[Contribution from the Chemical Laboratory of the Johns Hopkins University]

# THE HEAT OF FORMATION OF MOLECULAR HYDROGEN[1]

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The heat of association of atomic hydrogen has been measured by several indirect methods, the values obtained ranging from 90,000–107,000 calories. In this work a new determination has been made by a direct calorimetric method. The basic principle of this method can best be explained by reference to Fig. 1. Hydrogen is admitted to the discharge tube D at a known rate of flow by the capillary A. The partially dissociated gas passes through a small hole in B and is catalytically associated on the platinum calorimeter C. The temperature rise of the calorimeter gives the energy change of association. The percentage of atomic hydrogen causing the change is determined by the difference in the pressure of the gas before passing through the small hole under steady state conditions of no dissociation (that is, with no discharge) and the pressure of the steady state conditions of dissociation (that is, with discharge).

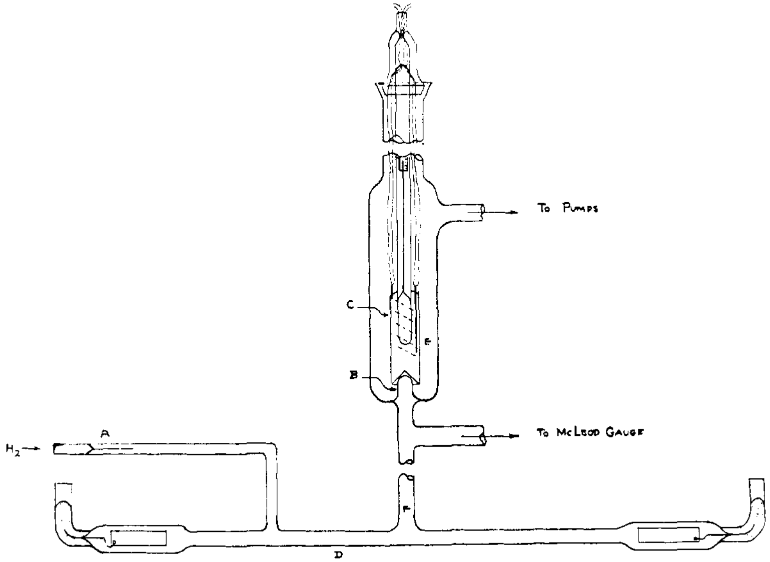

Fig. 1.—Diagrammatic sketch of apparatus.

This method employs the study of rates of effusion reported by one of us.[2] It was shown in this paper that the formula for the rate of effusion of a pure gas through a small hole could be employed experimentally to de-

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[1] This paper is an abstract of a thesis presented by L. Covell Copeland in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Johns Hopkins University.

[2] Weide and Bichowsky, This Journal, 48, 2529 (1926).

termine the percentage of thermal dissociation. As the present work deals with hydrogen dissociated in a discharge tube, the development of the final formula is given again.

The number of molecules of hydrogen, $N_N$, passing through a hole of area $s$ in $t$ seconds is[3]

$$N_N = N_0\, St\, P_N/\sqrt{2\pi K M_{H_2} T_N} \tag{1}$$

where $N_0$ is Avogadro's number, $M_{H_2}$ is the mass of a hydrogen molecule, $P_N$ is the pressure on the high pressure side of the small hole, and $T_N$ is the temperature of the hole. If the gas is partially dissociated the number of particles of dissociated gas will be equal to the sum of the molecular and atomic particles. It is most practical to measure the flow of gas before it is dissociated. Under conditions of equilibrium and no dissociation the number entering the apparatus is equal to the number passing through the small hole. When the gas is partially dissociated the number of molecules entering the apparatus under conditions of equilibrium is equal to the number of hydrogen molecules plus one-half the number of hydrogen atoms passing through the small holes. This number is $N_D$

$$N_D = N_{H_2} + \frac{1}{2}N_H = \frac{N_0\, St}{\sqrt{2\pi K T_D}}\left(\frac{P_{H_2}}{\sqrt{M_{H_2}}} + \frac{1}{2}\,\frac{P_H}{\sqrt{\frac{M_{H_2}}{2}}}\right) \tag{2}$$

Dividing equation (1) by equation (2) and substituting

$$P_D - \left(1 - \frac{1}{2}\sqrt{2}\right) P_H \text{ for } P_{H_2} + \frac{1}{2}\sqrt{2}\, P_H$$

(where $P_D$ is the total pressure of the dissociated gas)[4] and solving for $P_H$ equation (3) is obtained

$$P_H = 3.41\left(P_D - P_N \frac{N_D}{N_N}\sqrt{\frac{T_D}{T_N}}\right) \tag{3}$$

