NOTES

Thermodynamic Functions for Phosphine and the Phosphonium Ion

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The thermodynamic functions S° at 298°K., $H^\circ - H_0^\circ$, and $-(F^\circ - H_0^\circ)/T$ at temperatures from 298 to 1500°K. have been computed previously[1] for $PH_3(g)$ on the basis of earlier spectroscopic data.[2,3] More recently, spectroscopic and structural data for the phosphonium ion[4-6] and improved data for phosphine have been reported.[7-12]

The vibrational frequencies for phosphine are $\nu_1(1)\parallel = 2322.9$ cm.$^{-1}$; $\nu_2(1)\parallel = 990$ cm.$^{-1}$; $\nu_3(2)\perp = 2328$ cm.$^{-1}$ and $\nu_4(2)\perp = 1121$ cm.$^{-1}$.[7,8] The moments of inertia for PH_3[12,13] are $I_a = (7.16 \pm 0.05) \times 10^{-40}$ g. cm.^{2} and $I_b = I_c = 6.285 \times 10^{-40}$ g. cm.^{2}.

The vibrational frequencies obtained from the Raman spectra for the phosphonium ion, PH_4^+, (T_d symmetry) are $\nu_1(1) = 2304$ cm.$^{-1}$; $\nu_2(2) = 1040$ cm.$^{-1}$; $\nu_3(3) = 2370$ cm.$^{-1}$ and $\nu_4(3) = 930$ cm.$^{-1}$.[4,5] The r(P–H) distance for PH_4^+ obtained from the nuclear magnetic resonance measurements[6] on $PH_4I(s)$ is 1.42 ± 0.02 Å. Therefore, the moment of inertia, I, of PH_4^+ is $(9.00 \pm 0.25) \times 10^{-40}$ g. cm.^{2}.

The thermodynamic functions C_p°, $(H^\circ - H_0^\circ)/T$, $-(F^\circ - H_0^\circ)/T$, and S° have been calculated for phosphine and gaseous phosphonium ion in the temperature range from 200 to 1500° and 1000°K., respectively, by the rigid rotator-harmonic oscillator approximation for the ideal gas at a pressure of one atmosphere. The values of the thermodynamic functions are listed in Tables I and II.

Table I

Thermodynamic Functions for Phosphine in the Ideal Gas State in Cal./Deg.-Mole

T, °K.	C_p°	$(H^\circ - H_0^\circ)/T$	$-(F^\circ - H_0^\circ)/T$	S°
200	8.11	8.00	38.86	46.86
250	8.43	8.06	40.65	48.71
298.16	8.87	8.16	42.07	50.23
350	9.43	8.31	43.38	51.69
400	9.99	8.49	44.50	52.99
500	11.11	8.91	46.43	55.34
600	12.17	9.37	48.09	57.46
700	13.13	9.85	49.56	59.41
800	13.99	10.31	50.91	61.22
900	14.73	10.77	52.14	62.91
1000	15.37	11.20	53.30	64.50
1100	15.92	11.61	54.38	65.99
1200	16.38	11.99	55.41	67.40
1300	16.78	12.35	56.37	68.72
1400	17.12	12.68	57.30	69.98
1500	17.41	12.99	58.18	71.17

Table II

Thermodynamic Functions for the Phosphonium Ion in the Ideal Gas State in Cal./Deg./Mole

T, °K.	C_p°	$(H^\circ - H_0^\circ)/T$	$-(F^\circ - H_0^\circ)/T$	S°
200	8.41	8.05	37.14	45.19
250	9.13	8.20	38.94	47.14
298.16	10.01	8.42	40.40	48.82
400	11.98	9.09	42.95	52.04
500	13.73	9.85	45.05	54.90
600	15.28	10.64	46.91	57.55
700	16.63	11.40	48.60	60.00
800	17.81	12.13	50.17	62.30
900	18.83	12.83	51.64	64.47
1000	19.91	13.48	53.02	66.50

At the lower temperatures the thermodynamic functions for phosphine should be uncertain to less than ±0.1 cal./deg./mole. At temperatures near 1000°K. and above, neglect of anharmonicity and other effects can increase the uncertainties further. The uncertainties in $-(F^\circ - H_0^\circ)/T$ and S° for PH_4^+ resulting from the uncertainty in its moment of inertia amount to about ±0.1 cal./deg./mole. The uncertainties in the thermodynamic functions for PH_4^+ due to the inaccuracies in the vibrational frequencies are difficult to estimate, but they probably amount to several tenths of a cal./deg./mole.

