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A Test of the Third Law of Thermodynamics by Means of Two Crystalline Forms of Phosphine. The Heat Capacity, Heat of Vaporization and Vapor Pressure of Phosphine. Entropy of the Gas

C. C. STEPHENSON[1] AND W. F. GIAUQUE
Department of Chemistry, University of California, Berkeley, California

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The heat capacity of solid and liquid phosphine has been measured from 15°K to its boiling point, 185.38°K. Transitions were found at 30.29, 49.43 and 88.10°K. The heats of transition are 19.6, 185.7 and 115.8 cal./mole, respectively. The transition at 49.43°K had not previously been reported. In order to obtain complete conversion to the form of phosphine which is stable below 49.43°K it was necessary to keep the unstable form near 40°K for several days. A graph showing the rate of conversion to the stable form as a function of temperature has been given. The transition at 30.29°K occurs in the form of phosphine, unstable below 49.43°K. There is also a region of abnormally high heat capacity in the supercooled form between 30.29 and 35.66°K. At the latter temperature the heat capacity decreases abruptly by 15 percent without evidence of latent heat. The melting point was found to be 139.35°K and the heat of fusion 270.4 cal./mole. The heat of vaporization at the boiling point, 185.38°K, was determined calorimetrically. The value found was 3489 cal./mole. The vapor pressure of solid and liquid phosphine was measured and the results represented by the equations: Solid phosphine 128.67 to 139.35°K; $\log_{10} P(\text{int. cm Hg}) = -895.700/T + 6.86434$. Liquid phosphine 139.35 to 185.56°K; $\log_{10} P(\text{int. cm Hg}) = -1027.300/T - 0.0178530T + 0.000029135T^2 + 9.73075$. The entropy of the solid at 49.43°K may be obtained either from measurement on the stable or unstable form. The values are 8.14 and 8.13 cal./deg. per mole, respectively. While the extraordinarily close agreement is somewhat fortuitous, the measurements provide the most accurate existing verification of the third law of thermodynamics by means of two crystalline forms of a substance. The molal entropy of the ideal phosphine gas at the boiling point was found to be 46.39±0.1 cal./deg. per mole. The corresponding value at 298.1°K is 50.35 cal./deg. per mole. This may be compared with the value 50.5 calculated by Yost with the assistance of spectroscopic data and an estimated bond angle. The above entropy values neglect the nuclear spin entropy, $R \ln 16 = 5.509$ cal./deg. per mole, which should be added to obtain the absolute entropy. The values given are the ones which should be used in ordinary thermodynamic calculations. Phosphine is known to be a symmetrical top and the two equal moments of inertia are known from its band spectrum. It has not been found possible to evaluate the other moment of inertia in this manner. However, it can be calculated from the accurate entropy determination given above. The value found is $I_C = (7.9 \pm 0.8) \times 10^{-40}$ gram cm². The $P-H$ distance was found to be 1.45±0.02A and the bond angle, 98±5°.

IN this paper we will present the results of a low temperature investigation of phosphine. During this research a new form of phosphine, stable below 49.43°K, was discovered. By means of the new modification and the previously known form, which has now been shown to be unstable at low temperatures, it has been possible to obtain what we believe to be the most accurate verification of the third law of thermodynamics, using two crystalline forms of a substance.

The entropy of the gas has been evaluated from the calorimetric measurements. The entropy may also be obtained with the assistance of spectroscopic data. While the interpretation of the band spectrum of phosphine is not as complete as might be desired, nevertheless it has been possible to prove that the third law value of the entropy is in agreement with that given for the gas by quantum statistics.

[1] Charles A. Coffin Fellow, academic year 1934–35.

APPARATUS

The apparatus and methods employed in this research are similar to those used in previous investigations on condensed gases in this laboratory. The calorimeter is the one which has been given the laboratory designation Gold Calorimeter II.[2, 3] A full description of a similar calorimeter has been given by Giauque and Egan.[4] The temperatures were measured and heat introduced by means of a gold resistance thermometer heater. The resistance thermometer was calibrated during the measurements against copper constantan thermocouple W, which was soldered to the bottom of the calorimeter. This thermocouple had been compared with a hydrogen gas thermometer,[5] and oxygen and

[2] Giauque and Wiebe, J. Am. Chem. Soc. **50**, 101 (1928).
[3] Blue and Giauque, ibid. **57**, 991 (1935).
[4] Giauque and Egan, J. Chem. Phys. **5**, 45 (1937).
[5] Giauque, Buffington and Schulze, J. Am. Chem. Soc. **49**, 2343 (1927).

