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

Propylene. The Heat Capacity, Vapor Pressure, Heats of Fusion and Vaporization. The Third Law of Thermodynamics and Orientation Equilibrium in the Solid

BY T. M. POWELL AND W. F. GIAUQUE

Several cases are known where molecules containing somewhat similar atoms in otherwise equivalent positions enter the crystal lattice without appreciably distinguishing between the similar atoms. This situation which corresponds to thermodynamic equilibrium at the freezing point is sometimes unable to readjust itself to an ordered molecular arrangement as the temperature of the solid is lowered sufficiently to make this the stable state.

This effect was first observed by Johnston and Giauque[1] in the case of nitric oxide which polymerizes to N_2O_2. They showed that a residual entropy of $R \ln 2$ per mole of N_2O_2 remained near the absolute zero. The above explanation was advanced by Clayton and Giauque,[2] who investigated the similar effect in carbon monoxide. These authors pointed out that this was the usual case in molecules containing isotopes and was to be expected in other cases where the atoms are of somewhat similar size. In addition to the above cases this effect has been observed in the case of nitrous oxide NNO by Clusius[3] and Blue and Giauque.[4] Clayton and Giauque[2] also pointed out that this effect was to be expected in the case of certain carbon compounds.

The experimentally investigated cases mentioned above involve only lack of discrimination between atoms but it is evident that cases may occur where false equilibrium may exist at low temperatures with respect to groups of atoms. This paper is a report on a calorimetric investigation of propylene, $CH_2{=}CH{-}CH_3$, which shows that the CH_3 and CH_2 groups are located without discrimination when they enter the crystal lattice under equilibrium conditions at the freezing point. Propylene lacks the mechanism to rotate the molecule within the solid so as to produce an ordered arrangement corresponding to zero entropy as the absolute zero of temperature is approached.

The apparatus and method of measurement have been described previously.[4-8] The measure-

(1) Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).
(2) Clayton and Giauque, ibid., **54**, 2610 (1932).
(3) Clusius, Z. Elektrochem., **40**, 99 (1934).
(4) Blue and Giauque, THIS JOURNAL, **57**, 991 (1935).
(5) Giauque and Wiebe, ibid., **50**, 101 (1928).
(6) Giauque and Johnston, ibid., **51**, 2300 (1929).
(7) Giauque and Egan, J. Chem. Phys., **5**, 45 (1937).
(8) Giauque and Powell, THIS JOURNAL, **61**, 1970 (1939).

ments were made in a calorimeter with the laboratory designation Gold Calorimeter II.

Preparation and Purity of the Propylene.—A sample of propylene was donated by the Shell Development Company. Several heat capacity measurements in the region just below the melting point were made on the original sample and from the heat effect due to premelting the liquid soluble–solid insoluble impurity was estimated at 0.2 mole %. The material was then fractionated and subsequent calorimetric measurements of the premelting indicated that the impurity had been reduced to 0.02 mole %. Table I shows the several estimates of impurity as obtained by the total premelting which occurred up to the several temperatures.

TABLE I

PREMELTING DATA ON THE SAMPLE OF PROPYLENE

$\Delta, T°$ below m. p.	Premelting cal. mole^{-1}	% melted	Impurity mole %
3.77	0.94	0.132	0.022
2.34	1.49	.208	.022
1.06	3.06	.428	.021
0.265	9.76	1.37	.017
.109	34.2	4.8	.024
.063	60.4	8.5	.024
		Average	.022

The Vapor Pressure of Propylene.—The vapor pressure of propylene was measured by means of a mercury manometer and a standard meter with a cathometer used as a comparison instrument. The acceleration of gravity was taken as 979.973 cm. sec.$^{-2}$ for this location and the standard acceleration as 980.665 cm. sec.$^{-2}$.

The results have been represented by the equation, 165.8 to 225.9°K.

$$\log_{10} P_{\text{(inter. cm. Hg)}} = -\frac{1196.9}{T} - 3.92 \times 10^{-3}\, T + 8.07544 \quad (1)$$

The vapor pressure observations are compared with Equation 1 in Table II.

The temperatures are given to 0.001° only because the high relative accuracy permits the data to be used in obtaining derivatives.

From Equation 1 the boiling point of propylene was found to be 225.35°K.

A summary of observations on the melting point is given in Table III. The gradual increase with

TABLE II

VAPOR PRESSURE OF PROPYLENE 0°C. = 273.10°K.

