energy in the coil. Hence, it is expected that the Q value of the oscillator coil will be much smaller with Ag_2F samples than with AgF samples. Furthermore, the resonance signal from Ag_2F was obtained only at higher oscillation levels, because oscillation could not be sustained at lower levels. Nevertheless, the resonance signals from Ag_2F are of almost the same size as those from AgF. Consequently, the thermal relaxation time T_1 is expected to be much smaller in Ag_2F than in AgF. The decrease of T_1 values in Ag_2F could be attributed to the presence of defects. Actually, Hilsch, *et al.*,[10] suggested that the relatively large value of the residual resistivity of Ag_2F may be attributed to the presence of defects. The AgF sample used was extremely sensitive to the radiation in the visible region of the spectrum. In addition, it was prepared by a rapid precipitation process. As a consequence, the AgF sample must have had a large quantity of defects as well. In view of these facts, it seems natural to seek some other mechanisms that will explain the smaller T_1 value in Ag_2F. An explanation in terms of effects due to conduction electrons seems most plausible. As shown by Korringa,[20] the relaxation time T_1 is inversely proportional to the size of the Knight shift; *i.e.*, it is inversely proportional to the probability of finding conduction electrons at the nucleus. As mentioned above, this probability is expected to be rather small. Hence, the relaxation by the conduction electrons may not be the overwhelming contribution to T_1, even if the conduction electrons are really effective in reducing the T_1 value.

In the explanation of the result for Ag_2F, equation 1 cannot be utilized as such, because the simplifying assumptions on which equation 1 is based do not apply to this case. To obtain the appropriate theroretical expressions a study of Overhauser effect[13] and of the electrical resistivity perpendicular to the layers of Ag_2F as well as further T_1 measurements at different temperatures may be helpful.

Acknowledgments.—The author wishes to express his most sincere thanks to Professor J. M. Honig for his never failing interest during the course of this work and for his valuable advice. He thanks Dr. N. Muller for allowing him to use the magnet. He also thanks Dr. J. Richardson for many valuable discussions.

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(20) J. Korringa, *Physica*, **16**, 601 (1950); see also A. W. Overhauser, *Phys. Rev.*, **89**, 689 (1953).

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The Three Melting Points and Heats of Fusion of Phosgene. Entropy of Solids I and II, and Atomic Exchange Disorder in Solid II[1]

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Carbonyl chloride has been found to have three melting points at 145.37, 142.09 and 139.19°K. for solids I, II and III, respectively. Solid I is the form with the stable melting point. The calorimetric heats of fusion of the three forms at their respective melting points are (I) 1371.5 ± 1, (II) 1335.4 ± 1.5 and (III) 1131 ± 5 cal. mole^{-1}. The heat capacity data of solid I were combined with calorimetric measurements of Giauque and Jones on the liquid and the heat of fusion and vaporization to obtain the entropy of the ideal gas at the boiling point, 280.71°K., as 66.99 gibbs mole^{-1} (the value at 298.15°K. = 67.81 gbs. mole^{-1}). These are in complete agreement with the values 66.99 and 67.81 gbs. mole^{-1} calculated from quantum statistics and molecular data for the above two temperatures. It has been shown that the previous heat capacity measurements on $COCl_2$ by Giauque and Jones apply to solid II rather than to solid I. The entropy of solid II at its melting point is shown to be 20.24 gbs. mole^{-1}; however, the $\int_0^T C_p \, d \ln T$ gives only 20.04. The discrepancy of 0.20 gbs. mole^{-1} is well beyond experimental error and is attributed to atomic exchange disorder frozen into the crystal. This amount of entropy corresponds to 1.75% of the molecules with oxygen and chlorine atoms in exchanged positions. The energy change accompanying this dislocation is calculated to be 1330 cal. mole^{-1} for the case of a small fraction of exchanged atoms. The thermodynamic properties of solid II are corrected for the effect of frozen in disorder and tables of thermodynamic properties are given for solids I, II, liquid and gaseous $COCl_2$. For a pressure of one atmosphere it may be calculated that solid III has no equilibrium transition to solid I. Similarly there is no transition point between solids II and III. Calculation indicates that solid II becomes the stable form below about 40°K. but there is a considerable margin of possible error in this result due to the very small difference in heat content between solids I and II.

The purpose of this paper is to clear up some discrepancies in the thermodynamics of carbonyl chloride, $COCl_2$. Giauque and Jones[2] carried out a low temperature calorimetric investigation which was used to calculate the entropy of carbonyl chloride gas at the boiling point. The value was found[3] to be 1.63 gbs. mole^{-1} less than the entropy calculated by utilizing fundamental frequencies of the molecule as given by Thompson.[4] Assuming the correctness of Thompson's values the entropy shortage in $\int C_p \, d \ln T$ was explainable as unexpected residual disorder in the solid at limiting low temperatures.