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hydrogen vapor pressure thermometers,[6] by former investigators in this laboratory. At the conclusion of this research, the thermocouple was again checked against the triple point of hydrogen, hydrogen vapor pressures, the 43.76°K transition temperature of oxygen, and the triple point and vapor pressures of oxygen. The thermocouple gave temperatures which were low by the following amounts: 0.17° at the triple point of hydrogen, 13.95°K; 0.15° at the boiling point of hydrogen, 20.37°K; 0.13° at the transition temperature of oxygen, 43.76°K; 0.11° at the triple point of oxygen, 54.39°K; 0.01° at the boiling point of oxygen, 90.13°K. Suitable corrections were applied to the original calibration.

As is well known, small changes in physical state, which may produce a negligible effect on the electrical properties of metals at ordinary temperatures, commonly produce rather large effects at very low temperatures. The small low temperature deviations from the original calibration which was made nine years before these measurements demonstrate that very reliable copper constantan thermocouples can be made. It may be recalled, however, that Giauque, Buffington and Schulze[5] tested 58 spools of constantan wire at low temperatures, before selecting the particular wire from which this thermocouple was made.

It was considered unnecessary to reinvestigate the thermocouple above 90°K since not only was it in agreement at this temperature but the rapidly increasing dE/dT makes small changes in e.m.f. relatively less important at higher temperatures.

Preparation and Purity of Phosphine

Phosphine was prepared by the action of potassium hydroxide on phosphonium iodide. The phosphonium iodide was made from white phosphorus, iodine and water by the method of Baeyer.[7] The reaction is represented by the equation

$$9P+5I+16H_2O=5PH_4I+4H_3PO_4.$$

The yellowish brown product was sublimed into the generating flask to give clear colorless crystals.

To the phosphonium iodide, a twenty-five percent solution of potassium hydroxide was added slowly. The evolved phosphine was washed by hydrochloric acid to remove any P_2H_4, and then by a solution of potassium hydroxide to remove hydrochloric and hydroiodic acids. Finally, the gas was dried by KOH sticks and phosphorus pentoxide, and condensed in a liquid-air trap protected by a thin metal jacket. About 250 cc of liquid phosphine were prepared in this manner, and over half of this was discarded in the fore and end portions of several distillations. The solid phosphine was subjected to a high vacuum before the product was distilled into the calorimeter.

A series of short heat capacity measurements were made in the temperature region immediately below the melting point in order to determine the premelting effect due to liquid-soluble solid-insoluble impurity. From these measurements it was calculated that the impurity was less than four moles in one hundred thousand moles.

The gas prepared in the above manner was always spontaneously inflammable, although the moist gas, as it first came from the phosphonium iodide, was usually not. When the dry gas was moistened by bubbling through a trap containing water, it no longer ignited on contact with air. Since the dry gas was later shown to be very pure, it may be concluded that the pure gas is spontaneously inflammable. This confirms the similar observation of Ritchie.[8]

Vapor Pressure of Phosphine

The vapor pressure of phosphine was measured by means of a manometer 1.6 cm in diameter. The measurements were made by using a cathetometer as a comparison instrument in connection with a standard meter mounted in the manometer case. The pressure observations are corrected to international centimeters of mercury by means of data given in the *International Critical Tables*.[9] The standard accelera-

[6] Giauque, Johnston and Kelley, J. Am. Chem. Soc. **49**, 2367 (1927).
[7] Baeyer, Annalen **155**, 266 (1870).
[8] Ritchie, Proc. Roy. Soc. London **A128**, 551 (1930).
[9] *International Critical Tables* (McGraw-Hill Book Co., New York, 1926).

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TABLE I. *Vapor pressure of phosphine. (Boiling Point 185.38°K, 0°C=273.10°K.)*

T°K	P(int. cm Hg) (OBSERVED)	P OBS. $-P$ CALC.	T OBS. $-T$ CALC.
128.67	0.798	−0.002	+0.01 Solid
132.76	1.312	+ .001	0.00 Solid
136.10	1.921	+ .002	− .01 Solid
139.35	2.733	.000	.000 Triple point
144.521	4.477	+ .002	− .005 Liquid
148.960	6.635	+ .007	− .012 Liquid
152.549	8.939	+ .005	− .007 Liquid
156.699	12.380	.000	.000 Liquid
161.724	17.914	− .006	+ .005 Liquid
167.369	26.350	− .008	+ .005 Liquid
172.560	36.674	+ .005	− .002 Liquid
178.043	50.790	+ .002	− .001 Liquid
185.562	76.724	− .005	+ .001 Liquid

tion of gravity was taken as 980.665 cm/sec². The gravitational acceleration for this location, 979.973 cm/sec², was taken from the work of Sternewarte.[10]

The observations have been represented by the following equations: Solid phosphine from 128.67 to the melting point 139.35°K,

$$\log_{10} P_{(\text{int. cm Hg})} = -895.700/T + 6.86434. \quad (1)$$

Liquid phosphine from 139.35 to 185.56°K,

$$\log_{10} P_{(\text{int. cm Hg})} = -1027.300/T - 0.0178530T + 0.000029135T^2 + 9.73075. \quad (2)$$

The observed and calculated values are given in Table I. The boiling point was calculated from Eq. (2) to be 185.38°K.

