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THE HEAT OF FORMATION OF MOLECULAR OXYGEN

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Abstract

An apparatus has been constructed and described for the production of atomic oxygen and the direct determination of the heat of formation of molecular oxygen. A series of determinations have been conducted in the pressure range of 0.1 to 0.55 mm of mercury. The heat of formation of molecular oxygen was determined by these experiments as 131,000 (±6,000) calories or 5.7 (±0.3) volts per gram molecular weight. Several of the properties of atomic oxygen have been investigated including the possibility of long-lived metastable states.

Introduction

The dissociation energy of molecular oxygen has been determined by several indirect methods, the probable values ranging from 110,000 calories or 4.8 volts to 162,000 calories or 7.05 volts. In this work a direct calorimetric determination has been made. In preliminary reports by Bichowsky and the author[2] the presence of atomic oxygen in the gas issuing from a discharge tube was first demonstrated and a few of its properties determined. The method employed for the determination of the heat of association of atomic oxygen is the same as that used by Bichowsky and the author in their determination of the heat of formation of molecular hydrogen.[3]

Electrolytic oxygen was admitted to the electrodeless discharge bulb D, Fig. 1, at a determined rate of flow by the capillary A. The gas partially dissociated by the discharge from the high frequency current in H, passes through a set of orifices B and is associated on the palladium black surface of the calorimeter E. The temperature rise of the calorimeter above the temperature of the constant temperature bath I gives the energy of association of the partially dissociated gas. The percent of atomic oxygen in the gas is determined from the formula $2\alpha/(1+\alpha)=3.41(1-P_N/P_D)$ where α is the percent dissociation, P_N is the pressure of the gas on the high pressure side of the orifices B under steady state conditions of no dissociation, before the discharge is turned on, P_D is the pressure of the gas at the same point under the steady state conditions involving dissociation when the discharge is going. As the development of this formula from Knudsen's formula for the rate of flow of gas through a small orifice is given completely in a former paper[3] it will not be repeated here.

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[1] National Research Fellow in Chemistry.

[2] Bichowsky and Copeland, Nature **120**, 729 (1927); Phys. Rev. **31**, 1113(A) (1928).

[3] Bichowksy and Copeland, J.A.C.S. **50**, 1315 (1928).

Apparatus

The source of oxygen was a water-cooled electrolytic generator with nickel electrodes and CO_2-free potassium hydroxide solution as electrolyte. The rate of flow of gas into the apparatus was determined by capillary *A*. As the rate of flow of gas through a capillary is dependent on the pressure on the high pressure side, a manometer *M* was attached to the generator line which actuated a relay to control the D. C. current to the generator and thereby maintained the source of oxygen at constant pressure. Capillary *A* was also immersed in the constant temperature bath *I* (for simplification the sketch does not illustrate this). The rate of flow of oxygen into the apparatus was measured by means of the pipette and leveling bulb *L*. The volume of the pipette between the two scratches on the capillary tubes on either end was accurately known. In determining the rate of flow, stop-cock *K* was closed and the time required to fill the pipette with mercury from the leveling bulb was taken on a stop watch, care being taken to maintain constant pressure as indicated by manometer and relay.

