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

# Carbonyl Chloride. Entropy. Heat Capacity. Vapor Pressure. Heats of Fusion and Vaporization. Comments on Solid Sulfur Dioxide Structure

BY W. F. GIAUQUE AND W. M. JONES

This paper presents the results of a calorimetric investigation of carbonyl chloride covering the range from 15° K. to its boiling point. A comparison of the entropy calculated from molecular data with the entropy change obtained from the $\int_0^T C_p \, d\ln T$ leads to the conclusion that the planar phosgene molecule shows a nearly complete lack of discrimination between the positions of oxygen and chlorine in the crystal lattice.

**Apparatus and Method.**—The measurements were made in a vacuum calorimeter which has the laboratory designation Gold Calorimeter IV. A description has been given by Kemp and Giauque,[1] and a more detailed description of this type of calorimeter has been given by Giauque and Egan.[2] One calorie was taken equal to 4.1833 international joules.

The measurements on carbonyl chloride were made immediately after an investigation on nitromethane[3] and temperature scale comparisons presented in that connection apply to the present work. After the completion of all of the heat capacity and heat of fusion measurements, the resistance thermometer was broken due to a very unusual expansion of phosgene which occurred in the region extending some 25° below its melting point. A discussion of this expansion will be given below. A new resistance thermometer was installed prior to the measurements of the vapor pressure and heat of vaporization.

**Preparation and Purity of Carbonyl Chloride.**—About 500 cc. of Kahlbaum phosgene was fractionated in a vacuum jacketed column filled with glass helices for a length of approximately 75 cm. About three-fourths of the material was discarded. The sample employed weighed 185.5194 g. *in vacuo*, corresponding to 1.87537 moles. The molecular weight was taken as 98.924.

The change of melting point with the fraction melted was used to estimate the liquid soluble-solid insoluble impurity as 7 moles in 100,000 moles.

TABLE I

HEAT CAPACITY OF CARBONYL CHLORIDE. OBSERVED VALUES

0°C. = 273.10°K.

| $T$, °K. | $\Delta T$, °K. | $C_p$ cal. deg.$^{-1}$ mole$^{-1}$ | Ser. |
|---|---|---|---|
| 14.80 | 0.371 | 1.62 | I |
| 15.98 | 1.509 | 1.95 | I |
| 17.86 | 1.798 | 2.69 | I |
| 20.43 | 1.960 | 3.59 | I |
| 23.99 | 3.590 | 4.58 | I |
| 28.28 | 4.947 | 5.63 | I |
| 32.94 | 4.265 | 6.74 | I |
| 38.01 | 5.673 | 7.72 | I |
| 43.30 | 4.863 | 8.47 | I |
| 48.48 | 5.310 | 9.14 | I |
| 53.77 | 5.222 | 9.79 | I |
| 58.59 | 4.449 | 10.26 | I |
| 63.98 | 6.187 | 10.72 | I |
| 70.51 | 6.827 | 11.27 | I |
| 77.04 | 5.984 | 11.74 | I |
| 82.81 | 5.562 | 12.12 | I |
| 89.06 | 6.924 | 12.48 | I |
| 95.74 | 6.423 | 12.92 | I |
| 101.90 | 5.845 | 13.26 | I |
| 108.48 | 6.592 | 13.68 | I |
| 114.89 | 6.185 | 14.12 | I |
| 121.43 | 5.609 | 14.42* | I |
| 126.91 | 5.313 | 14.83* | I |
| 132.91 | 3.559 | 15.00* | I |
| 136.65 | 3.842 | 15.39* | I |
| 140.68 | 4.092 | 15.89* | I |
| 144.36 | Melting point | | |
| 148.38 | 4.006 | 24.98 | II |
| 152.68 | 4.505 | 24.81 | II |
| 157.51 | 4.967 | 24.64 | II |
| 163.06 | 5.980 | 24.46 | II |
| 169.34 | 6.402 | 24.32 | II |
| 175.74 | 6.252 | 24.20 | II |
| 182.01 | 6.107 | 24.14 | II |
| 188.20 | 5.985 | 23.99 | II |
| 194.89 | 5.856 | 23.88 | II |
| 200.94 | 5.750 | 23.79 | II |
| 206.89 | 5.636 | 23.78 | III |
| 207.10 | 5.628 | 23.74 | II |
| 211.86 | 5.522 | 23.77 | II |
| 217.74 | 5.946 | 23.77 | II |
| 224.10 | 6.369 | 23.78 | II |
| 230.59 | 6.217 | 23.77 | II |
| 236.90 | 6.007 | 23.86 | II |
| 243.39 | 6.467 | 23.92 | II |
| 250.11 | 6.328 | 23.94 | II |
| 256.59 | 5.627 | 23.99 | II |
| 262.76 | 6.065 | 24.00 | II |
| 269.21 | 5.955 | 24.00 | II |
| 274.89 | 4.275 | 24.09 | II |
| 279.40 | 3.664 | 24.03 | II |

