situation is complicated by the possibility of isotopes of all the light elements but the general agreement seems significant. Aston has pointed out that it is very difficult to prove the non-existence of other isotopes of oxygen with the mass spectrograph. However, this appears to be the most promising possibility for the estimation of the relative amount of O^{18}.

The presence of isotopes of oxygen will, of course, not affect chemical atomic weights except in the remote possibility of non-uniform distribution but before we can know the relationship between ordinary atomic weights and the results of the mass spectrograph, the amount of O^{18} must be known.

Another point of interest in connection with the new lines is as follows. If P, Q and R branches resulted from each of the triplet states of the oxygen molecule, we would have nine branches. Only four branches have been observed. This seems to indicate that the rotational momentum is required to change by an amount of plus or minus one that is, $\Delta j_k = \pm 1$ in addition to the usual requirement $\Delta j = \pm 1$ or 0. Professor R. S. Mulliken of the University of Chicago has called our attention to the similarity of the above selection rule to that in the atomic case where for line spectra $\Delta l = \pm 1$ and $\Delta j = \pm 1$ or 0.

Summary

The weak band in the atmospheric absorption of oxygen has been explained and demonstrates the existence of an isotope of oxygen, mass 18, present in small amount.

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

THE HEAT CAPACITY OF HYDROGEN IODIDE FROM 15°K. TO ITS BOILING POINT AND ITS HEAT OF VAPORIZATION. THE ENTROPY FROM SPECTROSCOPIC DATA

BY W. F. GIAUQUE AND R. WIEBE

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We have previously shown[1] that for hydrogen chloride and for hydrogen bromide the entropies as calculated for the gaseous state with the assistance of spectroscopic data are in agreement with those obtained from our calorimetric measurements and the third law of thermodynamics. This paper contains similar calorimetric data for hydrogen iodide, again leading to agreement between the two methods of obtaining the entropy.

Preparation of Hydrogen Iodide.—Hydrogen iodide was prepared directly from the elements in a manner very similar to that used for the preparation of hydrogen bromide. Iodine was sublimed into a large tube which was attached to a reaction tube containing a platinum spiral wound on quartz. The whole apparatus was then immersed in a water-bath which was kept at the boiling point by electrical heating of the platinum

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[1] Giauque and Wiebe, THIS JOURNAL, (a) **50**, 101 (1928); (b) **50**, 2193 (1928).

spiral to about 600°. Hydrogen was prepared by electrolysis and freed of oxygen by means of a nickel catalyst. Dry hydrogen was passed into the tube containing the iodine and became saturated at 100°. This left a large excess of hydrogen, which we considered desirable. The mixture passed over the hot platinum spiral and then through a trap surrounded by salt and ice to condense the considerable amount of unreacted iodine which was to be expected from the known equilibrium. The hydrogen iodide containing some iodine was finally condensed in a trap surrounded by liquid air, the hydrogen being allowed to escape. After a rough distillation had removed most of the iodine, the material was distilled into a bulb containing mercury which had been distilled onto the walls. This was very effective in eliminating all trace of color, leaving an exceptionally clear liquid. The hydrogen iodide, which could at most have contained only a trace of water, was then distilled into a bulb containing a sufficiently large amount of phosphorus pentoxide to bring it into intimate contact with all of the liquid. The drying continued for about a week. It was kept cold with the assistance of a carbon dioxide and ether bath. This solidified the hydrogen iodide which was, however, frequently melted and kept melted over considerable periods. The material was then distilled several times, the end fractions being discarded. All of the above operations were carried out in a vacuum-tight system which was evacuated by means of a mercury diffusion pump.

