THE SOLUBILITY OF CALCIUM SULPHATE IN PHOSPHORIC ACID SOLUTIONS¹

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The solubility of calcium sulphate in sulphuric acid has been investigated by Struve,² and more recently by Cameron and Breazeale.³ The latter found that there was an increasing solubility of calcium sulphate up to comparatively high concentrations of sulphuric acid, and that at 25° C a maximum was reached with about 75 grams of sulphuric acid per liter. The solubility then decreases in stronger acid solutions.

The solubility of calcium sulphate in nitric and hydrochloric acids has been studied by Banthisch,⁴ whose results show that there is an increasing solubility of gypsum in those acids, and it is probable that a maximum point would be reached at higher concentrations of the acids. With 72.36 grams of hydrochloric acid per liter he obtained a solubility of 17.275 grams of gypsum per liter, and with 225.14 grams of nitric acid per liter he obtained a solubility of 20.607 grams of gypsum per liter. Lunge's results⁵ with hydrochloric acid at 25° agree well with those of Banthisch, and show a marked tendency to a maximum in the solubility curve.

Banthisch has also studied the solubility effects of monochloroacetic acid, and formic acid on calcium sulphate,⁶ but the results are too few to make any generalization.

From these investigations of the solubility effects of these different acids on calcium sulphate it is found that there is either a maximum solubility of the salt, or else the curve tends to approach a maximum. Even in the case of sulphuric acid, where it might be expected that the solubility would

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² Zeit. anal. Chem. 9, 34 (1870).

³ Jour. Phys. Chem. 7, 571 (1903).

⁴ Jour. prakt. Chem. 137, 52 (1884).

⁵ Jour. Soc. Chem. Ind. 4, 31 (1885).

⁶ Jour. prakt. Chem. 137, 52 (1884).

decrease, owing to the presence of a common ion, there is a well defined maximum.

In nearly all cases where the solubility of gypsum has been studied in solutions of electrolytes with no common ion over wide ranges of concentration,¹ the solubility increases with increasing concentration of the electrolyte, until a maximum is reached. At still higher concentrations the solubility decreases again.

In this investigation the solubility of gypsum in various aqueous solutions of phosphoric acid was determined. A series of solutions of phosphoric acid of the strength indicated in the table was saturated with Kahlbaum's calcium sulphate. The bottles containing these solutions were immersed in a constant temperature bath at 25° C and kept in constant agitation for several weeks. The supernatant liquor was analyzed for phosphoric acid, for sulphates, and for calcium. In determining phosphoric acid a few grams of the solution were weighed out, diluted, and an aliquot part taken for analysis, precipitated as ammonium phosphomolybdate, and determined volumetrically. In determining sulphuric acid the sulphate was precipitated by barium chloride in a boiling hot solution. In the precipitation of the calcium from the solution strong in phosphoric acid, alcohol was used, and thus the greater part of the phosphoric acid was held in solution while the lime was precipitated. This precipitated calcium was then dissolved in hydrochloric acid, and precipitated again as oxalate, and weighed as oxide. The sulphate determinations calculated to calcium sulphate showed a tendency to run higher than those derived from the calcium determinations. This may be due to the known tendency of barium sulphate

¹ In NH_4Cl solutions, Cohn: Jour. prakt. Chem. 143, 43 (1887); Cameron and Brown: Jour. Phys. Chem. 9, 210 (1905). In NaCl solutions, Tilden and Shenstone: Proc. Roy. Soc. 38, 331 (1885); Cameron: Jour. Phys. Chem. 5, 556 (1901); Orloff: Jour. Russ. Phys. Chem. Soc. 34, 949 (1902); d'Anselme: Bull. Soc. Chim., Paris, (3) 29, 372 (1903). In MgCl_2 solutions, Cameron and Seidell: Jour. Phys. Chem. 5, 643 (1901). In NH_4NO_3 solutions, Cohn: l. c.; Cameron and Brown: l. c. In NaNO_3 solutions, Seidell and Smith: Jour. Phys. Chem. 8, 493 (1904).

to carry down foreign material in its precipitation, and to the incomplete precipitation of the calcium by the alcohol. The

Fig. 1

average variation of these two determinations is about 1 per cent, if the final solution given in the table be excluded.

The fact that equivalent amounts of lime and sulphuric acid have been found indicates that there is no reaction between phosphoric acid and gypsum to produce a phosphate of calcium, and also a microscopic examination of the solid phase showed only the characteristic crystals of gypsum.

In the following table the calcium sulphate figures are the means of the sulphate and of the calcium determinations.

SOLUBILITY OF GYPSUM IN PHOSPHORIC ACID SOLUTIONS AT 25°

Grams P_2O_5 per liter	Grams $CaSO_4$ per liter	Density of solutions $\frac{25^{\circ}}{25^{\circ}}$
0.0	2.126	—
5.0	3.138	1.002
10.5	3.734	1.007
21.4	4.456	1.016
46.3	5.760	1.035
105.3	7.318	1.075
145.1	7.920	1.106
204.9	8.383	1.145
312.0	7.965	1.221
395.7	6.848	1.230
494.6	5.573	1.344

These results show an increasing solubility of gypsum as the concentration of phosphoric acid increases up to about 230 grams of the acid per liter, when there is over 8 grams of gypsum in solution. Like hydrochloric and nitric acids, and unlike sulphuric acid small amounts of phosphoric acid markedly increase the solubility of calcium sulphate in dilute solution. This behavior of sulphuric acid may be attributed to the effect of the common sulphion. As the concentration of the phosphoric acid increases above 230 grams per liter, the curve shows a steady drop, till at about 500 grams of phosphoric acid per liter the solubility of calcium sulphate has decreased to about 5.5 grams per liter.

These results are in accord with the above generalization concerning the effect of electrolytes yielding no ion in common with those from gypsum.

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