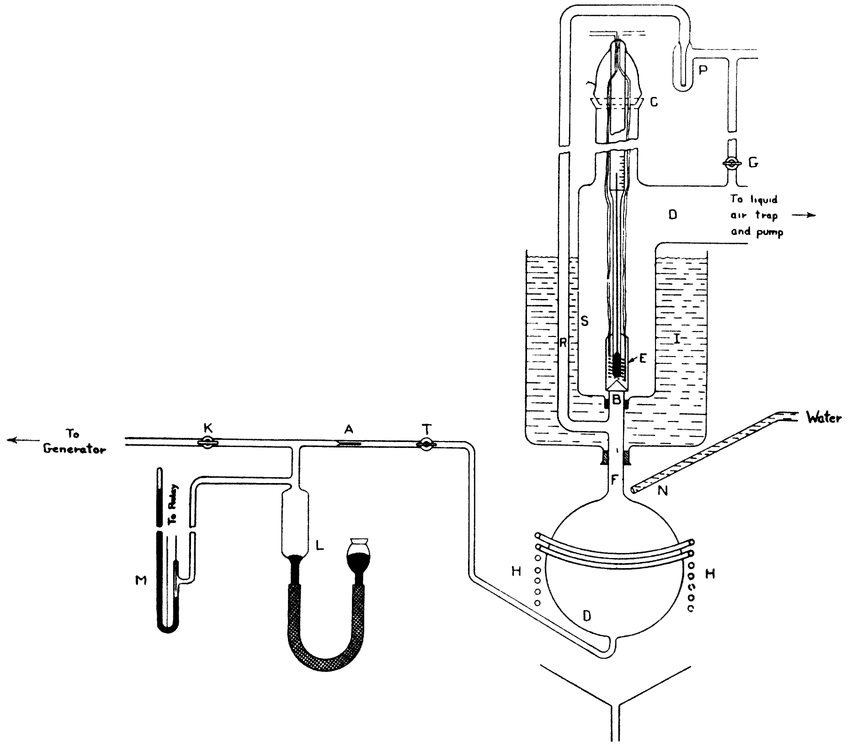

Fig. 1. Diagrammatic sketch of apparatus.

The discharge bulb *D* was made from a 500 cc round bottom flask. During an entire experiment this bulb was covered with running water from tap *N* discharging into the funnel placed beneath the bulb. The induction coil *H* was constructed of seven turns of 1/8 inch copper tubing through which water was circulated to keep it cool. The current was supplied from an induction furnace circuit which consisted of 3kva 1–100 transformer, two 0.035 microfarad oil condensers and a quenched spark gap. The dissociated gas left the discharge bulb through the tube *F* which was a 1 cm piece of tubing about 13 cm long and terminated in the set of orifices *B*.

The use of Knudsen's formula for the flow of gas through orifices is applicable only if the area of the orifice is small in comparison to the mean free path of the gas, and the thickness of the plate in which the orifice is made must also be small in comparison to the diameter of the hole. Thus at 0.1 of a mm pressure the diameter of these orifices and the thickness of the wall in which they were made had to be of the order of magnitude of 0.1 mm.

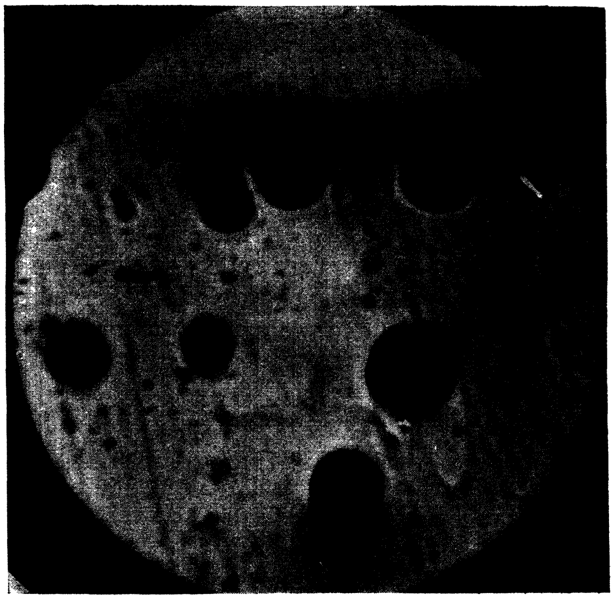

Fig. 2. Microphotograph of a portion of one set of orifices.
Largest holes 0.2 mm in diameter.

Sets of orifices containing 15 to 40 such holes were obtained in the following manner. The end of a piece of Pyrex tubing was blown out to give a large fragile bubble of glass about 0.1 mm in thickness. A small section of this thin glass was placed on a carbon plate and the end of a piece of 1 cm cross-section Pyrex tubing was heated to flowing temperature and then pressed against the thin glass thus sealing it to the end. A piece of 1/32 inch tungsten wire was mounted in the chuck of a jeweler's lathe and a fine centered point produced by burning it with an oxygen flame while the lathe was rotating. This fine drill was then heated red hot with an air flame and the thin wall lightly brought to the hot point. After considerable practice several very satisfactory sets of orifices were obtained. A microphotograph of a portion of one of these sets is shown in Fig. 2 in which the largest hole is about 0.2 mm in diameter. These orifices were sealed to tube *F* and fastened into the bottom of the calorimeter jacket *S* with sealing wax, to facilitate centering and replacement.