The experimental work of Giauque and Jones was rushed to completion in 1942 after they were engaged in war work and the haste left some unexplained occurrences which would normally have called for additional investigation. They comment on an expansion in the calorimeter, which strained the resistance thermometer over a region below the melting point and made it necessary to observe

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(1) This work was supported in part by the National Science Foundation.

(2) W. F. Giauque and W. M. Jones, THIS JOURNAL, **70**, 120 (1948).

(3) 1 gbs. (gibbs) = 1 defined cal./defined deg. K. See W. F. Giauque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, *ibid.*, **82**, 62 (1960).

(4) Thompson, *Trans. Faraday Soc.*, **37**, 251 (1941).

temperatures by means of a thermocouple. On one occasion an expansion of such severity occurred about 25° below the melting point that the resistance thermometer heater was broken. During the heat capacity series of Giauque and Jones from low temperatures an unexplained temperature rise occurred in the calorimeter equivalent to an amount of heat which we have calculated as 8.6 ± 0.5 cal. mole^{-1}. Accidental heat leak could not be excluded as a possibility. The average temperature during the small rise was 118.30° K. Giauque and Jones did not notice the work of Wahl[5] until after the publication of their paper in 1948. Wahl had observed long before that an unstable phase sometimes crystallizes from liquid carbonyl chloride. This suggested an explanation of the several above events and obviously necessitated a repetition of the calorimetry. Also Pitzer[6] questioned the lowest frequency which had been given by Thompson on the basis of a comparison with data on thiophosgene, and subsequently Catalano and Pitzer[7] made use of the "Matrix Isolation Method" to obtain data which led to a reassignment of the fundamentals with the elimination of one which Thompson had estimated as 230 cm.$^{-1}$. This reduced the entropy discrepancy to 0.36 gbs. mole^{-1} and made it desirable to find out whether this discrepancy was real or due to error caused by a misinterpretation of the phase in the calorimeter during some of the measurements of Giauque and Jones. The present work has given an entropy value in excellent agreement with the spectroscopic data of Catalano and Pitzer and has found that three crystalline forms can be produced from liquid carbonyl chloride. It also has been possible to show that Giauque and Jones[2] had a crystalline form which we have called solid II in the calorimeter during their low temperature heat capacity measurements rather than solid I which is the stable phase at the normal melting point.

Calorimetric Apparatus and Temperature Scale.—The measurements were made in Gold Calorimeter V.[8] Standard Thermocouple 102, of copper–constantan, was used as a temperature reference and a gold resistance thermometer heater was used for observing temperature changes with high precision, except over the region about 30° below the melting point, where strain due to expansion of the substance made it necessary to use the thermocouple directly. It has become evident that the liquid often solidifies to crystalline form II which evidently has a higher density than the stable form. Subsequent conversion is accompanied by a sufficient volume increase to strain the calorimeter over a temperature region extending for a considerable interval below the normal melting point. Immediately before the present work the thermocouple was checked against the triple and boiling points of hydrogen and nitrogen as described in the above reference.[8] 0°C. was taken as 273.15° K.

Sample of Carbonyl Chloride.—The sample of carbonyl chloride was the same as that used by Giauque and Jones.[2] It had been stored in a sealed glass container. The sample was opened without making contact with air and condensed into the calorimeter. The amount was determined as 165.194 g. *in vacuo*. The molecular weight was taken as 98.925.

The liquid soluble–solid insoluble impurity, as given by premelting heat measurements, was 0.037 mole% as mentioned later. The impurity as determined during the previous work[2] was 0.007 mole%. It seems probable that long standing in contact with the glass had caused a small amount of reaction with water, which is typically entrapped within glass.

The Three Melting Points and Crystalline Forms of Carbonyl Chloride.—As mentioned above, Wahl[5] observed that when liquid carbonyl chloride is cooled rapidly, an unstable solid phase crystallizes from the liquid. Because of this, a careful investigation was made of the phase behavior of carbonyl chloride near the melting region. This investigation showed that three different solid phases could be made to crystallize from the liquid.

In several experiments the liquid was cooled at the rate of about 0.5° per min. until a solid formed from the supercooled liquid in the range 130–135° K. This phase will be designated as solid III. We did not succeed in determining the melting point of this phase by the conventional method of observing the temperature as a function of the fraction melted. In every case when heat was introduced solid III converted spontaneously to a more stable form. Without allowing the material to solidify completely, the temperature of melting, with about 50% melted, was measured to be 139.16° K. A correction of 0.03° was added, on account of the known impurity, giving a melting point of 139.19 ± 0.1° K.

Solid III is very unstable. If allowed to stand a few degrees below its melting point, it converts to another form within an hour. Once started, the rate of conversion was fairly rapid, being complete within several minutes. The rate of conversion was undoubtedly increased by the presence of liquid. The stable solid I was the usual product of the conversion. However, another unstable phase, designated as solid II, was sometimes obtained.