* Temperature rise obtained with thermocouple.

**The Heat Capacity of Carbonyl Chloride.**—The heat capacity of the solid and liquid were measured in the usual manner except that the abnormal expansion of carbonyl chloride in the region below the melting point made it im-

---

(1) Kemp and Giauque, THIS JOURNAL, **59**, 79 (1937).

(2) Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

(3) Jones and Giauque, THIS JOURNAL, **69**, 983 (1947).

practicable to use the resistance thermometer-heater as a thermometer in this region. The heat capacity results are given in Table I. The five points immediately below the melting point are marked with asterisks because the temperature rise was obtained by means of the standard thermocouple on account of the thermometer strain mentioned above. These five points are of decreased accuracy and may be in error by as much as 1%.

The values given in Table II were obtained from a smooth curve through the data. They are believed to be accurate to 0.2% except at 20° K. where the error may be 1% and at 15° K. where it may be 5%.

TABLE II

HEAT CAPACITY OF CARBONYL CHLORIDE. VALUES TAKEN FROM SMOOTH CURVES THROUGH THE DATA

0°C. = 273.10°K.

| $T$, °K. | $C_p$, cal. deg.$^{-1}$ mole$^{-1}$ | $T$, °K. | $C_p$, cal. deg.$^{-1}$ mole$^{-1}$ |
|---|---|---|---|
| 15 | 1.67 | 150 | 24.91 |
| 20 | 3.46 | 160 | 24.56 |
| 30 | 6.05 | 170 | 24.31 |
| 40 | 8.02 | 180 | 24.11 |
| 50 | 9.33 | 190 | 23.95 |
| 60 | 10.39 | 200 | 23.83 |
| 70 | 11.23 | 210 | 23.77 |
| 80 | 11.93 | 220 | 23.77 |
| 90 | 12.57 | 230 | 23.81 |
| 100 | 13.18 | 240 | 23.87 |
| 110 | 13.77 | 250 | 23.94 |
| 120 | 14.35 | 260 | 23.99 |
| 130 | 14.93 | 270 | 24.04 |
| 140 | 15.51 | 280 | 24.09 |

When the vapor pressure became appreciable the liquid heat capacity values were corrected for the small amount of vaporization. The liquid densities used in computing the gas space above the liquid in the calorimeter were obtained from the I.C.T.[4]

TABLE III

MELTING POINT OF CARBONYL CHLORIDE

0°C. = 273.10°K.

