 2850° can be reconciled with the explosion experiments. If we refer to Table XV we see that we have found the dissociation at 2850° to be 9.2% at atmospheric pressure. This should be ample to account for the anomalies found by Siegel.

Siegel's objection that the dissociation of hydrogen could not account for the discrepancies observed at 2300–2400°, fails to apply to the present results. Siegel does not state his reasons for believing that the heat of dissociation is at least 150000 calories. Such a high value is at complete variance with all the experiments described in the present paper. With the value 84000 calories which we have adopted, the dissociation does not fall off nearly so rapidly at lower temperatures. This is readily seen from the following table:

T.	Siegel. $q = 150000$.		Langmuir. $q = 84000$.	
	x.	$\Delta C/C$.	x.	$\Delta C/C$.
2850	0.11	13.0%	0.092	11.0%
2300	0.0049	0.9%	0.014	2.6%

The figures in the second column represent the degree of dissociation calculated from Siegel's data, while those in the fourth column are taken from Table XV. The third and fifth columns give the increase in the "heat capacity of the system" $H_2O + MH_2$ referred to by Siegel. Thus, Siegel calculates that 11% dissociation at 2850° would increase the capacity by 13%. The other figures were obtained from this by proportion, taking into account, however, the effect of the temperature as was done in the preparation of Table XIX.

Thus, on Siegel's assumption of a high heat of dissociation, the effect of the dissociation is to increase the heat capacity at 2850° by 13%, but only by 0.9% at 2300°. It is evidently for this reason that he says that "surely the dissociation can play no part" at such low temperatures as 2300°.

Taking the values for the dissociation as calculated in the present paper, we find that the heat capacity would be increased 11% at 2850 and 2.6% at 2300°, an amount probably sufficient to account for the anomalies found by Siegel.

Thus, the explosion method gives additional evidence for the dissociation of hydrogen and confirms the substantial accuracy of the results.

11. Rate of Formation of Active Hydrogen.

It has been shown[1] that the disappearance of hydrogen in contact with a heated filament is caused by the deposition of atomic hydrogen on the bulb.

The present theory enables us to calculate the rate at which atomic hydrogen should be formed in contact with a tungsten wire. The rate at which atomic hydrogen is deposited on the bulb should naturally be less than that at which it is formed by the wire.

In the paper referred to, it was stated that the disappearance of hydrogen "was often quite marked when the wire was at a temperature as low as 1300° K.," but very few quantitative data at such low temperatures were given. By looking through the original notes of these experiments, I find that at low temperatures the highest rates of disappearance were as follows:

Experiment 160. Filament temperature 1200° K. In seven minutes the pressure fell from 16.4 to 15.6 microns, although at 1100° K. no decrease in pressure could be observed. The surface of the filament was 0.15 sq. cm. The rate of disappearance was 1.4 cubic millimeters of H_2 per minute per sq. cm. of surface.

Experiment 173. With the filament at 1270° the pressure decreased from 16.2 to 15.0 microns in three minutes. The surface of the filament was the same as before. This corresponds to a rate of 3.7 cubic mm. per minute per sq. cm.

In each case the hydrogen continued to disappear at a gradually decreasing rate for a half-hour or more. Because of this fatigue effect we shall here consider only the initial rates.

Let us now calculate the rate at which atomic hydrogen should have been produced by wires at these temperatures. In Equation 26 we may place $p_1 = 0$; $p_2 = P$ and may neglect the second term of the denominator at these low pressures and temperatures. Since the factor $\sqrt{2\pi R}$ is equal to 17.15 and α_1 is unity, we thus obtain

$$(76) \qquad K = 325. \sqrt{T_a T_1}\ \omega^2/P.$$

In this equation ω is the rate of dissociation of hydrogen in grams per second per sq. cm. of filament surface. Let R be the rate of dissociation of molecular hydrogen in cubic mm. per sq. cm. per minute. We then have

$$(77) \qquad R = 7.2 \times 10^8\ \omega$$

whence from (76), by placing $T_a = 300$

$$(78) \qquad R = 9.6 \times 10^6\ \sqrt{KP}\ T^{-1/4}.$$

[1] THIS JOURNAL, **34**, 1310 (1912).