TABLE I

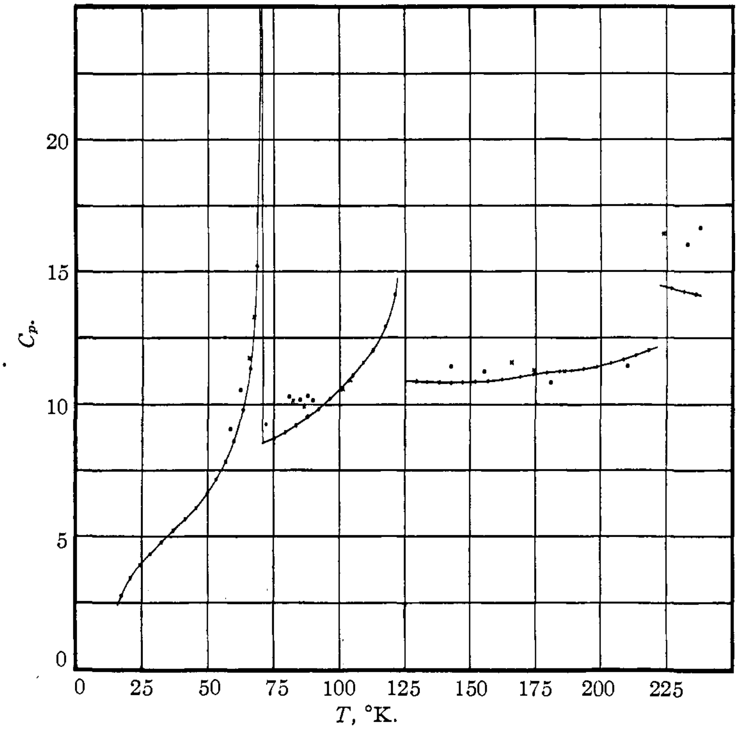
HEAT CAPACITY OF HYDROGEN IODIDE

Molecular weight, 127.94

T, °K.	ΔT	C_p/mole in cal./deg.
17.11	3.611	2.745
20.37	2.734	3.426
24.03	3.957	3.947
28.05	3.956	4.384
32.29	4.256	4.834
36.73	4.392	5.255
41.25	4.535	5.696
45.58	3.982	6.092
49.76	4.219	6.625
53.01	3.823	7.165
56.79	3.416	7.812
60.11	3.074	8.631
63.22	3.050	9.802
66.09	2.643	11.37
68.47	2.082	15.23
70.12	1.067	32.52
72.09	2.880	9.274
75.33	3.961	8.727
79.56	4.334	8.928
83.83	4.063	9.221
87.93	3.812	9.563
92.18	4.548	9.807
96.37	3.620	10.24
100.69	4.454	10.56
105.02	4.023	11.08
108.97	3.764	11.57
113.12	4.300	12.04
117.32	3.979	12.96
121.15	3.639	14.11
129.21	4.342	10.87
133.54	4.100	10.85
138.13	4.785	10.83
142.61	3.924	10.81
147.01	4.570	10.83
151.72	4.483	10.84
156.74	5.144	10.85
162.10	4.986	10.94
169.07	5.199	11.07
174.23	4.694	11.13
179.10	4.579	11.20
183.96	4.485	11.22
188.71	4.362	11.26
193.51	4.242	11.33
198.46	4.865	11.38
203.57	4.728	11.56
208.53	4.587	11.63
213.30	4.450	11.81
218.00	4.303	12.04
222.31	Melting point	
227.05	4.263	14.34
231.67	4.241	14.26
236.15	4.190	14.15
237.75	Boiling point	

Heat Capacity Measurements.—The calorimetric measurements were all made with gold calorimeter II. The calorimeter and experimental method have been described in our previous paper.[1a] 1.9662 moles of hydrogen iodide were used for the measurements. The data are given in Table I.

The data are shown graphically in Fig. 1, which also includes the data of Eucken and Karwat,[2] who investigated this substance from 58 °K. to its boiling point. Most of our data are accurate to two- or three-tenths of one per cent. Some points near 175 °K. are probably off by about five-tenths of one per cent. due to small distillation heat effects. The measurement at 17.11 °K. may be in error by one per cent.