The pressure at *B* was measured on a large thermostated McLeod gauge which was connected to the apparatus through *R*, a tube of 1 cm diameter. This gauge was read with a cathetometer. A liquid air trap *P* was inserted in the McLeod gauge line in order to keep mercury out of the apparatus because it destroyed the atomic gas and poisoned the catalytic surface of the calorimeter.

Stop-cock *G* was closed during the run but opened as a bypass to protect the fragile orifices when it was desired to change the pressure in the apparatus by more than a few cms. This bypass was also of assistance when evacuating the entire apparatus before starting a run.

The calorimeter *E* was constructed of a cylinder of platinum foil 1.5 cm in diameter and 4.5 cm long. This cylinder was closed at the bottom end by a platinum foil cone and sealed to the bulb of a Beckmann thermometer with Wood's metal. A coil of enameled nichrome wire with enameled copper potential and current leads was sealed in the Wood's metal. This coil was for the calibration of the calorimeter. On the conical surface of the calorimeter was deposited electrolytically an even layer of palladium black. The Beckmann thermometer and calorimeter were sealed into the upper section of a ground joint *C* with sealing wax. Tube *D* served to conduct the gas to the conventional liquid air trap, mercury pump, fore pump, and low pressure McLeod gauge. The thermostat *I* consisted of an inverted bottle from which the bottom had been removed. It was fastened to *F* with a rubber stopper and supported separately. In addition to what is shown in Fig. 1, the thermostat contained a toluene thermoregulator, stirrer, lamp, Bechmann thermometer, cooling coil, and capillary *A*. The temperature of the water in the thermostat could be maintained constant to within 0.01°C.

SOME QUALITATIVE PROPERTIES OF ATOMIC OXYGEN

The first experiments[2] made on the study of atomic oxygen made use of a discharge tube containing aluminum electrodes for dissociating the gas. The electrodeless discharge produced a much larger percentage of atomic gas due to the absence of any metal that could produce a "clean up" effect. This fact is in accord with the observations of Kurt and Phipps.[4] Also in agreement with these authors it was found that water vapor was necessary for the establishment of dissociation. This fact was demonstrated very convincingly in the following manner. A 500 cc long-neck distilling flask was evacuated and then filled with moist oxygen gas to a pressure of about 0.2 mm and sealed off from the apparatus. When this bulb was held in the induction coil of the oscillating circuit a greenish blue discharge with a red center appeared that showed in the hand spectroscope, the line spectra of O I and the first three members of the Balmer series against a dark back-

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[4] Kurt and Phipps, Phys. Rev. **34**, 1357 (1929).

ground. If the neck of the bulb was now placed in liquid air the entire character of the discharge slowly changed, the lines fading out and a banded background developing till finally $H\alpha$ the last to disappear, left nothing but a banded spectra. When the liquid air was removed, the reverse phenomena took place till at the end of a few minutes nothing but line spectra again remained. There were also a few specks of foreign material on the sides of the bulb that were incandescent when the line spectra were present and invisible when the band spectra were predominant. If the neck of the bulb was first cooled in liquid air and then placed in the exciting field, the first flash showed red and then immediately changed to the blue banded spectra. The interpretation is that the removal of water vapor by freezing it out with liquid air either prevented the dissociation of the O_2 molecule or, in analogy to Wood's[5] explanation of the role of water vapor in the production of atomic hydrogen, the removal of water vapor exposed the dry glass walls which were sufficiently catalytic for the recombination of oxygen atoms to cause their complete removal. In either case excited atoms were not present in the dry bulb in sufficient number to produce detectable line spectra or cause the foreign particles to glow by the heat of recombination of oxygen. The energy of the discharge was then taken up in the excitation of the molecules as shown by the ensuing band spectra. As another illustration of the necessity of water vapor it should be mentioned that when liquid air was applied to the inlet line of the apparatus between A and D during the discharge there was a gradual decrease in pressure and a steady drop in the temperature of the calorimeter indicating a decreased percentage of dissociation. Both of these readings returned to their former value when the liquid air was removed.

