

which gives for dilute liquid solutions a quantitative connection between the temperature coefficient of solubility and the heat of solution, does not apply.

SHEFFIELD CHEMICAL LABORATORY,
YALE UNIVERSITY, NEW HAVEN, CONN.

THE DISSOCIATION OF HYDROGEN INTO ATOMS.

Part I. Experimental.

BY IRVING LANGMUIR AND G. M. J. MACKAY.
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Some early measurements¹ of the heat loss by convection from heated tungsten wires in hydrogen showed that the loss increased at an abnormally high rate when extremely high temperatures were reached.

A little later² a series of measurements on the heat convection from various kinds of wires in different gases led to a general theory of convection from hot bodies, which makes possible the approximate calculation of heat losses from a wire at any temperature in any gas which behaves normally.

With hydrogen, the theory led to results in close agreement with the experiments, up to temperatures of about 2300° K. Above this, however, the observed heat loss increased rapidly until at 3300° K., it was over four times the calculated value.

This fact suggested that the hydrogen was partly dissociated into atoms at these high temperatures.

In a subsequent paper,³ the theory of heat conduction in a dissociating gas was developed to apply to this case.⁴ It was shown that the power required to heat the wire could be expressed as the sum of two terms, thus:

$$W = W_C + W_D \quad (1)$$

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

² Langmuir, *Phys. Rev.*, **34**, 401 (1912).

³ Langmuir, *THIS JOURNAL*, **34**, 860 (1912).

⁴ At the time of publication of the above mentioned paper, I was unaware that Nernst had previously (Boltzman, *Festschrift*, 1904, p. 904) developed a quantitative theory of the heat conduction in a dissociating gas, and had shown that the heat conductivity of nitrogen peroxide, determined by Magnanini, agreed well with that calculated by his equations from the known degree of dissociation of this substance. Nernst showed that the effect of the dissociation is to increase the heat conductivity of a gas by an amount equal to

$$Dq \frac{dc}{dT}.$$

He does not, however, show that this leads to the very simple and useful form of equation developed by the writer, namely,

$$W_D = SDq(C-C').$$

Nernst points out that the heat conductivity of gases may be used not only to detect dissociation qualitatively, as R. Goldschmidt (Thesis, Brussels, 1901) had shown, but in some cases to determine the degree of dissociation quantitatively. (I. LANGMUIR.)

Here W is the total power (in watts per centimeter) required to maintain the wire at a given temperature T_2 .

W_C represents the part which is carried by ordinary heat conduction and follows the usual laws of heat convection, namely:¹

$$W_C = S \int_{T_1}^{T_2} k dT = S(\varphi_2 - \varphi_1) \quad (2)$$

S is called the shape factor and depends on the diameter of the wire and the nature of the gas, but is independent of the temperature of the wire. k is the coefficient of heat conductivity of the gas, W_D represents that part of the heat loss which is dependent on the dissociation of the gas. It was shown that W_D could be expressed thus:

$$W_D = SDq_1C_1 \quad (3)$$

where S is the shape factor, D is the diffusion coefficient of hydrogen atoms through molecular hydrogen, q_1 is the heat of formation of hydrogen molecules from 1 g. of hydrogen atoms, and C_1 is the concentration of hydrogen atoms (grams per cc.) in the gas immediately in contact with the hot wire.

The experiments gave W directly (after subtracting the heat radiated from the hot wire). The value of W_C could be calculated by (2) and thus equation (1) led to a determination of W_D . By substituting in (3) the values of S and W_D , the product Dq_1C_1 was obtained from the results of the experiments.

It was then necessary to estimate the approximate value of D . This was done by guessing the probable free path of hydrogen atoms through hydrogen molecules by analogy with other gases and by then substituting this value in an equation, derived from the kinetic theory, which expresses the diffusion coefficient in terms of the normal free path.

Having thus chosen D and dividing this into the known value of Dq_1C_1 , the product q_1C_1 was found. Van't Hoff's equation gives a relation between q_1 and the temperature coefficient of C_1 . Since q_1 is nearly independent of the temperature, the temperature coefficient of C_1 must be practically equal to that of q_1C_1 , so that in this way q_1 could be found. From this, the value C_1 and the degree of dissociation was then calculated.