| Date and time | % Melted | $T$, °K., resistance thermometer | $T$, °K., thermocouple |
|---|---|---|---|
| 11/1/42 | Heated into | | |
| 12:45 a.m. | melting point | | |
| 2:45 a.m. | 3 | 145.272 | 145.27 |
| 3:45 a.m. | 3 | 145.272 | 145.27 |
| 4:00 a.m. | Supplied heat | | |
| 5:00 a.m. | 10 | 145.332 | 145.33 |
| 6:00 a.m. | 10 | 145.330 | 145.32 |
| 7:00 a.m. | 10 | 145.329 | 145.32 |
| 7:15 a.m. | Supplied heat | | |
| 9:00 a.m. | 25 | 145.339 | 145.34 |
| 9:45 a.m. | 25 | 145.338 | 145.34 |
| 10:00 a.m. | Supplied heat | | |
| 11:30 a.m. | 40 | 145.338 | 145.35 |
| 11/2/42 | | | |
| 12:30 p.m. | 40 | 145.337 | 145.34 |

Accepted value 145.34 ± 0.05° K.

**The Melting Point of Carbonyl Chloride.**—The equilibrium melting point temperature was observed as a function of the fraction of the phosgene melted. A summary of the observations is given in Table III. The strain in the resistance thermometer which developed in the region below the melting point disappeared as soon as the melting point was reached, as might be expected.

**Heat of Fusion of Carbonyl Chloride.**—The data relating to the two determinations of the heat of fusion of carbonyl chloride are given in Table IV. The measurements were started somewhat below the melting point and ended somewhat above, and a correction for $\int C_p dT$ was applied.

TABLE IV

HEAT OF FUSION OF CARBONYL CHLORIDE

Melting point, 145.34°K.

| Temperature interval, °K. | Corrected heat input | Pre-melting | Cal./mole $\int C_p dT$ | $\Delta H$ fusion |
|---|---|---|---|---|
| 144.360–146.263 | 1405.4 | 3.2 | 38.6 | 1370.0 |
| 143.046–147.110 | 1450.6 | 1.3 | 80.4 | 1371.5 |

Mean 1371 ± 2

**Vapor Pressure of Carbonyl Chloride.**—The vapor pressure was measured by means of a mercury manometer, 1.6 cm. i. d., which could be attached to the glass line leading to the calorimeter. After each determination, the calorimeter was shut off from the manometer. The material in the manometer and connecting lines was then condensed, and the lines were pumped out. This was done as a precaution against error which would result if some phosgene reacted with the mercury, although a preliminary experiment did not detect this reaction.

The data of Cawood and Patterson[5] were used for correcting for capillary depression. The standard acceleration of gravity was taken as 980.665

TABLE V

VAPOR PRESSURE OF CARBONYL CHLORIDE

Boiling point 280.66°K.; 0°C. = 273.10°K.

| $T$, °K. | $P$, obs. int. cm. | $P_{obs.} - P_{calcd.}$ | $T_{obs.} - T_{calcd.}$ |
|---|---|---|---|
| 215.481 | 2.475 | +0.002 | −0.012 |
| 221.449 | 3.732 | − .002 | + .009 |
| 227.317 | 5.467 | + .003 | − .009 |
| 233.743 | 8.075 | − .011 | + .024 |
| 240.968 | 12.212 | + .003 | − .005 |
| 247.573 | 17.388 | + .024 | − .028 |
| 255.322 | 25.550 | − .002 | + .002 |
| 264.013 | 38.188 | .000 | .000 |
| 272.147 | 54.128 | + .002 | − .001 |
| 277.048 | 66.007 | − .002 | + .001 |
| 281.103 | 77.312 | + .004 | − .001 |

$dP/PdT = 0.038443$ deg.$^{-1}$ at 280.66°K.

---

(4) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1926.

(5) Cawood and Patterson, *Trans. Faraday Soc.*, **29**, 522 (1933).

cm. sec.$^{-2}$, and the local value(6) used was 979.973 cm. sec.$^{-2}$.

The vapor pressure observations have been represented by the following equation for the range 215 to 281° K.

$$\log_{10}P_{(\text{Int. cm.})} = -(1690.3/T) + 9.68020 - 0.0078981T + 0.0000055847T^2$$

A summary of the observations including a comparison with the above equation is given in Table V. The above equation gives the boiling point as 280.66° K.