Although these experiments do not show any optimum pressure for dissociation as mentioned by Kurt and Phipps,[4] it should be noted that any dependence of dissociation at the orifices on pressure is probably completely masked by the changes in the surface conditions of exit tube F which was frequently changed throughout the course of these experiments and by changes in the rate of flow of gas through the apparatus.

Mercury vapor is very readily oxidized to the yellow form of mercuric oxide by atomic oxygen. Unless liquid air is maintained on the traps on all lines leading to a source of mercury vapor the cooler portions of the apparatus soon become coated with a yellow sheen due to this oxide.

Traces of nitrogen give the familiar greenish afterglow due to the metastable molecules. At the same time some compound is formed, possibly an oxide of nitrogen which will travel through the liquid air traps and react with mercury leaving a dirty black deposit[6] that destroys the use of McLeod gauges. For the above reasons tank oxygen could not be used in these experiments.

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[5] Wood, Proc. Roy. Soc. **102,** 1 (1922).

[6] This black deposit may be removed without disassembling the apparatus even if it can not be heated, by filling the contaminated section with a few tenths of a millimeter of hydrogen and passing a discharge through that portion with an induction coil such as is used in testing for leaks.

Atomic oxygen like atomic hydrogen will cause small specks of substances, catalytic for the recombination, to glow white-hot in the dissipation of the energy of this reaction. A rough qualitative study of five metals was made to find a suitable catalyst for the surface of the calorimeter. Wires of these metals about 0.002 inches in diameter and 1 inch long were mounted on magnetic probes in another apparatus so they could be moved towards or away from the discharge bulb in vacuum. It was found that palladium, platinum and nickel were readily heated to glowing by the atomic oxygen but that copper and tungsten* were not visible affected. Palladium was apparently the most active and both palladium and platinum wires could be melted by bringing them too close to the discharge or increasing the flow of gas suddenly. Although it was necessary to bring the wires to within 10 cm of the discharge bulb to start them glowing, after they were hot they could be removed as far away as 35 cm from the discharge bulb in the direction the gas was flowing where they would still glow visibly and apparently indefinitely. This initial lag which was always present if the wire for any reason became cooled is believed to be due to a surface layer of gas or water vapor which prevented the reaction taking place except at high concentrations of atomic gas. Once the reaction was started the temperature of the wire kept its surface free until it was allowed to cool again. Platinum was first chosen at the most practical catalyst for recombination but subsequent experiments showed it was not sufficiently effective. Every collision of an oxygen atom did not mean capture for recombination. (See blank experiments) Palladium black however both because of its greater area and its greater activity was found to be sufficiently effective.

EXPERIMENTS ON HEAT OF FORMATION

At the beginning of all experiments the capillary *A* was closed off by the stop-cock *T* and the bypass *G* was opened. The apparatus was then evacuated until the McLeod guage showed a "flat guage," approximately 10^{-6} mm. Stopcock *T* was then opened and the bypass *G* closed. The following readings were taken periodically; the pressure on both sides of the orifices, temperature of the bath, the temperature of the calorimeter and the laboratory air temperature. Occasional checks on the rate of flow were made. When steady-state conditions were obtained, which generally required one to two hours, readings of all temperatures and pressures were taken every 10 minutes for a period from half an hour to an hour. If these readings showed no appreciable drift the discharge was turned on and the process of obtaining steady state readings repeated. After the discharge was turned off a new steady state set of readings was obtained and at the same time the calibration of the calorimeter was made by passing sufficient current from a 12 volt storage battery through a variable resistance and ammeter and the heating coil of the calorimeter to maintain the temperature of the Beckmann thermometer at the same point as it was during the discharge. These ammeter

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* In atomic hydrogen tungsten wires glow and platinum wires do not glow except with a large excess of oxygen. (See Wood, ref. 5).

readings and the reading of the potential drop across the heating coil gave an amount of energy per minute which was equal to that received by the calorimeter per minute during the discharge. The following computations are for Experiment 1.

Rate of flow of oxygen corrected to normal temperature and pressure 0.66014 cc/min.

Average pressure at B during last half hour of steady state of discharge 0.3544 mm.

