tween the helical and random coil forms of ribonuclease that the helical form is relatively less stable in water than it is in deuterium oxide. Since the helical form presumably owes most of its stability to internal H-bonding, this result indicates less extensive internal H-bonding for the hydrogen compound in water. However, this protein transformation is relatively more complex than the previous example and interpretation is correspondingly more difficult.

Very little definite information is available on the role of the solvent in establishing the observed ratios of relative H-bonding. General zero-point energy arguments lead to the prediction that for isolated gaseous molecules internal hydrogen bonding by deuterium would be greater than that by hydrogen. In agreement with this Potter, Bender and Ritter[28] find the heat of dimerization of gaseous acetic acid-d_4 to be 300 calories greater than that of ordinary acetic acid and, at temperatures below about 140°, this leads to greater dimerization of the deuterium compound. However, there is also a measurable entropy difference for the two dimerizations so that zero-point energy considerations do not tell the whole story.

We know of no measurements of relative internal H-bonding in the gas state. But tentatively we can assume that, as with acetic acid dimerization, the bonding by deuterium will be slightly stronger. The implication of the present work then is that the H-bonding of the *solvent* deuterium oxide can be enough greater than that of water to reverse the normal prediction for internal H-bonding. Some direct studies of this proposal are in progress.

[28] A. E. Potter, Jr., P. Bender and H. L. Ritter, *J. Phys. Chem.*, **59**, 250 (1955).

ITHACA, N. Y.

[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING UNIVERSITY OF CALIFORNIA, BERKELEY]

Phosphoryl Chloride. Entropy. Low Temperature Heat Capacity. Heats of Fusion and Vaporization. Vapor Pressure[1]

BY J. B. OTT AND W. F. GIAUQUE

RECEIVED SEPTEMBER 15, 1959

The heat capacity of phosphoryl chloride has been measured from 13 to 304°K. The heat of fusion at the triple point, 274.33°K., was determined as 3132 cal. mole^{-1}. The heat of vaporization at 298.15°K. and a pressure of 3.092 int. cm. was found to be 9220 cal. mole^{-1}. The calorimetric data were used to calculate the entropy of the ideal gas at 1 atm. and 298.15° K. as 77.75 gibbs mole^{-1}. A selected assignment of the fundamental frequencies of $POCl_3$ was used to calculate a value of 77.77 gibbs mole^{-1}.

This paper describes a low temperature calorimetric investigation of phosphoryl chloride, $POCl_3$, for the purpose of determining its entropy. This molecule is a somewhat unsymmetrical tetrahedron, and while it was expected that the crystal would attain perfect order at low temperatures, there was at least a small possibility of the type of disorder found[2] in perchloryl fluoride, ClO_3F.

Calorimetric Apparatus and Temperature Scale.—The measurements were made in Gold Calorimeter V. This designation is used for the rebuilt calorimeter IVA.[2] The calorimeter is similar to the one described by Giauque and Egan.[3] The bottom, in which a welding crack had developed, was replaced, and a new gold resistance thermometer-heater was wound on the outside surface. The calorimeter weighed 453.2 g. before the resistance thermometer was added. The capacity to the top of the small platinum access tube was 135.37 cm.^{3} at 20°. The platinum tube was 1.4 cm. long, 0.24 cm. i.d. The standard thermocouple was attached by means of a detachable thermocouple well, as described by Busey and Giauque.[4]

The standard copper–constantan thermocouple No. 102 was compared with the triple (13.94° K.) and boiling (20.36° K.) points of hydrogen, and the triple (63.15° K.) and boiling (77.34° K.) points of nitrogen. Appropriate corrections were made for the deviations. 0° was taken as 273.15° K.

Sample of Phosphoryl Chloride.—Reagent grade Baker and Adamson phosphoryl chloride was selected as a starting material. The label specified 0.01% sulfate and 0.001% iron. It probably would also contain some hydrogen chloride and phosphoric acid from hydrolysis with moisture. This material was put in a vacuum jacketed distillation column and refluxed for two days. Air was removed by pumping a small amount of the material through a capillary during the initial refluxing. The material remaining was distilled at a reflux ratio of 125:1. Of 400 cc. distilled, the central 150 cc. fraction was used for the calorimetric measurements. The column has been described by Koehler and Giauque.[2] The condensation coil at the top was maintained at 20°. This held the distillation pressure of $POCl_3$ inside the calorimeter at about 2.5 cm.