The degree of dissociation of hydrogen into atoms (at atmospheric pressure) was thus calculated to be 1.2% at 2300° K., and 44% at 3100° K., and 84% at 3500° K. The heat of formation of the molecules from the atoms was given at 130,000 calories (for 2 g. of hydrogen).

These results seemed to conflict seriously with the measurements of the specific heat of hydrogen obtained by the explosion method. Pier² had

¹ *Phys. Rev.*, *l. c.*

² *Z. Elektrochem.*, **15**, 536 (1909).

concluded from his experiments that the mean specific heat of hydrogen from room temperature up to 2500° K. could be represented by the equation

$$C_v = 4.70 + 0.00045t$$

On the other hand, Bjerrum¹ found that the specific heat of water vapor was abnormally large at temperatures above 2000° K.

The method adopted by Bjerrum was one in which it was not possible to distinguish between variations in the specific heat of water vapor and of hydrogen. An increase of perhaps 10–20% in the specific heat of hydrogen at 3000° would, therefore, be quite consistent with Bjerrum's experiments.

A dissociation as high as 44% at 3100° K. would, however, lead to an apparent specific heat of H_2 two or three times greater than the usually accepted value.

One explanation of this discrepancy might be that the velocity of the hydrogen dissociation is so small that during the short time of an explosion, equilibrium was not reached, whereas in the other experiments, the catalytic action of the hot tungsten wire caused the dissociation to approach the equilibrium more closely.

It seems, however, improbable that the velocity of the reaction would be so slow at temperatures as high as 3100° K. Bjerrum's experiments, therefore, seem to indicate that the degree of dissociation is considerably less than the values obtained by the methods described above.

If we examine the chain of reasoning by which the results were obtained we see that there is one extremely weak link, namely, the method by which the diffusion coefficient D was obtained.

It is true that this method would give a fair degree of accuracy if applied to almost any pair of ordinary gases at ordinary temperatures, but a good deal of uncertainty arises when it is applied to a dissociating gas. In fact, under such conditions, the diffusion coefficient might be very much greater than that calculated in the usual way. An example of such a case is already known in the abnormally great mobility of the hydrogen and hydroxyl ions in aqueous solutions. A larger value for the diffusion coefficient would lead to lower values for the dissociation and might thus remove the discrepancy between the previous calculations and Bjerrum's results.

Qualitative Evidence for the Dissociation of H_2 .

H. von Wartenberg,² after pointing out the discrepancy between the former calculations and the results of the explosion method criticises the heat conductivity method as follows:

"Die Fehlerquellen der Methode sind zu gross, als dass man die Zahlen

¹ *Z. physik. Chem.*, **79**, 513 (1912).

² *Z. Elektrochem.*, **19**, 901 (1913).

auch nur als annähernd richtig betrachten könnte, wenn auch eine geringe Dissociation des H_2 von etwa 2100° nicht als ausgeschlossen erscheint. Sichere Zahlen wird wohl nur die Explosionsmethode geben können."

As far as accurate quantitative determinations of the degree of dissociation of most complex gases are concerned, we feel that von Wartenberg's preference for the explosion method is justified, but for qualitative evidence of dissociation, especially of elementary gases, we consider that the heat conductivity method has great advantages over the explosion method. The fact that mixtures of gases must be employed in the latter method, so complicates the phenomena that there is considerable uncertainty in the interpretation of results. Furthermore, it will be shown that the conductivity method, in some cases, is very much more sensitive than the explosion method.

The qualitative evidence of dissociation of hydrogen obtained by the heat conduction method and already published, may be briefly summarized as follows:

1. The heat loss from tungsten wires (or platinum wires up to 1750°) in nitrogen, mercury vapor, argon, and carbon monoxide varies with the temperature accurately, as expressed by equation (2).

2. The heat loss in hydrogen follows accurately the same law up to about 1900° K. and then rapidly increases, until at 3500° K. it is over four times its calculated value.

3. No secondary electrical effects which might cause a similar increase can be detected.

4. At lower pressures the heat loss from tungsten wires in hydrogen becomes actually *greater* than at atmospheric pressure. This does not occur with other gases.