Substituting in this the values of K from Table XV and taking the values of P and T given above, we obtain the values given below as "R cal." For comparison these are placed side by side with those found by experiment.

	T.	R calc.	R obs.
Expt. 160................	1200	9.8	1.4
Expt. 173................	1270	27.4	3.7

These results indicate that under the most favorable conditions realized in the experiment, only about one-seventh of the hydrogen dissociated was deposited as "active hydrogen" on the bulb. In the great majority of cases the fatigue effect made the observed rate of clean-up much slower.

The fact that the observed rates are less than the calculated, yet of the same order of magnitude, is a satisfactory confirmation of the theory that the disappearance and activation of hydrogen are caused by its dissociation into atoms.

There is thus quantitative evidence of the dissociation of hydrogen over the whole range of temperature from 1200° to 3500°. The substantial agreement of the calculated and observed results over such a wide range proves that the value we have found for the heat of dissociation, namely, 84000 calories, cannot be far from correct.[1]

12. Experiments with Mixtures of Hydrogen and Nitrogen.

Some experiments have been made to determine the heat losses from tungsten wires in mixtures of nitrogen and hydrogen. The wire was the same as that previously used in the experiments with hydrogen. The bulbs, after being exhausted in the usual way, were filled with the mixture of gases, the *total* pressure in each case being 600 mm. Mixtures containing 1.25, 3.0, 10.0 and 30% of hydrogen were used. The results given in Table XX were obtained by subtracting from the observed watts per centimeter, the energy radiated (W_R). These figures are directly comparable with those given in Table I of Part I.

TABLE XX.

Diam. of wire 0.00706 cm.   Total pressure 600 mm.

T.	W_R	Watts per cm., carried by mixture.				W_C in N_2. $S = 1.36$.	W_C in H_2. $S = 1.18$.
		$p_0 = 7.5$ mm.	$p_0 = 18$ mm.	$p_0 = 60$ mm.	$p_0 = 180$ mm.		
1800	0.38	1.45	1.52	2.06	....	1.40	7.4
2000	0.65	1.75	1.85	2.40	....	1.70	9.0
2200	1.06	2.10	2.30	2.86	4.5	2.02	10.7
2400	1.60	2.60	2.95	3.70	5.8	2.36	12.6
2600	2.33	3.35	3.70	4.92	7.9	2.75	14.5
2800	3.30	4.23	4.70	6.78	11.4	3.14	16.8
3000	4.46	5.15	6.20	9.30	....	3.58	19.1

[1] For example, it now becomes impossible to reconcile our experiments with the value $q_2 = 63000$ calculated according to the method of Bohr, *Phil. Mag.*, **26**, 863 (1913); **27**, 188 (1914).

TABLE XXI.

Observed and Calculated Values of W_D.

T.	$p_o = 7.5$ mm.		$p_o = 18$ mm.		$p_o = 60$ mm.		$p_o = 180$ mm.	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
1800	—0.01	....	—0.03	....	+0.08	....	...	...
2000	+0.06	0.03	—0.05	0.04	0.00	0.08	...	...
2200	0.00	0.08	+0.05	0.13	0.00	0.24	—0.1	0.4
2400	+0.15	0.20	+0.33	0.32	0.36	0.60	+0.4	1.0
2600	0.45	0.41	0.60	0.65	1.00	1.23	1.6	2.2
2800	0.93	0.72	1.18	1.20	2.30	2.30	4.2	4.2
3000	1.37	1.10	2.20	1.92	4.18	3.96	...	...

To obtain the heat carried from the wire by the dissociation, it is necessary to subtract W_C. In the last two columns of Table XX are the calculated values of W_C for pure nitrogen and hydrogen at pressures of 600 mm. These are obtained by multiplying S by the values of $\varphi_2 - \varphi_1$ given in Tables III and IV. For the mixture of hydrogen and nitrogen W_C was found by interpolating linearly between the values calculated for the pure gases. By subtracting these results from the watts per cm. of Table XX the values of W_D given in Table XXI as "cal." were obtained. The smallness of the differences at lower temperatures shows that the heat carried by convection in mixtures of gases is approximately an additive function of the partial pressures (the total pressure remaining constant).