Premelting heat capacity measurements indicated that the material contained 0.02 mole % of liquid soluble-solid insoluble impurity.

Heat Capacity of Phosphoryl Chloride.—The heat capacities were measured in the usual manner. 202.187 g. corrected to *vacuo* were distilled into the calorimeter. The molecular weight was taken as 153.346. One atmosphere of helium was added at 10° to purge the filling tube and to essentially prevent later diffusion into it. The helium also provided good heat transfer within the calorimeter. One defined calorie was taken as 4.1840 absolute joules. Two series of measurements were made on the solid. The resistance thermometer-heater showed evidence of strain for about 50° below the melting point. The standard thermocouple was used for temperature observations in this region. The data are given in Table I. The values are

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[1] This work was supported in part by the National Science Foundation.

[2] J. K. Koehler and W. F. Giauque, THIS JOURNAL, **80**, 2659 (1958).

[3] W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[4] R. H. Busey and W. F. Giauque, THIS JOURNAL, **74**, 4443 (1952).

TABLE I

OBSERVED HEAT CAPACITY OF PHOSPHORYL CHLORIDE[a]

T, °K.	C_p, gibbs mole^{-1}	Series	T, °K.	C_p, gibbs mole^{-1}	Series
14.07	1.999	I	182.48	22.20	I
15.63	2.562	I	189.95	22.64	I
17.81	3.328	I	197.47	23.13	I
20.57	4.410	I	205.02	23.58	I
23.69	5.350	I	212.64	24.02	I
28.24	6.601	I	220.28	24.48	I
33.14	7.759	I	222.43	24.62[b]	II
37.50	8.626	I	227.97	24.95[b]	I
42.07	9.351	I	229.14	25.00[b]	II
47.10	10.09	I	235.82	25.43[b]	I
52.67	10.82	I	236.30	25.39[b]	II
58.31	11.52	I	243.56	25.83[b]	II
64.15	12.23	I	243.64	25.93[b]	I
70.35	12.95	I	250.96	26.22[b]	II
77.03	13.59	I	251.11	26.37[b]	I
84.34	14.34	I	256.73	26.60[b]	I
91.69	15.06	I	258.32	26.65[b]	II
99.08	15.76	I	261.41	27.26[b]	I
106.56	16.44	I	264.83	27.33[b,c]	II
114.08	17.11	I	266.02	27.58[b]	I
121.74	17.75	I	270.38	30.61[b,d]	II
129.49	18.35	I	274.33	M.p.	
137.09	18.95	I	280.85	33.01	III
144.65	19.51	I	284.90	33.00	IV
152.44	20.10	I	288.45	33.06	III
160.18	20.67	I	292.69	33.06	IV
167.62	21.19	I	295.96	33.13	III
175.05	21.70	I	300.19	33.21	IV

[a] Mol. wt. = 153.346. 1.3185 moles in calorimeter. [b] Temperature rise obtained from thermocouple. [c] ΔT = 5.726°K. [d] ΔT = 5.158°K. Both [c] and [d] used for impurity calculation.

given in gibbs mole$^{-1.5}$ and the conversion to absolute temperature is 0°C. = 273.15°K. in all data given.

The Melting Point of Phosphoryl Chloride.—The triple point was determined as a function of the fraction X melted and the values extrapolated by means of a plot of T *vs.* $1/X$. The measurements were made under the vapor pressure of $POCl_3$. The data are given in Table II together with the values of other observers.

TABLE II

TRIPLE POINT OF PHOSPHORYL CHLORIDE[a]

% Melted	T, °K. resist. therm.	T, °K. thermocoup.
20	274.268	274.259
45	274.298	274.300
75	274.311	274.316

[a] Extrapolated and accepted value = 274.33 ± 0.05° K. Values due to other observers are: 274.40,[6] 274.33,[7] 274.35° K.[8]

Heat of Fusion of Phosphoryl Chloride.—Three determinations of the heat of fusion were made in the usual manner of starting energy input at a temperature somewhat below the melting point and ending it somewhat above. Correction was made for any premelting which had occurred before the starting temperature. The data are given in Table III.