The evidence of dissociation is, however, not at all limited to the abnormal heat conductivity.

A large amount of evidence of a chemical nature has gradually accumulated in this laboratory, which proves, beyond doubt, that hydrogen at low pressures, upon coming in contact with a heated metallic wire, is chemically activated and can, under proper conditions, retain its activity several days. A very brief review of this evidence will be of interest.

1. It has been shown¹ that when a wire of tungsten, platinum or palladium is heated to a temperature above 1300° K. in hydrogen at very low pressure (0.001 to 0.020 mm.), the hydrogen slowly disappears. There is a distinct fatigue effect, but the substitution of a new section of wire does not restore the action. The hydrogen is not absorbed by the wire, but is deposited on the glass, especially where this is cooled by liquid air. If the cooled portions are heated, ordinary hydrogen is liberated which will

¹ "A Chemically Active Modification of Hydrogen," Langmuir, THIS JOURNAL, 34, 1310 (1912).

not recondense on replacing liquid air. The hydrogen may deposit on cooled glass surfaces, even in tubing at a considerable distance from the bulb. This hydrogen has remarkable chemical activity and will react with oxygen and phosphorus at room temperature. These effects are not due to the catalytic effect of finely divided metal deposits. The active hydrogen is not affected by an electrostatic field and therefore does not consist of hydrogen ions.

2. The active hydrogen thus produced can diffuse through long tubes (at low pressures) and can then dissolve in platinum (at 50°) and cause a marked increase in its electrical resistance and corresponding decrease in its temperature coefficient. Ordinary hydrogen, under similar conditions, will not do this. These effects have been described in some detail by Freeman.¹

3. It has been found that tungstic oxide, WO_3 , platinum oxide, PtO_2 ,² and many other substances, placed in a bulb containing a tungsten filament and hydrogen at very low pressures, rapidly become chemically reduced when the filament is heated to a temperature exceeding about $1700^{\circ} K$. although otherwise they are not acted on by hydrogen.

Many of these phenomena have been studied quantitatively in some detail, and the results seem consistently to be in accord with the theory that a portion of the hydrogen which comes into contact with the hot wire is dissociated into atoms. These, perhaps because of strong unsaturated chemical affinity, tend to adhere to glass surfaces even at room temperature. Some, however, leave the glass and wander further. Gradually the glass surfaces become charged with hydrogen atoms to such an extent that any fresh atoms striking the surface, combine, even at liquid air temperatures, with those already present. In case the atoms strike a metal surface such as platinum, they dissolve in it up to a considerable concentration.

The foregoing results afford satisfactory proof that hydrogen, particularly at low pressures, is readily dissociated into atoms by metallic wires at very high temperatures.

There is, however, good reason to suspect that the actual values for the degree of dissociation previously given are considerably too high. The cause of this was thought to be an incorrect assumption as to the diffusion coefficient of hydrogen atoms through molecular hydrogen.

The remainder of the present paper deals with the results obtained by two methods which lead to more or less quantitative data on the dissociation, without necessitating any assumptions as to the magnitude of the diffusion coefficient.

¹ THIS JOURNAL, 35, 927 (1913).

² Formed and deposited on the bulb by heating Pt at very high temperature in O_2 at low pressure or by passing a glow discharge between Pt electrodes in O_2 at low pressure.

The first method is based on measurements of the total heat losses from tungsten wires at a series of different pressures, ranging from 10 mm. up to atmospheric pressure. If the previous results were correct, that is, that hydrogen is 44% dissociated at atmospheric pressure and 3100° K., then, at a pressure of 10 mm., the dissociation should be 96.5%. A further rise in temperature could then only slightly increase the degree of dissociation, for it is already close to the limit of 100%. We see, then, from equation (3), that the heat loss under these conditions would have only a very small temperature coefficient. It was hoped, at the outset of these experiments, that the actual degree of dissociation could be determined from the decrease in the temperature coefficient of W_D as the pressure was progressively lowered.

