[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITY OF OXYGEN FROM 12°K. TO ITS BOILING POINT AND ITS HEAT OF VAPORIZATION. THE ENTROPY FROM SPECTROSCOPIC DATA

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The investigation reported in this paper concerns the entropy of oxygen. Aside from its importance as an element, oxygen is particularly interesting in that its three known crystalline forms, as well as the liquid and the gaseous states, are strongly paramagnetic. The main interest lies in the magnetic behavior of the gaseous state and that of the crystalline state stable below 23.66°K. The fact that the gas has a positive magnetic susceptibility indicates a multiplicity in the quantum states which would lead to a considerable effect in the entropy. The paramagnetism of the solid state suggests the possibility that the application of the third law of thermodynamics in the ordinary manner to the calorimetric data of oxygen may not include a contribution to the entropy[1] arising from a random distribution of magnetons in the solid state. It may be said in advance that this latter effect does not contribute appreciably to the entropy of solid oxygen at the temperatures of liquid hydrogen. This is in rather sharp distinction to the case of $Gd_2(SO_4)_3{\cdot}8H_2O$, where the experimental data show[1c] that the magnetons are contributing over eight cal. per deg. per mole to the entropy of this substance at a temperature of 1.3°K.

The experimental procedure is based upon a calorimetric investigation of the various forms of oxygen from a temperature of 11.75°K. to the gaseous state at the boiling point. From the measurements the entropy of oxygen was calculated and found to be in agreement with that calculated from spectroscopic data. The purpose necessitated the attainment of high accuracy in the calorimetric measurements.

Preparation and Purification of the Oxygen

The oxygen was prepared by electrolysis of a sodium hydroxide solution in an electrolytic cell which operated on a current of four hundred amperes. Although generated in a commercial cell, there was little reason to expect impurities other than hydrogen and ozone since the electrolyte in the cell had been in service for a number of years (sufficient to bring about the removal of objectional impurities, if any) and was protected from contact with the air. From the generator the oxygen was carried under pressure to the purifying train. Special high vacuum stopcocks were employed and these were greased with rubber stopcock grease previously saturated with oxygen gas at 150°. Before use the entire purifying train was tested and found to hold a vacuum of 10^{-5} mm. of mercury. Adsorbed gases were removed by warming and sparking the glass

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[1] (a) Schottky, *Physik. Z.*, **22**, 1 (1921); (b) **23**, 9 (1922); (c) Giauque, THIS JOURNAL, **49**, 1870 (1927).

line a number of times and by evacuating it over a period of several days. Finally, a continuous stream of oxygen gas was passed through the line for several hours before any was collected. The train consisted of a tower of potassium hydroxide sticks to remove moisture, a long column of oxidized copper turnings heated to 400° in an electric furnace to remove hydrogen, two more towers of potassium hydroxide sticks, a tube filled with amalgamated copper turnings to decompose ozone (the potassium hydroxide and the copper oxide are also catalytic agents in the decomposition of ozone), two meters of tubing packed alternately with plugs of glass wool and of phosphorus pentoxide, and several bulbs, for use in fractionally distilling the liquid. We relied on the fractionation as the most reliable portion of the process for the removal of the final traces of impurity. The liquid oxygen was subjected to four steps in the fractionation. In each step only the middle portion was saved. About 600 cc. of liquid oxygen initially collected was reduced to a little over 100 cc. of final product which was distilled into the calorimeter. Before heat capacity measurements were begun, the oxygen in the calorimeter, frozen by the aid of liquid hydrogen, was evacuated with a mercury vapor pump for an hour or so to remove any last trace of hydrogen. Kahlbaum's phosphorus pentoxide was employed and Baker and Adamson's C. P. potassium hydroxide as reagents.

This method of purification is substantially that followed by Baxter and Starkweather[2] in their precise density determinations. We are using their value for the density of oxygen. We made no analysis of the oxygen; however, the shape of the heat capacity curve below the melting point and the sharpness of the melting point temperatures showed qualitatively that the oxygen was very pure. Oxygen was prepared on five different occasions. The various preparations of oxygen will be referred to by the designations I, II, III, IV and V.

Experimental Procedure

The experimental procedure in measuring heat capacities and in working up the data corresponded in the main to that of Giauque and Wiebe[3] in their measurements on the halogen acids and we employed the same gold calorimeter, II, and other portions of the same apparatus employed by them. The essential features of the method consisted in introducing a measured amount of heat electrically to the substance contained in the vacuum-jacketed calorimeter and measuring the temperature rise on a sensitive gold resistance thermometer calibrated at frequent intervals against a standard thermocouple soldered to the bottom of the calorimeter. The methods differed in certain important respects from those of Giauque and Wiebe. We will briefly outline some of these changes.

Timing.—To replace stop-watch and hand control of the electrical energy input circuits, a timing mechanism[4] that opened and closed the circuits electrically in response to time signals was designed. The time signals were obtained through the courtesy of the Astronomy Department of the University of California. By calibration it was shown that the heating intervals were thus timed within a maximum limit of error of 3×10^{-3} seconds in an absolute sense, which affected the final heat capacity values in the most unfavorable circumstances by only one part per hundred thousand. Measurements were made with sidereal time but this was corrected to solar time by the equation 1 solar second = 1.002738 sidereal seconds.

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[2] Baxter and Starkweather, *Proc. Nat. Acad. Sci.*, **12**, 699 (1926).

[3] Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928).

[4] Johnston, *J. Opt. Soc. Am.*, 17, 381 (1928).

Amount of Material Present in the Calorimeter.—The apparatus for measuring the amount of material present in the calorimeter during heat capacity measurements is shown in Fig. 1. The measuring bulb A is made from a five-liter pyrex round-bottomed flask and is supported in the hemispherical casting B. The internal diameter of B is a half inch larger than the external diameter of A and the intervening space is filled with a cast of Woods metal, C, poured when A was clamped in position. To the top and bottom of A are fused the small-diameter glass tubes D and E which bear etched scales marking volume intervals of 0.1 cc. The volume included between these two scales was determined by two calibrations which gave agreement to 0.13 cc. The calibrations were made by weighing mercury. The usual precautions in exact volume calibration were taken and the small volume effect due to distortion of the bulb by mercury pressure was evaluated. After calibration the lower end, E, was fused to a glass tube extending to the bottom of the six-liter cast-iron mercury reservoir F. This whole apparatus was immersed in a 25° thermostat which maintained a temperature constant to 0.01°.

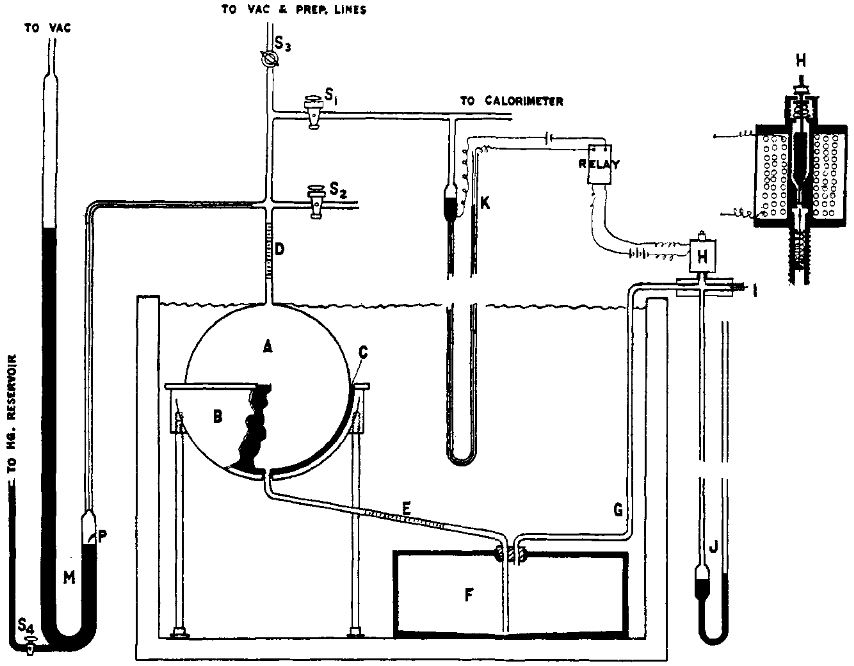

Fig. 1.