It is shown experimentally that, by using a capillary to control the rate of flow of hydrogen, the rate of flow when the gas was dissociated $N_D$ was equal to the rate of flow when there was no dissociation $N_N$. Also, the temperature of the small holes did not vary more than 5°K. Therefore the fraction $(N_D/N_N)\sqrt{T_D/T_N}$ may be set equal to one and formula (3) reduces to

$$P_H = 3.41\,(P_D - P_N) \tag{4}$$

If $\alpha$ is used to represent the percentage of dissociated gas, $2\alpha$ equals $P_H$ and $1 + \alpha = P_D$

$$\frac{2\alpha}{1+\alpha} = \frac{P_H}{P_D} = 3.41\left(1 - \frac{P_N}{P_D}\right)$$

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[3] Jeans, "The Dynamical Theory of Gases," Cambridge University Press, Cambridge, England, 4th ed., 1925, p. 121.

[4] $P_D = P_{H_2} + P_H$

$P_D - P_H = P_{H_2}$

$P_D - P_H + \frac{1}{2}\sqrt{2}\,P_H = P_D - \left(1 - \frac{1}{2}\sqrt{2}\right)P_H = P_{H_2} + \frac{1}{2}\sqrt{2}\,P_H.$

Solving for $\alpha$ the percentage of atomic hydrogen flowing through the small hole is obtained.

## Apparatus

The capillary A served to control the rate of flow of hydrogen into the apparatus. An automatic electrolytic hydrogen generator fitted with nickel electrodes and a 30% solution of potassium hydroxide as electrolyte was used as a source of moist hydrogen. As this generator, because of its automatic action, used only sufficient current to equalize the flow of hydrogen through the capillary, it was possible to use a second hydrogen generator connected in series with the first to measure the rate of flow. The discharge tube D was a Wood's tube,[5] so constructed that it could be immersed in a water-bath. The tube received its energy from an alternating current transformer delivering about 1000 volts and 0.2 of an ampere. The dissociated gas left the discharge tube through F, which was a section of one cm. tubing 25 cm. long. The tube F terminates in the small hole system B which was ring-sealed into the calorimeter jacket E. To obtain the maximum percentage of dissociation, the pressure in the discharge tube was maintained below 0.5 mm. of mercury. Since the theory on which this work is based demands that the small hole be small in comparison with the mean free path of the gas, the size of the hole was seriously limited.

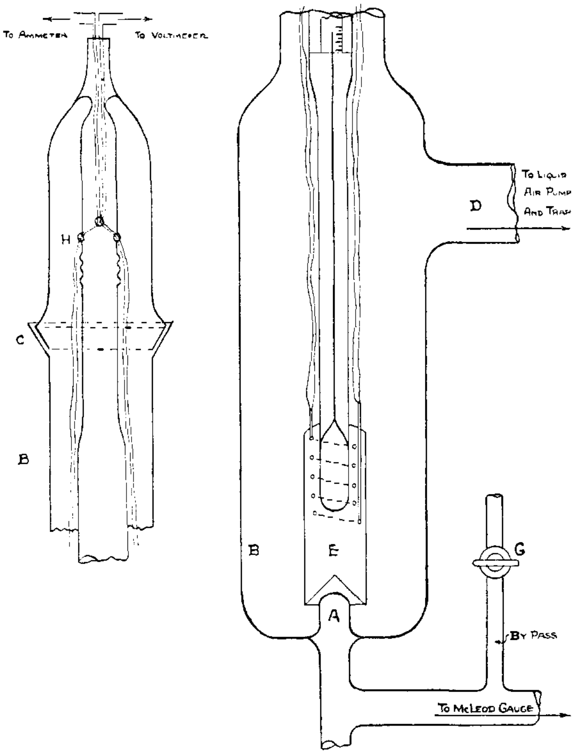

Fig. 2.—Sectional diagram of calorimeter and jacket.

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[5] Wood, *Phil. Mag.*, **42**, 729 (1921); *Proc. Roy. Soc.* (*London*), **102**, 1 (1923).

In order to obtain a sufficient flow of gas to give the desired accuracy in the calorimetric data, it was necessary to use a multiple system of small holes. The arrangement used consisted of nine small holes with diameters between 0.125 and 0.25 mm. These holes were constructed by rounding off one end of a piece of one cm. pyrex tubing which was then blown out until it was thin enough to work readily in a soft air flame. This thin wall was backed with sealing wax and the holes, first countersunk with a diamond drill, were completed with a drill made from 0.125 mm. tungsten wire. The sealing wax was removed by dissolving it in alcohol.