The experiments to be described have shown, however, that even at 10 mm. pressure the temperature coefficient of W_D is practically as great as at atmospheric pressure, showing that even at these low pressures the hydrogen around the wire is not nearly completely dissociated. These experiments, however, give an upper limit to the degree of dissociation.

In the second method, measurements were made at very much lower pressures, from 0.01 mm. up to 0.2. At the lowest pressures, the conditions should become very simple, for the molecules travel in straight lines directly from filament to bulb. Under such conditions, the hydrogen atoms produced practically never return to the filament without having struck the bulb many times and having had ample opportunity of recombining. The filament is, therefore, struck only by hydrogen molecules, and from the formula

$$m = \sqrt{\frac{M}{2\pi RT}} p^{\frac{1}{2}} \quad (5)$$

the rate at which the hydrogen molecules reach the surface may be calculated. If, then, the heat loss be determined by experiment, the energy carried away by each molecule can be calculated. If, by heating the filament to very high temperatures, a condition could be reached in which every hydrogen molecule which strikes the filament becomes dissociated, then those experiments would lead to a direct determination of the heat of formation (heat absorbed by dissociation) of hydrogen molecules. In the absence of definite evidence that the dissociation is complete, the method gives at least a lower limit for the heat of formation.

Experiments on the Heat Losses from Tungsten Wires in Hydrogen.

1. *Higher Pressures.*—In the experiments upon which the former calculations of the dissociation were based, the measurements of heat loss

¹ Here m is the rate (in grams per sq. cm. per second), at which the hydrogen comes into contact with the filament. M is the molecular weight of H_2 (*i. e.*, 2), T is the temperature of the bulb, and p is the pressure of the hydrogen in the bulb. The derivation of this equation has been given in a previous paper (*Phys. Rev., N. S.*, 2, 329 (1913)) and *Physik. Z.*, 14, 1273 (1913).

were made from short pieces of tungsten wire mounted vertically in a large glass tube open at the lower end, through which a fairly rapid stream of hydrogen passed. The temperature in most cases was determined from the resistance. The relation between resistance and temperature was, however, found by measurement of the intrinsic brilliancy of pieces of the same wire mounted in exhausted bulbs.

In the present experiments, it was desired to employ a series of different pressures of hydrogen around the filament, and furthermore, to avoid injury to the wire by impurities in the hydrogen.

The method adopted was therefore to mount single loop filaments of pure tungsten wire in large heater lamp bulbs (cylindrical bulbs about 25 cm. long and 7 cm. diameter) which were filled with pure, dry hydrogen at various pressures. These were then set up on the photometer bench and a series of simultaneous measurements of candle power, current and voltage were made. The color of the light emitted was also accurately matched against that from a standard lamp viewed through a special blue glass.¹

Before filling the bulbs with hydrogen, they were exhausted to 0.1 micron pressure for an hour while heated to 360°, and the filaments were heated to a high temperature to drive off gases. The hydrogen was prepared electrolytically and was freed from oxygen and water vapor with extreme care.

Thirty lamps were made up for these experiments. Fifteen of these were filled with hydrogen at the following pressures: 1, 10, 25, 50, 100, 200 and 750 mm. Six were exhausted to a good vacuum in order to determine the amount of energy radiated. The remainder were filled with pure nitrogen at various pressures, to compare the heat loss in this gas with that in hydrogen.

The wire used in all lamps was 0.00706 cm. diameter. In every case it was welded to nickel leads with tungsten or molybdenum tips. The length of wire used in the hydrogen lamps ranged from 5 to 9 cm. and in the vacuum and nitrogen lamps, from 6 to 12 cm. It was necessary to use rather short lengths in hydrogen in order to be able to heat the wire to the melting point without using voltages over 200 volts.

Temperature Measurements.—The temperatures were determined, as has been usual in this laboratory, by the relation

$$T = \frac{11230}{7.029 - \log H} \quad (6)$$

where H is the intrinsic brilliancy of the filament in international candle power per sq. cm. of projected area. On this scale the melting point of

¹ This method has proved extremely accurate and serviceable as a means of comparing the temperatures of tungsten filaments. It is described in some detail by Langmuir and Orange, *Proc. Amer. Inst. Elect. Eng.*, 32, 1895 (1913).

tungsten proves to be 3540° K. (by direct experiment). This value we consider to be more probable than the lower values usually given.