Solid II was ordinarily obtained by crystallization from the liquid after rapid supercooling to about 140° K. and then cooling at the rate of about 1° per hr. This phase would usually start to crystallize between 135 and 140° K.

The melting point of solid II was determined with 9.9 and 27.7% melted before spontaneous conversion occurred. The data are given in Table I.

TABLE I

MELTING POINT OF CARBONYL CHLORIDE SOLID II

0° C. = 273.15° K.

% melted	T, °K.[a]
9.9	142.00
27.7	142.06

[a] Extrapolated value 142.09 ± 0.05° K.

Solid II is considerably more stable than solid III. It could be kept at the melting point for several days and a more extensive set of observations would have been possible had not some accident, due to unknown causes, but unconnected with the properties of carbonyl chloride, terminated the experiments. Solid II was cooled to 130° K. and there was no apparent conversion at this temperature. An attempt to cool this phase to very low temperatures would have been made had it not been for the accident mentioned above. After calorimetric measurements, including the heats of fusion of solids I and II, had been made, it was found that these phases had almost identical

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(5) W. Wahl, *Proc. Roy. Soc.* (*London*), **A89**, 327 (1914).

(6) K. S. Pitzer, private communication.

(7) E. Catalano and K. S. Pitzer, THIS JOURNAL, **80**, 1051 (1958).

(8) J. B. Ott and W. F. Giauque, *ibid.*, **83**, 1308 (1960).

heat contents and it became of interest to make a detailed study of the unexplained heat evolution data of Giauque and Jones[2] near 118.30° K., as mentioned above. Their data books show the following: The heat capacity measurement at T_{av} = 114.89° K. with a temperature rise of 6.185° showed normal heat transfer rates with the surrounding heavy copper-lead "block" both at the beginning and end of the measurement. The only suspicious circumstance was that the measurement was about 0.5% high. The data were checked repeatedly without the detection of possible error but it is a suspicious circumstance that this slightly high point should occur just before the unexplained heat evolution which will be identified later as a transition. The "block" was heated in preparation for a subsequent heat capacity measurement, and almost immediately following this, and before the heat capacity measurement could be started, it was found that the calorimeter was warming spontaneously. Fortunately the observations on the temperature of the calorimeter and its surroundings were continued for a period of 2 hr., at which time the drift of the calorimeter temperature had slowed to a rate corresponding quite accurately to the known heat transfer rate between the calorimeter and its surrounding "block." A careful evaluation of the spontaneous heat evolution gave a value of 8.6 ± 0.5 cal. mole^{-1} at 118.30° K. It will be shown later that this is the difference in heat content of solid II over that of solid I at that temperature.

It became evident that the heat capacity measurements of Giauque and Jones[2] below 118.3° K. apply to pure solid II and that their results above this temperature were made on solid I. The fact that the almost identical heat capacity curves cross at a very small angle at about this temperature helped to obscure this fact. The possibility that the calorimeter contained a mixture of solids I and II below 118.3° K. is ruled out by the magnitude of the rate of heat evolution when recrystallization started. It is evident that no appreciable interface between crystals of solids I and II could have existed during observations near 118.0° K., where the rate of change of the calorimeter temperature corresponded accurately to the difference in temperature between the calorimeter and its surrounding "block."

When either solids II or III were allowed to stand, they eventually converted to solid I, which is definitely a more stable phase.

It was interesting to see some evidence in these experiments that crystal nuclei persisted after the material was melted. The crystallization behavior seems to depend on the previous solid phase. When solid I was the last one obtained before melting, it was desirable to warm the liquid about 25° above the melting point to avoid the reappearance of solid I during subsequent cooling. Occasionally solids II or III were obtained without this procedure but they were very unstable and usually converted to solid I before any measurements could be made.

The Heat Capacity of Carbonyl Chloride.—Heat capacity measurements were made on solid I and two observations on the supercooled liquid were obtained over the range 137 to 145° K. One atmosphere of helium gas was added to the calorimeter at the melting point to purge the filling tube and prevent condensation in the filling tube during subsequent temperature changes. The helium gas also served to ensure temperature equilibrium. The measurements on the liquid overlap the previous work of Giauque and Jones.[2] The agreement in the region of overlap is about 0.1%. As mentioned above, the temperature measurements for values in the range from 118° K. to the melting point were obtained with the thermocouple alone because of strain in the resistance thermometer-heater. One defined cal. has been taken as 4.1840 absolute joules.

Two observations were obtained on the heat capacity of solid II. The heat capacity data are given in Table II.