When the heat capacity measurements were completed and it was desired to measure the amount of substance present in the calorimeter, pressure was applied through the bicycle valve I to force mercury into Bulb A. A portion of the substance in the calorimeter was then vaporized by supplying heat and gas was collected in the bulb A. At the same time pressure was released in F by action of the electromagnetic valve H, whose action is described more fully in the next title, so that the mercury returned to the reservoir and the gas collected in A at atmospheric pressure. When A was almost filled with gas, as evidenced by the mercury height in the capillary manometer J, which was calibrated against an empirical scale, the vaporization was stopped and S_1 was closed. Further pressure was released in F by hand manipulation of the valves and the mercury meniscus was brought into the lower scale E. The pressure was then read on the constant dead-space, large-diameter manometer M which was enclosed in an air-jacketed case and was connected to A through capillary tubing to diminish volume external to the thermostat. The pressure was read with the aid of a standard meter scale and a Société Génévoise Cathetometer. This process was repeated until all of the material in the calorimeter was vaporized. It ordinarily required about eighteen repetitions to complete the measurement. These measurements included a small amount of gas in the line external to the thermostat. Although neither volume nor temperature of this portion of the gas was known to the same accuracy as that enclosed in the thermostat, the amount was small compared to that in A; moreover, it was largely canceled out since ordinarily gas at nearly the same pressure occupied this space both before A was filled with gas and after. The final of the 18-odd measurements included gas in the entire line volume, including the calorimeter. The calorimeter was warmed up to room temperature before this final measurement and it was usually possible to arrange that this should be a measurement of gas at low pressure so that the uncertainty of this volume introduced a negligible uncertainty into the total amount.

The following equation was employed for calculating the amount of gas from the PVT relationship.

$$\text{Amount in moles} = V{\cdot}P{\cdot}\frac{d}{M}\cdot\frac{1}{1+kT}\cdot[1+\alpha(1-P)]$$

where V = volume in liters, P = pressure in international atmospheres, d = density of the gas per liter at standard conditions, M = molecular weight, k = mean coefficient of thermal expansion for the range from 0 to 25°, T = temperature in °C. and α = the coefficient of deviation from Boyle's Law per atmosphere. In deriving P from the measured pressure, corrections were applied as given in "International Critical Tables,"[5] for temperature of mercury and of the standard meter scale and for capillary depression as measured by meniscus height. The gravitational acceleration was taken as 979.973 cm./sec.^{2} as given by Sternwarte[6] for this locality. The values used for the remaining constants employed in this equation are as follows: $d = 1.42898$,[2] $k = 0.003672$,[7] $\alpha = -0.00087$.[8] Any error in these constants will, of course, affect all of the heat capacity determinations alike. However, the uncertainty in these constants is so small that error from this source may be neglected.

Measurements of Heat of Vaporization

The heat of vaporization was measured by what corresponds to Method II in the paper of Giauque and Wiebe. The absorption bulb of their measurements was necessarily replaced in this work by the measuring bulb A described under the previous heading and the heating interval was chosen of such a length as not quite to fill the bulb.

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[5] "International Critical Tables," McGraw-Hill Book Co., New York, 1926, Vol. I.

[6] Landolt, Börnstein and Roth, "Physikalisch-Chemische Tabellen," Berlin, 1923.

[7] We used the value employed by Baxter and Starkweather. This is close to the value (0.003674) obtained by Jolly, *Pogg. Ann.*, Jubelband, 96 (1874).

[8] Batuecas, Maverick and Schlatter, *J. chim. phys.*, **22**, 131 (1925).

The automatic pressure control by the electromagnetic valve H maintained a pressure constant to about 0.1 mm. of mercury during the measurement. This resulted in constancy of temperature and consequently of resistance in the combined resistance thermometer heater by which the energy was supplied to the calorimeter. A very constant energy current was thus maintained and it was possible to read this factor with great accuracy in the course of the measurements. The construction of H is shown more clearly in the inset to the right of the diagram of Fig. 1. The basic ideas in the construction of this valve and in the electrical set-up are due to Smith.[9] When the pressure registered in the line leading from the calorimeter exceeds a certain predetermined value, an electrical circuit is completed through contact of the mercury with a platinum wire at K. Through a relay this energizes the magnet at H whose armature depresses the stem of a bicycle valve and releases air pressure from the reservoir F. This causes mercury to flow from A and lowers the line pressure. With proper adjustment at H, the regulator can be made very sensitive. The contact at K was adjustable and by this device heats of vaporization could be measured at any desired pressure. However, in this research, all measurements were made at a pressure of 760 mm. of mercury.

Attainment of Low Temperature.—Low temperatures were obtained by liquefaction of hydrogen and subsequent evaporation at low pressures in the manner of Giauque and Wiebe[10] but between the calorimetric apparatus and the vacuum pump of 150 cubic feet displacement mentioned in their article, a battery of three large Nelson oil vacuum pumps connected in parallel was included. These had a total displacement of 12 cubic feet per minute and were capable of producing a vacuum of better than 10^{-3} mm. of mercury in a non-gassing system. With their aid, a maximum temperature lowering to 10.7°K. was produced, although no heat capacity measurements were begun below about 11.7°K. The accuracy of the low temperature measurements was improved by breaking the vacuum in the space surrounding the calorimeter while cooling down, by use of helium gas at low pressure in preference to hydrogen gas. The helium was adsorbed to a much smaller degree than was the hydrogen and it was thus possible to regain a high vacuum in a much shorter interval following the cooling and to operate with a greatly reduced heat leak during the early measurements.

Temperature Scale.—The temperature intervals in the heat capacity measurements were determined from readings of a gold resistance thermometer wound on the exterior surface of the calorimeter and calibrated at short intervals in the course of heat capacity measurements by comparison with a standard copper constantan thermocouple W soldered to the bottom of the calorimeter. The method of treating the calibration data was that described by Giauque and Wiebe. The temperature scale for thermocouple W was fixed in terms of the hydrogen gas thermometer by Giauque, Buffington and Schulze,[11] and in terms of the hydrogen vapor pressure thermometer by Giauque, Johnston and Kelley,[12] for which it was the direct standard of comparison. These authors also found it in agreement with the oxygen vapor pressure thermometer. In the course of the heat capacity measurements, it was again compared with the oxygen vapor pressure thermometer and found to be in agreement and at the end of the measurements it was compared a second time with the hydrogen vapor pressure thermometer and found in agreement. The temperatures given by thermocouple W are believed to be correct to within 0.05°. All fixed temperature points recorded in the data that follow, such as transition points, melting points and boiling and vapor pressure points, are based directly on the temperature readings of thermocouple W. The readings taken from the resistance

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[9] Smith, *Ind. Eng. Chem.*, **16**, 22 (1924).