The temperatures were also determined by two auxiliary methods: by measurement of the resistance and by matching the color of the emitted light against that of a standard provided with a blue screen. In both these methods, however, the primary standard of temperature was the one given above, based on the intrinsic brilliancy of the filament.

It was found in nearly all experiments that the three methods gave concordant results. The presence of hydrogen or nitrogen did not change either the resistance or the color of the light emitted from a filament set up at a given intrinsic brilliancy. Discordant results were obtained only in the experiments in vacuum or low pressures of gas after the filament had been heated some time above 3200° K. and had evaporated so that the bulb had blackened and the diameter of wire had changed.

In order to avoid errors in temperature due to the cooling effect of the leads, the candle power was usually determined through a slit, one or two centimeters wide, placed horizontally in front of the lamp. In this way, the intrinsic brilliancy can be determined with accuracy.

At temperatures below 1800° K., the candle power determinations were too inaccurate to be suitable for temperature measurements. The temperatures were, therefore, found in these cases from the resistance, proper correction being made for the cooling effects of the leads.

Before making measurements on the lamps, they were thoroughly aged by running them for 24 hours with the filaments at a temperature of about 2400° K. With the hydrogen and nitrogen of the purity used in these experiments, this treatment produced no perceptible injury of the filament. During the first few hours of aging, the filament, even in vacuum lamps, undergoes slight changes in resistance, and it was with this object, as well as to test the purity of the gases, that the lamps were subjected to the aging process.

The lamps were then set up on the photometer one by one, and measurements of current, voltage, candle power and color were made. About 30 to 50 sets of readings were taken with each lamp, raising the voltage usually in steps of 2.5 to 5 volts at a time. The temperature was thus gradually raised from 800° K., up to about 2900° . Then a series of points was taken at descending temperatures and finally the temperatures were raised to temperatures of 3000° and more, frequently repeating some of the measurements at lower temperatures to see if the filament had undergone any change. The readings up to 3000° K. could be taken without haste, as the filament undergoes only relatively slow changes below this temperature. Above this temperature the readings were taken as rapidly as possible, and at wider intervals (usually 10 volts). These precautions were especially necessary with the lamps containing less than 100 mm. of

gas. In those containing nearly atmospheric pressure of either hydrogen or nitrogen, there was never any perceptible darkening of the bulb, and the loss of material from the filament was extremely small, even when the temperature was raised several times very close to the melting point of the filament.

From the data thus obtained, the power consumption (in watts per centimeter of length), the temperature, and the resistance (per centimeter) were determined. The watts per cm. were plotted on semi-logarithmic paper against temperature and smooth curves drawn through the points.

Most of the points fitted very closely (within 1 or 2%) with the smoothed curves, and it was only rarely, at very low and at very high temperatures, that deviations as great as 5% were observed.

The results of these experiments are summarized in Table I. The energy *radiated* from the filament per second (in watts per centimeter of length) is given in the second column under the heading W_R . This was obtained from the lamps with well exhausted bulbs. The resistance (in ohms per centimeter) of the filament is given in the third column headed R. These values represent the averages of all the lamps. There was no appreciable difference in R for the gas filled and the vacuum lamps. The next six columns contain the data obtained from the bulbs containing hydrogen. The figures give directly the energy carried from the filament by the gas, the values tabulated being obtained by subtracting W_R from the observed total power consumption (in watts per cm.).

The last five columns contain similar data obtained from the nitrogen filled lamps.

Simple observation of these figures show the very striking difference in the effects in the two gases. In nitrogen, the values decrease steadily as the pressure is reduced, and in hydrogen, at the lower temperatures, the same decrease is observed. But at higher temperatures, in hydrogen, the power consumption is considerably greater at lower pressures than at atmospheric pressure.

The conclusions drawn from these measurements will be considered later, together with the results obtained at still lower pressures.

