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.

(16) A. P. Altshuller, This Journal, **77**, 3480 (1955).

2715 E. 116th St.
Cleveland 20, Ohio

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

By Emma Fessenden and S. Z. Lewin

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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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(1) J. J. Berzelius, *Pogg. Ann.*, **1**, 18 (1824).

(2) W. Plato, *Z. physik. Chem.*, **58**, 350 (1907).

(3) A. N. Campbell and A. J. R. Campbell, *Trans. Faraday Soc.*, **35**, 241 (1939).

(4) C. W. Bunn, "Chemical Crystallography," Oxford, London, 1946, p. 135.

ratio of Ba:Cl:F was varied, and the composition of the precipitate was determined when precipitation occurred in the presence and in the absence of sulfate ions. All precipitations in this series were carried out at room temperature, and the precipitate was allowed to remain in contact with the mother liquor for three days before filtering. A barium nitrate solution of appropriate concentration was first mixed with an appropriate barium chloride solution, and this mixture was then treated with a potassium fluoride solution that did, or did not, contain a very small amount of dissolved sulfate. All concentrations refer to the final mixture before precipitation had occurred.

For the following Ba:Cl:F ratios, the precipitate consisted entirely of BaF_2 when precipitation took place in the absence of sulfate: 1:1:2, 1.5:1:2, 2:1:3, 4:1:1. At a ratio of 1:1:1, the precipitate was largely BaF_2, with some BaClF, and at a ratio of 1:2:1, the precipitate contained no BaF_2, being entirely BaClF. When precipitation took place in the presence of a trace of sulfate, however, the solid phase consisted of approximately equal amounts of BaClF and BaF_2 in the cases of the 1.5:1:2 and 2:1:3 mixtures. The 1:1:1 mixture showed an increased yield of BaClF, together with a small yield of Ba_2ClF_3; and the 1:1:2 mixture showed no BaClF, but some Ba_2ClF_3 in addition to the BaF_2. The precipitate from the 4:1:1 mixture remained practically pure BaF_2. In the case of the 1:2:1 mixture, a trace of sulfate changed the composition of the precipitate from pure BaClF to practically pure Ba_2ClF_3. The general trend of these data may be summarized by the generalization that precipitation in the presence of sulfate tends to produce BaClF at the expense of BaF_2, and of Ba_2ClF_3 at the expense of BaClF.

It has been observed that heating an equimolar mixture of $BaCl_2$ and BaF_2 in a muffle furnace at 900° for several hours results in the formation of pure BaClF, and similar treatment of an equimolar mixture of BaClF and BaF_2 gives pure Ba_2ClF_3. The latter compound, if fused by heating to 1100° and then cooled rapidly by removal from the furnace, reverts to a mixture of BaClF plus BaF_2.

Treatment of Ba_2ClF_3 with boiling water does not affect it, whereas similar treatment of BaClF converts it to $BaF_2 + BaCl_2$. Dilute acids and alkalies decompose Ba_2ClF_3; sodium chloride solution converts the compound into BaClF, and NaF solution converts it to BaF_2. Barium nitrate solution also converts Ba_2ClF_3 into BaF_2.

Discussion

The present X-ray data clearly show that a solid phase having the same analytical composition as the eutectic of Plato and Campbell and Campbell, but corresponding to a single, discrete phase, may be obtained by prolonged heating of dry BaClF and BaF_2, or by precipitation from aqueous solution in the presence of sulfate. Its crystal lattice is rhombohedral with $a = 11.4$ and $\alpha = 107°20'$, in contrast to the cubic lattice of BaF_2 ($a = 6.184$) and the tetragonal lattice of BaClF ($a = 4.38$, $c = 7.22$). The same phase, with identical Bragg angles, is a constituent of the precipitates obtained from solutions having different Cl^- to F^- ratios, and it is clearly not a solid solution of BaClF in BaF_2.

It is evident that the chlorotrifluoride was not encountered by Plato because it does not crystallize from a melt that is allowed to cool rapidly, as was the case in his cooling curve studies. It does form if the solid mixture is maintained at a high temperature for a prolonged period. It was not found by Campbell and Campbell because it does not precipitate from aqueous solutions in the absence of sulfate ions.

Under conditions such that only BaF_2 is formed in the absence of sulfate, a trace of the latter produces a high yield of BaClF. When only BaClF is precipitated in the absence of sulfate, a trace of the latter produces a high yield of the chlorotrifluoride at the expense of the former. No explanation can be offered at present for this remarkable effect of sulfate in catalyzing the precipitation of barium chlorofluoride and barium chlorotrifluoride.

DEPARTMENT OF CHEMISTRY
NEW YORK UNIVERSITY
NEW YORK, N. Y.

The Structure of the Salt $3NaPO_3 \cdot KPO_3$

BY E. J. GRIFFITH AND J. R. VAN WAZER

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Recently a new inorganic phosphate, $3NaPO_3 \cdot KPO_3$, was reported by Morey.[1] It is the purpose of this work to classify the structure of the new salt. Modern theory[2] limits the probable existence of species other than chains or rings in compositions with M_2O/P_2O_5 ratios of unity. M refers to any univalent cation.

A salt was prepared as directed by Morey and the salt yielded an X-ray pattern with the same maxima as the one reported, except that the pattern reported by Morey contains sodium trimetaphosphate as an impurity. The salt next was dissolved in water, acidified to *p*H 2.5, and titrated with standard base. This titration showed the salt to contain 0.075 equivalent of weak acid per mole of $3NaPO_3 \cdot KPO_3$, indicating that it was either very long chains or rings containing a trace of linear molecules.

Intrinsic viscosities were run on the original salt, but the value was too small to be measured accurately. This is proof that the salt has a relatively low molecular weight in aqueous solution.

Next, another sample of the salt was dissolved in water, and then precipitated from solution with methanol. A crystalline product was obtained that had an X-ray pattern very similar to the X-ray pattern of the original salt. The differences in the X-ray patterns were: the relative intensities were not the same in both patterns, and the maxima were broader in the pattern obtained from the sample which was precipitated from solution. The maxima occurred at identical spacings, however. The differences in the patterns are attributable to the smaller crystallite size of the sample which was precipitated from solution. The salt is not destroyed when dissolved in water and precipitated with methanol.

Another sample of the salt was dissolved in water and ion exchanged with the hydrogen form of a pulverized Dowex-50 ion-exchange resin, neutralized with sodium hydroxide, and precipitated with methanol. The resulting product was sodium tripolyphosphate hexahydrate. This result indicates that during the treatment the original compound was hydrolyzed, since very little weak acid function was found in the original salt. There was a 40-fold increase in the weak acid function during the ion-exchange process with the acidic resin. The neutral sodium form of the ion-exchange resin does not accelerate the hydrolysis of condensed phosphates. A Dowex-50 ion-exchange resin was prepared in the sodium form, and the original salt converted en-

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[1] G. W. Morey, THIS JOURNAL, **76**, 4724 (1954).

[2] J. R. Van Wazer and K. A. Holst, *ibid.*, **72**, 639 (1950).