[10] *Cf.* Latimer, Buffington and Hoenshel, THIS JOURNAL, **47**, 1571 (1925).

[11] Giauque, Buffington and Schulze, *ibid.*, **49**, 2343 (1927).

[12] Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

thermometer should represent the temperature intervals correctly to within 0.001 to 0.003° since over a short interval the absolute error of calibration should not vary appreciably and since the resistance readings are reproducible to 0.001 ohm, which corresponds to 0.001° over nearly the entire temperature range above 35°K. At lower temperatures, errors in the temperature interval may be larger and may approximate 0.01 to 0.05° at the very lowest temperatures, where dR/dT rapidly diminishes. Two different resistance thermometers of nearly similar character and dimensions were employed in the course of the measurements.

Corrections to the Experimental Data.—In addition to corrections involving only physical constants of the substances measured, the following experimental corrections were applied because of conditions peculiar to the method and apparatus.

(a) A correction amounting normally to about 0.2 of 1% of the total heat input was applied for heat generated in a resistance of 55,000 ohms shunted across the thermometer heater terminals for purposes of measuring the potential drop. This correction could be applied with high accuracy.

(b) A correction was applied for heat generated in a pair of No. 40 copper leads one inch in length bridging the vacuum space surrounding the calorimeter and connecting the gold resistance thermometer ends with the so-called thermometer terminals which were in thermal contact with the surrounding jacket. It was assumed that half the heat generated in this pair of leads went to the calorimeter and that half was conducted to the surrounding jacket. This entire correction amounts to only about 0.02 of 1% of the total energy.

(c) A correction amounting to 0.2 of 1% at liquid-air temperatures and increasing several fold at lower temperatures was applied for heat interchange between the calorimeter and its surroundings during the heating period. This correction was obtained from measurements of warming rates before and after each run and could be applied with an error not over from 10 to 20% of the correction.

(d) A supplementary correction was applied to make allowance for the temperature head of the resistance thermometer from radiation and conduction during resistance measurements. This correction was evaluated through the application of Newton's Law of Heat Transfer combined with certain assumptions involved in the geometry of the apparatus. It affected the specific heats by less than 0.05 of 1% over the greater portion of the temperature range investigated, and introduced an uncertainty of 0.01 or 0.02% into the final data.

(e) Correction was applied for heat spent in vaporizing material into the 70-odd cc. of line volume adjacent to the calorimeter. This correction was effective over about the last thirty degrees of the heat capacity range investigated. It amounted to about 1% of the total energy input for the heat capacity measurement at the highest temperature, but its importance dwindled rapidly for the measurements at lower temperatures.

The correction itself might be in error by as much as 10%. In applying this correction we used the data of Cath,[13] in agreement with our own[12] for oxygen. Allowance was made for the vapor space within the calorimeter, for which we employed the densities of liquid oxygen given by Mattias and Onnes.[14]

(f) A correction amounting to from 10% to 15% of the total energy supplied was necessary to take account of the heat capacity of the empty calorimeter. This was evaluated from heat capacity measurements carried out on the empty calorimeter with the same care as those carried out on the substances investigated. The heat capacity of the empty calorimeter was determined in three separate series of measurements carried out, respectively, before, during and after the period covered by the measurements. A smooth curve fitted the experimental values to within 0.1 of 1% with almost no exceptions.

In measuring heats of transition, fusion and vaporization the heat interchange correction corresponding to corrections (c) and (d) was applied graphically by plotting, respectively, temperatures of calorimeter and of surrounding jacket against time elapsing during the measurement. From the area between the two curves thus obtained and with the further employment of an empirical heat interchange factor experimentally determined as a function of temperature difference between calorimeter and surroundings, the correction was applied. In one or two instances the magnitude of this correction exceeded 1%. More often it was about 0.2 or 0.3 of 1%. This correction introduced an uncertainty of about 10% of its value.

Probable Errors

Heat Capacity Measurements.—The expression for obtaining the heat capacities from the experimental data takes the form

$$C_p \text{ (at } T) = \frac{\left(\frac{\epsilon \cdot I \cdot t}{\Delta T} \cdot W\right) - C_c}{A}$$

where ϵ = voltage across heater terminals during heat input, I = amperes through heater during heat input, t = the time of heat input in seconds, W = factor for converting joules to calories. This factor is taken from "International Critical Tables."[5]

We express our results in terms of the 15° calories: C_c = heat capacity of the empty calorimeter, A = amount of material present in the calorimeter. By means of a White double potentiometer, ϵ was known to within 0.05 of 1% and I to within 0.02%.

The factor "t" is known with very high accuracy. In the most un-

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[13] Cath, *Comm. Phys. Lab. Univ. Leiden,* 152d (1918).

[14] Mattias and Onnes, *ibid.*, 117 (1911).

favorable circumstances, its limit of error has been mentioned as of about 0.001 of 1%.

ΔT is determined from resistance measurements made with the White potentiometer. As the temperature interval was usually between 4 and 5°, 0.05 of 1% appears a reasonable limit of error in this factor. To this must be added a possible error of 0.1 of 1% for uncertainty of temperature scale on the resistance thermometer. It should be mentioned that this latter error will have little effect on the entropy since if the temperature coefficient of resistance is too high in some temperature region, it must be too low by a corresponding amount in some adjacent temperature region.

The correction for heat capacity of the calorimeter has been discussed under the heading correction (f). The uncertainty present in this factor may introduce an error of from 0.01 to 0.03 of 1% in the final values of C_p.

Error in the amount of material present in the calorimeter is introduced by each of three factors, pressure, volume and temperature of the gas. From a consideration of these combined factors, the amount of gas measured cannot be in error by more than 0.03 of 1% for an individual measurement and must average to a somewhat smaller limit over the eighteen-odd measurements involved in obtaining A.

The limits of error present in these factors combined with those introduced in the corrections (a), (b), (c), (d) and (e) thus cannot introduce a greater maximum error than about 0.4 of 1% into individual specific heat points and that only for the highly improbable assumption that all errors are present at a maximum and in the same sign. The probable error should not exceed half of this figure. As a matter of fact C_p values obtained with this apparatus rarely deviate from a smooth curve drawn through the points by over 0.1 of 1% in the region above 35°K.; 0.2 of 1% appears to be a reasonable limit to the error of the smooth curves through our data. The statements here made apply only for the temperature region above 35°K. Below that temperature the inaccuracy increases, due in part to the increase in the relative importance of the various correction factors, to the smaller heat capacities but principally to the decreasing $\mathrm{d}R/\mathrm{d}T$ of the resistance thermometer. At 20°K. the values for C_p may be as much as 0.7 of 1% in error and at 12° the errors of measurement may be as high as 5%.

Heats of Transition, Fusion and Vaporization.—The heats of transition and fusion contain about the same probable error as do the specific heats. The heats of vaporization are somewhat more accurate, however, due to a smaller contribution from several factors that introduce the major inaccuracies. The more important of these favorable influences are the small, almost negligible, ΔT; the nearly constant energy current, I; the smaller correction for extraneous heat capacity and the smaller inaccuracy remaining in the heat interchange correction. The mean of the several determinations of heats of vaporization is believed to be correct to within 0.1 of 1%.