The vapor pressure of liquid phosphine has been measured by Henning and Stock.[11] For corresponding pressures, the vapor pressure equation of Henning and Stock gives temperatures which are higher by the following amounts than those given by the above equation: at 150°K, 0.09°; at 160°K, 0.10°; at 170°K, 0.12°; at 178°K, 0.18°; at the boiling point, 0.27°. The two temperature scales have been shown to be consistent to 0.03° from 160°K to 195°K by the vapor pressures of HCl.[2] The higher temperatures given by Henning and Stock may be due to an impurity in their sample. The heat of vaporization calculated from the vapor pressure equation of this research is in better agreement with the calorimetric value than that calculated from the equation of Henning and Stock, which is evidence that their equation is somewhat in error near the boiling point.

[10] Landolt, Börnstein and Roth, *Physikalische-chemische Tabellen* (Verlag Julius Springer, Berlin, 1923).
[11] Henning and Stock, Zeits. f. Physik **4**, 226 (1921).

TABLE II. *Melting point of phosphine.*

DATE AND TIME	% MELTED	T°K RESISTANCE THERMOMETER	T°K THERMO-COUPLE	PRESSURE (int. cm Hg)
4/20/35 9:45 P.M.	Heated into melting point			
10:51 P.M.	9	139.321	139.31	2.730
4/21/35 12:04 A.M.	Supplied heat			
2:05 A.M.	12	139.333	139.32	2.730
2:45 A.M.	Supplied heat			
4:56 A.M.	20	139.343	139.35	2.731
5:26 A.M.	Supplied heat			
8:22 A.M.	30	139.347	139.35	2.733
9:08 A.M.	Supplied heat			
11:19 A.M.	40	139.346	139.36	2.735
12:01 P.M.	Supplied heat			
2:12 P.M.	65	139.350	139.35	
	Accepted values		139.35	2.733

MELTING POINT OF PHOSPHINE

Table II gives a summary of the observed melting point temperatures and pressures.

Table III contains a summary of measurements of the melting and boiling point temperatures for phosphine.

THE TRANSITION OF PHOSPHINE

Clusius[14] has measured the heat capacity of phosphine to the temperatures of liquid hydrogen. He found transitions at 88.5 and 30.3°K. He has published his heat capacity results only in graphical form. Two somewhat similar regions of high heat capacity are shown, one near 35°K and the other about 50°K.

The present investigation confirms the existence of the two transitions reported by Clusius and the region of high heat capacity at 35°K.

TABLE III. *Melting and boiling point temperatures of phosphine.*

MELTING POINT °K	BOILING POINT °K	OBSERVER
140.6	188	Olszewsky[12] (1886)
——	186.9	McIntosh and Steele[13] (1904)
——	185.65	Henning and Stock[11] (1921)
139.7	——	Clusius[14] (1933)
139.35	185.38	This research

[12] Olszewsky, Phil. Mag. (5) **39**, 188 (1895).
[13] McIntosh and Steele, Proc. Roy. Soc. **73**, 450 (1904).
[14] Clusius, Zeits. f. Elektrochem. **39**, 598 (1933).

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However, we have found that another transition exists at 49.43°K. The previous observations below this temperature refer to an unstable modification. The small rise in heat capacity shown in Clusius' graph near 50°K indicates that one or two percent of the stable form was present during his measurements. All of the transitions have been carefully reinvestigated.

The Transition Temperature at 88.10°K

From cooling and warming curves it was found that phosphine can be superheated or supercooled one or two tenths of a degree above or below 88.10°K. Table IV contains a summary of the measurements.

The Transition Temperature at 49.43°K and the Rate of Transformation

When phosphine is cooled slowly below 49.43°K it undergoes a transformation to another form. If cooled with sufficient rapidity, the high temperature form may be completely supercooled and kept at liquid hydrogen temperatures with practically no conversion. On warming, the supercooled form begins to change spontaneously into the stable low temperature form at about 36°K. The rate of the transformation reaches a maximum at about 40°K and becomes too small to measure at 47°K. Complete conversion to the stable form requires two to three days near 40°K. Fig. 1 shows the variation of the rate of transformation with temperature. This is indicated approximately by a graph of the warming rates at various temperatures. The heat leak from the surroundings was negligible during the measurements, which were made with between 50 and 60 percent transformed.