×, Eucken and Karwat; ●, Giauque and Wiebe.

Fig. 1.—Heat capacity in calories per mole of hydrogen iodide.

The Transitions of Hydrogen Iodide.—Hydrogen iodide has two gradual transitions similar to those found for hydrogen bromide. In our previous discussion of the transitions of hydrogen bromide, we mentioned that lack of equilibrium was a factor, although we believed that the transitions would be gradual even with complete equilibrium. We have

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[2] Eucken and Karwat, *Z. physik. Chem.*, **112**, 467 (1924).

learned nothing from hydrogen iodide to change this opinion but some measurements on the transition occurring near 125°K. supply interesting information concerning the difficulty in obtaining true equilibrium and also show that a considerable amount of energy is absorbed within a very small temperature range if not at a definite temperature. Starting at a temperature of 122.99°K., 55.8 cal. per mole of substance was added over a period of ten minutes. At two minutes after energy input ceased, the temperature was 125.73°K., and this decreased at a gradually diminishing rate to 125.64°K. in seventy minutes, at which time the rate of decrease was 0.0004° per minute. The current was again passed through the heater adding 56.6 cal. per mole over a period of ten minutes. At two minutes after energy input ceased, the temperature was 125.88°K. and decreased to 125.64°K. in twenty minutes, at which time the rate of decrease was 0.004° per minute or ten times the previous rate at this temperature. At fifty minutes it had decreased to 125.60° and the rate of decrease was 0.0008° per minute. It is evident that as the transition approaches completion, equilibrium is obtained more readily. The results suggest the following possibility: the transition starts as a changing thermal equilibrium between energy states of the hydrogen iodide molecule, both in the same crystal lattice, but when a sufficient concentration of the higher energy state has been reached, the system becomes unstable and changes to a new crystalline form. This question could be investigated by X-ray measurements of crystal structure, although care might be necessary in cooling the hydrogen iodide slowly through the transition range if our conditions were to be duplicated. Simon and Simson[3] have found by X-ray analysis that the somewhat similar transition of ammonium chloride is not accompanied by a change in crystalline form and they conclude that it represents an equilibrium between molecular energy states.

It seems probable that many substances will have a change of phase induced by an increasing concentration of molecules with some degree of freedom excited in addition to the ordinary vibration.

The heat capacity measurements in the transition ranges were not used in obtaining the entropy, for which purpose separate determinations of total heat input over the whole range were obtained. The values are given in Table II.

TABLE II

HEAT ABSORBED IN TRANSITION REGIONS OF HYDROGEN IODIDE

Temp. interval, °K.	60.90–72.23	62.09–75.42	113.75–129.63	113.26–129.11
Heat absorbed, cal./mole	150.8	167.4	394.6	393.8

Heat of Fusion.—Two determinations of the heat of fusion gave 687.1 and 685.5 cal. per mole, respectively. The average is 686.3 ± 0.8

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[3] Simon and Simson, *Naturwissenschaften*, **38,** 880 (1926).

cal. per mole. Comparison with the results of previous observers is made in Table III.

TABLE III

HEAT OF FUSION OF HYDROGEN IODIDE

Melting point, 222.31°K. Molecular weight, 127.94

Heat of fusion, cal./mole	Observer
552	Beckman and Waentig[4] (1910)
732, 688 (weighted mean, 726)	Eucken and Karwat[2] (1924)
687.1, 685.5 (mean, 686.3 ± 0.8)	Giauque and Wiebe (1929)

Melting- and Boiling-Point Temperatures of Hydrogen Iodide.—The melting point was observed with one-fourth, one-half and two-thirds of the material melted, respectively. The observations covered a period of six hours. The maximum deviation was 0.006° on the thermocouple and 0.004° on the resistance thermometer. The average deviation was 0.003° on the thermocouple and 0.002° on the resistance thermometer. The melting-point temperature was found to be 222.31 ± 0.05°K.