TABLE III

HEAT OF FUSION OF PHOSPHORYL CHLORIDE[a]

Temp. interv., °K.	Heat input, corr.	Pre-melting	$\int C_p dT$	$\Delta H_{\text{fus.}}$, cal./mole
273.05–280.09	3334	19.7	223	3131
268.35–277.42	3391	2.2	263	3130
268.53–277.21	3385	2.4	252	3135

[a] M.p., 274.33°K. Average value, 3132 ± 3

Vapor Pressure of Phosphoryl Chloride.—It was necessary to have an accurate value of the vapor pressure at the temperature used for the calorimeter measurement of the heat of vaporization in order to calculate the entropy. Only a few points were measured in the range 280–298° K. because the apparatus, which was similar to that described by Giauque and Egan,[3] did not permit observations above room temperature. The measurements were made with a Société Génévoise cathetometer, accurate to 0.001 cm., used as a comparison instrument against a standard meter bar. The data were compared with values obtained from a straight line plot of $(\ln P + \Delta C_p/R \ln T)$ *vs.* $(1/T)$, where $\Delta C_p = C_p(g) - C_p(l) = 13.0$ gbs. mole^{-1}.

$$\frac{d \ln P}{d\,(1/T)} = -\frac{(\Delta H_0 - \Delta C_p T)}{R\left(1 - \left(\frac{V_1 P}{RT}\right)\right)}$$

$\Delta H_{\text{vap.}} = \Delta H_0 - 13.0\ T$, V_1 = molal volume of liquid, and the term V_1P/RT is almost completely negligible at the low pressures involved.

$$\frac{d\left(\ln P + \frac{\Delta C_p}{R} \ln T\right)}{d(1/T)} = \frac{-\Delta H_0}{R}$$

which may be evaluated from the calorimetric data. It was found that a systematic deviation in the vapor pressure values existed in a direction to indicate that a pressure of 0.026 cm. of inert gas was present. Previous measurements in this Laboratory have shown that it is extremely difficult to make vapor pressure measurements to a high percentage accuracy when the pressure is low, due to the great difficulty in completely removing inert gases. In the present case we made the rough assumption that the partial pressure of the inert gas remained constant over the small interval measured to obtain an approximate value of the inert gas pressure. The effect of the correction of 0.026 cm. on the final entropy value is only about 0.015 gbs. mole^{-1}.

The original and the corrected observations are given in Table IV along with deviations from the best straight line, with the calculated slope, through the data.

Heat of Vaporization of Phosphoryl Chloride.—The heat of vaporization was measured a little below 25° where the pressure is only about 3 cm. In order to stabilize the vaporization process, a capillary tube was calibrated so that the flow balanced the heat input when the effluent gas was completely condensed in liquid nitrogen. The condensation occurred in a weighing bulb, which could be attached to the capillary by means of a ground glass joint. Corrections were made for

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TABLE IV

VAPOR PRESSURE OF PHOSPHORYL CHLORIDE

T, °K., resist. therm.	P obsd. inter. cm.	P obsd., − P corr.	P obsd. − P calcd., corr.
280.129	1.181	1.155	+0.002
285.153	1.550	1.524	− .009
289.966	2.043	2.017	+ .019
294.215	2.499	2.473	− .033
298.238	3.150	3.124	+ .019
298.15	Calcd. = 3.092		

TABLE V

HEAT OF VAPORIZATION OF PHOSPHORYL CHLORIDE AT 298.15°K.

Moles vaporiz.	Time energy input, min.	ΔH vap., cal./mole
0.15187	70	9219
.15199	70	9222
.15723	70	9219
	Average value	9220 ± 5

TABLE VI

CALCULATION OF THE ENTROPY (GIBBS/MOLE) OF $POCl_3$ FROM THE CALORIMETRIC DATA

0–15°K., extrap.	0.86
15–274.33°K. graph.	38.15
Fusion, 3132/274.33	11.42
274.33 − 298.15°K., graph.	2.75
Vaporization 9220/298.15	30.92
Entropy of actual gas at 0.04068 atm. and 298.15°K.	84.10
$S_{\text{ideal}} - S_{\text{real}}$ est.	0.01
Compress. from 0.04068 to 1 atm.	−6.36
Entropy of ideal gas at 1 atm. and 298.15°K.	77.75 gbs./mole