TABLE II

HEAT CAPACITY OF CARBONYL CHLORIDE

0° C. = 273.15° K., mol. wt. $COCl_2$ = 98.925; 1.6699 moles in calorimeter, gibbs mole^{-1}

T, °K.	C_p, gbs. mole^{-1}	T, °K.	C_p, gbs. mole^{-1}	T, °K.	C_p, gbs. mole^{-1}
Solid I				133.51	15.26[b,c,d]
12.61	1.319	54.37	9.965	139.41	16.08[b,c,d]
14.38	1.822	59.97	10.52	145.37	M.P.I.
16.27	2.371	65.89	10.98	Solid II	
18.19	3.472[a]	72.08	11.46	132.83	14.87[b]
20.63	3.685	79.22	11.93	135.96	15.13[b]
23.61	4.885	86.97	12.36	142.09	M.P.II
27.02	5.440[a]	94.71	12.82	Liquid	
30.75	6.412	102.22	13.26	139.95	25.28
34.90	7.281	109.82	13.73	145.55	25.04
39.33	8.074	117.48	14.17[b]	152.47	24.84
44.10	8.837	123.64	14.61[b]	160.55	24.62
49.24	9.449	128.51	14.87[b]		

[a] Value not used, time of energy input uncertain. [b] Temperature rise obtained from thermocouple. [c] Used for impurity calculation. [d] The measurements on solid I at 133.51 and 139.41° K., and those on solid II at 132.83 and 135.96° K. had temperature rises of 5.112, 6.765, 2.821 and 3.429°, respectively. After correction for the effect of impurity, these four values become 15.14, 15.52, 14.87, 15.03 gbs. mole^{-1}.

The measurements at 133.51 and 139.41° K. on solid I were used for the calculation of the liquid soluble–solid insoluble impurity. A simple, almost linear extrapolation of the observations at lower temperatures where no premelting occurred gave 0.037 mole% from each of these points.

Heats of Fusion of Carbonyl Chloride.—The heats of fusion were measured in the usual manner of starting several degrees below each melting point and terminating energy input at a temperature somewhat above. Only one determination, 1373 cal. mole^{-1}, of the heat of fusion of solid I was made because it agrees with the 1371 cal. mole^{-1} value of Giauque and Jones.[2]

Since the heat capacity of solid III was not obtained before measurements were terminated by the accident mentioned above, its heat of fusion is somewhat uncertain due to the $\int C_p dt$ for the 5.6° interval below its melting point. However, it seems unlikely that its heat capacity would differ much from the values for solids I and II which differ from each other only by small amounts. The correction was made by assuming that the heat capacity of solid III was the same as that of solid I. The corrections for the amounts of premelting at the start of the fusion measurements on solids II and III were made on the basis of the same amount of impurity as determined from the data on solid I.

During the measurement of the heat of fusion of solid III it converted to solid I, as could be observed by the rapid change in calorimeter temperature to the higher melting point. This, of course, caused no difficulty in the calorimetric determination, since the final state was liquid.

Similarly solid II converted to solid I during the third determination of its heat of fusion; however, solid II remained throughout the melting during the first and second determinations.

Confirmation that solid II converted to solid I during the measurements of Giauque and Jones was obtained as follows:

Assume Solid II = Solid I (1)

$$\Delta H_{118.30°\text{K.}} = -8.6 \pm 0.5 \text{ cal. mole}^{-1}$$

From $\int \Delta C_p \mathrm{d}T$, $\Delta H_{142.09°\text{K.}} = -5.4$ cal. mole^{-1}

$$\text{Solid I} = \text{Liquid} \quad (2)$$

$$\Delta H_{145.37°\text{K.}} = 1371.5 \pm 1 \text{ cal. mole}^{-1} \text{ at m.p.}$$

From $\int \Delta C_p \mathrm{d}T$, $\Delta H_{142.09°\text{K.}} = 1340.8$ cal. mole^{1}

Combining equations 1 and 2

$$\text{Solid II} = \text{Liquid} \quad (3)$$

$$\Delta H_{142.09} = 1335.4 \pm 1.5 \text{ cal. mole}^{-1} \text{ at m.p.}$$

This value is in excellent agreement with the average, 1335.7 ± 2, of three less accurate direct determinations of the heat of fusion of solid II, summarized in Table III, and confirms the interpretation of the measurements of Giauque and Jones.