Table VI gives a comparison of the melting and boiling points with those of other observers.

TABLE VI

MELTING AND BOILING POINTS OF CARBONYL CHLORIDE

| Melting point, °K. | Boiling point, °K. | Observer |
|---|---|---|
| | 281.3 | Beckmann(7) (1907) |
| 155.1 | | Erdmann(8) (1908) |
| | 280.79 | Paternò and Mazzucchelli(9) (1920) |
| | 281.5 | Nikitin(10) (1920) |
| 147.1 | | Atkinson, Heycock, and Pope(11) (1920) |
| | 280.74 | Germann and Taylor(12) (1926) |
| 145.34 ± 0.05 | 280.66 ± 0.05 | This research |

**Heat of Vaporization of Carbonyl Chloride.**—The heat of vaporization of carbonyl chloride was measured directly by adding heat to the calorimeter and removing the gas at constant pressure. By means of a capillary system the pressure could be held at approximately one atmosphere while the gas was condensed in small weighed bulbs by cooling them with liquid air. Heat-capacity corrections were made to take into account the small difference in the initial and final temperatures which were measured before and after energy input. Corrections were also applied for heat leak and for the evaporation required to fill the space previously occupied by evaporated liquid.

The heat of vaporization was also calculated from the vapor pressure data by means of the equation $\mathrm{d}P/\mathrm{d}T = \Delta H/T\Delta V$ and Berthelot's equation of state.

$$\Delta H = \frac{RT^2\mathrm{d}\ln P}{\mathrm{d}T}\left[1 - \frac{9\,PT_c}{128\,P_cT}\left(1 - \frac{6\,T_c^2}{T^2}\right) - \frac{PV_{\text{liq.}}}{RT}\right]$$

The critical constants were taken from Germann and Taylor(12): $T_c$ = 455° K. and $P_c$ = 56 atm. The molal volume of the liquid at the boiling point was taken at 69.2 cc. from the "I.C.T." The use of Berthelot's equation introduced a correction of 192 cal. mole$^{-1}$ for gas imperfection.

The heat of vaporization data are summarized in Table VII.

TABLE VII

HEAT OF VAPORIZATION OF CARBONYL CHLORIDE AT ITS BOILING POINT 280.66°K.

| Moles vaporized | Time of energy input, minutes | $\Delta H$ vaporization cal. mole$^{-1}$ |
|---|---|---|
| 0.15098 | 40 | 5831 |
| .15261 | 40 | 5834 |
| .15916 | 40 | 5836 |
| .13241 | 35 | 5825 |
| | Mean | 5832 ± 6 |
| From the vapor pressure equation assuming a Berthelot gas | | 5825 |

The value for the heat of vaporization obtained from the vapor pressure data agrees very well with the direct determinations but can be given no weight in comparison with these more reliable values. However the agreement is evidence in support of the use of Berthelot's equation in correcting for the effect of gas imperfection on the entropy of the carbonyl chloride gas as will be done below.

**The Entropy of Carbonyl Chloride.**—The calculation of the entropy of carbonyl chloride from the calorimetric measurements is summarized in Table VIII.

TABLE VIII

CALCULATION OF THE ENTROPY OF CARBONYL CHLORIDE FROM THE CALORIMETRIC MEASUREMENTS

| | Calories per degree per mole |
|---|---|
| 0–15° K., extrapolation | 0.64 |
| 15–145.34° K., graphical | 19.78 |
| Fusion, 1371/145.34 | 9.43 |
| 145.34–280.66° K., graphical | 15.87 |
| Vaporization, 5832/280.66 | 20.78 |
| | 66.50 ± 0.15 |
| Correction for gas imperfection | 0.13 |
| $S$ (ideal gas at 280.66° K.) − $S$ (solid at 0° K.) = | 66.63 |

The structure of the carbonyl chloride molecule has been determined by Brockway, Beach and Pauling(13) by electron diffraction measurements. They give the following results; C–O = 1.28 × 10$^{-8}$ cm., C–Cl = 1.68 × 10$^{-8}$ cm. and the Cl–C–Cl angle = 117°. From these values the moments of inertia may be calculated as 105.4 × 10$^{-40}$, 240.1 × 10$^{-40}$ and 345.5 × 10$^{-40}$ g. cm.$^2$.