Table IV. *The transition temperature at 88.10°K.*

Time	% Transformed	T°K Resistance Thermometer	Thermocouple
0	Cooled approximately half-way through the transition		
1:44		87.99	87.98
5:00	Cooled below the transition temperature and conversion completed		
5:30	Heat added		
8:12	17	88.20	88.20
8:23	Heat added		
13:36	33	88.22	88.23
13:51	Heat added		
17:20	50	88.25	88.24
17:28	Heat added		
20:35	67	88.31	88.34
20:43	Heat added. Transition complete		
24:34	Cooled partially back through the transition		
31:30		87.99	88.03
		Accepted value	88.10±.10°

Clusius[14] gives 88.5°K for this temperature.

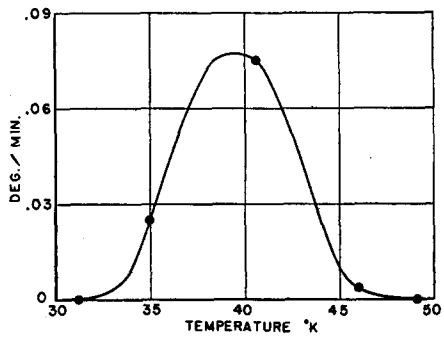

Fig. 1. Variation of the rate of transformation of phosphine with temperature ordinates: warming rate of the calorimeter in deg. per min. with 50 percent transformed.

To determine the transition temperature, sufficient energy was added to the low temperature form to cause approximately 50 percent conversion. The temperatures attained in three separate measurements were: 49.44°K, after an equilibrium period of 12 hours; 49.40°K, equilibrium period, 6 hours; 49.45°K, equilibrium period, 7 hours. The average of these values, 49.43°K, has been taken as the transition temperature.

The transition temperature could not be reached by allowing the supercooled phosphine to warm spontaneously due to the slow rate of conversion; the highest temperature reached in this way was 47.3°K. It was possible to heat the low temperature form 0.25° above the transition temperature before conversion began.

The Transition Temperature at 30.29°K

A transition occurred in the unstable form at 30.29°. No supercooling or superheating could be detected at this temperature. Table V contains a summary of the temperature measurements.

The Region of High Heat Capacity Near 36°K

Above the transition at 30.29°K the heat capacity curve shows an abnormal rise, followed by a rather abrupt decrease near 35.66°K.

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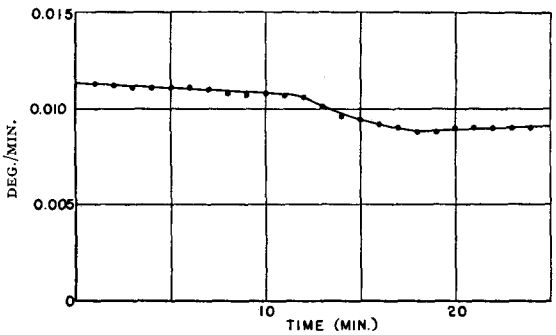

FIG. 2. Cooling rate curve for phosphine near 35.66°K. The temperature was 35.66°K at 15.5 minutes on scale.

Within the limit of accuracy of the observations there was no isothermal absorption of heat near the region of sudden change and for this reason the phenomenon was studied by means of cooling and warming rates near 36°K. When the rate of cooling or warming is plotted against time, a break is found at 35.66°K extending over the comparatively small region of ±0.03°. Fig. 2 shows one of these cooling curves.

The curve indicates that the heat capacity drops by approximately 15 percent within 0.06°, and no doubt this region would be smaller if the equilibrium were instantaneous. There is no indication of an isothermal heat effect, or of superheating or supercooling.

MEASUREMENT OF AMOUNT OF PHOSPHINE

The amount of phosphine used in the calorimetric measurements was determined in a thermostated bulb of about 5 liters capacity. The apparatus and procedure have been described[15] previously.

During the experiments, some of the same phosphine on which the calorimetric measurements were made was used by Long and Gulbransen[16] for their data of state measurements on this substance. From their data and Ritchie's[8] density measurements at 0°C we have calculated the coefficient, α, of deviation from Boyle's law at one atmosphere and 298.1°K to be -0.0074 per atmos where $PV=P_0V_0(1+\alpha P)$. In calculating this value we made use of the molecular weight 34.044 rather than the value 34.000 obtained by Ritchie and used by Long and Gulbransen in presenting their data. Essentially the calculation assumes that Ritchie's density measurements were correct but that the extrapolation of the PV product to zero pressure is in error. The molal volume of an ideal gas at 0°C = 273.10°K and 1 atmos. was taken as 22411.5 cc. 2.446 moles of phosphine were used for the measurements.

[15] Giauque and Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).