TABLE III

HEATS OF FUSION OF CARBONYL CHLORIDE IN CAL. MOLE^{-1}

Temp. interval, °K.	Corr. heat input	Premelt. heat	$\int C_p \mathrm{d}T$	ΔH_{fusion}
Solid I, m.p. = 145.37°K.				
142.79–155.79	1667.6	5.7	300.3	1373.0
The values obtained by Giauque and Jones[2] were				1370.0
				1371.5
			Accep. value	1371.5 ± 1
Solid II, m.p. = 142.09°K.				
137.78–147.56	1532.6	3.2	202.7	1333.1
137.71–147.69	1539.1	3.2	206.9	1335.4
137.84–147.94	1546.6	3.2	211.3	1338.5
			Av.	1335.7 ± 2
Accepted value calculated above from the heat of fusion of solid I and $\Delta H_{\text{transition I} \rightarrow \text{II}}$				1335.4 ± 1.5
Solid III, m.p. = 139.19°K.				
133.56–146.85	1407.9	2.3	279.7	1131 ± 5

The Entropy of Carbonyl Chloride.—The calculation of the entropy is summarized in Table IV. The correction for gas imperfection at the boiling point was made by assuming a Berthelot gas. T_c = 455° K., P_c = 56 atm.[9]

$$S_{\text{ideal}} - S_{\text{real}} = 27RT_c^3P/32T^3P_c = 0.13 \text{ gbs. mole}^{-1}$$

The data for the heat capacity of the liquid and the heat of vaporization were taken from the work of Giauque and Jones.[2] However, their heat capacity data, melting and boiling points were corrected from 0° C. = 273.10° K. to 0° C. = 273.15° K. The value for 298.15° K. was obtained by using the statistical data for the gas above the boiling point.

From Table IV below the entropy values obtained from the molecular data for the boiling point, 280.71° K., and 298.15° K. were 66.99 and 67.81 gbs. mole^{-1}, in agreement with the calorimetric data. This shows that solid I of carbonyl chloride attained perfect order at limiting low temperatures.

The Entropy of Solid II.—The entropy of solid II at its melting point, 142.09°K., may be evaluated by subtracting the entropy of fusion from the known entropy of the liquid, 29.64 gbs. mole^{-1} at this temperature. The result, 29.64 − 9.40 = 20.24 gbs. mole^{-1}.

TABLE IV

CALCULATION OF THE ENTROPY OF CARBONYL CHLORIDE FROM THE CALORIMETRIC MEASUREMENTS

Solid I	Gibbs mole^{-1}
0–15°K., extrap.	0.76
15–145.37°K., graph.	20.02
Fusion, 1371.5/145.37	9.43
145.37–280.71°K., graph.	15.87
Vaporiz. 5832/280.71	20.78
Entropy of real gas at b.p.	66.86 ± 0.05
Corr. for gas imperfection	0.13
Calorimetric entropy of ideal gas at b.p.	66.99
280.71–298.15°K., molecular data	0.82
Calorim. entropy of ideal gas at 298.15°K.	67.81

When the $\int_0^T C_p \, \mathrm{d} \ln T$ is computed from the heat capacity values on solid II, the value obtained, 20.04 gbs.mole^{-1}, is short by the amount 0.20 gbs.mole^{-1}, which is well outside the limit of error on the measurement of 20 gbs.mole^{-1} Any assumption of error would have to face the following facts: The data on solid II are smooth and thus a systematic error causing the results of Giauque and Jones to be low by an average of 1% would be required. Errors in measuring the amount investigated or the calorimetric energy are eliminated by the fact that the measurements of Giauque and Jones agree with the present work to about 0.1% where the same quantities were measured in the respective researches. The temperature scale was checked in each research and, since the major increases in entropy happen to be roughly linear with temperature, an error of over a degree, which would be required, is ruled out. There appears to be no alternative except to accept as an experimental fact that the $\int_0^T C_p \, \mathrm{d} \ln T$ is deficient to the extent of 0.20 gbs.mole^{-1}. Such a result is equivalent to frozen in disorder.

In the earlier work of Giauque and Jones the similar assumption of disorder in the solid which

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(9) A. F. O. Germann and Q. W. Taylor, THIS JOURNAL, **48**, 1154 (1926).

they investigated at low temperatures was based on incorrect information as mentioned above. However, the present limited data on solid II are surrounded by such substantial agreement between all other calorimetric and quantum statistical values as to force acceptance of a limited amount of disorder in solid II. Failure of crystal structures to distinguish between C, N, O and F atoms in otherwise equivalent positions within molecules has been demonstrated by means of entropy discrepancies in previous researches in this Laboratory, and it is not improbable that various cases of at least some degree of atomic exchange between elements in adjacent rows of the periodic system will be found.

It is of interest to repeat the comment of Giauque and Jones[2] after they had examined a scale model of carbonyl chloride. "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 $R \ln 3 = 2.18$ cal. deg.$^{-1}$ mole^{-1} of residual entropy." The present data indicate that order in solid II is nearly complete with respect to the above atomic exchange when the crystal is formed at the melting point; at lower temperatures the potential maximum to be surmounted, in eliminating the residual amount of disorder in accordance with thermodynamic equilibrium, is too large to give a rate within the limitations of ordinary calorimetry.