The spectrum of phosgene has been investigated by Marton(14) (infrared), Henri and Howell(15) (ultraviolet), Dadieu and Kohlrausch(16) (Raman),

---

(6) Landolt, Börnstein and Roth, "Physik. chem. Tabellen," Verlag Julius Springer, Berlin, 1923.

(7) Beckmann, *Z. anorg. Chem.*, **55**, 370 (1907).

(8) Erdmann, *Ann.*, **362**, 148 (1908).

(9) Paternò and Mazzucchelli, *Gazz. chim. ital.*, **50**, I, 30 (1920).

(10) Nikitin, *J. Russ. Phys.-Chem. Soc.*, **52**, 235 (1920).

(11) Atkinson, Heycock and Pope, *J. Chem. Soc.*, **117**, 1410 (1920).

(12) Germann and Taylor, THIS JOURNAL, **48**, 1154 (1926).

(13) Brockway, Beach and Pauling, *ibid.*, **57**, 2693 (1935).

(14) Marton, *Z. physik. Chem.*, **117**, 97 (1925).

(15) Henri and Howell, *Proc. Roy. Soc.* (*London*), **128A**, 190 (1930).

(16) Dadieu and Kohlrausch, *Ber.*, **139**, 717 (1930).

Ananthakrishnan[17] (Raman), Bailey and Hale[18] (infrared).

The most important work is that of Ananthakrishnan since the polarization estimates on his Raman lines are important in assigning the observed frequencies to the several modes of motion. Only five of the six fundamental frequencies were observed in the Raman spectrum, although all were expected. Thompson[19] has reviewed the data and compared it with that on thiophosgene which he has measured, and in which case he found all six fundamental frequencies. As the two phosgenes are very similar he was able to make a good estimate of the unobserved non-planar deformation frequency as 230 cm.$^{-1}$. Thompson estimates that the error involved in the uncertainty of his choice would be less than 0.1 cal. deg.$^{-1}$ mole$^{-1}$ in a statistical entropy calculation. The fundamentals are given by Thompson as 1827, 845, 570, 444, 302 and (230) cm.$^{-1}$. The symmetry number of the molecule is two.

The calculation of the entropy of carbonyl chloride gas from molecular data is given below. The physical constants used are taken from the "I.C.T." The calculations are in essential agreement with results derived from equations given by Thompson.[19]

| | 280.66° K. | 298.10° K. |
|---|---|---|
| $S$ translation | 39.39 | 39.69 |
| $S$ rotation | 24.45 | 24.63 |
| $S$ vibration | 4.42 | 4.81 |
| $S$ ideal gas, 1 atmos. cal. deg.$^{-1}$ mole$^{-1}$ | 68.26 | 69.13 |

$$S \text{ (molecular data)} - \int_0^{280.66} C_p \, d\ln T = 68.26 - 66.63 = 1.63$$

The only appreciable uncertainty in the above calculation is the 230 cm.$^{-1}$ frequency. In order to eliminate the discrepancy it would be necessary to assume a value of about 900 cm.$^{-1}$ instead of 230 cm.$^{-1}$. Not only does this appear unreasonable but the polarization analysis of Ananthakrishnan[17] appears to eliminate possible reassignment of the observed frequencies so as to permit the inclusion of a 900 cm.$^{-1}$ value with the five observed frequencies.