Lower Pressures.—In these experiments, measurements of the power consumption were made at a series of temperatures, with pressures ranging from 0.01 mm. up to 13 mm. The measurements were made while the lamps containing the filaments were connected to a vacuum system consisting of two McLeod gages (one for lower and one for higher pressures) and a Gaede mercury pump. The lamps were first exhausted at 360° for an hour and a trap immersed in liquid air placed directly below the lamps condensed the moisture given off from the glass.

The candle power was measured during the experiments by a portable Weber photometer. The characteristics in vacuum at temperatures

ranging from 1500 to 2500° K. were first determined and then a few centimeters (pressure) of pure hydrogen was admitted to the system and pumped out to a pressure of 13 mm. A series of measurements of current, voltage and candle power was again made. In this way, in the first experiment, the characteristics were measured at pressures of 13.1, 6.5, 2.5, 1.2, 0.53, 0.218, 0.102 and 0.045, 0.020 and 0.010 mm. and at 0.0001 mm. In a second experiment, measurements at a few pressures were made as a check on the preceding.

In the third experiment, made a few weeks later, a much more complete series of measurements was made, extending the range of observations from 1100° to 2900° K. Higher temperatures were avoided, in order not to cause any evaporation of the filament. The pressures employed in this set of tests were 4.4, 1.10, 0.207, 0.039, 0.015 and 0.00007 mm. At each pressure about 30 readings at different temperatures were taken.

The results of the third experiment were in excellent agreement with those of the first two. Since the former covered so much wider a range, only these results are given in this paper.

The tungsten wire used for these experiments was taken from the same spool as that used in the experiments at higher pressures.

The filament was mounted horizontally in a straight piece 9.85 cm. long. Because of the cooling effect of the leads, it was assumed that the effective length of the wire for calculation of the watts per centimeter was 9.4 cm. The bulb was a cylindrical bulb with rounded ends, about 10 cm. diameter and 18 cm. long, and the filament was supported in its axis.

TABLE II.

| Temp. ° K. | W _R . | R. | Heat carried by hydrogen watts per cm. | | | | |
|---------------|------------------|------|--|-------------|--------------|--------------|--------------|
| | | | 4.40 mm. | 1.10 mm. | 0.207 mm. | 0.039 mm. | 0.015 mm. |
| 1100 | 0.022 | 0.60 | 0.26 | 0.09 | 0.020 | 0.004 | 0.002 |
| 1200 | 0.037 | 0.70 | 0.31 | 0.11 | 0.024 | 0.005 | 0.002 |
| 1300 | 0.060 | 0.80 | 0.36 | 0.13 | 0.030 | 0.006 | 0.002 |
| 1400 | 0.095 | 0.89 | 0.41 | 0.16 | 0.038 | 0.007 | 0.003 |
| 1500 | 0.138 | 0.98 | 0.47 | 0.19 | 0.050 | 0.009 | 0.004 |
| 1600 | 0.192 | 1.07 | 0.55 | 0.22 | 0.066 | 0.012 | 0.006 |
| 1700 | 0.268 | 1.15 | 0.65 | 0.28 | 0.088 | 0.019 | 0.008 |
| 1800 | 0.36 | 1.24 | 0.82 | 0.36 | 0.125 | 0.032 | 0.012 |
| 1900 | 0.48 | 1.33 | 1.09 | 0.52 | 0.21 | 0.06 | 0.019 |
| 2000 | 0.62 | 1.42 | 1.44 | 0.85 | 0.34 | 0.10 | 0.031 |
| 2100 | 0.78 | 1.52 | 2.06 | 1.27 | 0.53 | 0.16 | 0.055 |
| 2200 | 0.98 | 1.62 | 2.98 | 1.81 | 0.73 | 0.22 | 0.092 |
| 2300 | 1.23 | 1.72 | 4.37 | 2.62 | 0.99 | 0.29 | 0.120 |
| 2400 | 1.55 | 1.82 | 5.98 | 3.56 | 1.27 | 0.37 | 0.148 |
| 2500 | 1.82 | 1.92 | 8.21 | 4.85 | 1.58 | 0.42 | 0.178 |
| 2600 | 2.20 | 2.02 | 11.0 | 5.49 | 1.82 | 0.48 | 0.189 |
| 2700 | 2.67 | 2.12 | .. | 6.23 | 1.96 | 0.50 | 0.191 |
| 2800 | 3.20 | 2.23 | .. | 6.97 | 1.98 | 0.50 | 0.191 |
| 2900 | 3.80 | 2.34 | .. | 7.61 | 1.99 | 0.50 | 0.191 |

The data obtained by these experiments are given in Table II. In the second and third columns are given the characteristics of the filament in good vacuum (0.00007 mm.). W_R is expressed in watts per centimeter, and R in ohms per centimeter. The figures in the other columns give the differences between the observed power consumption at different pressures and those in vacuum.