T, °K.	$P_{obsd.}$ int. cm. Hg.	$P_{obsd.} - P_{calcd.}$	$T_{obsd.} - T_{calcd.}$
165.764	1.598	−0.006	+0.039
172.721	2.941	− .001	+ .005
176.465	3.992	.002	− .005
179.951	5.232	− .001	+ .003
184.486	7.319	− .000	+ .001
189.451	10.354	+ .001	− .002
195.583	15.452	+ .002	− .003
202.665	23.731	+ .008	− .006
207.395	30.996	− .002	+ .001
213.343	42.547	− .002	+ .001
220.228	59.830	− .051	+ .018
225.925	77.992	+ .001	− .000

the % melted corresponds to the 0.02 mole % of impurity mentioned above.

TABLE III

MELTING POINT OF PROPYLENE 0°C. = 273.10°K.

% melted	T, °K. Thermocouple	T, °K. Resistance thermometer
4.8	87.76	87.748
8.5	87.81	87.794
45	87.82	87.836
82	87.84	87.849
94	87.85	87.852
Accepted value	87.85	

In Table IV the melting and boiling points are compared with those obtained by previous observers.

TABLE IV

MELTING AND BOILING POINTS OF PROPYLENE

M. p., T, °K.	B. p., T, °K.	Observer
..	225.3	Burrell and Robertson[9] (1915)
87.9	226.1	Maass and Wright[10] (1921)
..	225.3	Trautz and Winkler[11] (1922)
88.2	....	Huffman, Parks and Barmore[12] (1931)
..	225.34	Kistiakowsky, et al.[12a] (1935)
..	225.45	Ashdown, Harris and Armstrong[13] (1936)
87.85	225.35	This research

The Calorimetric Observations.—The heat capacity measurements on solid and liquid propylene are recorded in Table V. The results on the liquid were corrected for vaporization into the small gas space when the vapor pressure made the effect appreciable. In making this correction

(9) Burrell and Robertson, THIS JOURNAL, **37**, 2188 (1915).

(10) Maass and Wright, ibid., **43**, 1098 (1921).

(11) Trautz and Winkler, J. prakt. Chem., **104**, 37 (1922).

(12) Huffman, Parks and Barmore, THIS JOURNAL, **53**, 3876 (1931).

(12a) Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 876 (1935).

(13) Ashdown, Harris and Armstrong, ibid., **58**, 850 (1936).

the measurements of Maass and Wright[10] on the density of liquid propylene were utilized. A small pressure of helium gas was used to facilitate thermal equilibrium in the solid. The amount of propylene taken for the measurements was determined by condensing the material in a steel bomb equipped with a valve and weighing at room temperature: 64.227 g. equivalent to 1.5264 moles was used for the measurements; 4.1832 international joules was taken equal to 1 calorie (15°).

TABLE V

THE HEAT CAPACITY OF PROPYLENE

0°C. = 273.10°K. Molecular weight = 42.078. 1.5264 moles were in the calorimeter.

T, °K.	ΔT approx.	C_p cal. deg.$^{-1}$ mole^{-1}	T, °K.	ΔT approx.	C_p cal. deg.$^{-1}$ mole^{-1}
14.18	1.3	1.141	87.85	Melting point	
16.66	3.6	1.588	93.91	4.4	22.03
19.63	2.4	2.201	98.66	5.1	21.76
22.81	3.9	3.057	104.18	5.8	21.49
26.23	2.9	3.891	109.98	5.7	21.35
29.87	4.2	4.686	115.64	5.5	21.14
33.62	3.3	5.607	128.09	6.0	20.99
37.46	4.3	6.468	134.56	6.6	20.93
41.29	3.8	7.175	141.21	6.4	20.81
45.53	4.7	7.85	154.97	6.8	20.83
50.66	5.5	8.71	161.88	6.6	20.82
55.96	4.9	9.44	169.01	7.2	20.87
61.25	5.6	10.26	176.71	7.0	20.98
66.61	5.0	10.98	187.77	6.7	21.06
71.45	4.6	11.61	194.66	6.5	21.19
76.49	5.4	12.29	201.77	7.0	21.42
76.59	5.3	12.41[a]	209.18	6.8	21.55
81.69	4.8	13.40[a]	216.41	6.6	21.61
84.87	1.4	14.20[a]	223.40	6.3	21.86
86.17	1.3	16.10[a]	225.35	Boiling point	

[a] Values include premelting heat effect.

Results taken from a smooth curve through the data are given in Table VI. The curve should represent the heat capacity to 0.1–0.2% above 35°K. At 20°K. the error may be 1% and at 15°K. several %.

The data are shown graphically in Fig. 1 where the dotted curve below the melting point shows the rise in heat capacity due to the premelting resulting from 0.02 mole % of impurity.