To calculate the values of W_D for mixtures of gases according to our theory we need to start from Equation 27. From this we can eliminate p_1 and p_2 as before, by means of Equation 30. The significance of P and p_2, however, is now somewhat different, so we must proceed from this point in a slightly different way. In Equation 30, P is the total pressure, and p_1 the partial pressure of atomic hydrogen. We then have

$$(79) \qquad p_2 = p_o - \tfrac{1}{2}p_1$$

where p_o is the partial pressure of molecular hydrogen before dissociation occurs and p_2 is the partial pressure of molecular hydrogen after dissociation.

In the present case we may place $T_a = T_2$; P = 600, S = 1.34, and $q_1 = 42000$. From (30) we thus find

$$(80) \qquad p_1 = 946 W_D/(D_o \sqrt{T}).$$

Combining (79) and (80) with (27), we find

$$(81) \qquad K = \frac{W^2{}_D \, (946/D_o \sqrt{T} + E)^2}{p_o - W_D \, (473/D_o \sqrt{T} + E)}$$

where E is given by (34).

By trial it was found that (81) gives the best agreement between the observed and calculated values of W_D if D_o is placed equal to 2.5.

Calculating E by (54) it is evident that E is negligible compared to

$473/2.5\sqrt{T}$ over the whole range of temperatures covered by the experiments. Equation 81 thus simplifies to

$$(82) \qquad W_D = \sqrt{\frac{Kp_0 T}{144000}} \times \sqrt{1 - \frac{190}{p_0 \sqrt{T}}} W_D.$$

This quadratic equation can be conveniently solved for W_D by using a series of approximations, since the second radical is always close to unity. In this way, by taking K from Table XV, the values of W_D for different temperatures and partial pressures have been calculated. The results are placed side by side with the observed values in Table XXI.

The agreement is entirely satisfactory, considering the crudeness of some of the assumptions made.

The theory receives additional confirmation through the fact that the observed values of W_D increase in proportion to the square root of the partial pressure as demanded by the theory, whereas at lower temperatures the observed values of W_C increase linearly with the partial pressure.

From the value of D_0 we may conclude by (29) that the diffusion coefficient of hydrogen atoms through nitrogen at high temperatures and atmospheric pressure is

$$(83) \qquad\qquad D = 2.5 \, (T_a/273)^{3/2}.$$

Comparing this with (69) we see that the ratio of the diffusion coefficient of hydrogen atoms through hydrogen to that through nitrogen is $9.6/2.5 = 3.84$.

If we calculate the free path of hydrogen atoms through nitrogen according to the principles of the kinetic theory, using Equations 20 and 21 on page 865 of the "paper of 1912," we obtain

$$(84) \qquad\qquad D_{cal.} = 2.16 \, (T/273)^{3/2}.$$

This agrees well with the diffusion coefficient calculated from the experiments (Equation 83). We have previously remarked that the observed rate of diffusion of hydrogen atoms through molecular hydrogen was found to be 4.2 times greater than that calculated. Evidently hydrogen atoms behave abnormally when diffusing through molecular hydrogen, but not when diffusing through nitrogen. This is probably caused by the hydrogen atoms going, we might say, through the hydrogen molecules by combining with one atom in a molecule with which it collides and thus liberating the other. This effect is probably entirely analogous to the abnormal mobility of the H and OH ions in aqueous solutions.

13. Summary.

1. Previous calculations of the degree of dissociation of hydrogen, from experiments on the heat losses from tungsten wires in hydrogen, conflicted rather seriously with Bjerrum's determinations of the specific heat of hydrogen by the explosion method. The weak point in the method

of calculation was a rather arbitrary assumption regarding the diffusion coefficient of atomic hydrogen through ordinary hydrogen.

2. This apparent discrepancy suggested that the actual amount of dissociation might be somewhat less than that previously calculated, but did not indicate that the abnormal heat conductivity of hydrogen at high temperatures was not due to dissociation.

3. The qualitative evidence of such a dissociation seems conclusive. Thus, not only does hydrogen show an entirely abnormal increase in heat conductivity, but this heat conductivity actually increases as the pressure is lowered.