[16] Long and Gulbransen, J. Am. Chem. Soc. **56**, 203 (1936).

HEAT CAPACITY OF PHOSPHINE

The heat capacity results are given in Table VI. For the calculation of energy, 1.0004 absolute joules were taken equal to 1 international joule and 4.185 absolute joules were taken equal to 1 calorie. The data are shown in Fig. 3.

Before Series III and IV were taken, the calorimeter was kept, in each case, near 40°K for 48 hours. Complete conversion was assured by the absence of any heat effect due to the transition in the unstable form at 30.29°K.

The heat capacities of the unstable form from 30.29°K to 35.66°K and the heat of transition

TABLE V. *Transition temperature of phosphine.*

Date and Time	% Transformed	T°K Resistance Thermometer	T°K Thermocouple
Series 1			
5/7/35 9:04 P.M.	Heated into transition		
9:17 P.M.	40	30.289	30.25
9:38 P.M.	Heat added		
10:01 P.M.	60	30.288	30.25
10:08 P.M.	Heat added		
10:40 P.M.	90	30.293	30.27
Series 2			
5/23/35 9:21 P.M.	Heated into transition		
9:48 P.M.	25	30.284	30.28
Series 3			
5/25/35 1:13 A.M.	Heated into transition		
1:27 A.M.	65	30.290	30.34
Series 4			
8/7/35 7:00 P.M.	Cooled partially through transition		
9:30 P.M.		30.275	30.33
		Accepted value	30.29

Clusius[14] gives 30.3°K for this temperature.

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at 30.29°K depended to some extent upon the rate of cooling between 50 and 35°K. The rate of cooling before the measurements on the form unstable below 49.43°K is given in Table VII.

The discussion of the effect of different rates of cooling is given later.

A heat capacity measurement, which has not been given in Table VI, was made between 49.09 and 51.33°K at the end of Series I. This measurement was high because it included a heat effect due to the transition of a small amount of the stable form which was present. The data indicate that 1.6 percent of the unstable form had gone over to the stable modification. Most of this conversion took place during the heat capacity measurements from 36°K to 47°K; consequently, the measurements in this region for Series I may be in error by one or two percent.

It is estimated from the rate of transformation and the time of cooling that below 36°K, the high temperature form contained less than 0.2 percent of the stable modification for Series I, less than 0.1 percent for Series V and X, and less than 0.4 percent for Series VII.

The measurements of Series II were made after cooling only to 44.7°K. The absence of any heat effect at 49.43°K shows that the high temperature form underwent no appreciable conversion during these measurements.

TABLE VI. *Heat capacity of phosphine. (Molecular weight, 34.044; 0°C=273.10°K.)*

T°K	ΔT	C_p CAL./DEG./MOLE	SERIES	T°K	ΔT	C_p CAL./DEG./MOLE	SERIES
			Form stable below 49.43°K				
15.80	2.615	1.076	IV	33.31	3.824	4.169	III
16.65	2.694	1.197	III	33.41	3.644	4.188	IV
18.63	2.955	1.562	IV	37.13	3.835	4.886	IV
19.49	2.993	1.679	III	37.29	4.075	4.893	III
21.71	3.175	2.090	IV	41.12	3.985	5.571	IV
22.66	3.340	2.259	III	41.50	4.432	5.602	III
25.04	3.525	2.692	IV	45.10	3.974	6.314	IV
26.00	3.404	2.847	III	45.86	4.291	6.469	III
28.62	3.667	3.300	IV	47.85	1.517	6.982	IV
29.94	3.333	3.550	IV	49.43	Transition		
			Form stable above 49.43°K				
17.71	2.747	1.987	V	47.52	3.255	10.51	I
18.81	3.386	2.200	I	48.66	2.553	10.68	II
20.58	2.930	2.641	V	51.14	2.414	10.87	II
22.31	3.743	3.054	I	54.45	4.217	11.10	II
23.65	3.248	3.431	V	58.19	4.832	11.34	VI
24.77	3.898	3.776	VII	63.40	5.570	11.56	VI
25.55	2.776	3.992	I	68.77	5.203	11.75	VI
26.94	3.396	4.551	V	74.33	5.922	11.90	VI
27.62	1.803	4.827	VII	80.07	5.569	11.98	VI
28.06	2.201	5.040	I	85.25	4.841	12.22	VI
29.05	1.035	5.594	VII	88.10	Transition		
29.29	1.321	5.809	V	92.69	5.115	11.15	VIII
30.29	Transition			98.01	5.389	11.21	VIII
31.34	1.006	8.20	I	103.50	5.184	11.22	VIII
31.65	2.314	8.80	V	109.39	5.414	11.26	VIII
32.22	3.141	8.73	VII	114.96	5.193	11.32	VIII
32.31	0.944	8.65	I	120.28	4.998	11.38	VIII
33.46	1.360	9.38	I	125.82	4.772	11.53	VIII
34.21	2.817	10.16	V	131.27	4.573	11.57	VIII
34.55	0.822	10.25	I	135.72	4.063	11.69	VIII
34.84	2.136	10.55	VII	139.35	Melting point		
35.33	0.741	11.35	I	146.11	5.449	14.58	IX
35.66	Abrupt decrease in heat capacity			151.69	5.293	14.51	IX
36.12	0.844	9.61	I	157.11	5.175	14.47	IX
36.49	1.136	9.55	VII	162.43	5.040	14.46	IX
40.87	3.018	9.84	I	167.64	4.919	14.44	IX
44.17	3.499	10.18	I	172.71	4.798	14.45	IX
46.04	2.723	10.41	II	177.69	4.677	14.48	IX
				182.73	4.558	14.48	IX
				185.38	Boiling point		