From low temperature heat capacity measurements[14,15] the entropy of phosphine at the b.p., 185.38°K., has been calculated to be 46.39 ± 0.1 cal./deg./mole. The statistical thermodynamic value for the entropy at 185.38°K. is 43.26 ± 0.01 cal./deg./mole. The agreement is quite good, but the calorimetric value for S° does appear to be about 0.1 cal./deg./mole too high.

The previous statistical thermodynamic values[1] for $-(F^\circ - H_0^\circ)/T$ for PH_3 are 0.03 to 0.06 cal./deg./mole higher in the temperature range from 298 to 1500°K. than the values calculated in this work. The previous statistical value[1] of S° for PH_3 at 298.16°K. is 0.03 cal./deg./mole too low. The values of S° above 298°K. have not been given previously. The entropy of the reaction

$$PH_3(g) + H^+(g) \longrightarrow PH_4^+(g)$$

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at 298.16°K. now can be calculated. The entropies of $PH_3(g)$ and $PH_4^+(g)$ at 298.16°K. from Tables I and II are 50.23 and 48.82 cal./deg./mole. The entropy of $H^+(g)$ from the Sackur–Tetrode equation is 26.01 cal./deg./mole. Thus the entropy of the protonation reaction is −27.42 cal./deg./mole. The entropy of the protonation of $NH_3(g)$ is −27.55 cal./deg./mole.[16] Consequently, the entropies of the two protonation reactions are very nearly the same.

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X-Ray Diffraction Study of the Precipitation of Barium from Solutions Containing Chloride, Fluoride and Sulfate. Formation and Properties of Barium Chlorotrifluoride

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The precipitation of BaClF from concentrated mixtures of the chloride and fluoride of barium has been reported as early as 1824[1]. Plato[2] studied the system BaF_2–$BaCl_2$ by means of cooling curves, and found evidence only for the existence of BaClF, and of solid solutions between $BaCl_2$ and BaClF, and between BaF_2 and BaClF. An equimolar eutectic mixture of BaF_2 and BaClF was reported. Campbell and Campbell[3] investigated the system BaF_2–$BaCl_2$–H_2O and showed that BaClF and solid solutions of $BaCl_2$–BaClF precipitated under various conditions, in agreement with the phase diagram of Plato. In neither of these investigations was evidence found for the formation of any chlorofluoride other than BaClF.

In the course of some studies of the precipitation of barium sulfate from solutions containing fluoride and chloride ions, we have identified in the precipitates a compound having the formula Ba_2ClF_3, and this observation has prompted an investigation of the conditions of formation and properties of this substance. The results of this work have disclosed why Plato and Campbell and Campbell did not encounter the chlorotrifluoride in their experiments.

Experimental

All reagents employed for the precipitations were of analytical grade; weighings were made to ±0.05 g. on a torsion balance. Samples were prepared for X-ray diffraction measurements by grinding until they could pass a No. 325 mesh screen.

Diffraction patterns were recorded with a North American Philips Diffractometer, using a copper target and a nickel foil filter. The tube was run at 35 kv. and 15 ma., and spectra were recorded at a scale factor of 16, multiplier 1, time constant 4. The divergent and scatter slits were set at 1°, and the receiving slit at 0.006″.

Pure Ba_2ClF_3 was made by heating an intimate equimolar mixture of BaClF and BaF_2 at 900° in a muffle furnace, and maintaining the mixture at that temperature overnight. The powder pattern of this reaction mixture showed no remaining BaF_2 or BaClF, whereas mixtures of these two components in other molar ratios than 1:1 showed diffraction peaks characteristic of the reagent that was present in excess, in addition to those of the new species.