The heat capacity of propylene, above 68.9°K., has been measured by Huffman, Parks and Barmore.[12] The observations agree well with the present results, as may be seen from a comparison included in Table VI.

The observations on the heat of fusion are given in Table VII. The runs started several degrees below the melting point and ended somewhat

TABLE VI

THE HEAT CAPACITY OF PROPYLENE

0°C. = 273.10°K. Molecular weight = 42.078.

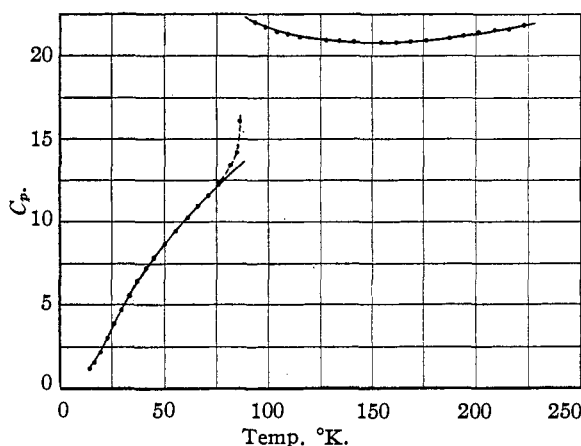| T, °K.	C_p cal. deg.$^{-1}$ mole^{-1}	% dev., H. P. and B. This research	T, °K.	C_p cal. deg.$^{-1}$ mole^{-1}	% dev.. H. P. and B. This research
15	1.27		100	21.70	−0.3
20	2.29		110	21.33	−0.7
25	3.59		120	21.08	−1.3
30	4.78		130	20.93	−1.1
35	5.92		140	20.85	−1.1
40	6.92		150	20.82	−0.9
45	7.78		160	20.83	− .8
50	8.56		170	20.89	− .6
60	10.05		180	20.98	− .2
70	11.45	0.9	190	21.13	.0
80	12.79		200	21.32	.0
			210	21.52	.0
87.85	13.83	Melting point	220	21.75	
87.85	22.33		225.35	21.89	(B. p.)
90	22.21	0.0	230	22.01	

Fig. 1.—Heat capacity in calories per degree per mole of propylene.

above. The correction for the heat capacity was of course made on the basis that premelting as shown in Table I is included in the heat of fusion.

TABLE VII

HEAT OF FUSION OF PROPYLENE

Melting point, 87.85°K. Molecular weight, 42.078.

Run	$T_1° - T_2°$	Heat input cal. mole^{-1}	$\int C_p \, dT$ cal. mole^{-1}	Pre-melting at T_1, cal. mole^{-1}	ΔH Fusion cal. mole^{-1}
1	83.131–93.912	914.59	198.69	1.38	717.2
2	82.812–91.626	868.75	152.35	1.30	717.7
3	84.398–92.692	871.17	154.37	2.06	718.1
4	83.099–91.698	865.95	149.95	1.38	717.3
				Average	717.6

The heat of fusion also has been measured by Huffman, Parks and Barmore,[12] who obtained the value 701.4 cal. mole^{-1}. This value is 2% less

than the one obtained in the present research. As the heat capacity in the earlier work had not been measured to temperatures sufficiently below the melting point to permit an estimate of the effect of impurity, it is presumed that the deviation is due to unconsidered premelting rather than to error in the actual calorimetric observation.

For measurements of the heat of vaporization the amount evaporated was measured by means of a 5-liter thermostatted bulb, initially filled with mercury which was removed automatically as the gas was accepted at constant pressure. This apparatus has been described previously.[6] At the conclusion of energy input the line leading from the calorimeter was closed, the mercury was lowered to a suitable calibration mark and a pressure observation was taken. The propylene from three such observations was collected and weighed in the steel bomb mentioned above. From these data a value of the gas density was calculated. The data are collected in Table VIII.

TABLE VIII

GAS DENSITY OF PROPYLENE AT 25°

Bulb volume, cc.	Pressure inter. cm. Hg	Total amt., g.
5330.9	71.574	
5358.5	73.233	26.823
5320.9	74.120	

$$P_0 V_0 = RT = 22411.5 \times \frac{298.10}{273.10} \text{ cc. atm.}$$

$$PV = RT(1 + \lambda P)$$
$$\lambda = -0.0149 \text{ atm.}^{-1}$$

The density calculated to 1 atmosphere was 1.7461 g./l. at 25.00°. Before and after the measuring bulb was connected to the calorimeter the temperature was not exactly the vaporization temperature and suitable corrections were applied for the effect of temperature change on calorimetric heat content and the small amount of gas in the connecting line. The measurements of the heat of vaporization are given in Table IX.