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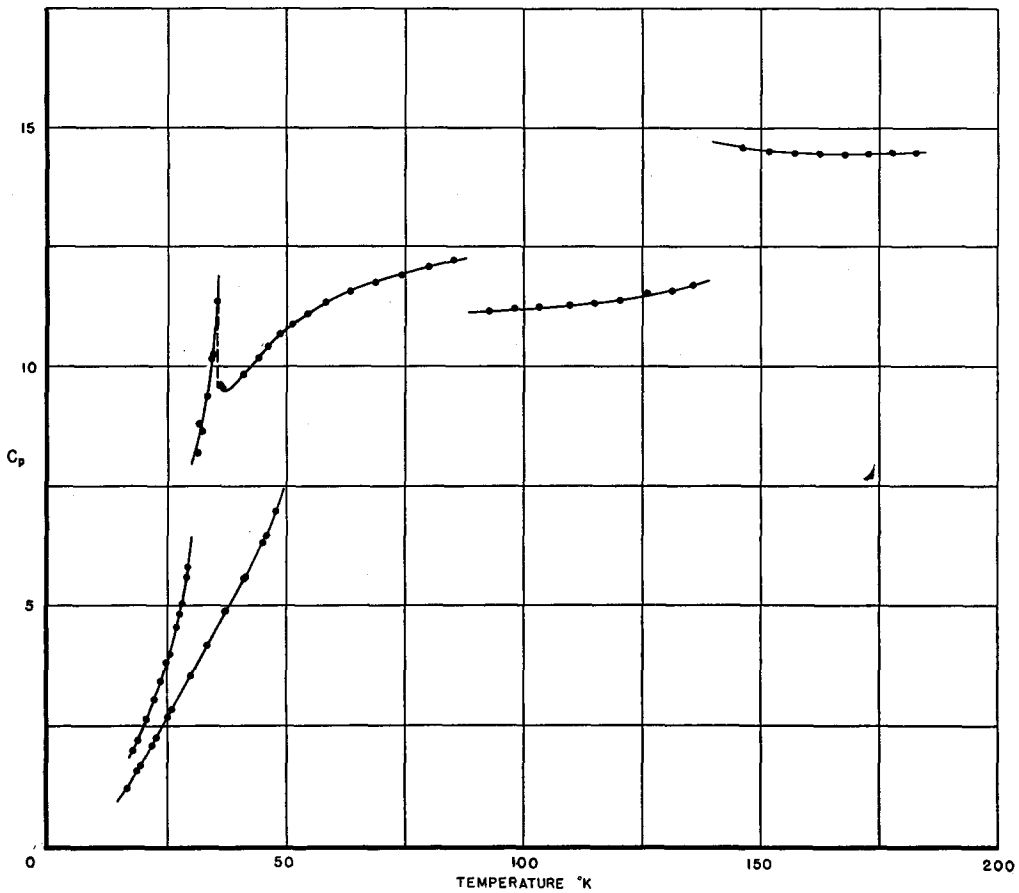

FIG. 3. Heat capacity in calories per degree per mole of phosphine.

Points taken from smooth curves through the data are summarized in Table VIII.

Another series of measurements was made from 15°K to 50°K after half of the phosphine had been allowed to undergo transformation to the stable form. These measurements were affected by the greater rate of conversion caused by the larger amount of the stable form present, and it was not possible to obtain results as accurate as those given for the other series. The results of this series will be discussed below.

A comparison of the results of Clusius[14] with those of the present investigation is not possible since the preliminary publication of his results is in graphical form.

THE HEAT OF TRANSITION AT 30.29°K

A summary of the measurements of the heat of transition at 30.29°K is given in Table IX.