The boiling point was found to be 237.75 ± 0.05°K. This was obtained from measurements of pressure and temperature made in connection with the heat of vaporization determinations. The values obtained for the melting- and boiling-point temperatures by various observers are summarized in Table IV.

TABLE IV

MELTING- AND BOILING-POINT TEMPERATURES OF HYDROGEN IODIDE

Melting point, °K.	Melting point, °K.	Observer
222.3	238.96 (730.4 mm.)	(1897) Estreicher[5]
222.8	236.4 (751.4 mm.)	(1900) Ladenburg and Krügel[6]
222.3	237.4	(1906) McIntosh, Steel and Archibald[7]
227.1	....	(1911) Bagster[8]
222.4	237.3	(1924) Henglein[9]
223.1	237.1	(1925) Miravalles and Moles[10]
222.31 ± 0.05	237.75 ± 0.05	(1929) Giauque and Wiebe

Measurement of Amount of Hydrogen Iodide.—The amount of hydrogen iodide was measured by absorption in 30% sodium hydroxide after passing through a very small mercury trap, as was described for hydrogen chloride.[1a] However, in this case we met a difficulty which was not encountered in the measurements on hydrogen chloride or hydrogen bromide. It was noticed that very small bubbles of gas rose slowly through the

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[4] Beckmann and Waentig, *Z. anorg. chem.*, **67**, 17 (1910).

[5] Estreicher, *Z. physik. Chem.*, **20**, 605 (1896).

[6] Ladenburg and Krügel, *Ber.*, **33**, 637 (1900).

[7] McIntosh, Steele and Archibald, *Z. physik. Chem.*, **55**, 129 (1906).

[8] Bagster, *Tab. Ann.*, 82 (1911).

[9] Henglein, *Z. Physik*, **18**, 64 (1924).

[10] Miravalles and Moles, *Anales soc. españ. fís. quím.*, **23**, 509 (1925).

sodium hydroxide to the surface and on testing the gas in the absorption bulb it proved to be hydrogen. The dissolved mercury was in the form of the very stable iodide complex which could not be precipitated by the addition of sulfide ion. Consequently the analysis was carried out by means of a zinc–copper couple. The effectiveness of this method was tested by duplicating the solutions except that known amounts of mercuric iodide complex were present. It was found that the method (in the rather rough manner in which we used it and for the amounts concerned) gave results 10% too low and the analyses were calculated on this basis. This was sufficiently accurate for our purpose since the total correction for hydrogen lost proved to be almost negligible. However, the evolution of hydrogen gave rise to another more serious difficulty, since during the initial weighing of the absorption bulb, the gas space was filled with air; while during the final weighing, it was nearly all hydrogen. The relative amounts of air and hydrogen in the gas space were determined and the correction was made. The total correction due to these two effects was about 0.2 of 1%.

Heat of Vaporization.—The heat of vaporization was measured by Method II, as described for the hydrogen chloride measurements.[1a] The data are given in Table V.

TABLE V

HEAT OF VAPORIZATION OF HYDROGEN IODIDE

Boiling point, 237.75°K. Molecular weight, 127.94

HI evap., moles	0.1777	0.3014	0.3010	0.3000	
Type of run	II	II	II	II	
Time of energy input, min.	55	75	75	75	
ΔH at 760 mm., cal./mole	4718	4719	4732	4726	Mean, 4724 ± 5

Comparison with the results of previous observers is made in Table VI. All of the results listed are from calorimetric determinations.

TABLE VI

HEAT OF VAPORIZATION OF HYDROGEN IODIDE

Heat of vap., cal./mole	Observer
4480	(1908) Elliot and McIntosh[11]
4340	(1910) Estreicher and Schnerr[12]
4950	(1912) Beckmann[13]
5885	(1916) Cederberg[14]
4724 ± 5	(1929) Giauque and Wiebe

The Entropy of Hydrogen Iodide from the Third Law.—The entropy was obtained by graphical integration of the heat capacity against the

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[11] Elliot and McIntosh, *J. phys. chem.*, **12,** 163 (1908).