Figure 2 is a sketch of the calorimeter jacket and the calorimeter. B is the calorimeter jacket, which consisted of an 18-cm. length of 6-cm. tubing surmounted by a length of 4-cm. tubing containing a ground glass joint C. From one side of the calorimeter jacket a 2.5 cm. piece of tubing, D, served to conduct the gases through a liquid air trap to the pumps. A stopcock G was installed for by-passing the gas around the calorimeter. The calorimeter E was constructed of a cylinder of platinum foil 9.5 cm. long and 2 cm. in diameter. This cylinder was closed at the bottom end by a platinum foil cone and sealed around the bulb of a Beckmann thermometer by Wood's metal. The Beckmann and calorimeter were supported from the top by means of a graded seal H, one end of which was sealed to the Beckmann and the other end ring-sealed to the upper portion of the ground glass joint as shown in Fig. 2. This means of support was adopted because it afforded the minimum amount of heat loss through conduction. The ground glass joint facilitated the removal of the Beckmann and calorimeter to set the Beckmann. For the purpose of determining the heat capacity of the Beckmann and calorimeter, a coil of nichrome wire was immersed in the Wood's metal of the calorimeter at the time the calorimeter was assembled. Two fine copper enameled wires connected the resistance unit through a Weston milliammeter to a 6-volt storage battery. Two other wires were connected to a Weston 3-volt voltmeter. The calorimeter jacket was covered with asbestos paper as far as the ground glass joint. A slit was cut from this covering in order to read the Beckmann. Pressure measurements were made with a McLeod gage which was read with a cathetometer.

## Experiments

It was found that two hours of continuous discharge were necessary to give a steady pressure in the discharge tube. The pressures reported here are the average of the corrected pressures observed during the third hour of a continuous run. The pressure on the low pressure side of the small hole (that is, around the calorimeter) was 0.005 mm. The temperature of the calorimeter was recorded every minute by plotting directly degrees

### EXPERIMENT 1

| | |
|---|---|
| Rate of flow of hydrogen corrected to normal temperature and pressure | 10.77 cc./10 min. |
| Pressure in discharge tube with no current | 0.24006 mm. |
| Pressure in discharge tube with current | 0.27687 mm. |

$$\frac{2\alpha}{1+\alpha} = \frac{P_H}{P_D} = \frac{3.41\ (0.27687 - 0.24006)}{0.27687} = 0.4531$$

$$\alpha = 29.3 \text{ per cent. of } H_2 \text{ dissociated}$$

$$10.77 \text{ cc./10 min.} \times 0.293 = 3.155 \text{ cc. of dissociated } H_2 \text{ in ten minutes}$$

$$\text{Calorimetric data} = 15.03 \text{ cal./10 min.}$$

$$\frac{22{,}412}{3.155} \times 15.02 = 106{,}900 \text{ cal./gr. mol. wt.}$$

Beckmann against time. The resulting curves were corrected for cooling effect and their calorimetric values computed from the specific heat of the calorimeter, which was found to be 7.763 cal./deg. Fig. 3 shows the temperature curves used in one experiment.

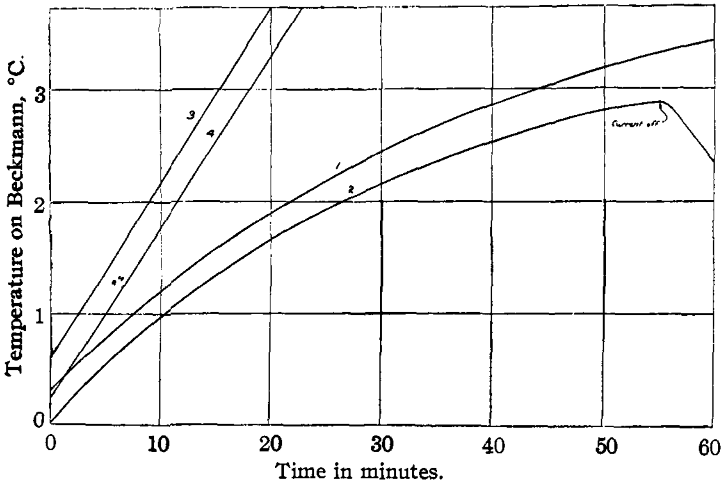

Fig. 3.—1, Temperature curve with discharge on; 2, temperature curve of calibration; 3, curve 1, corrected; 4, curve 2, corrected.