The heat of transition was highest for the slowest rate of cooling in the above series. When the heat of transition is high, the heat capacity curve in the region from 30.29 to 35.66°K is correspondingly low. No heat capacities were taken in Series X, but the rate of cooling was the same as in Series V, so the heat capacity of that series was assumed in order to make the $\int C_p dT$ corrections. The small variations mentioned above produce a negligible effect in evaluating the entropy. In any case, the effect of the variation in the heat of transition is

TABLE VII. *Rate of cooling from 50°K to 35°K.*

SERIES	I	V	VII	X
T, °K		Time in minutes		
50	0	0	0	0
45	12	6	18	6
30	25	13	38	13
35	39	23	62	23

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TABLE VIII. *Heat capacity of phosphine. Values taken from smooth curves through the data.*

T°K	C_p CAL./DEG./MOLE	T°K	C_p CAL./DEG./MOLE
Form stable below 49.43°K			
15	0.96	35	4.48
20	1.79	40	5.38
25	2.66	45	6.31
30	3.56		
Form stable above 49.43°K			
15	1.56	90	11.15
20	2.46	100	11.21
25	3.85	110	11.28
30	6.23	120	11.37
35	10.90	130	11.53
40	9.77	140	14.75
45	10.32	150	14.52
50	10.78	160	14.45
60	11.42	170	14.44
70	11.79	180	14.46
80	12.06	185	14.49

practically compensated by the change in the heat capacity. This is shown in Table X by separate entropy calculations made for three different series of measurements over this region.

The general character of the heat capacity curves between 25 and 35°K is of the type usually associated with molecular rotation in the solid state.

One measurement of the heat of transition was made on a mixture of 52 percent of the high temperature form and 48 percent of the stable form; the relative amounts were determined by assuming that the heat capacity of the mixture below the transition at 30.29°K is equal to the sum of the heat capacities of the two forms. The value obtained was 10.34 cal./mole of the mixture, or 19.8 cal./mole for 100 percent of the high temperature form.

HEATS OF TRANSITION AND FUSION

Table XI contains the results of the determinations of the heat of fusion and heats of transition at 49.43°K and 88.10°K.

THE HEAT OF VAPORIZATION OF PHOSPHINE

The heat of vaporization was measured by adding energy and accepting the gas evolved in the five liter measuring bulb referred to above. The pressure was kept constant to about a

TABLE IX. *Heat of transition at 30.29°K.*

TEMPERATURE INTERVAL	CORRECTED HEAT INPUT/MOLE	$\int C_p dT$	ΔH CAL./MOLE	SERIES
30.157–30.832	25.06	5.13	19.93	I
30.094–30.645	23.60	4.25	19.35	X
30.036–30.592	23.53	4.17	19.36	X
29.946–30.500	23.19	3.94	19.25	V
29.840–30.647	25.93	5.72	20.21	VII
		Average value	19.6±0.4	

Clusius[14] gives 19.5 cal./mole.

TABLE X. *Entropy change from 30.29°K to 35.66°K.*

SERIES	I	V	VII
Heat of transition/30.29°K	0.658	0.636	0.667
30.29°K–35.66°K	1.500	1.559	1.514
	2.158	2.195	2.181

TABLE XI. *Heat of transition and fusion of phosphine. Transition at 49.43°K*

TEMPERATURE INTERVAL	CORRECTED HEAT INPUT/MOLE	$\int C_p dT$	ΔH CAL./MOLE
49.076–50.209	196.52	11.03	185.5
48.639–51.138	210.04	24.26	185.8
	Accepted value		185.7±.2
Transition at 88.10°K			
87.652–89.625	137.96	22.49	115.5
87.555–89.271	135.51	19.74	115.8
87.482–89.725	141.46	25.70	115.8
87.372–90.009	146.13	30.22	115.9
	Accepted value		115.8±.1
Fusion at 139.35°K			
137.917–142.576	334.54	64.37	270.2
138.224–141.177	310.75	40.23	270.5
137.891–140.863	310.19	39.55	270.6
	Accepted value		270.4±.2

Clusius[14] has given 114.0 cal./mole for the heat of transition at 88.10°K and 267.3 cal./mole for the heat of fusion.