A large amount of chemical evidence has also been accumulated. If hydrogen at low pressures comes into contact with metallic wires at temperatures above 1300° K., part of the hydrogen is converted into an active modification which remains adsorbed on glass surfaces for long periods of time. This active hydrogen can react at room temperature with oxygen or with many reducible substances, or can dissolve in metals such as platinum. There are good reasons for thinking that this active hydrogen is hydrogen in the atomic condition.

4. A series of experiments were made to measure, more accurately than hitherto, the heat losses from a tungsten wire at temperatures from 800° to 3500° K. and at pressures of hydrogen ranging from 0.01 mm. up to atmospheric pressure. Similar experiments were made with nitrogen.

5. At temperatures below that at which dissociation occurs the heat loss from the wires decreases steadily as the pressure is lowered. Only at pressures above 200 mm. do convection currents play any important part. Below this pressure the decrease in the heat loss is due to the temperature discontinuity, first observed by Smoluchowski. The theory of this effect is developed for the case of small wires at very high temperatures and the results are found to be in good agreement with the experiments.

6. The normal heat conductivity is separated from the abnormal effect due to dissociation, and a table is prepared (Table III) giving the heat carried from the wire by the dissociation, at various temperatures and pressures. With nitrogen there is no abnormal increase in heat loss at high temperatures.

7. The following theory of the phenomena occuring in and around the wire is proposed:

The dissociation of the hydrogen does not occur in the space around the wire, nor by the impact of molecules against its surface, but takes place only among the hydrogen molecules which have been absorbed (dissolved?) by the metal of the wire. Within the metal the reaction occurs so rapidly that equilibrium may be assumed to prevail at all times.

The equilibrium constant within the metal may, however, be very different from that in the gas phase.

It is assumed that there is no "adsorption film" on the surface of the wire through which the hydrogen has to diffuse, but that the absorption takes place by the collision of the molecules (or atoms) against the surface of the wire. A certain proportion of the molecules striking the surface may be reflected without absorption. Thus, of all the hydrogen molecules striking against the surface, we assume that a certain fraction α_2 is absorbed, while the fraction $1 - \alpha_2$ is reflected. Similarly, of all the hydrogen atoms striking the surface, the fraction α_1 is absorbed.

In general, the partial pressures of atomic hydrogen in the gas immediately surrounding the wire will not be that corresponding to the equilibrium at the temperature of the wire. The difference between these two partial pressures may be looked upon as a "drop in concentration" at the surface of the wire strictly analogous to Smoluchowski's "temperature drop" in the case of heat conduction and to Kundt and Warburg's "slip" in the case of experiments on the viscosity of gases.

The partial pressure of atomic hydrogen immediately around the wire depends on: 1st, the rate at which atomic hydrogen escapes from the wire; 2nd, the rate at which atomic hydrogen is absorbed by the wire; and 3rd, the rate at which it can diffuse away from the wire.

8. From the viewpoint of this theory it has been possible, by thermodynamical reasoning, to develop a quantitative theory by which the dissociation constant K (in the gas phase) may be calculated in terms of W_D the heat carried from the filament by dissociation; q_1 the heat of reaction; D the diffusion coefficient, and the two coefficients α_1 and α_2.

The resulting general Equation 31 is of the form (neglecting constant factors)

$$K = \frac{(W/q)^2 \, (P/D + 1/\alpha_1)^2}{P - (W/q) \, (P/D + 1/\alpha_2)}$$

where P is the total pressure.

9. By comparing this equation with the experimental data, it is found possible to so choose the quantities K, q, D, α_1 and α_2 that the resulting equation agrees excellently with the experiments at all temperatures and pressures. At the same time, the values of K conform to the thermodynamical requirement given by van't Hoff's equation

$$d \ln K/dT = q/RT^2.$$

The agreement between the theory and the experiments is shown in Tables XVII and XVIII, where the observed and calculated values of W are placed side by side.