[12] Estreicher and Schnerr, *Krakauer Anz.*, 345 (1910).

[13] Beckmann, *Z. anorg. chem.*, **74,** 300 (1912).

[14] Cederberg, *Ber. chem. affin.*, Berlin, **1916.**

logarithm of the absolute temperature. The method used for the two gradual transitions was the same as that previously described for hydrogen bromide. All energy above a value of 16 cal. per degree per mole was divided by the temperature selected as a center of gravity on a $(C_p - 16)$ against T plot. The temperatures selected are not to be confused with the transition temperature of ordinary "sharp transitions," nor are the heats to be taken as heats of transition, especially since the value of 16 cal. per degree subtracted over the range was purely arbitrary.

The extrapolation below 15.3°K. was carried out by means of a Debye curve with an $h\nu/k = 73$. The similarity of the heat capacity curve to those of hydrogen chloride and hydrogen bromide gives us considerable confidence in the extrapolation of the somewhat greater amount of entropy due to the lower characteristic frequency of this substance. A summary of the entropy calculation is given in Table VII.

TABLE VII

CALCULATION OF THE MOLAL ENTROPY OF HYDROGEN IODIDE GAS

0–15.3°K., extrapolation	1.085	
Transition 18.6/70.1	0.265	
Transition 192.4/125.6	1.531	
Transitions are $\int (C_p - 16)dT$, 15.3–222.31°K., graphical	20.99	
Fusion, 686.3/222.31	3.087	
222.31–237.75°K., graphical	0.958	
Vaporization, 4724/237.75	19.87	
Entropy at the boiling point.	47.8	± 0.1 E. U.

There are practically no data for use in making a correction for gas imperfection at the boiling point. We will, however, assume a very uncertain additive correction of 0.1 E. U., as was done in the case of hydrogen chloride and hydrogen bromide.

The Entropy of Hydrogen Iodide from Spectroscopic Data.—The only measurements on the rotational states of hydrogen iodide are those of Czerny,[15] who obtained only four lines of the pure rotation band. These are sufficient to determine the moment of inertia with some accuracy but are hardly enough to justify a calculation of the entropy from the individual energy states, as was possible with hydrogen chloride and hydrogen bromide, although Czerny gives a formula which could be used for extrapolation. However, for the case of a polar diamagnetic gas, we may use the approximate formula for rotational entropy obtained by Sackur and Tetrode, namely, $S_R = R + R \ln 8\pi^2 IT/h^2$, where I represents the moment of inertia of the molecule and h is Planck's constant. This value added to the translational entropy obtained from the Sackur equation should give a theoretical value for the entropy which is sufficiently accurate for comparison with our calorimetric value.

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[15] Czerny, (a) *Z. Physik*, **44**, 235 (1927); (b) **45**, 476 (1927).

The value obtained for the entropy of ideal hydrogen iodide gas at the temperature of the boiling point and a pressure of one atmosphere is 47.8 or 47.5 cal. per degree per mole, corresponding, respectively, to the use of the Tetrode or Lewis constant for the Sackur equation. The results are given in Table VIII, which also summarizes the results for the other halogen acids.

TABLE VIII

COMPARISON OF SPECTROSCOPIC AND THIRD-LAW VALUES OF THE ENTROPY OF THE HYDROGEN HALIDES

		Spectroscopic		Third-law	
	T, ° K.	Tetrode const.	Lewis const.	Actual gas	Corr. to ideal state
Hydrogen chloride	188.07	41.47	41.15	41.2 ± 0.1	41.3
	298.1	44.64	44.32	....	44.5
Hydrogen bromide	206.38	44.92	44.60	44.9 ± 0.1	45.0
	298.1	47.48	47.16	....	47.6
Hydrogen iodide	237.75	47.8	47.5	47.8 ± 0.1	47.9
	298.1	49.4	49.1	....	49.5

Table VIII contains two minor corrections to our previously published spectroscopic values. The value for hydrogen chloride at its boiling point has been increased by 0.02 E. U. The value for hydrogen bromide at 298.1°K. has been lowered by 0.05 E. U. Both these corrections are due to the detection of arithmetical errors in our previous calculations. The theoretical calculations should be accurate to 0.01 E. U.