### Experiment 2

| | |
|---|---|
| Rate of flow of hydrogen corrected to normal temperature and pressure | 10.10 cc./10 min. |
| Pressure in discharge tube with no current | 0.23877 mm. |
| Pressure in discharge tube with current | 0.27094 mm. |

$$\frac{2\alpha}{1+\alpha} = \frac{P_H}{P_D} = \frac{3.41\ (0.27094 - 0.23877)}{0.27094} = 0.4049$$

$\alpha$ = 25.38 per cent. of $H_2$ dissociated

10.10 cc./10 min. × 0.2538 = 2.56 cc. of dissociated $H_2$ in 10 min.

Calorimetric data = 11.8 cal./10 min.

$$\frac{22{,}412}{2.56} \times 11.80 = 103{,}100 \text{ cal./gr. mol. wt.}$$

### Experiment 3

| | |
|---|---|
| Rate of flow of hydrogen corrected to normal temperature and pressure | 10.56 cc./10 min. |
| Pressure in discharge tube with no current | 0.24289 mm. |
| Pressure in discharge tube with current | 0.27598 mm. |

$$\frac{2\alpha}{1+\alpha} = \frac{P_H}{P_D} = \frac{3.41\ (0.27598 - 0.24289)}{0.27598} = 0.40326$$

$\alpha$ = 25.25 per cent. of $H_2$ dissociated

10.56 cc./10 min. × 0.2525 = 2.66 cc. of dissociated $H_2$ in 10 min.

Calorimetric data = 12.6 cal./10 min.

$$\frac{22{,}412}{2.66} \times 12.6 = 105{,}810 \text{ cal./gr. mol. wt.}$$

As a check on this method a blank experiment was carried out. A piece of platinum wire gauze was inserted in the tube leading from the discharge tube to the small holes at the point F in Fig. 1. The purpose of this gauze was to associate all the atomic hydrogen before it reached the small hole system and calorimeter. The results of this experiment showed that there was no observable difference of pressure between the steady state of discharge and the steady state of no discharge, and that there was no observable heat effect in the calorimeter. We feel that these results prove that the observed pressure change in the reported experiments were due to atomic hydrogen which was completely associated by the platinum gauze, and that there was no thermal leakage from the Wood's tube to the calorimeter.

## Discussion

The reported values of the heat of association of atomic hydrogen are as follows: Langmuir,[6] from the energy loss of a tungsten filament heated in hydrogen, 90,000 cal.; Frank,[7] from the energy absorbed by molecular hydrogen from electron impact, 80,000–100,000 cal.; Olsen and Glockler,[8] from a study of ionization potentials, 73,000 cal.; Wohl,[9] from the energy of a detonating gas mixture, 96,000 cal.; Bodenstein and Jung,[10] from calculations on the heat of formation of hydrogen bromide investigated by Herzfeld,[11] 107,000 cal.; Whitmer,[12] from band spectra of hydrogen, 100,100 cal.; Dieke and Hopfield,[13] also from band spectra of hydrogen, 101,000 cal.; Condon,[14] from a study of wave mechanics, 101,400 cal.; this method average, 105,270 cal.

The possible experimental errors introduced by the limits of the accuracy of the recorded data are as follows:

| Source of error | Possible % error in results | Source of error | Possible % error in results |
|---|---|---|---|
| Rate of flow of hydrogen | 0.25 | Calibration of calorimeter | 1.25 |
| Steady state pressures | 3.00 | Limiting experimental error | 3.28 |
| Temperature rise of calorimeter | 0.34 | Experimental deviation from the mean | 1.1 |

The following theoretical assumptions are involved in this method. (I) The gas on the high pressure side of the small hole has a distribution of velocity that will permit the use of equation (1). (II) The observed pres-

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[6] Langmuir, THIS JOURNAL, **36**, 1708 (1914); **37**, 417 (1915).

[7] Frank, *Physik. Z.*, **22**, 467 (1921).

[8] Olsen and Glockler, *Proc. Nat. Acad. Sci.*, **9**, 122 (1923).

[9] Wohl, *Z. Electrochemie*, **30**, 49 (1924).

[10] Bodenstein and Jung, *Z. physik. Chem.*, **121**, 127 (1926).

[11] Herzfeld, *Ann. Physik.*, **59**, 635 (1919).

[12] Whitmer, *Proc. Nat. Acad. Sci.*, **12**, 238 (1926).

[13] Dieke and Hopfield, *Z. Physik*, **40**, 239 (1926).

[14] Condon, *Proc. Nat. Acad. Sci.*, 13, 469 (1927).

sure change is due solely to the percentage of monatomic hydrogen passing through the small hole. (III) The calorimeter records the total energy of recombination of the dissociated gas that passes through the small holes and only this energy.