Discussion of Experimental Results.

The experimental data contained in Tables I and II give, as a function of both temperature and pressure, the total heat carried by the surrounding hydrogen from a heated tungsten filament in this gas.

It has been shown in the previous papers that this energy carried by the gas can be resolved into two parts, W_C and W_D .

$$W = W_C + W_D \quad (1)$$

The temperature coefficient of W_C is given by

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

where

$$\varphi = \int_0^T k d'T.$$

In the previous paper, S was calculated from results obtained with gases other than hydrogen. This method of calculation of S , although giving an approximation good enough for most purposes, may be open to criticism. In the present case, therefore, it has been thought better to determine S directly from the experimental results of Tables I and II.

The values of $\varphi_2 - \varphi_1$ were taken from the data given in the previous paper,¹ in which φ was calculated from the heat conductivity of hydrogen as determined by Eucken² and from the measurements of the viscosity of hydrogen by Fisher³.

By trial a value of S was found, which, when multiplied by $\varphi_2 - \varphi_1$, would give the best agreement with the values of W observed at temperatures so low that W_D was negligible. At higher temperatures, W_D was obtained by subtracting $S(\varphi_2 - \varphi_1)$ from W . The logarithm of W_D was plotted against $1/T$ from the data at rather low temperatures (1700–2500° K.). It is only in this range of temperatures that the calculated values of W_D are materially affected by errors in the value S . By trial a value of S was finally chosen which would give most nearly a straight line relation between $\log W_D$ and $1/T$.

These values of S have been used to calculate W_D and the results are given in Table III.

¹ *Physic. Rev. l. c.*

² *Physik. Z.*, 12, 1101 (1911).

³ *Physic. Rev.*, 24, 385 (1907).

TABLE IV.
 "W_D" from Experiments with Nitrogen.

| T ₁ ° K. | $\varphi_2 - \varphi_1$ watts per cm. | 750 mm. S= 1.41. | 200 mm. S= 1.15. | 100 mm. S= 1.06. | 50 mm. S= 0.75. | 10 mm. S= 0.43. | 1 mm. S= 0.10. |
|------------------------|---|---------------------------|---------------------------|---------------------------|--------------------------|--------------------------|-------------------------|
| 1100 | 0.43 | | | -0.06 | | | |
| 1200 | 0.49 | | | -0.04 | | | |
| 1300 | 0.56 | | | -0.01 | | | +0.03 |
| 1400 | 0.63 | | | -0.04 | | +0.03 | +0.04 |
| 1500 | 0.73 | | | +0.01 | | +0.03 | +0.04 |
| 1600 | 0.82 | | | +0.03 | | +0.03 | +0.04 |
| 1700 | 0.92 | | | +0.03 | | +0.04 | +0.04 |
| 1800 | 1.03 | | | +0.03 | | +0.06 | +0.03 |
| 1900 | 1.13 | | | +0.02 | | +0.07 | +0.03 |
| 2000 | 1.25 | -0.11 | +0.02 | +0.01 | +0.07 | +0.06 | +0.02 |
| 2100 | 1.36 | -0.04 | +0.04 | +0.01 | +0.06 | +0.06 | +0.01 |
| 2200 | 1.49 | -0.01 | +0.05 | 0.00 | +0.04 | +0.04 | 0.00 |
| 2300 | 1.61 | -0.01 | +0.06 | +0.02 | +0.05 | +0.03 | 0.00 |
| 2400 | 1.74 | +0.01 | +0.06 | +0.02 | +0.04 | +0.00 | -0.01 |
| 2500 | 1.87 | +0.04 | +0.07 | +0.02 | +0.02 | +0.02 | -0.03 |
| 2600 | 2.02 | +0.05 | +0.04 | -0.00 | 0.00 | -0.06 | -0.03 |
| 2700 | 2.16 | +0.07 | +0.04 | -0.02 | -0.02 | -0.09 | -0.05 |
| 2800 | 2.31 | +0.08 | +0.02 | -0.03 | -0.04 | -0.10 | -0.06 |
| 2900 | 2.47 | +0.08 | 0.00 | -0.04 | -0.07 | -0.10 | -0.07 |
| 3000 | 2.63 | +0.13 | -0.02 | -0.07 | -0.10 | -0.11 | -0.08 |
| 3100 | 2.79 | +0.12 | -0.04 | | -0.12 | | |
| 3200 | 2.96 | +0.13 | -0.08 | | -0.16 | | |
| 3300 | 3.13 | +0.13 | -0.11 | | -0.29 | | |
| 3400 | 3.31 | +0.09 | -0.14 | | -0.22 | | |
| 3500 | 3.49 | +0.08 | -0.18 | | -0.26 | | |