TABLE VII

THERMODYNAMIC PROPERTIES OF SOLID AND LIQUID PHOSPHORYL CHLORIDE (in gibbs mole^{-1})

T, °K.	C_p^0	S^0	$-(F^0 - H_0^0)/T$	$(H^0 - H_0^0)/T$
15	2.308	0.857	0.220	0.637
20	4.148	1.772	0.488	1.284
25	5.740	2.882	0.854	2.028
30	7.038	4.046	1.289	2.757
35	8.150	5.217	1.767	3.450
40	9.038	6.366	2.270	4.096
45	9.784	7.474	2.787	4.687
50	10.466	8.541	3.310	5.231
55	11.112	9.569	3.832	5.737
60	11.728	10.562	4.352	6.210
70	12.877	12.459	5.376	7.083
80	13.909	14.246	6.374	7.872
90	14.895	15.941	7.344	8.597
100	15.843	17.560	8.285	9.275
110	16.753	19.113	9.199	9.914
120	17.604	20.607	10.088	10.519
130	18.387	22.048	10.953	11.095
140	19.155	23.439	11.795	11.644
150	19.914	24.787	12.617	12.170
160	20.653	26.096	13.418	12.678
170	21.353	27.369	14.202	13.167
180	22.021	28.609	14.968	13.641
190	22.659	29.816	15.718	14.098
200	23.276	30.994	16.452	14.542
210	23.879	32.144	17.173	14.971
220	24.477	33.269	17.878	15.391
230	25.061	34.370	18.572	15.798
240	25.627	35.449	19.252	16.197
250	26.205	36.507	19.921	16.586
260	26.788	37.546	20.579	16.967
270	27.397	38.568	21.227	17.341
273.15	27.596	38.887	21.429	17.458
274.33	27.672	39.006	21.504	17.502(s)
274.33	33.046	50.423	21.504	28.919(l)
280	33.001	51.099	22.096	29.003
290	33.040	52.257	23.117	29.140
298.15	33.169	53.174	23.926	29.248
300	33.216	53.379	24.107	29.272

TABLE VIII

THERMODYNAMIC PROPERTIES OF PHOSPHORYL 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	43.461	35.512	7.949
20	7.950	45.747	37.798	7.949
25	7.957	47.522	39.572	7.950
30	7.984	48.975	41.022	7.953
35	8.048	50.209	42.248	7.961
40	8.161	51.291	43.313	7.978
45	8.328	52.261	44.254	8.007
50	8.548	53.150	45.100	8.050
55	8.812	53.976	45.869	8.107
60	9.112	54.756	46.578	8.178
70	9.785	56.210	47.851	8.359
80	10.508	57.563	48.981	8.582
90	11.241	58.844	50.007	8.837
100	11.960	60.065	50.952	9.113
110	12.654	61.238	51.834	9.404
120	13.316	62.367	52.665	9.702
130	13.946	63.459	53.454	10.005
140	14.541	64.514	54.207	10.307
150	15.102	65.536	54.927	10.609
160	15.630	66.528	55.621	10.907
170	16.125	67.490	56.292	11.198
180	16.590	68.425	56.940	11.485
190	17.024	69.334	57.568	11.766
200	17.430	70.218	58.179	12.039
210	17.813	71.078	58.773	12.305
220	18.170	71.916	59.352	12.564
230	18.503	72.731	59.916	12.815
240	18.815	73.523	60.465	13.058
250	19.109	74.298	61.003	13.295
260	19.385	75.053	61.530	13.523
270	19.644	75.789	62.044	13.745
273.15	19.723	76.018	62.204	13.814
274.33	19.752	76.104	62.264	13.840
280	19.889	76.508	62.548	13.960
290	20.120	77.210	63.041	14.169
298.15	20.298	77.770	63.436	14.334
300	20.336	77.896	63.525	14.371
310	20.542	78.566	63.999	14.567
320	20.736	79.221	64.465	14.756
330	20.920	79.863	64.922	14.941
340	21.096	80.490	65.371	15.119
350	21.262	81.103	65.811	15.292
360	21.419	81.705	66.245	15.460
370	21.570	82.293	66.670	15.623
380	21.713	82.871	67.089	15.782
390	21.850	83.436	67.500	15.936
400	21.980	83.992	67.907	16.085
450	22.549	86.614	69.842	16.772
500	23.007	89.015	71.641	17.374

heat leak and the effect of small changes of temperature on the residual material. Correction also was made for the fact that the volume previously filled with liquid became available for gas. The values for ΔH were corrected to 298.15°K. over the small temperature range. The values are given in Table V.