Heat Capacity Data.—Four series of measurements were carried out to determine the heat capacities of solid and liquid oxygen. Each was carried out with a different lot of oxygen and the preparation numbers corresponding to these four lots will serve to describe the series. Series

TABLE I

HEAT CAPACITY OF OXYGEN

Molecular weight, 32.000. Series I, 3.8387 moles; Series II, 3.7762 moles; Series IV, 3.9498 moles; Series V, 3.7929 moles.

Series	T, °K.	ΔT, °K.	C_p/mole in cal./deg.
V	12.97	2.445	1.10
IV	14.14	1.389	1.52
V	15.12	1.685	1.60
IV	15.57	1.323	1.79
II	16.66	1.324	2.33
V	16.80	1.496	2.18
IV	16.94	1.120	2.25
IV	18.13	1.120	2.67
II	18.32	1.604	2.71
V	18.45	1.676	2.79
IV	19.34	1.197	3.07
II	20.26	1.596	3.50
V	20.33	1.923	3.52
IV	20.85	1.494	3.60
II	21.84	1.317	4.20
IV	22.24	1.238	4.27
V	22.24	1.776	4.40
Transition at 23.66°			
IV	25.02	0.905	5.42
II	25.61	1.618	5.57
V	25.61	1.981	5.47
IV	26.75	2.494	5.75
V	28.00	2.781	6.05
II	28.08	2.405	6.42
IV	29.88	3.699	6.61
II	30.63	2.582	6.94
V	31.08	3.260	6.93
IV	33.05	2.580	7.52
II	33.33	2.787	7.73
V	34.41	3.244	8.08
IV	35.57	2.423	8.26
II	35.77	2.290	8.49
V	37.59	3.037	9.08
IV	37.85	2.024	9.12
II	38.47	2.936	9.80
IV	39.99	2.122	9.80
V	40.18	2.090	9.92
II	40.67	1.474	10.16
V	42.21	1.903	10.73
Transition at 43.76°			
IV	45.90	3.825	11.02
II	47.76	2.055	11.07
V	48.11	3.723	11.01
IV	48.97	2.208	10.99
II	50.55	3.152	11.01
V	51.68	3.338	11.03
IV	52.12	3.979	11.06
Melting Point at 54.39°			
V	56.95	3.360	12.76
II	57.95	3.056	12.72
V	60.97	4.596	12.71
II	61.48	3.944	12.71
II	65.57	2.887	12.71
V	65.92	4.282	12.71
I	68.77	3.277	12.73
II	69.12	4.159	12.75
V	70.67	5.104	12.77
I	71.38	3.245	12.78
II	73.31	3.848	12.81
I	74.95	3.767	12.85
V	75.86	5.070	12.80
II	77.58	4.632	12.84
I	78.68	3.640	12.83
V	81.13	5.395	12.88
II	82.31	4.748	12.86
I	82.96	4.681	12.88
I	84.79	3.704	12.93
V	86.43	5.151	12.91
II	86.61	4.619	12.95
II	86.97	4.526	12.92
I	87.32	3.924	12.91
V	90.33	2.612	12.99

I was carried out only for liquid oxygen; Series IV only for solid as a short circuit developed during the heat of fusion determinations. Series II and V covered both solid and liquid. Series V covered the extremes of the temperature interval investigated, as its measurements extended from 11.75°K. to 91.64°K. The individual results are tabulated in Table I. Column 1 gives the series number, Col. 2 the mean absolute temperature, Col. 3 the temperature interval covered and Col. 4 the heat capacity in calories per mole per degree.

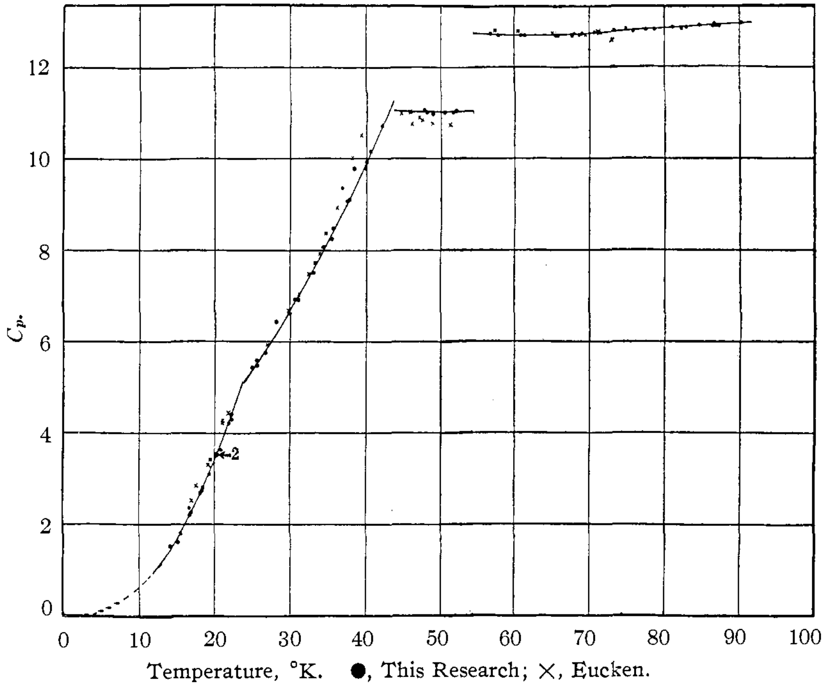

Fig. 2.—Heat capacity in calories per mole of oxygen.

These data are reproduced graphically in Fig. 2, where the dark circles represent the values obtained in the individual measurements. The various series of measurements are in good agreement for liquid oxygen as only six of the twenty-four measurements secured over that range lie off the smooth curve by more than 0.1 of 1%. The largest deviation is 0.3 of 1%. This curve is believed to represent the correct heat capacity for liquid oxygen to within 0.2 of 1%. The initial downward slope of the curve with a subsequent upward trend may indicate the presence of an equilibrium between polymerized and unpolymerized molecules with small heat of dissociation as predicted by Lewis.[15] This comment

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[15] Lewis, This Journal, **46**, 2027 (1924).

is in keeping with the minimum observed in the heat capacity data for water; see, for example, the data given by Barnes.[16]

The same degree of accuracy cannot be claimed for the curves representing the heat capacities of solid oxygen as for the liquid since the various series do not lead to quite the same close agreement, particularly for the two forms stable at lower temperatures. We cannot reconcile this small disagreement with what is believed to be the normal accuracy of the experimental method, particularly since repeated measurements made in determining the heat capacity of the empty calorimeter—an essentially more difficult measurement for the attainment of accuracy—and the various measurements for the liquid and for other substances all yielded individual values in good agreement with the respective curves. We suspect that the somewhat poorer agreement for solid oxygen may be due to some characteristics in its behavior observed by Wahl,[17] who found that liquid oxygen becomes viscous close to its freezing point and readily supercools to a glass interfused with crystals of the solid modification stable just below the melting point. When cooled to the transition (at 43.76°K. by our measurements), Wahl reports that the crystal modification stable below that temperature is formed almost instantaneously from the supercooled glass. This crystal form cracks badly and appears to have a considerably greater density than the higher temperature form. The latter property would lead to poorer thermal conductivity within the calorimeter and would increase the difficulties attendant on the attainment of accuracy. The former property might result in slight differences in physical composition in various instances. The comparative sharpness of transition and melting points discussed in the next section precludes the possibility of our having had more than traces of a physical form other than the respective pure crystals. Lest we convey an exaggerated impression of the irregularities in heat capacity to which we are referring, it should be mentioned that the individual measurements for the various solid modifications seldom were off the curves drawn by more than a very few tenths of one per cent., but the number of points that deviated over wider limits and the average deviations as well were considerably larger than for the other measurements. Due to the large number of points obtained, the curve for Solid I (43.76°K. to the melting point) is believed to be correct to within 0.3 of 1%, that for Solid II (23.66°K. to 43.76°K.) to within 0.5 of 1%, and that for Solid III (below 23.66°K.) to within 1% at its upper extremity but increases in uncertainty with temperature lowering and may be in error by 5% at the lowest temperature the measurements attained. In drawing the curves low weight has been given to certain measurements for which experimental

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[16] Barnes, *Trans. Roy. Soc. London,* **199,** 149 (1902).