In obtaining the third law value given for hydrogen iodide at 298.1°K. (25°), it was assumed that $C_p = 7/2R$ between 237.75 and 298.1°K. This assumption is justified by the nearly complete absence of vibrational energy, as may be shown from the molecular vibrational frequency as estimated by Czerny.[15]

According to Redlich[16] the value of the chemical constant of hydrogen iodide obtained by Eucken, Karwat and Fried[17] leads to a value of 50.69 cal. per degree per mole for this substance. Eucken, Karwat and Fried had placed the error at ±0.7 E. U.

Our measurements support the Tetrode constant for the Sackur equation and also indicate that the third law of thermodynamics is, in fact, an exact law.

We express our thanks to Dr. H. L. Johnston for assistance in making the measurements on hydrogen iodide and to Prof. R. T. Birge for discussions of the spectroscopic data.

Summary

The heat capacity of solid and of liquid hydrogen iodide has been measured from 15.3°K. to its boiling point.

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

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

The melting point was found to be 222.31 ± 0.05°K.; the boiling point, 237.75 ± 0.05°K.

The heat of fusion is 686.3 ± 0.8 cal. per mole. The heat of vaporization at the boiling point is 4724 ± 5 cal. per mole.

Two regions of high heat capacity were found in the solid state which appear to be internal transitions of the molecule; however, one of these, in particular, after progressing over a considerable temperature range, seems to develop into the ordinary or sharp transition type.

The entropy has been calculated from the experimental data and the third law of thermodynamics.

The entropy has also been calculated from spectroscopic data. The two methods lead to the same value within the limit of our experimental error, thus supporting the validity of each method.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. VI. OXIDATION OF HYDROGEN PEROXIDE BY CERIC SULFATE. INDIRECT DETERMINATION OF LEAD

BY N. HOWELL FURMAN AND JOHN H. WALLACE, JR.

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Introduction

Some of the uses of ceric sulfate in volumetric analysis have been described in other papers of this series[1] and in those of other investigators.[2] Von Knorre[3] made use of the reaction

$$2Ce(SO_4)_2 + H_2O_2 = Ce_2(SO_4)_3 + H_2SO_4 + O_2$$

in the determination of cerium. He added an excess of hydrogen peroxide (freshly standardized) to the ceric solution and determined the excess of the former with 0.1 *N* permanganate solution. Atanasiu and Stefanescu have published data for a single potentiometric titration of hydrogen peroxide with ceric sulfate in sulfuric acid solution. Our observations have been made with various acids and with a variety of different concentrations of acid.

Experimental

The apparatus was similar to that described in previous papers of this series; a bright platinum wire and a N calomel electrode made up the electrode system.

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[1] N. H. Furman, THIS JOURNAL, **50**, 755, 1675 (1928); Furman and Evans, *ibid.*, **51**, 1128 (1929).

[2] H. H. Willard and Philena Young, *ibid.*, **50**, 1322, 1334, 1368, 1372, 1379 (1928); **51**, 139, 149 (1929); *Ind. Eng. Chem.*, **20**, 972 (1928); I. A. Atanasiu, *Bull. soc. roum. chim.*, **30**, 1 (1928); Atanasiu and V. Stefanescu, *Ber.*, **61**, 1343 (1928); H. Rathsberg, *ibid.*, **61**, 1664 (1928).

[3] V. Knorre, *Z. angew. Chem.*, **10**, 685, 717 (1897); *Ber.*, **33**, 1924 (1900).