Zaslow, Atoji and Lipscomb[10] cooled a crystal of carbonyl chloride to the temperature of liquid nitrogen, permitted it to stand at temperatures as high as 113°K. for as long as 72 hr. and made X-ray determinations of the crystal structure. They found a perfectly ordered structure. Since the above technique has a high probability of producing one of the known unstable forms, or even an additional unknown unstable form, we cannot be certain that this structural determination applies to solid I. When small unstable crystals are deposited under the above conditions, the conversion rate may be negligible. There is evidence that the chance of starting a crystallization process depends on the total volume of substance and it seems reasonable that when unstable crystalline forms are deposited under the above conditions the probability of conversion may be very low. If the above X-ray examination applies to solid II, the small amount of atomic exchange disorder may have been outside the decision limits of the X-ray methods utilized.

The Thermodynamic Properties of Carbonyl Chloride.—The values of the entropy and other thermodynamic properties of the gas derived from a quantum statistical calculation were obtained in the usual manner. The constants recommended by Rossini, *et al.*,[11] and DuMond and Cohen[12] were used except that they were corrected from 0° C. = 273.160° K. to 0° C. = 273.15° K.

The molecular data utilized are summarized in Table V.

TABLE V

MOLECULAR DATA FOR CARBONYL CHLORIDE

Moments of inertia[13]

Average values weighted for isotopes in g. cm.^{2} molecule^{-1}

$I_a = 106.90 \times 10^{-40}$
$I_b = 244.89 \times 10^{-40}$
$I_c = 352.91 \times 10^{-40}$

Vibrational frequencies[7] in cm.$^{-1}$

$V_1 = 570$ $V_4 = 849$
$V_2 = 1827$ $V_5 = 440$
$V_3 = 285$ $V_6 = 585$

The thermodynamic properties for the ideal gas are given in Table VI and those for solid I and the liquid are given in Table VII.

TABLE VI

THERMODYNAMIC PROPERTIES OF CARBONYL CHLORIDE GAS IN GIBBS MOLE^{-1}

T, °K.	$C_p{}^0$	S^0	$-(F^0 - H_0{}^0)/T$	$(H^0 - H_0{}^0)/T$
15	7.949	40.566	32.616	7.949
20	7.949	42.852	34.903	7.949
25	7.949	44.626	36.677	7.949
30	7.950	46.075	38.126	7.949
35	7.951	47.301	39.352	7.949
40	7.957	48.363	40.413	7.950
45	7.968	49.301	41.350	7.951
50	7.987	50.141	42.187	7.954
55	8.016	50.904	42.946	7.958
60	8.056	51.602	43.638	7.964
70	8.169	52.852	44.867	7.985
80	8.322	53.953	45.936	8.017
90	8.512	54.944	46.883	8.061
100	8.733	55.852	47.735	8.117
110	8.979	56.695	48.511	8.184
120	9.245	57.488	49.227	8.261
130	9.526	58.240	49.891	8.349
140	9.816	58.955	50.513	8.442
145.37	9.973	59.238	50.832	8.496
150	10.110	59.643	51.099	8.544
160	10.408	60.305	51.654	8.651
170	10.703	60.945	52.182	8.763
180	10.996	61.565	52.686	8.879
190	11.281	62.166	53.169	8.997
200	11.559	62.752	53.633	9.119
210	11.829	63.323	54.081	9.242
220	12.090	63.879	54.514	9.365
230	12.341	64.422	54.933	9.489
240	12.582	64.953	55.340	9.613
250	12.812	65.471	55.735	9.736
260	13.033	65.978	56.119	9.859
270	13.245	66.474	56.493	9.981
280	13.447	66.959	56.858	10.101
280.71	13.460	66.993	56.884	10.109
290	13.639	67.435	57.215	10.220
298.15	13.791	67.814	57.499	10.315
300	13.824	67.900	57.563	10.337
350	14.631	70.093	59.199	10.894
400	15.284	72.095	60.689	11.406
450	15.820	73.923	62.058	11.865
500	16.270	75.614	63.330	12.284