[17] Wahl, *Proc. Roy. Soc. London,* **88,** 61 (1913).

conditions were less favorable, as shown by entries in the data books, and no weight has been given to two points obtained in Series I for Solid II which we could not substantiate in the later series when special care was given to those particular temperatures.

The graph includes the results of Eucken[18] shown by crosses. For Solid III Eucken is higher than our curve by amounts ranging from 6 to 14%, with an average deviation of 10%. Eucken's results are in agreement with ours for Solid II up to about 34°K. Above this temperature they deviate sharply and at 39°K. are about 9% above the curve. For Solid I Eucken obtains values lower than ours by about 2% on the average. For liquid oxygen the values of Eucken begin about 0.4 of 1% higher and approach the curve. His last point at about 73°K. is 1% lower than the curve. It seems probable that much of the discrepancy between Eucken's measurements and this investigation is due to his temperature scale between the liquid hydrogen and liquid air regions. It can be noticed that his measurements for Solid I are low and those for Solid II are high. This would be in accord with the fact that he recorded 42.5°K. for the I–II transition against the value of 43.76 ± 0.05°K. This transition temperature is very easily measured.

Melting and Transition Temperature.—The melting point was determined in one series of measurements with Preparation IV. The transition temperatures were both determined with Preparation III.

In determining the melting point the oxygen was first cooled below 40°K. and then warmed through the transition (Solid II to Solid I) in order to avoid the presence of supercooled liquid so far as possible. After warming into the melting point, twelve measurements were taken over a period of sixty-five hours and with different proportions of solid melted. The thermocouple showed an extreme difference of 0.05° and the resistance thermometer, which is essentially the more reproducible of the two, showed a maximum change of 0.015°. From these measurements the melting point was selected as 54.39 ± 0.05°K.

In determining the temperature of the higher transition seven measurements were taken over a period of eight hours. The thermocouple showed an extreme variation of 0.04° and the resistance thermometer a variation of 0.015°. From these measurements the value 43.76 ± 0.05°K. was obtained.

The lower transition temperature was studied over a period of five hours. Due to the low heat capacities of the portions of the apparatus, the low heat of transition and the difficulty of maintaining adequate constancy in the temperature of the surroundings at this temperature the same constancy of results could not be expected as for the higher temperatures. Both thermocouple and resistance thermometer showed a temperature

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[18] Eucken, *Ber. physik. Ges.*, **18**, 4 (1916).

variation of 0.1° among the eleven measurements carried out, in the course of which the percentage of oxygen transformed was increased from about 15% to about 65%. The value was 23.66 ± 0.1°K.

TABLE II

MELTING AND TRANSITION TEMPERATURES OF OXYGEN

Observer	Transition Temp., °K.	Transition Temp., °K.	M. p., °K.
This research	23.66 ± 0.10	43.76 ± 0.05	54.39 ± 0.05
(1916) Eucken[18]	23.5	42.5	54.1
(1911) Onnes and Crommelin[19]	..	..	54.7
(1911) Dewar[20]	..	..	54
(1903) Estreicher[21]	..	..	46

Heats of Fusion and Transition.—The heats of fusion and transition were measured in the usual manner, starting the heat input at a temperature a little below the melting point and ending at a temperature a little above. Correction was applied for $\int C_p dT$. The results are shown in Table III.

TABLE III

HEATS OF FUSION AND TRANSITION OF OXYGEN

Series I, 3.8387 moles; Series II, 3.7762 moles; Series IV, 3.9493 moles; Series V, 3.7929 moles.

Series	Temp. interval	Corr. total heat input (cal.)	$\int C_p dT$	ΔH, cal. per mole	Mean
		Fusion at 54.39°			
II	52.73–56.40	591.84	190.15	106.37	106.3 ± 0.3
V	53.86–55.24	499.20	96.66	106.13	
		Transition at 43.76°			
II	41.78–45.09	827.70	154.40	178.28	
IV	41.12–43.98	836.90	136.48	177.34	177.6 ± 0.5
V	43.20–46.20	814.58	142.09	177.29	
		Transition at 23.66°			
II	22.68–24.65	125.82	41.08	22.44	
IV	22.87–24.55	125.72[a]	36.91	(22.3–22.5)[a]	22.42 ± 0.1
V	23.16–24.60	115.63	30.68	22.40	

[a] Due to partial loss of vacuum during this measurement, a heat interchange correction amounting to one calorie in the total energy was rendered uncertain by 100%. Choosing the extreme limits for the uncertainty of the correction, we get the limiting values of ΔH included in the table.

Eucken[18] obtained 15.7 and 19.2 in two determinations of the lower transition heat, 166.7 and 168.0 in two determinations of the higher transition heat and 105.5 in one determination of the heat of fusion.

Heat of Vaporization.—The heat of vaporization was measured in the

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[19] Onnes and Crommelin, *Comm. Phys. Lab. Univ. Leiden*, No. 121c (1911).

[20] Dewar, *Proc. Roy. Soc. London*, **85A**, 597 (1911).

[21] Estreicher, *Bull. intern. acad. sci. Cracovie*, 836 (1903).

manner described earlier in this paper. The pressure was maintained constant at 76 cm. of mercury within 0.1 mm. All measurements were made with Preparation I. Heat was supplied for thirty-five minutes in the first measurement and for thirty-seven minutes in those following. The results are shown in Table IV.

TABLE IV

HEAT OF VAPORIZATION OF OXYGEN

Boiling point, 90.13°K.

This research		Other observers	
Moles O_2 evaporated	ΔH, 760 cm. of Hg in cal./mole	Observer	ΔH
0.20513	1629.4	(1925) Dana[22]	1631.7[b]
.20944	1627.8	(1916) Eucken[18]	1600[c]
.20871	1629.2	(1914) Keesom[23]	1625
.20714	(1635.4)[a]	(1911) Barschall[24]	1641
.20808	1629.2	(1906) Alt[25]	1629
.20688	1628.5	(1906) Dewar[26]	1635
Value chosen, 1628.8 ± 1.6		(1904) Estreicher[27]	1850
		(1903) Shearer[28]	1905

[a] The value in parentheses was given no weight in arriving at this value.

[b] This is a mean of 24 determinations varying from 1629.9 to 1638.5. 0.2 of 1% (3.3 calories) is claimed as the limit of error for the mean. We have corrected Dana's values to the "International Critical Tables" value for the mechanical equivalent of heat and to Baxter and Starkweather's value for the density of oxygen to correspond to the present work.