The results in Table III were obtained from the data in Tables I and II, merely by subtracting the product of S (given at the head of each column of Table III) by $\varphi_2 - \varphi_1$ (given in second column of Table III).

The data on the heat losses from tungsten wires in nitrogen given in Table I, was used in a similar way to calculate $W - W_C$ and the results are given in Table IV. The values of $\varphi_2 - \varphi_1$ in this table are calculated from the viscosity and heat conductivity of nitrogen.¹

A comparison of Tables III and IV shows clearly the very great difference between hydrogen and nitrogen. With nitrogen the heat loss increases with the temperature very nearly proportionally to $\varphi_2 - \varphi_1$. The differences observed and tabulated are not greater than the possible experimental errors. In the case of hydrogen, up to temperatures of 1500-1700° K., the results are similar to those of nitrogen; that is, there is no evidence that the differences between W and W_C are anything more than experimental errors. But at very high temperatures W_D increases

¹ See *Physic. Rev.*, *l. c.*

very rapidly, and becomes 50 or 100 times as large as the possible experimental error.

In the second part of this paper, these data will be used to calculate the degree of dissociation and the heat of formation of hydrogen molecules. The experiments at low pressures lead to a somewhat detailed knowledge of the mechanism of the reaction taking place on the surface of the wire.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, N. Y.

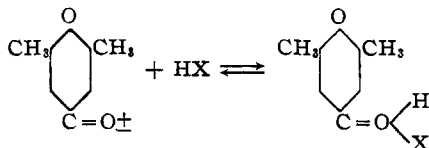
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THE ADDITION COMPOUNDS OF ORGANIC ACIDS IN PAIRS.

By JAMES KENDALL.

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In a recent communication¹ the author has shown, by the application of the freezing-point method, that a large number of organic acids form addition compounds with dimethylpyrone, and that these compounds are to be regarded as true oxonium salts. The reaction is best expressed by the equation:



The formation of an equimolecular addition compound is thus considered to be due to the basic (or unsaturated) properties of the group $>\text{C} = \text{O}^{\pm}$, in which oxygen functions as a quadrivalent atom.

This same group, $>\text{C} = \text{O}^{\pm}$, is present in all organic acids themselves. Consequently it appeared probable that, if the acidic properties of an organic acid could be sufficiently suppressed, the basic nature of the group $>\text{C} = \text{O}^{\pm}$ would become evident and formation of addition compounds with other substances could be obtained. Now the acidic properties of a weak acid can obviously be reduced to a minimum by the presence of a second, much stronger acid. In the present investigation, therefore, the validity of the general conclusions drawn in the previous paper is tested by this method—the examination of systems containing two organic acids of widely divergent strengths.

The experimental details and the main principles of the method followed have already been described in full. The formation of an addition compound can be immediately deduced from the freezing-point curve of a two-component system by the appearance of a maximum on the curve; the position of the maximum indicates the composition of the compound.

¹ Kendall, *THIS JOURNAL*, 36, 1222 (1914).