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TABLE VII

THERMODYNAMIC FUNCTIONS OF SOLID I AND LIQUID CARBONYL CHLORIDE IN GIBBS MOLE^{-1}

T, °K.	C_p	S	$-(F - H_0^0)/T$	$(H - H_0^0)/T$
15	1.970	0.759	0.199	0.560
20	3.473	1.531	.431	1.100
25	4.915	2.461	.742	1.719
30	6.209	3.474	1.113	2.361
35	7.294	4.515	1.524	2.991
40	8.193	5.549	1.963	3.586
45	8.931	6.559	2.418	4.141
50	9.535	7.532	2.881	4.651
55	10.043	8.465	3.346	5.119
60	10.499	9.359	3.810	5.549
70	11.306	11.040	4.725	6.315
80	11.979	12.595	5.612	6.983
90	12.535	14.038	6.470	7.568
100	13.123	15.390	7.295	8.095
110	13.735	16.669	8.089	8.580
120	14.334	17.890	8.855	9.035
130	14.934	19.061	9.596	9.465
139.19	15.477	20.098	10.258	9.840
140	15.525	20.190	10.313	9.877
142.09	15.648	20.420	10.460	9.960
145.37	15.845	20.780	10.689	10.091
		Liquid		
139.19	25.308	29.119	9.844	19.275
140	25.269	29.268	9.958	19.310
142.09	25.183	29.641	10.245	19.396
145.37	25.056	30.214	10.689	19.525
150	24.902	30.998	11.304	19.694
160	24.570	32.594	12.585	20.009
170	24.307	34.075	13.806	20.269
180	24.149	35.460	14.971	20.489
190	23.972	36.761	16.084	20.677
200	23.810	37.986	17.149	20.837
210	23.770	39.146	18.169	20.977
220	23.773	40.252	19.148	21.105
230	23.787	41.309	20.088	21.221
240	23.876	42.324	20.994	21.330
250	23.955	43.300	21.867	21.433
260	24.006	44.240	22.709	21.531
270	24.011	45.147	23.524	21.623
280	24.059	46.020	24.312	21.708
280.71	24.062	46.081	24.367	21.714

Calculation of the Effects of Interatomic Disorder in Solid II of Carbonyl Chloride.—It may be shown that a residual entropy of 0.20 gbs.mole^{-1} corresponds to only 1.75% of the oxygen atoms in carbonyl chloride exchanging positions with chlorine atoms. While the calculation of a case with a large amount of disorder would be quite complex, this near limiting case may be approximated in a very simple manner.

Consider a single disoriented molecule in an otherwise completely ordered domain. The oxygen will have equal probability of occupying either chlorine position, thus the distribution function

$$Q = 1 + 2e^{-\epsilon/kT}$$

where ϵ is the difference in energy required to exchange the oxygen and chlorine atoms. Considering the whole system $\Delta S_{\text{disorder}} = R \ln Q + RT \dfrac{\mathrm{d} \ln Q}{\mathrm{d}T} = 0.20$ gbs. mole^{-1} at 142.09° K., $\dfrac{\epsilon}{kT}$ is found to be 4.72 at 142.09° K. and $N\epsilon = 1330$ cal. mole^{-1}, where N = Avogadro's number.

We may now use this quantity to calculate the corrections to the observed heat capacity and other thermodynamic properties to place them on the basis of equilibrium results which would be observed if the amount of disorder could adjust with temperature in accordance with the requirements of thermodynamic equilibrium. The above formula neglects the interaction between disordered states and those originating in other degrees of freedom; however, the fact that the function is set to give the correct entropy at the melting point should largely compensate for any such interactions.

$$\Delta C_p = -R \frac{\mathrm{d}}{\mathrm{d}T} \frac{\mathrm{d} \ln Q}{\mathrm{d}\, 1/T}$$

$$\Delta F = -RT \ln Q$$

$$\Delta H = RT^2 \frac{\mathrm{d} \ln Q}{\mathrm{d}T}$$

The several corrections are shown in Table VIII and they have been combined with the heat capacity observations on solid II in deriving the thermodynamic properties which solid II would have if thermodynamic equilibrium could be obtained. These values are given in Table IX.

TABLE VIII

CONTRIBUTION TO THERMODYNAMIC PROPERTIES OF SOLID II OF CARBONYL CHLORIDE DUE TO INTERATOMIC EXCHANGE DISORDER IN GIBBS MOLE^{-1}

T, °K.	C_p	S	$-(F - H_0^0)/T$	$(H - H_0^0)/T$
50	0.001	0.000	0.000	0.000
55	.003	.000	.000	.000
60	.007	.001	.000	.001
70	.025	.003	.000	.003
80	.064	.009	.001	.008
90	.128	.019	.002	.017
100	.217	.037	.005	.032
110	.331	.064	.009	.055
120	.457	.097	.015	.082
130	.594	.139	.023	.116
139.19	.721	.182	.032	.150
140	.734	.188	.033	.155
142.09	.762	.199	.035	.164

Investigation of the Possibility of Transition Points between Solids I, II and III.—Some conclusions can be drawn concerning possible equilibrium transition points between solid phases I, II and III of carbonyl chloride at one atmosphere. At higher temperatures, both by theoretical expectation, and by actual experiments on solids I and II, the heat capacities of the three solid phases should be very similar. On this approximate assumption, $\Delta C_p = 0$, and ΔS and ΔH for the transition between solid III and either of the other forms will be independent of temperature. Thus the temperature of any possible transition may be estimated by $T_{\text{transition}} = \Delta H/\Delta S$.