Average pressure at B during last half hour of steady state of no discharge 0.3099 mm.

$$2\alpha/(1+\alpha) = 3.41(0.3544 - 0.3099)/0.3544 = 0.4282$$

$$= 27.24 \text{ percent of dissociated } O_2$$

0.660 cc/mm × 0.2724 = 0.180 cc dissociated O_2/min.

0.123 amps at 0.60 volts required to maintain the calorimeter at the temperature obtained during discharge.

0.123 amps × 0.60 volts × 60 = 4.428 joules/min
= 1.058 calories/min

22,412 cc/gr mol. wt × 1.058 calories/mm ÷ 0.180 cc/min
= 131,645 calories/gr molecular wt.

Table I gives the recorded data and results of fifteen experiments and one blank experiment, which will be explained later, arranged in the chronological order in which they were performed. Column 2 gives cc/min which is the rate of flow of oxygen corrected to normal temperature and pressure. Column 3 (P_D) gives the average pressure of the steady state during discharge and Column 4(P_N) the average pressure of the steady state after discharge. Column 5 gives the percent dissociation calculated from the pressure differences. Column 6 cal/min gives the energy in calories per minute required in the calibration of the calorimeter to bring it to the same tem-

TABLE I.

Experiment number	cc/min	P_D mm of Hg	P_N mm of Hg	Percent Dissociation	cal/min	ΔH cal/mol
1	0.660	0.3544	0.3099	27.24	1.058	131,645
2	0.660	0.3522	0.3109	24.94	0.964	131,267
3	0.660	0.3085	0.3087	0.00	0.000	
4	0.667	0.2036	0.1789	26.15	1.222	156,985
	0.667	0.2032	0.1789	25.67	1.200	156,987
5	0.667	0.2012	0.1792	22.92	1.048	153,611
6	0.378	0.1088	0.0998	16.46	0.454	163,244
7	0.373	0.1089	0.0995	17.35	0.474	164,201
8	0.815	0.2455	0.2189	22.70	1.272	154,045
9	0.111	0.3766	0.3245	30.86	0.203	132,886
	0.111	0.3757	0.3245	30.27	0.188	125,489
10	0.168	0.5555	0.4813	29.51	0.288	130,381
11	0.064	0.2152	0.1905	24.38	0.121	172,360
12	1.129	0.5533	0.4867	25.84	0.176	135,023
13	1.129	0.5560	0.4846	28.03	0.177	125,239
14	0.947	0.4657	0.4150	22.76	0.130	135,197
15	0.947	0.4661	0.4163	22.06	0.127	134,633
16	0.361	0.1784	0.1626	17.87	0.456	159,382

perature as it was during the steady state of discharge. Lastly are listed the computed values of the heat of formation in calories per gram molecular weight. In Experiments 4 and 9 two separate steady states were obtained with the discharge on, involving different temperatures of the calorimeter. For this reason two separate computations were made on these experiments.

Blank experiments. In experiment 3 a strip of platinum foil coated with palladium black was inserted in tube *F*. The purpose of this foil was to associate all the atomic oxygen before it reached the orifices 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. These results show that the observed pressure change in the other experiments was due to atomic oxygen which was completely associated by the palladium black surface to molecular oxygen and that there was no thermal leakage from the electrodeless discharge or exciting circuit to the calorimeter. These results were not obtained with a clean platinum surface in place of the palladium black. In the first experiments on this problem a shiny platinum surface was left on the calorimeter. Very inconsistent values were obtained for the heat of formation ranging from 50,000 to 150,000 calories. A similar blank with shiny platinum showed that only about 30% of the atoms were being associated. In all subsequent experiments the palladium black surface has been used. Whenever the calorimeter was removed a new surface of palladium black was deposited. This precaution was followed because one experiment not reported here, conducted after the apparatus had been standing for some time without liquid air on the traps, gave a value of 100,000 calories. Subsequent examination of the calorimeter surface showed an iridescently colored surface and minute drops of mercury visible with the aid of the microscope.