We believe that the explanation of the discrepancy lies in the random orientation of the carbonyl chloride molecules in the crystal lattice. This planar molecule does not differ greatly from an equilateral triangle, with the carbon atom off center, and despite its appreciable electric moment it appears necessary to assume that the oxygen can occupy any of three positions. Complete randomness in this respect would correspond to $R$ ln3 = 2.18 cal. deg.$^{-1}$ mole$^{-1}$ of residual entropy, instead of the value 1.63 given above, but some approach to order has been noted in cases of random orientation in CO and NNO and it is reasonable to assume that some regularity may be attained in the present case.

We have mentioned the abnormal expansion which occurred in solid phosgene in the region below its melting point and it seems probable that this is related to the partial attainment of molecular orientation equilibrium in the solid.

In the some two score condensed gases which have been investigated in this Laboratory with similar calorimeters the only one we can recall which caused a disturbance of this kind was sulfur dioxide. To quote from Giauque and Stephenson[20]: "At 175° K., about 20° below the melting point of sulfur dioxide, the resistance thermometer began to give slightly high values, and just below the melting point the abnormal increase in resistance reached 0.1% of the total resistance. As soon as a portion of the sulfur dioxide was melted, the resistance returned to its normal value. No completely satisfactory explanation of this stretching effect can be offered; none of the many other condensed gases investigated in this calorimeter have caused such a disturbance."

It would seem to be more than a coincidence that the above behavior should occur in these two molecules, since, among all those investigated, only sulfur dioxide like carbonyl chloride is a triangular molecule with elements of the first and second rows of the periodic system at the apexes of the triangle. Accordingly we suggest that when carbonyl chloride and sulfur dioxide are first solidified the amount of random orientation present at the freezing point is reduced by subsequent cooling. This causes dimensional changes in the solid which are not reversed in macroscopic detail when the substance is slowly warmed, thus producing the strain observed in the calorimeter.

In the case of sulfur dioxide the electron diffraction investigation of Schomaker and Stevenson[21] combined with the entropy measurements of Giauque and Stephenson[20] make it certain that perfect order is attained at low temperatures. However the characteristics of sulfur dioxide in the region below its melting point give some basis for the suspicion that it has disorder of the molecular orientation type.

The sulfur dioxide molecule is too far from an equilateral triangle to make it appear probable that simple orientation of the triangle would be the explanation in this case. The crystal structure of sulfur dioxide is unknown; however, it is of interest to speculate about a type of plausible crystalline arrangement which would be in accord with the experimental observations.

If adjacent sulfur dioxide molecules are paired, with their molecular planes 90° apart, and with the O–O sides of the triangles together, the two sulfur and four oxygen atoms would approximate a sphere. If the oxygen atoms were at the corners of a square there would be three orientation

---

[17] Ananthakrishnan, *Proc. Ind. Acad.*, **5A**, 285 (1937).

[18] Bailey and Hale, *Phil. Mag.*, **25**, 98 (1938).

[19] Thompson, *Trans. Faraday Soc.*, **37**, 251 (1941).

[20] Giauque and Stephenson, THIS JOURNAL, **60**, 1389 (1938).

[21] Schomaker and Stevenson, *ibid.*, **62**, 1270 (1940).

positions exchanging oxygen and sulfur atoms for each pair of sulfur dioxide molecules. It is also of interest that, if the oxygen atoms in such an arrangement were located on a staggered square, which is more probable, orientation disorder could result due to rotation of oxygen atoms alone with two possibilities per pair of sulfur dioxide molecules. It is also possible that both types of disorder could occur simultaneously.

In any of the above cases it is reasonable, not only that a good deal of orientation disorder should be present at the freezing point, but also that potential barriers between the several positions should be small enough to permit the attainment of perfect order as the solid is cooled, as was shown by the entropy determination.

It is obviously of interest to have a crystal structure investigation of solid sulfur dioxide. The observations should be made on the solid cooled to at least the temperature liquid air since, if the above explanation of the abnormal expansion of solid sulfur dioxide is correct, disorder near the freezing point may complicate structural observations.