[c] Eucken states that on account of his experimental procedure, his heat of vaporization probably corresponds to a pressure higher than atmospheric.

Entropy from the Heat Capacity Data.—We have calculated the entropy of oxygen gas at the boiling point of oxygen, making use of the heat capacity data. In making the extrapolation below 11.75°K. the Debye function with $\beta\nu = 90.9$ has been used. It has been assumed that the oxygen molecule is acting as a unit at these low temperatures. The extrapolated entropy of 0.32 entropy units is very unlikely to contribute an appreciable error. Lewis and Gibson[29] made a similar calculation from the data of Eucken.[18] In Table V is summarized the entropy contribution of the various $\int C_p d \ln T$'s and ΔH's, both from our own data and from those of Eucken. The temperatures recorded in the first column are the present transition, melting and boiling point values. The entropy

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[22] Dana, *Proc. Am. Acad. Arts. Sci.*, **60**, 241 (1925).

[23] Keesom, *Comm. Phys. Lab. Univ. Leiden*, 137e (1914).

[24] Barschall, *Z. Electrochem.*, 17, 345 (1911).

[25] Alt, *Ann. Physik*, **19**, 739 (1906).

[26] Dewar, *Proc. Roy. Soc. London*, **76A**, 325 (1906).

[27] Estreicher, *Bull. intern. acad. sci. Cracovie*, 183 (1904).

[28] Shearer, *Phys. Rev.*, 17, 469 (1903).

[29] Lewis and Gibson, THIS JOURNAL, **39**, 2554 (1917).

contributions calculated by Lewis and Gibson of course make use of the corresponding temperatures determined by Eucken.

TABLE V

CALCULATION OF THE ENTROPY OF OXYGEN GAS

	This research, cal. per deg. per mole		Eucken, by Lewis and Gibson
0 to 11.75°K., extrapolation	0.321	Total 2.018	2.20
11.75 to 23.66°K., graphical	1.697		
Transition, 22.42/23.66	0.948		0.74
23.66 to 43.76°K., graphical	4.661		4.58
Transition, 177.6/43.76	4.058		3.94
43.76 to 54.39°K., graphical	2.397		2.62
Fusion, 106.3/54.39	1.954		1.95
54.39 to 90.13°K., graphical	6.462		6.52
Vaporization, 1628.8/90.13	18.07		17.72
Entropy of actual gas at boiling point	40.57 ± 0.1 E. U.		40.27

In order to make a comparison of this entropy value with that calculated from spectroscopic data, which is the primary purpose of this paper, it is necessary that the experimental value given above be corrected to the hypothetical perfect gas state. This may be done with the aid of Berthelot's equation and the thermodynamic equations involving the successive processes of expansion of the actual gas to zero pressure and of compression of perfect gas from zero pressure to one atmosphere. These lead to a net correction of $27T_c^3P/32T^3P_c$, as shown by Giauque and Wiebe.[3] With the aid of the critical data of Onnes, Dorsman and Holst,[30] namely, $T_c = 154.3$°K. and $P_c = 49.7$ atmospheres, $+0.17$ entropy units is obtained as the value of this correction for oxygen gas at its boiling point. Hence the entropy of the hypothetical perfect oxygen gas at 90.13°K. is 40.74 E.U.

Entropy from Spectroscopic Data.—Dieke and Babcock[31] have obtained measurements of the fine structure of the atmospheric absorption bands of oxygen. Recently Mulliken[32] has given an interpretation which is satisfactory for the strong bands in this absorption and more recently Giauque and Johnston[33] have extended Mulliken's interpretation to include the weak A′ band as well and so obtained a complete interpretation of the atmospheric bands. In the light of Mulliken's interpretation, the normal state of the molecule in oxygen gas is what is described by spectroscopists as a triplet *s* level. This means that the molecules in oxygen gas are differentiated into three forms of small energy difference characterized by the coupling between the angular momentum of electron spin

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[30] Onnes, Dorsman and Holst, *Comm. Phys. Lab. Univ. Leiden*, 145b (1914).

[31] Dieke and Babcock, *Proc. Nat. Acad. Sci.*, **13**, 670 (1927).

[32] Mulliken, *Phys. Rev.*, **32**, 880 (1928).

[33] Giauque and Johnston, THIS JOURNAL, **51**, 1436 (1929).

of the two unbalanced electrons in the oxygen molecule and the angular momentum of the rotating molecule. This coupling may be represented by drawing the momenta vectors oriented with respect to one another in parallel position, in anti-parallel position and in a position approximately at right angles. The molecules are further differentiated with respect to vibrational states with $n = {}^1/_2, {}^3/_2, {}^5/_2, \ldots\ldots$ The energy difference between the lowest state, the ${}^1/_2$ state, and the next higher state, the ${}^3/_2$ state, is sufficiently large (1554 wave numbers)[34] that at the boiling point of oxygen the number of molecules in the ${}^3/_2$ state is entirely negligible as shown by application of the Boltzmann factor. A still further differentiation of the oxygen molecules results from the quantized distribution of rotational energy among the various molecules. Characteristic of a homopolar molecule whose atoms have no nuclear spin, the alternately quantized rotation states are missing in oxygen, as in the diatomic helium molecule. This statement is supported by the quantum interpretation necessary to explain the Schumann bands of oxygen and by the interpretations of the atmospheric bands referred to above. The rotation states containing even-numbered units of angular momentum are missing and those present correspond to $j_k = 1, 3, 5, \ldots$ where j_k here is identical with the number of units of momentum possessed due to rotation of the molecule.

A further differentiation results due to the presence of isotopic molecules composed of an atom of oxygen of mass 16 combined with an atom of oxygen of mass 18 as shown by the interpretation[33] of the weak A′ band. However, the very low intensities of the lines of the weak A′ band when compared quantitatively with the intensities of the corresponding lines of the strong A band show that this isotope molecule is present in such a small amount as to have a negligible influence on the entropy.

The utilization of the energy levels of molecules, as obtained from spectroscopic data, in the calculation of entropy has been discussed by Giauque and Wiebe.[3] The equation

$$S_{\mathrm{E+R+V}} = R\left[\ln \Sigma_{e,n,m}p_{e,n,m}e^{-\epsilon_{e,n,m}/kT} + \frac{1}{kT}\,\frac{\Sigma_{e,n,m}p_{e,n,m}\epsilon_{e,n,m}e^{-\epsilon_{e,n,m}/kT}}{\Sigma_{e,n,m}p_{e,n,m}e^{-\epsilon_{e,n,m}/kT}}\right]$$

permits the calculation of the entropy due to all energy absorption other than that of translation. $\epsilon_{e,n,m}$ represents the energy of a certain state fixed with respect to the electronic configuration, the molecular vibration and molecular rotation; $p_{e,n,m}$ represents the corresponding *a priori* probability, or statistical weight of such a state, and $\Sigma_{e,n,m}$ indicates that terms within the summation sign are summed over all electronic, vibrational and rotational states of the molecule until it is apparent that further terms will add no appreciable contribution to the summation;

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[34] *Cf.* Birge, *Bull. Nat. Research Council,* 11, 332 (1926).

k represents the Boltzmann constant and **e** the base of the natural logarithms.

To the above entropy must be added the entropy due to the translation as given by the Sackur equation[35]

$$S_T = \frac{3}{2}R \ln M + \frac{3}{2}R \ln T + R \ln V + S_1$$

where R is the gas constant, T is the temperature on the absolute scale, M the molecular weight and V the molal volume in cc. $S_1 = 11.06$ cal. per degree per mole.

