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.

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

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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).

tirely to the sodium form with it, and then precipitated from solution with methanol. The resulting product was sodium trimetaphosphate. This means that the original salt is a trimetaphosphate.

Since the original salt is not destroyed by dissolution and may be precipitated from solution with methanol, it is possible to prepare the original salt in aqueous solution as well as from a melt. A solution of sodium trimetaphosphate was prepared by dissolving 51.0 g. of sodium trimetaphosphate in 300 ml. of water to which 12.4 g. of potassium chloride and 2.0 g. of KOH were added. Methanol was added to the solution until precipitation ceased. The white precipitate was redissolved and reprecipitated. It was dried at 30° and X-rayed. The X-ray pattern was identical to the pattern obtained from the original $3NaPO_3 \cdot KPO_3$ which had been dissolved in water and precipitated from solution with methanol. This is proof that the salt prepared by Morey is a trimetaphosphate which may be prepared from a melt or from an aqueous solution.

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Activity of Hydrochloric Acid in Mixtures with Cobalt(II) and Nickel(II) Chlorides

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Of the various methods for the determination of the activity of hydrochloric acid, measurement of the electromotive force of cells employing hydrogen and silver–silver chloride electrodes has proved to be the most satisfactory up to comparatively high acid concentrations. The cell $H_2/HCl\ (m_1),\ MCl_x\ (m_2)/AgCl–Ag$ has also been used extensively to determine the activity of hydrochloric acid in hydrochloric acid–salt mixtures.[1] However, in general there has been no independent confirmation of the activity values in such acid–salt systems by another method.

Recently the activity of hydrochloric acid in mixtures with cobalt and nickel chlorides has been determined by vapor pressure measurements,[2] and since the results seriously disagreed with some activity values obtained by the electromotive force measurements of an earlier investigation, it seemed worthwhile in view of the importance of the above cell to reexamine its suitability for activity measurements in these transition metal halide solutions at high salt and acid activities. As an independent check on the results the hydrochloric acid activities were also determined from the distribution coefficients of HCl between benzene and the aqueous mixtures.[3]

Experimental

Solutions.—The salt-acid mixtures were prepared 7 molal in HCl and analyzed as described elsewhere.[2]

Electromotive Force Measurements.—All experiments were made at 30°. The hydrogen electrodes were of the usual platinized platinum type. Silver–silver chloride electrodes were constructed by electrolytically depositing silver on platinum spirals and chloridizing according to the recommendations of Janz and Taniguchi.[4] In order to prevent diffusion of silver ions to the hydrogen electrode, the silver–silver chloride electrode was enclosed in a tube fitted with a fine-porosity fritted-glass disc at one end. Silver chloride–saturated solution was aspirated up until the level inside the tube was slightly below that outside.

The partial pressure of the presaturated hydrogen gas was calculated from the barometric pressure and the data of Moore, *et al.*,[2] for the water and HCl vapor pressures. Approximately two hours were required to saturate the solutions with hydrogen.

Potential comparisons were made using a Rubicon Type B potentiometer. A value of 0.21912 volt was taken as the standard potential of the cell.[5] The value of the neglected liquid junction potential was probably small in all cases.[6]

Distribution Experiments.—Equal volume (50 ml.) amounts of benzene and the acid-salt mixtures were sealed in glass tubes and agitated mechanically for 24 hours at 30°. The shaking was stopped and the solutions allowed to stand for an additional 12 hours before sampling for analysis.

Weighed samples of the benzene phase were re-extracted with known amounts of aqueous potassium nitrate solution, and samples of the resulting aqueous phase were then titrated potentiometrically with silver nitrate to a null endpoint by the procedure of Kolthoff and Kuroda.[7] Since it has been shown that over the molality range of 7.2×10^{-6} to 2.73×10^{-1} in benzene the aqueous phase activity of HCl is proportional to its concentration in benzene,[3] the HCl activities were calculated according to the equation

$$a(\mathrm{HCl}) = 2.96 \times 10^6 m(\mathrm{HCl}) \qquad (1)$$

Discussion of Results

Reasonably good agreement was obtained among all three methods (Fig. 1). These results confirm the vapor pressure measurements previously reported[2] and independently demonstrate the suitability of the electromotive force method in determining hydrochloric acid activities in transition metal salt solutions of high acid and salt activity.

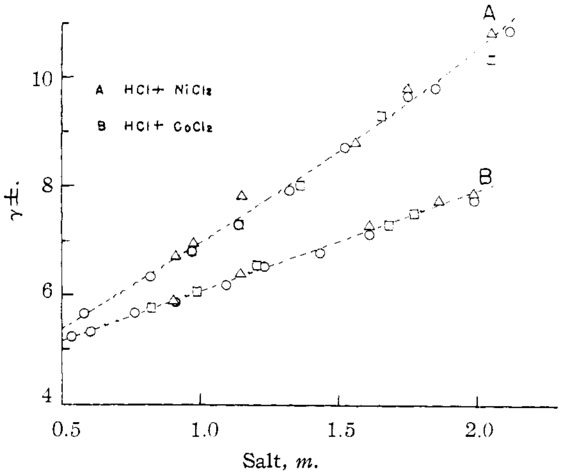

Fig. 1.—HCl activity coefficients of 7 molal HCl in presence of $CoCl_2$ and $NiCl_2$: ○, vapor pressure measurements; △, benzene extraction measurements; □, electromotive force measurements.

Acknowledgment.—This work was supported

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