The Entropy of Phosphoryl Chloride from the Calorimetric Data.—The entropy was calculated in the usual manner by graphical integration and a Debye extrapolation. The data are summarized in Table VI.

The microwave data of Williams, Sheridan and Gordy,[9] and the vibrational fundamentals as given by Ziomek, Piotrowsky and Walsh,[10,11] were used to calculate a statistical value of the entropy of $POCl_3$ gas.

Williams, Sheridan and Gordy found it necessary to combine their data with the electron diffraction data of Brockway and Beach[12] in order to obtain the moment of inertia about the symmetry axis

$$I_1 = 422.3 \times 10^{-40} \text{ g. cm.}^2 \text{ molecule}^{-1}$$
$$I_2 = 419.2 \times 10^{-40}$$
$$I_3 = 578.7 \times 10^{-40}$$

We have obtained the above values from a weighted average of the several isotopic species. $I_1 \neq I_2$ due to isotopic loss of symmetry.

Ziomek, Piotrowsky and Walsh calculate a value for the entropy at 298.16°K. as 77.38 gbs. mole^{-1}. This value must be in error since the experimental result, 77.75 gbs. mole^{-1}, is greater than the above value, whereas it must be equal or less than the value derived from quantum data. Ziomek, Piotrowsky and Walsh do not state which of the fundamentals were given a double weight. We have used their values for the fundamentals and the weights listed to bring the calorimetric and spectroscopic values into agreement. The fundamental frequencies in cm.$^{-1}$ are

$$\nu_1 = 1290,\ \nu_2 = 486,\ \nu_3 = 337,\ \nu_4 = 581(2),$$
$$\nu_5 = 267(2),\ \nu_6 = 193(2)$$

These give a value of 77.77 *vs.* the experimental value 77.75 gbs. mole^{-1}. These values do not include the contributions due to isotopic mixing or nuclear spin. The result of Ziomek, Piotrowsky and Walsh corresponds to a reversal of ν_3 and ν_5 with respect to the double weight.

The above data were used to calculate values for the thermodynamic properties of phosphoryl chloride gas. The thermodynamic properties for condensed phases and the gas are given in Tables VII and VIII, respectively.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS, THE STATE UNIVERSITY]

Counterion Binding by Polyelectrolytes. V. The Effect of Binding of Univalent Cations by Polyphosphates on the Intrinsic Viscosity(1)

BY PHILIP D. ROSS AND ULRICH P. STRAUSS

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The effect of alkali metal ions on the molecular dimensions of a long-chain polyphosphate has been determined by viscosity measurements at 0° in aqueous solutions maintained at 0.2 ionic strength with tetramethylammonium bromide. All alkali metal ions depress the intrinsic viscosity, but in different ways. It is shown that the intrinsic viscosity is not a unique function of either the degree of ionization of the polyphosphate or the degree of binding of the alkali metal ions. This result indicates the existence of specific solvent incompatibilities of site-bound ion-pairs. The previous explanation of the dependence of the binding constants for the association of the cations with PO_3^--groups on the cation concentration in terms of the molecular dimensions of the polymer chain has been confirmed.

One of the most characteristic and best known properties of polyelectrolytes is the strong dependence of their molecular dimensions on their degree of ionization.(2) More recently, phase separation and viscosity studies on long-chain polyphosphates have shown that the solvent incompatibilities of site-bound $LiPO_3$ and $NaPO_3$ groups were different and that such differences had a pronounced effect, comparable to that of the degree of ionization, on the molecular dimensions of the polyelectrolyte.(3) However, since the degree of binding of the Li^+ and Na^+ ions was not quantitatively known, the conclusions concerning the molecular dimensions were necessarily only qualitative. In the meantime, the binding of Li^+,

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