Since the flow of gas through the apparatus imparts an added velocity to the gas in the direction of the hole, the validity of assumption (I) is brought into question. One cc. of hydrogen, measured at atmospheric pressure, flowing through a tube 0.85 cm.$^2$ in cross section, at a pressure of 0.25 mm. has a velocity of about 70 cm./sec. Since the average velocity of a hydrogen molecule at 300°K. is about 210,000 cm./sec., this superposed unidirectional flow can have little effect on the distribution of velocities. Of even less importance is the effect on distribution of velocities of the recombination of the hydrogen atoms on the walls and through ternary collisions in the region in front of the small holes. The rate of recombination of monatomic hydrogen is not known but supposing as an upper limit that it is proportional to the concentration of atomic hydrogen, and supposing the gas leaving the discharge tube to be pure atomic hydrogen, about 1.5% of the atomic hydrogen would combine in the cm. in front of the holes. The amount passing through the tube is 1 cc. of $H_2$ or 2 cc. of H per minute. The limiting rate of combination is $2.7 \times 10^{19} \times 0.25/760 \times 0.015 \times 2/60 = 4.4 \times 10^{12}$ atoms per sec. But the total number of collisions of the hydrogen atoms per cc. per sec. at these pressures is of the order of $2 \times 10^{29} \times 0.25/760 = 6.6 \times 10^{25}$; therefore the proportion of collisions resulting in chemical reaction is negligible.

Assumption (II) requires that under the conditions of this experiment there is no $H_3$ or any species of hydrogen other than H and $H_2$.

Recent experiments[15] seem to render improbable the existence of $H_3$ under these conditions. If it were present our results would have been lowered because of the higher concentration of H present than was assumed. They would also have to be varied because the heat reaction $H + H_2 = H_3$ is small. The two partial corrections would tend to cancel. That there is no pressure drop due to some effect of the discharge other than that due to a gas which recombines on platinum is shown by the blank experiment.

Although a known impurity of about 3% of water vapor was present, the probability of dissociated water vapor in an atmosphere of hydrogen, at a distance of 25 cm. from the discharge tube is exceedingly small. Since the same amount of water vapor passed the small holes during discharge and when there was no discharge, it had no effect on the pressure measurements.

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[15] (a) Paneth, Klever and Petros, *Z. Electrochem.*, **33**, 102 (1927); (b) Smallwood and Urey, THIS JOURNAL, **50**, 620 (1928); (c) Bach, *Ber.*, **58B**, 1388 (1926); (d) Scanavy-Grigoriewa, *Z. anorg. allgem. Chem.*, **159**, 55 (1927).

Assumption (III) requires that there be no heat effect not due to combination of hydrogen on the calorimeter. This is proved by the blank experiment. It also requires that all the monatomic hydrogen passing through the small holes recombine on the platinum calorimeter. The mean free path at the pressures in the calorimeter is long enough to insure that every hydrogen atom will strike the calorimeter at least once. From the geometry the probable number of collisions is at least 3. The coefficient of recombination of hydrogen atoms on a platinum surface is not known but all qualitative information indicates it is very high. If it is above 80%, the error introduced is less than 1%. Such incomplete recombination would mean that our value was too low.

This determination was made at constant pressure. The corresponding value at constant volume would be some 600 calories smaller.

## Summary

A new direct method for the determination of the heat of formation of molecular hydrogen has been described. The mathematical theory and a description of the apparatus have been given.

The results of three experiments and one blank determination have been presented with a discussion of the possible experimental and theoretical errors.

The value of the heat of formation of molecular hydrogen has been determined by this method as 105,000 ± 3500 calories.

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[Contribution from the Chemistry Laboratory of the University of Michigan]

# CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. I. PREPARATION AND STANDARDIZATION OF SOLUTIONS. DETERMINATION OF CALCIUM

By H. H. Willard and Philena Young[1]

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## Introduction

The use of ceric salts as oxidizing agents has been suggested by a number of authors. Lange[2] in referring to the oxidizing properties of ceric sulfate recommends it as a volumetric reagent; Sonnenschein[3] suggests it instead of permanganate for the titration of iron; A. Job[4] speaks of the stability and strong oxidizing properties of acid solutions of ceric salts and of their possible use in cases where permanganate is not applicable as in the esti-

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[1] From a dissertation submitted by Philena Young to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Lange, *J. prakt. Chem.*, **82**, 129 (1861).

[3] Sonnenschein, *Ber.*, **3**, 631 (1870).

[4] Job, *Compt. rend.*, **128**, 101 (1899).