It is not our intention to place too much emphasis on the particular structure suggested to explain possible random orientation in solid sulfur dioxide but rather to illustrate the possiblity of orientation disorder in such a substance.

Kemp and Giauque[22] found very slow thermal equilibrium in their measurements on carbonyl sulfide. In the 75° interval below the melting point, 134.31° K., it took about ten times the usual period to obtain temperature equilibrium after an energy input. The entropy calculations show that the substance attains perfect order at very low temperatures but they expressed the opinion that random orientation of the sulfur and oxygen ends of the molecule characterizes thermodynamic equilibrium at the higher temperatures. The difficulty of such a molecular rotation within the solid was believed to be responsible for the slow thermal equilibrium.

In the case of carbonyl chloride it is probable that a somewhat greater approach to order would be possible with excessively slow cooling, extending over months or years, but the attainment of order in cases of this type often involves coöperation of molecules sufficiently to make the rate drop off rather sharply with temperature. The phenomenon is much the same as the decrease in entropy, and thus the increased order, which accompanies the annealing of a glass. A glass must be annealed above a rather definite temperature or the process will not occur at an appreciable rate. The entropy associated with structural randomness, corresponding to thermodynamic equilibrium in the annealing region of a system, which is non-crystalline in certain respects, will remain when the substance is cooled to very low temperatures.

The solids of carbon monoxide, nitric oxide, nitrous oxide, water and evidently carbonyl chloride, are those known to remain amorphous or glass-like with respect to molecular orientation within their semi-crystalline frameworks, even when considerable time is allowed for thermal equilibrium.

The molecule thiocarbonyl chloride is so nearly an equilateral triangle, with the carbon atom near the center, that it seems safe to predict that it would have a residual entropy of $R \ln 3$ and the same situation should exist with carbonyl fluoride.

## Summary

The heat capacity of solid and liquid carbonyl chloride (phosgene) has been determined from 15 to 280° K.

The melting point is 145.34° K. (0° C. = 273.10° K.). The heat of fusion is 1371 cal. mole$^{-1}$.

The vapor pressure of liquid carbonyl chloride has been measured from 215 to 281° K. The data are represented by the equation, $\log_{10} P_{(\text{int cm.})} = -(1690.3/T) + 9.68020 - 0.0078981T + 5.5847 \times 10^{-6}T^2$.

The boiling point is 280.66° K., and the heat of vaporization at this temperature is 5832 cal. mole$^{-1}$.

The calorimetric measurements have been used to calculate the increase in entropy between 0° and 280.66° K. as 66.63 cal. deg.$^{-1}$ mole$^{-1}$.

A calculation of the entropy of carbonyl chloride gas at 280.66° K. from molecular data leads to a value of 68.26 cal. deg.$^{-1}$ mole$^{-1}$.

The 1.63 cal. deg.$^{-1}$ mole$^{-1}$ discrepancy between the above results is interpreted as due to random orientation of the planar triangular carbonyl chloride molecule in the solid at low temperatures. The maximum value for this effect would be $R \ln 3 = 2.18$ cal. deg.$^{-1}$ mole$^{-1}$ so that some approach to order is indicated.

The entropy of carbonyl chloride is calculated from molecular data to be 69.13 cal. deg.$^{-1}$ mole$^{-1}$ at 298.1° K. and this value, which does not include the entropy due to nuclear spin or the isotope effect, is the most reliable value to use in thermodynamic calculations.

A comparison of the similar anomalous behavior of carbonyl chloride and sulfur dioxide, in the region below their melting points, leads us to infer that sulfur dioxide also has some random orientation in the solid although the data on this substance indicate that it becomes perfectly ordered at very low temperatures. These two molecules each have atoms of the first and second rows of the periodic system at the apexes of their triangular structures.

BERKELEY, CALIFORNIA

RECEIVED JUNE 18, 1947

---

[22] Kemp and Giauque, THIS JOURNAL, 59, 79 (1937).