TABLE IX

HEAT OF VAPORIZATION OF PROPYLENE

Boiling point, 225.35°K.

Run	Moles evaporated	Time of energy input, min.	ΔH vap. cal. mole^{-1}
1	0.20483	54	4400
2	.21618	57	4405
3	.21744	57	4405
4	.20770	56	4399
		Average	4402

The entropy calculation from 0°K. to the boiling point is summarized in Table X.

TABLE X

SUMMARY OF ENTROPY CALCULATION

0–15°K. Debye function, $hc\nu/k =$ 100	0.482
15–87.85°K., graphical	11.543
Fusion, 717.6/87.85	8.168
87.85–225.35°K., graphical	20.014
Vaporization, 4402/225.35	19.534
Actual gas at boiling point	59.74 ± 0.1
Correction for gas imperfection	0.19
Ideal gas at 225.35°K.	59.93
$\int_{225.35}^{298.1} C_p(\text{gas})\, d \ln T$ from molecular data	3.0
Ideal gas at 298.1°K.	62.9 cal. deg.$^{-1}$ mole^{-1}

The correction for gas imperfection was made by means of an equation of state to be published shortly by Mr. E. E. Roper,[14] who has kindly calculated the value of $S_{\text{ideal}} - S_{\text{actual}}$ for us from his data.

The molecular data on propylene are not known very accurately but Kassel[15] has calculated the translational and rotational entropy by assuming values for interatomic distances which should be reasonably accurate. (Values used were C—C, 1.53×10^{-8} cm.; C=C, 1.35×10^{-8} cm.; C—H, 1.1×10^{-8} cm.; with tetrahedral angles.) From these data and the assumption of free rotation of the methyl group he obtains

$$S_{\text{(Trans. + rot.)}} = 11.73 + 9/2\, R \ln T$$

However, Pitzer[16] has predicted that the rotation of the methyl group is hindered and has given tables,[17] based on the assumption of a reasonable type of potential function, which readily allow calculation of the entropy difference of a hindered rotator and a freely rotating group. These tables are expressed as functions of the moments of inertia of the rotating groups and the number and height of the potential barriers.

Kistiakowsky[18] has investigated the heat capacity of propylene gas and has reached the conclusion that the potential barrier lies between 600 and 800 cal. per mole for the rotation of the methyl group. Using 700 cal. per mole and taking the value 4.7×10^{-40} g. cm.^{2} as the moment of inertia for the methyl group, the entropy associated with translation and rotation was calcu-

(14) Personal communication.
(15) Kassel, *J. Chem. Phys.*, **4**, 435 (1936).
(16) Pitzer, *ibid.*, **5**, 473 (1937).
(17) Pitzer, *ibid.*, **5**, 469 (1937).
(18) Kistiakowsky, *ibid.*, **6**, 900 (1938).

lated. The entropy due to vibration was calculated from levels suggested by E. B. Wilson and used by Kistiakowsky. The values in cm.$^{-1}$ and the statistical weights are: 432, (1); 580 (1); 700, (1); 900, (3); 920, (1); 1100, (1); 1200, (1); 1247, (1); 1300, (1); 1415, (2); 1648, (1); 3000, (6). The entropy calculation is summarized in Table XI.

TABLE XI

THE ENTROPY OF PROPYLENE FROM MOLECULAR DATA

	223.35°K.	298.1°K.
$S_{\text{(Trans. + rot.)}}$ assuming free rotation	60.17	62.67
Correction for hindered rotation	−0.23	−1.00
$S_{\text{vib.}}$ harmonic	1.08	2.37
S of ideal gas in cal. deg.$^{-1}$ mole^{-1}	61.0 ± 0.3	64.0

The experimental value of the entropy calculated in Table X is 59.90 cal. deg.$^{-1}$ mole^{-1} or 1.1 units less than the calculated value, 61.0 cal. deg.$^{-1}$ mole^{-1}, given in Table XI. The discrepancy is outside the combined limits of error of the theoretical calculation and the experimental determination, and it is believed to be due to random end for end orientation of CH_2=CH—CH_3 in the crystal lattice. Complete lack of discrimination between the CH_2 and CH_3 groups would correspond to a discrepancy of $R \ln 2 = 1.38$ cal. deg.$^{-1}$ mole^{-1}.