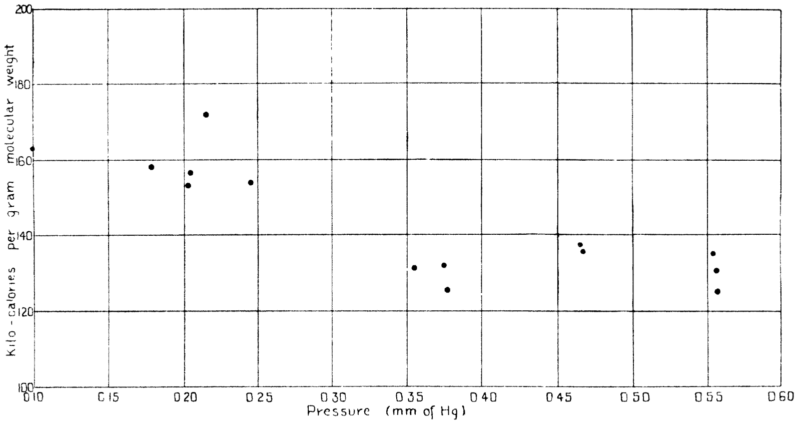

Fig. 3. ΔH-pressure plot of Table I.

As a check on the possibility that the field of coil *H* might cause a temperature rise in the calorimeter not noticed in the blank experiment the oscillating current was allowed to pass through the coil when the pressure was too low to excite a discharge, 10^{-4} mm and also when the pressure was so high that only a faint glow was visible, 10 mm. In both cases there was no discernable temperature rise in the calorimeter. There was no appreciable stray discharge to the calorimeter. To demonstrate this fact an auxiliary electrode was sealed into a side arm on *F* and grounded through a galvanometer. No current passed through the galvanometer during the discharge.

In all these experiments the pressure of the low pressure side of the small holes was about 1/80th of that on the high pressure side.

DISCUSSION

It should be noted that all values obtained from experiments where the pressure was below 0.3 of a mm are higher and not as consistent as the values obtained from those experiments conducted at higher pressures. Fig. 3 is a plot of all values of Table I in kilocalories as abscissas against pressure

TABLE II.

Author	Source	Value cal/gr mol.wt.
Warburg[8]	Photochemical formation of O_3	138,000
Born and Gerloch[9]	“ “ “	162,000
Eucken[10]	Heat of formation of CO	253,000–423,000
Wulf[11,12]	Ionization potentials	56,000–138,000
Hogness and Lunn[13]	Ionization potentials of O_2	150,000
Birge and Sponer[14]	Absorption bands of O_2	162,000
Birge[15,16,17,18]	“ “ “	138,000
Herzberg[19]	“ “ “	149,500
Kassel[20,21]	Decomposition of O_3	110,000
Mecke[22,23,24]	Predissociation in NO_2 bands	128,000
Henri[25]	Predissociation in SO_2 bands	126,400
Kaplan[26]	Birge's paper	131,000
Kondratjew[27]	Predissociation in NO_2 bands	118,000
Rodebush and Troxel[28]	Direct calorimeter measurement	131,000
Baxter[29]	Predissociation bands of NO_2	115,000
Average value of nine high pressure runs of this paper		131,300

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[7] Copeland, J.A.C.S. **52,** 2580 (1930).

[8] Warburg, Zeits. f. Electrochemie **26,** 58 (1920).

[9] Born and Gerloch, Zeits. f. Physik **5,** 433 (1921).

[10] Eucken, Ann. d. Chemie **440,** 111 (1924).

[11] Wulf, J.A.C.S. **47,** 1944 (1925).

[12] Wulf, Proc. Nat. Acad. Sci. **14,** 615 (1928).

[13] Hogness and Lunn, Phys. Rev. **27,** 733 (1926).

[14] Birge and Sponer, Phys. Rev. **28,** 259 (1926).

[15] Birge, Phys. Rev. **27,** 641 (1926).

[16] Birge, Nature **122,** 842 (1928).

[17] Birge, Phys. Rev. **34,** 1062 (1929).

[18] Birge, Trans. Faraday Soc. (1929).

[19] Herzberg, Zeits. f. Phys. Chemie **4B,** 223 (1929).

[20] Kassel, Phys. Rev. **34,** 817 (1929).

[21] Kassel, Zeits. f. Phys. Chemie **2B,** 264 (1929).