10. The values of the quantities K, q, D, α_1 and α_2 which were used in these calculations, and which were found to give the best agreement between experiment and theory, are as follows:

Dissociation Constant K.—Let us define the dissociation constant K by the equation:

$$(22) \qquad\qquad K = p_1^2/p_2$$

p_1 and p_2 being the partial pressures (in mm.) of atomic and molecular hydrogen, respectively. Then it is found that

$$(65) \qquad\qquad \log_{10} K = 7.77 - 19700/T.$$

Values of K calculated from this equation for temperatures from 1200 to 4000° have been given in Table XV, together with the corresponding degrees of dissociation at pressures of 760 mm. and 1 mm. The following is a comparison of these results with those obtained previously (in the year 1912):

<div align="center">DEGREE OF DISSOCIATION AT 760 MM.</div>

Temp. °K.	2000	2300	2500	3100	3500
Results in 1912	0.0013	0.012	0.039	0.44	0.84
Results in 1915	0.0033	0.014	0.031	0.17	0.34

In the range from 2200–2600°, the results are nearly identical, but at higher and lower temperatures the differences become large.

Heat of Formation of Hydrogen Molecules.—By applying van't Hoff's equation to the foregoing data, we find the heat of reaction for two grams of hydrogen to be

<div align="center">84000 calories at constant volume
90000 calories at constant pressure</div>

In 1912 the value given was 130000 calories at constant volume.

Diffusion Coefficient of Atomic Hydrogen in Molecular Hydrogen.— This quantity is found to be

$$(70) \qquad\qquad D = 2.14 \; 10^{-3} \; T^{3/2}.$$

This result is 4.2 times greater than that found previously by calculation from the principles of the kinetic theory. This difference suggests that the hydrogen molecules are more or less "transparent" to hydrogen atoms. The effect is probably quite analogous to that of the abnormal mobility of the H and OH ions in aqueous solutions.

The Coefficients α_1 and α_2.—The coefficient α_1 is found to be constant and equal to unity, while α_2 is apparently constant and equal to 0.68. In other words, *all the hydrogen atoms striking the filament are absorbed by it and 68% of all the hydrogen molecules are absorbed.* The velocity of the reaction is thus determined practically entirely by the equilibrium conditions within the wire. The fact that these coefficients are found to be so nearly equal to unity is excellent evidence that in the present theory we are actually dealing with the fundamental factors determining the velocity of the reaction.

11. Other possible theories of the mechanism of the reaction are discussed, but no other is found which agrees at all well with the facts.

12. The apparent increase in specific heat caused by the dissociation is calculated. Even at temperatures as low as 2000° the effect should be perceptible. The magnitude of the effects found is, according to statements of Seigel, of the right order to account fully for certain anomalies in the experiments of Bjerrum. Therefore, the results of the explosion method, instead of conflicting with the present determinations of the degree of dissociation, may be regarded as additional evidence in their favor.

13. The rate at which hydrogen at very low pressures is dissociated by a tungsten wire at 1200–1500° has been calculated according to the theory and is found to be 8–10 times greater than the *greatest* observed rate at which active hydrogen was deposited on glass surfaces. In view of the marked fatigue effects characteristic of this adsorption of active hydrogen by glass, the agreement is close enough to lend further support to the theory. The quantitative evidence of the dissociation of hydrogen may therefore be said to extend over a temperature range from 1200 to 3500° K., in which the degree of dissociation increases in the ratio 1:170000.

14. Experiments on the heat losses from tungsten wires in mixtures of nitrogen and hydrogen yield results also in accord with the theory. See Table XXI. The diffusion coefficient of hydrogen atoms through nitrogen is found to be

$$D = 2.5 \ (T/273)^{3/2}$$

which is in excellent agreement with a value calculated by the kinetic theory.

SCHENECTADY, N. Y.

THE FREE ENERGY OF SOME CARBON COMPOUNDS.

BY GILBERT N. LEWIS AND MERLE RANDALL.

Elementary Forms of Carbon.

Of the numerous known forms of carbon only two, graphite and diamond, appear to be true chemical individuals. Indeed it is possible that substances like coal, charcoal, and coke should be regarded, not as elementary carbon, but as mixtures of hydrocarbons of low hydrogen content. Passing from benzene through naphthalene to more unsaturated compounds of higher molecular weight there seems to be no limit to the ratio between the number of carbon atoms to the number of hydrogen atoms in a hydrocarbon molecule. However, there are certain of the so-called amorphous forms of carbon, such as the one produced by the decomposition of pure carbon monoxide, which must be regarded as pure, but of which the properties vary according to the method of preparation. They