This is the first case where false equilibrium due to random orientation of groups of atoms has been demonstrated and it leads to the conclusion that a similar effect is to be expected in all organic molecules where CH_3 and CH_2 groups occupy otherwise equivalent positions in a molecule. In larger molecules, with higher melting points than the 87.85°K. melting point of propylene, random orientation is still more likely to represent thermodynamic equilibrium when the substance solidifies, and the chance of attaining an ordered arrangement as the temperature is lowered is less. Moreover, it seems necessary to conclude that when one or more double bonds are unsymmetrically placed in internal positions in otherwise symmetrical hydrocarbons, a similar disorder will occur and an appropriate correction should be made to the entropy value obtained by the ordinary application of the third law of thermodynamics.

The most reliable value of the entropy for use in the thermodynamic calculations is 64.0 cal.

deg.$^{-1}$ mole^{-1}. This value does not include the contribution due to nuclear spin.

We thank the Shell Development Company for donating the propylene used for these measurements and Dr. R. A. Ruehrwein for assistance with the experimental work.

Summary

The heat capacity of solid and liquid propylene has been measured from 14 to 226°K.

The melting and boiling points are 87.85 and 225.35°K., respectively. (0°C. = 273.10°K.)

The heats of fusion and vaporization were measured calorimetrically and were found to be 717.6 and 4402 cal./mole, respectively.

The vapor pressure of propylene was measured from 165.8 to 225.9°K. and the results have been represented by the equation

$$\log_{10} P_{(\text{inter. cm. Hg})} = -\frac{1196.9}{T} - 3.92 \times 10^{-3}T + 8.07544$$

The gas density of propylene was determined to

be 1.7461 grams per liter at 25.00°C. and 1 atmosphere.

The calorimetric data have been used to calculate the entropy of propylene gas and the value at the boiling point was found to be 59.93 cal. deg.$^{-1}$ mole^{-1}. The value calculated for this temperature from available molecular data is 61.0 ± 0.3 cal. deg.$^{-1}$ mole^{-1}. The entropy discrepancy is interpreted as due to random end for end orientation of CH_2=CH—CH_3 molecules in the crystal lattice.

It is concluded that unsymmetrically placed double bonds in otherwise symmetrical hydrocarbons will lead to a disordered arrangement in the crystal lattice and a suitable entropy correction should be made to the $\int C_p \, d \ln T$.

The most reliable value for the entropy of propylene gas at 298.1°K. and 1 atmosphere is 64.0 cal. deg.$^{-1}$ mole^{-1}, calculated from molecular data.

The Vapor Pressure of Aqueous Solutions of Sulfuric Acid

BY S. SHANKMAN AND A. R. GORDON

The growing importance of the isopiestic method of investigating the thermodynamic properties of aqueous solutions has emphasized the need for reliable standards. In their pioneer work in this field, Sinclair and Robinson[1] adopted potassium chloride as reference substance, but, more recently, Scatchard, Hamer and Wood[2] have selected sodium chloride for their standard curve. While sodium chloride is eminently suitable for the dilute range of concentration, it cannot be employed for solutions in which the activity of the water is less than 0.75; sulfuric acid would seem to be the obvious alternative to serve as standard when studying the more concentrated range. While the vapor pressure and e. m. f. data for sulfuric acid solutions are of high precision and are in satisfactory agreement up to 3 molal, the case is somewhat different for higher concentrations. The vapor pressure measurements of Collins[3] (which are usually quoted in

the literature) are not of the highest accuracy, and, moreover, are in disagreement with the e. m. f. measurements. We have therefore measured the vapor pressure of sulfuric acid solutions at 25° for concentrations from 2 molal to 23 molal by the static method.

Experimental

The apparatus was similar to that of Gibson and Adams[4]; we may say at once that we can fully substantiate their claims as to its convenience and accuracy. Since it has been discussed adequately, no lengthy description is needed here; its essential feature is that it is possible to measure the vapor pressure of the solution, the vapor pressure of the pure solvent, and the differential vapor pressure lowering by a suitable manipulation of stopcocks (see Fig. 1 of ref. 4).

In our apparatus, the flasks, containing about 25 cc. of solution or solvent, were of approximately 75 cc. capacity, and were placed symmetrically with respect to regulator, heater and stirrer in a water-bath controlled to 0.01°. The internal diameter of the manometer tubing was 15 mm.; the heights of the manometer liquid were measured by comparing them through a telescope with a vertical plate glass scale, placed immediately in front of the two legs of

(1) D. A. Sinclair, J. Phys. Chem., 37, 495 (1933); R. A. Robinson and D. A. Sinclair, THIS JOURNAL, 56, 1830 (1934).

(2) G. Scatchard, W. J. Hamer and S. E. Wood, ibid., 60, 3061 (1938).

(3) E. M. Collins, J. Phys. Chem., 37, 1191 (1933).

(4) R. E. Gibson and L. H. Adams, THIS JOURNAL, 55, 2679 (1933).