[22] Mecke, Naturwissenchaften **51,** 996 (1929).

in millimeters of mercury as ordinates. In a former note[7] the value obtained at low pressures was presented. Since that time the last eleven experiments given here have been made. Since the high pressure values are consistent among themselves within the experimental limits of accuracy over a range of pressure from 0.35 mm of mercury to 0.56 mm of mercury, the average of these results is taken as the correct value. It is quite possible that the high values at low pressures are due to excess energy from metastable oxygen atoms which would have a longer life at lower pressures due to the fewer number of collisions. It was on this assumption that the high pressure measurements were made. Further confirmation of this point was sought by making a few runs with the discharge bulb moved 42 cm away from the calorimeter. Under these conditions it would be expected that there will be a decrease in the percentage of the atoms in the metastable state, by the time they reached the calorimeter. Also there will be a decrease in the total number of atoms. Unfortunately experiments made with longer paths have not proved to be sufficiently reliable to draw any conclusions.

Table II gives the reported values of the heat of formation of molecular oxygen and the experimental source from which the computation was made.

All values of experiments made at pressures above 0.3 mm of mercury agree within 6,000 calories of their average which is therefore taken as the experimental error.

It is of considerable interest that the preliminary report of Rodebush and Troxel is also from a direct calorimetric determination which differs but slightly from the method reported here. The agreement of our results is of more significance because of the differences in the method which include a fundamentally different application of Knudsen's formula for the measurement of the percent of dissociation. This result agrees also with that of Kaplan's and within the experimental limits with those of Mecke and Henri.

For a discussion of the theoretical assumptions involved in this method the reader is referred to the paper of Bichowsky and Copeland.[3] In addition to what is stated there concerning the validity of the use of Knudsen's formula it should be mentioned that in this work it was found that the ratio of the rate of flow of oxygen to the pressure was a constant for each set of orifices over the range of pressures used.

The author wishes to acknowledge his indebtedness to Dr. F. R. Bichowsky who first suggested this problem and the method used. He also wishes to acknowledge the valuable assistance received from Mr. Foster Rieke including the final perfection of the method of making the sets of orifices. He

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[23] Mecke, Nature **125,** 526 (1930).

[24] Mecke, Zeits. f. Phys. Chemie **7B,** 108 (1930).

[25] Henri, Nature **125,** 275 (1930).

[26] Kaplan, Phys. Rev. **35,** 436 (1930).

[27] Kondratjew, Zeits. f. Phys. Chemie **7B,** 70 (1930).

[28] Rodebush and Troxel, J.A.C.S. **52,** 3467 (1930).

[29] Baxter, J.A.C.S. **52,** 3468 (1930).

is indebted to Professor L. C. Graton for the microphotographs. In conclusion he also wishes to thank Professor E. C. Kemble and the other members of the Physics Department of Harvard University for their valuable assistance in the direction of the activities of his fellowship.

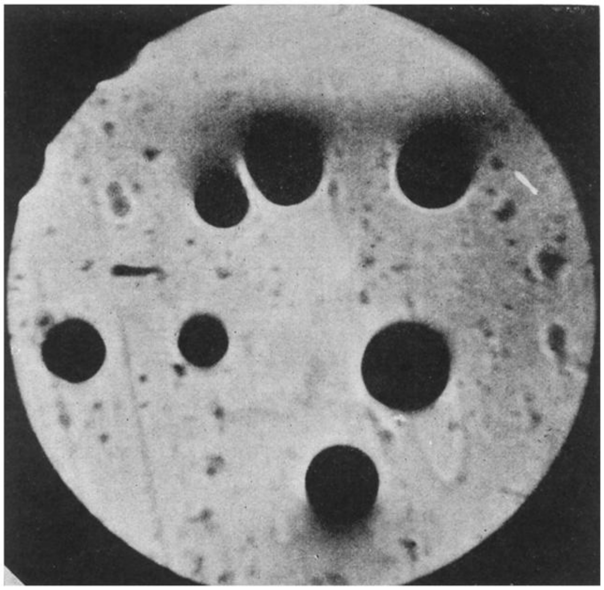

Fig. 2. Microphotograph of a portion of one set of orifices. Largest holes 0.2 mm in diameter.