The d values and relative intensities of the diffraction pattern of barium chlorotrifluoride are given in Table I. It has been found possible to index the lines up to $2\theta = 34°$ on the basis of hexagonal symmetry, with the parameters $a = 18.4$ and $c = 12.5$ Å. Beyond this angle, the possible sets of indices for each reflection are so numerous that unique assignments cannot be made on the basis of a powder diagram alone. The indices shown in the table all satisfy the relationships: $h - k + l, h + 2k + l, -2h - k + l = 3n$, thus establishing that the true unit cell is rhombohedral,[4] with $a = 11.4$ Å., and $\alpha = 107° 20'$.

Table I

Diffraction Data for Ba_2ClF_3

d			
Expt.	Calcd.	Rel. intens.	hkl
9.2	9.2	Weak	110
5.32	5.31	2	300
4.60	4.60	1	220
4.16	4.15	2	003
3.80	3.80	30	113
3.60	3.61	7	312
3.48	3.47	100	410
3.28	3.28	60	303
3.09	3.09	50	501
3.07	3.07	20	330
2.67	2.66	50	600

Other lines, with relative intensities given in parentheses, were observed at d = 2.55 (4), 2.47 (20), 2.30 (4), 2.24 (1), 2.20 (4), 2.18 (40), 2.113 (4), 2.085 (20), 2.015 (20), 2.010 (40), 1.885 (40), 1.811 (10), 1.789 (40), 1.741 (10).

A series of experiments was conducted in which barium chloride solutions were precipitated by the addition of a sodium or potassium fluoride solution containing, in some cases, dissolved sodium sulfate. The precipitates were analyzed by means of their powder diffraction patterns, and the relative amounts of the several solid phases were estimated on the basis of the intensities of the strongest lines free of interference from the other species. All concentrations refer to the final solution before precipitation.

Solutions that were 0.1 M in $BaCl_2$ and 0.1 to 0.25 M in NaF gave precipitates that consisted of BaClF and BaF_2 if precipitation took place at room temperature, and of BaF_2 alone if the precipitation took place at the boiling point. This is to be expected from the fact that BaClF is decomposed by hot water into $BaCl_2 + BaF_2$. In the following experiments, $BaSO_4$ was precipitated together with the barium halides.

The precipitate consisted principally of Ba_2ClF_3, plus some $BaSO_4$, if a solution 0.075 M in $BaCl_2$, 0.10 M in NaF and 0.025 M in Na_2SO_4 was prepared at the boiling point, and the precipitate was digested in the hot solution for five hours. The precipitate obtained under identical conditions, but digested in the hot solution for only one-half hour, consisted principally of BaClF, and contained small amounts of Ba_2ClF_3 and $BaSO_4$. Thus, in hot solution, and at a Ba: Cl:F ratio (after precipitation of the $BaSO_4$) of 1:2:2, BaClF precipitates more readily than Ba_2ClF_3, but is converted into the latter during digestion. If the same solution is prepared at room temperature, and the precipitate is digested overnight at room temperature, it is found to consist of Ba_2ClF_3 plus some $BaSO_4$, but with no detectable BaClF.

The composition of the precipitate depends upon the relative proportions of Ba^{++}, Cl^- and F^- remaining after precipitation of any $BaSO_4$. Thus, in precipitations carried out at room temperature followed by room temperature digestion overnight, at a Ba:Cl:F ratio of 1:6:4 the solid phase contained only a small amount of Ba_2ClF_3 in addition to the $BaSO_4$, and there was no BaClF or BaF_2. If the fluoride concentration was reduced, so that the relative concentrations were 1:6:2, the precipitate contained only BaClF in addition to the $BaSO_4$. At a ratio of 1:3:2, the precipitate was mainly BaClF, with a small amount of Ba_2ClF_3 in addition to the $BaSO_4$.

In order to investigate further the role played by the $BaSO_4$, a series of precipitations was carried out in which the

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