TABLE XII. *Heat of vaporization of phosphine, boiling point, 185.38°K.*

AMOUNT EVAPORATED, MOLES	TIME OF ENERGY INPUT, MINUTES	ΔH AT 760 MM. CAL./MOLE
0.20631	45	3486
0.21263	46	3489
0.21666	47	3486
0.21840	47	3491
0.21376	47	3490
	Accepted value	3489±3
From the vapor pressure equation of this research		3472
From the vapor pressure equation given by Henning and Stock[11]		3408

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TABLE XIII. *The entropy of phosphine, molecular weight 34.044.*

	Form Stable above 49.43°K		Form Stable below 49.43°K	
0–15°K, Debye function	$h\nu/k=99$	0.495	$h\nu/k=114$	0.338
Graphical	15–30.29°K	2.185	15–49.43°K	4.041
Transition	19.6/30.29	0.647	185.7/49.43	3.757
Graphical	30.29–49.43	4.800	—	—
Entropy at 49.43°K		8.13		8.14
Graphical, 49.43–88.10°K		6.705		
Transition, 115.8/88.10		1.314		
Graphical, 88.10–139.35°K		5.194		
Fusion, 270.4/139.35		1.940		
Graphical, 139.35–185.38°K		4.140		
Vaporization, 3489/185.38		18.82		
Entropy of actual gas at boiling point		46.25		
Correction for gas imperfection		+0.14		
Entropy for ideal gas at boiling point		46.39±0.1 cal. per deg. per mole.		

millimeter of mercury. A summary of the data is given in Table XII.

The heat of vaporization was calculated from the vapor pressure equations using the equation of state given by Long and Gulbransen.[16] This equation of state was corrected to the generally accepted molecular weight 34.044 rather than the value 34.000 used by the above authors.

THE ENTROPY FROM CALORIMETRIC DATA

An itemized account of the calculation of the entropy of phosphine is given in Table XIII. The entropy correction for gas imperfection was made by using Berthelot's equation of state, with $T_c=324.1$°K and $P_c=64$ atmos.[17]

The almost exact agreement of the entropies at 49.43°K for the two paths is undoubtedly fortuitous; the individual values may be in error by several hundredths of an entropy unit. The close agreement of the two values is an excellent verification of the third law of thermodynamics.

As mentioned above, one series of heat capacity measurements was made from 15 to 50°K with half each of the stable and unstable forms. The entropy value at 49.43°K, obtained from these measurements, agrees with the above value to 0.1 cal./deg. per mole. As the amount converted was measured in terms of the heat evolved during the partial transformation, the above entropy agreement is of interest in that it indicates that the process of conversion of the unstable to the stable form is accomplished by the formation of distinct phases. Since the character of the heat capacity curves of the two forms below 49.43°K indicates molecular rotation in the unstable form and no molecular rotation in the stable form, we had considered the possibility that the slow transformation at low temperatures might have involved the loss of molecular rotation in a gradual and homogeneous manner throughout the solid. The random distribution accompanying such a process would preclude an entropy agreement such as that given above.

THE ENTROPY FROM SPECTROSCOPIC DATA

Phosphine has a symmetrical pyramidal form, in which the principal moments of inertia $I_A=I_B\neq I_C$. The value $I_A=6.221\times10^{-40}$ gram cm^2 has been made certain by the measurements of Wright and Randall.[18] The value of I_C has not been determined experimentally, but Yost[19] has calculated a value of 8.26×10^{-40} gram cm^2 by making the plausible assumption that the bond angle is 100°. He then calculated $S_{298.1}=50.5\pm1.0$ for phosphine. The nuclear spin entropy, $R\ln 16=5.509$, is not included in this value.

By using the fundamental frequencies, 990, 1121, and 2327 cm^{-1}, observed by Fung and

[17] *International Critical Tables*, Vol. 3, p. 248.

[18] Wright and Randall, Phys. Rev. **44**, 391 (1933).

[19] Yost, J. Chem. Phys. **2**, 624 (1934).

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Barker[20] and the frequency 2340 cm^{-1} calculated from valence forces by Howard[21] the entropy change of phosphine gas from 185.38°K to 298.1°K is found to be 3.96 cal./deg. per mole. This, added to the experimental value $S_{185.38}=46.39$, gives $S_{298.1}=50.35$ cal./deg. per mole, which agrees with the value given by Yost.

It is quite unlikely that any lack of equilibrium exists in the solid which would cause a discrepancy between the calorimetric and spectroscopic values, since the entropies given by the two paths below 50°K are in accord. The experimental value of the entropy of phosphine may therefore be used with confidence in thermodynamic calculations. In addition, the constants of the phosphine molecule may be obtained from the experimental entropy value, the familiar Sackur-Tetrode equation, and the value of I_A. For I_C, the value $7.9\times10^{-40}\pm0.8\times10^{-40}$ gram cm^2 is calculated; for the P−H distance, 1.45 ± 0.02A; and for the bond angle, $98\pm5°$. The value found for I_C definitely eliminates the possibility that phosphine is a spherical top, as suggested by Fung and Barker.

We thank Dr. Roy Overstreet for assistance with the experimental work.

[20] Fung and Barker, Phys. Rev. **45**, 238 (1934).
[21] Howard, J. Chem. Phys. **3**, 207 (1935).

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