For the summations indicated above values were obtained from the data of Dieke and Babcock[31] for the energies corresponding to the first twenty-six rotation states in the normal oxygen molecule. Only odd-numbered values of j_k are present as explained previously. In keeping with the nomenclature of Mulliken,[32] F_1, F_2 and F_3 represent the three kinds of molecules resulting from differences in coupling between the angular momentum due to rotation of the molecule as a whole and the angular momentum due to spin of the electrons. F_1 represents the coupling with spin parallel to rotation, F_2 the coupling with spin approximately at right angles to the rotation vector and F_3 the coupling with spin antiparallel to rotation. j represents the total resultant angular momentum of the molecule and is given by the vector sum of j_k and s. Here s equals 1 and results from spin of the two unpaired electrons each electron contributing $^1/_2$ unit of angular momentum. The *a priori* probabilities necessary for use in the entropy equation given above are obtained from the values of j here listed by the relationship $p_{e,m,n} = 2j + 1$, as given by the wave mechanics. The energies for the molecules possessed of the F_2 coupling are derived by the use of the energy equation given by Dieke and Babcock,[31] with the constants derived from their P_1 and R_1 branches. The energies for molecules of corresponding j_k with F_1 or F_3 couplings were calculated from the F_2 energies by subtracting the approximate energy differences which exist between the F_2 and the F_1 or F_3 states. Several of these differences are tabulated by Mulliken and they have been smoothed out and extrapolated to higher j_k states by a graphical method.

TABLE VI

SUMS IN THE ENTROPY EQUATION FOR OXYGEN

$n = 1/2$, $T = 90.13$°K.

e	$\Sigma_{1/2,m} p_{1/2,m} \mathbf{e}^{(-\epsilon_{1/2,m}/kT)}$	$(1/kT)\Sigma_{1/2,m} \epsilon_{1/2m} p_{1/2m} \mathbf{e}^{(-\epsilon_{1/2,m}/kT)}$
F_1	28.574	24.635
F_2	21.686	21.748
F_3	17.333	18.990
$\Sigma_{e,1/2,m}$	67.593	65.373

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[35] (a) Sackur, *Ann. Physik*, **36**, 598 (1911); (b) Tetrode, *ibid.*, **38**, 434 (1912); (c) Ehrenfest and Trkal, *Proc. Acad. Sci., Amsterdam*, **23**, 162 (1920).

In Table VI we show the values obtained for the sums which appear in the entropy equation for $T = 90.13$°K. The sums are not affected within the numbers of decimals used by the inclusion of higher j_k states.

It is interesting to note that the oxygen molecules are quite unevenly distributed between the F_1, F_2 and F_3 states at the boiling point of oxygen gas. The distribution is 42.3% of F_1, 32.1% of F_2 and 25.6% of F_3. This uneven distribution is almost entirely due to the differences in the *a priori* probabilities. These differences are more pronounced for the low rotation states. The energies of the various states are nearly identical. We have calculated the contributions to these sums from the next higher vibration state and found them negligible for this temperature. Putting these sums into the entropy equation

$$S_{E+R+V} = 10.29 \text{ entropy units}$$

Combining this value with the 30.39 entropy units found for the contribution due to translation of the molecules as calculated with the Sackur[35a] equation for a monatomic gas, we find for the entropy of the hypothetical perfect oxygen gas at 1 atmosphere pressure and 90.13° K. the value 40.68 cal./deg. mole. The result of a similar calculation for a temperature of 298.1°K. is given in Table VII.

TABLE VII

SUMS IN THE ENTROPY EQUATION FOR OXYGEN

$T = 298.1$°K.

e	$\Sigma_{n,m} p_{n,m} e^{(-\epsilon_{n,m}/kT)}$	$1/kT \Sigma_{n,m} \epsilon_{n,m} p_{n,m} e^{(-\epsilon_{n,m}/kT)}$
$n = 1/2$, F_1	83.831	77.959
$n = 1/2$, F_2	72.882	72.628
$n = 1/2$, F_3	63.155	67.363
	219.868	217.950
$n = 3/2$, $\Sigma_{e,n,m}$	0.125	1.055
$n = 5/2$, $\Sigma_{e,n,m}$	.000	0.001
$\Sigma_{e,n,m}$	219.993	219.006

This leads to a value of $S_{298.1} = 49.03$ E.U.

It will be of interest to compare the above method of calculating the rotational entropy with that proposed by Tetrode,[35b] who derived the equation $S_R = R \ln IT + S_2$ for the rotational entropy of a rigid molecule, where I is the moment of inertia in g.cm.^{2} and $S_2 = 177.68$. The above formula was derived for infinite temperature but for practical purposes holds quite well at ordinary temperatures. However, while this formula correctly represents the entropy of the molecular situation assumed by Tetrode, it fails to consider a number of factors which are now recognized as important in molecular behavior. Two of these are encountered in the case of the oxygen molecule. First, the triplet multiplicity of the various states of the oxygen molecule leads to an increase in the entropy of $R \ln 3$ for the limiting case and by a slightly smaller amount at ordinary temperatures. Second, the homopolar character of the molecule combined with the non-spinning character of the oxygen nuclei results in the exclusion of alternate rotation states. This leads to a smaller entropy by $R \ln 2$ for the limiting case. The net result of the above is that the rotational entropy of the oxygen molecule would be given approximately by

$$S_R = R \ln IT + R \ln \frac{3}{2} + S_2$$

The theoretical and experimental values are given in Table VIII. The "spectroscopic" values are those derived by the summation method.

TABLE VIII

COMPARISON OF SPECTROSCOPIC AND THIRD LAW VALUES OF THE ENTROPY OF OXYGEN

T, °K		90.13	298.1
Spectroscopic, cal. per deg. per mole		40.68	49.03
Third law	Actual gas	40.57 ± 0.1	....
	Corrected to ideal state	40.7	49.1

The third law value given for 298.1°K. was obtained by adding the 0.17 E.U. correction for gas imperfection estimated by means of Berthelot's equation and the spectroscopic difference to the value obtained for the actual gas at the boiling point. The entropy was also calculated by utilizing the thermodynamic equation $dP/dT = \Delta S/\Delta V$ and vapor pressure measurements in place of the direct entropy of vaporization. The vapor pressure equation of Cath[13]

$$\log_{10} P(\text{atmos.}) = -\frac{419.31}{T} + 5.2365 - 0.00648T$$

was taken to represent the data. Later measurements[12] agree very closely with this equation. This was combined with Berthelot's equation, for which the constants have been given previously. For convenience the calculation was carried out at 71.40°K., where the vapor pressure of oxygen is 6.046 cm. and the molal volume of the liquid is 25.9 cc. from the work of Mattias and Onnes.[14]

The entropy of vaporization at this temperature and pressure was found to be 24.58 E.U., to which must be added a correction of 0.03 E.U. for gas imperfection of the Berthelot gas at this temperature and pressure. The entropy of the liquid at 71.40°K. was found to be 19.50 E.U. The entropy change accompanying the compression of ideal gas from 6.046 cm. to one atmosphere is -5.03 E.U. The increase in entropy on heating ideal gas from 71.40°K. to the boiling point at 90.13°K. is 1.62 E.U. when we assume a C_p of $^7/_2R$, which should be nearly correct. Then at 90.13°K., $S_{O_2} = 19.50 + 24.58 + 0.03 - 5.03 + 1.62 = 40.70$ E.U.