TABLE IX

THERMODYNAMIC PROPERTIES OF EQUILIBRIUM SOLID II OF CARBONYL CHLORIDE IN GIBBS MOLE^{-1}

T, °K.	$C_{p\text{meas}}$	$C_{p\text{corr.}}$	S	$-(F - H_0^0)/T$	$(H - H_0^0)/T$
15	1.674	1.674	0.600	0.156	0.444
20	3.446	3.446	1.339	.354	0.985
25	4.844	4.844	2.264	.642	1.622
30	6.059	6.059	3.256	.994	2.262
35	7.173	7.173	4.276	1.390	2.886
40	8.028	8.028	5.292	1.814	3.478
45	8.718	8.718	6.278	2.255	4.023
50	9.344	9.345	7.229	2.705	4.524
55	9.907	9.910	8.146	3.158	4.988
60	10.389	10.386	9.030	3.610	5.420
70	11.228	11.253	10.698	4.504	6.194
80	11.931	11.994	12.251	5.376	6.875
90	12.567	12.695	13.704	6.221	7.483
100	13.191	13.408	15.078	7.038	8.040
110	13.763	14.094	16.389	7.829	8.560
120	14.273	14.730	17.642	8.594	9.048
130	14.755	15.349	18.846	9.387	9.459
139.19	15.177	15.898	19.910	9.999	9.911
140	15.213	15.947	20.005	10.057	9.948
142.09	15.308	16.070	20.243	10.203	10.040

The fact that the liquid comes to equilibrium with all solid phases enables the calculation of their free energies of transition.

Solid I = Solid III
$\Delta F = 57.1$ cal. mole^{-1} at 139.19°K.
$\Delta H = 182$ cal. mole^{-1}
$\Delta S = 0.90$ gbs. mole^{-1}
$T_{(\text{transition})}? = 202$°K.

Since this temperature is far above the melting points it is evident that solid III is always metastable with respect to solid I at one atmosphere.

Solid II = Solid III
$\Delta H = 177$ cal. mole^{-1}
$\Delta S = 1.08$ gbs. mole^{-1}
$T_{(\text{transition})}? = 164$°K.

Since 164° K. is also far above the melting region, it is evident that no transition point exists between solids II and III at one atmosphere.

Solid I = Solid II
$\Delta F = 30.6$ cal. mole^{-1}
$\Delta H = 5.4$ cal. mole^{-1}
$\Delta S = -0.18$ gbs. mole^{-1}

all at 142.09° K.

From Tables VII and IX, and the above data, $\Delta H_0^0 = -5.9$ cal. mole^{-1} and ΔF may be calculated for the above transition as a function of temperature. Since ΔH_0^0 is negative, it is evident that solid II would be stable at the absolute zero, where $\Delta F = \Delta H_0^0$, and that ΔF must pass through zero at some low temperature. Calculation gives $\Delta F = 0$ at about 40° K. This calculation is not very accurate because ΔH_0^0 happens to be such a small negative quantity, derived as a difference of large quantities involved in combining data on solids I and II. The estimated heat of transition at 40° K. is about 10 cal. mole^{-1}.

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Preparation and X-Ray Diffraction Data[1] for Some Rare Earth Stannates

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A series of eight rare earth stannates and yttrium stannate isostructural with pyrochlore have been prepared by solid state reaction at elevated temperatures. The general formula for these compounds is $A_2Sn_2O_7$ where A is Nd, Sm, Pr, La, Gd, Er, Eu, Yb or Y. Lattice constants calculated from X-ray powder diffraction data are given. The lanthanide contraction is demonstrated. A linear relationship is developed between lattice constant and ionic radius.

Oxide compounds isostructural with cubic pyrochlore have been the subject of recent investigations. Bystrom[2] first showed by X-ray diffraction powder diagrams that the paraelectric form of cadmium niobate has this structure. Interest in this compound and other isostructural oxides was stimulated as a result of the discovery by Cook and Jaffe[3a,3b] that it is ferroelectric below room temperature. Jona, Shirane and Pepinsky[4] have refined the structure reported by Bystrom with data collected on single crystals. Its space group is Fd3m with 8 formula weights per unit cell. The structure of $Cd_2Nb_2O_7$ is viewed as a three dimensional network of corner-sharing (NbO_6) octahedra. The Cd ions and the seventh oxygen ion occupy large open spaces in the network. The network of linked octahedra results in an Nb:O ratio of 2:6.

Investigations of systems yielding $A_2B_2O_7$ compounds isostructural with pyrochlore have been made by Roth[5] and Aleshin and Roy.[6]

Roth has prepared $La_2Sn_2O_7$, showing these to be cubic pyrochlores. Padurow and Schusterius[7] have referred to pyrochlore phases in the system La_2O_3–SnO_2–TiO_2. Dielectric measurements as a function of temperature have been made by Marzullo and Bunting[8] on several compositions studied

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