This value, which might be expected to contain a possible error of several tenths of an entropy unit, happens to be in excellent agreement with the theoretical value 40.68 E.U. and the more direct experimental value 40.74 E.U. This may be taken as a substantiation of the use of Berthelot's equation to represent gas imperfection.

Eucken, Karwat and Fried[36,37] have given the value $S_{298.1} = 49.04 \pm 0.2$ E.U. for oxygen.

This latter value is in excellent agreement with the theoretical value, although rather fortuitously so, as may be seen from the comparison made in Table V. In making the above calculation, Eucken, Karwat and Fried used the value 1629 obtained from an average of the available data rather than the value 1599 used by Lewis and Gibson in computing the entropy of vaporization given in Table V. Their selected value is identical with our experimental value.

It is well worth noting that the extended Tetrode equation leads to values which are practically identical with those calculated by the more reliable summation method. The value obtained at 90.13 is high by 0.02 E.U. while that at 298.1°K. is in exact agreement. While this close agreement is partially due to the fortuitous canceling of several effects it is to be expected that the Tetrode equation properly extended where necessary will usually give values correct to within a few hundredths of an entropy unit per mole at ordinary temperatures.

It is suggested that entropy values deduced from reliable spectroscopic data are preferable as a basis for thermodynamic calculations to the less accurate values obtained from heat capacity measurements and the third law. The values of the entropy obtained from spectroscopic data are for the ideal state of a gas, which is also the state of reference used in tabulating thermodynamic data.

The Paramagnetism of Solid Oxygen.—The magnetic susceptibility of solid oxygen has been investigated by Onnes and Perrier.[38] The susceptibility of the crystalline form stable below the boiling point of hydrogen has a very small positive temperature coefficient and appears to be approaching the absolute zero with a temperature coefficient of zero. From this some conclusions may be drawn as to the change in entropy with magnetic field strength. We have the thermodynamic equation[39]

$$\left(\frac{\partial S}{\partial \mathfrak{H}}\right)_{P,T} = \mathfrak{H}\left(\frac{\partial x}{\partial \mathrm{T}}\right)_{P,\mathfrak{H}}$$

from which it is evident that a zero temperature coefficient of susceptibility corresponds to no change in entropy as the magnetic field strength is increased. While this in itself is not proof that the contribution to the

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[36] Eucken, Karwat and Fried, *Z. Physik*, **29**, 1 (1924).

[37] "Thermodynamik und die freie Energie chemischer Substanzen," von Lewis und Randall, übersetzt von Redlich, Julius Springer, Wien, 1927.

[38] Onnes and Perrier, *Comm. Phys. Lab. Univ. Leiden*, 116 (1910); 124A (1911); Perrier and Onnes, *ibid.*, 139C (1914).

[39] Giauque, This Journal, **49**, 1864 (1927).

entropy due to the magnetic system of the oxygen molecule is practically zero in this particular solid state, it is the condition imposed by the third law of thermodynamics for zero entropy in such systems. However, the agreement of the entropy calculated from our calorimetric measurements with that obtained from spectroscopic data shows that the magnetons in solid oxygen have little randomness at the temperatures of liquid hydrogen. It is therefore concluded that the magnetons have coupled with each other into what may be considered as a magneton crystal within the molecular crystal lattice of oxygen. The strong paramagnetism of solid oxygen must be regarded as due to what corresponds to a Paschen–Back effect in the solid—that is, a destruction of the coupling by the applied field as is observed in the case of some gaseous ions. This does not mean that the magneton crystal has been largely broken down by the fields of about 16,000 gauss which have been used for the susceptibility determinations, since the intensity of magnetization obtained is only 0.25% of the saturation value for two Bohr magnetons.

The small positive susceptibility obtained for many substances, and which has little temperature coefficient, may be due to the initial effect of the coupling breakdown which a sufficiently strong field could produce.

We wish to thank Mr. J. O. Clayton for assistance in making many of the measurements.

Summary

The heat capacities of the three crystalline forms of solid oxygen and of the liquid have been measured from 11.75°K. to the boiling point. The curves through the data are believed to represent the heat capacity of liquid oxygen to within 0.2 of 1%; of Solid I to within 0.3 of 1%; of Solid II to within 0.5 of 1%. For Solid III the inaccuracy of the curve may be somewhat larger, ranging from 1% at the upper extremity (23.66°K.) to possibly 5% at 12°K.

The transition temperatures were determined to be 23.66 ± 0.10°K. and 43.76 ± 0.05°K., respectively. The melting point was found to be 54.39 ± 0.05°K. and the boiling point 90.13 ± 0.05°K.

Calorimetric measurements were made of the heats of transition, fusion and vaporization. Arranged in order of the transition at 23.66°, the transition at 43.76°, fusion and vaporization, these values are 22.42 ± 0.1, 177.6 ± 0.5, 106.3 ± 0.3 and 1628.8 ± 1.6 calories per mole, respectively.

The entropy of oxygen gas at 90.13°K. and 1 atmosphere was calculated from the above data and the third law of thermodynamics, and found to be 40.57 ± 0.1 calories per degree per mole. Corrected to the ideal state with the aid of Berthelot's equation, a correction which amounted to +0.17 cal./degree/mole, this value was compared with that calculated by the accurate "summation" method from the molecular spectra of

oxygen gas. The two values are in almost exact agreement, showing that the triplet character of the oxygen molecule due to the unbalanced angular momentum of its two spinning electrons has contributed approximately *R* ln 3 to the entropy of gaseous oxygen, and also that the absence of alternate rotation levels in the oxygen molecule due to its homopolar nature results in an entropy of *R* ln 2 less than would be the case for a polar molecule of the same moment of inertia.

The entropy of oxygen gas at 298.1°K. was calculated by the "summation" method from the spectral data and found to be 49.03 calories per mole per degree. We believe that this is the best value for use in thermodynamic calculations.

It is also shown that the magnetons in the crystalline form of oxygen stable below 23.66°K. are not contributing appreciably to the entropy and must, therefore, be coupled in a non-random manner into what may be regarded as a magneton crystal within the ordinary molecular crystal lattice.

It is shown that the existing magnetic susceptibility data on solid oxygen are in agreement with the requirement of the third law of thermodynamics for zero entropy in magnetic systems, namely, that the temperature coefficient of the magnetic susceptibility should approach zero as the absolute zero of temperature is approached.

It is concluded that the large positive susceptibility of solid oxygen is due to the initial effect of a coupling breakdown induced by the applied field in analogy to the Paschen-Back effect in gaseous ions.

The general agreement of the various physical facts concerning the oxygen molecule in relation to the entropy and particularly the close agreement of the entropy as obtained by the two methods support our confidence that the third law of thermodynamics is an exact law.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XXX. HALOGEN SUBSTITUTION PRODUCTS OF MONOGERMANE[1]

BY L. M. DENNIS AND P. R. JUDY

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Most of the possible halogen substitution products of methane and monosilane (SiH_4) of the types RHX_3, RH_2X_2 and RH_3X, have been prepared.[2] The purpose of the present investigation was the preparation and study of some of the analogous compounds of germanium.

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[1] This article is based upon part of the thesis presented to the Faculty of the Graduate School of Cornell University by P. R. Judy in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] See Landolt-Börnstein, "Physikalisch-chemische Tabellen," **1923**, Vol. I, p. 356.