Short Communications

The Solubility of Calcium Oxalate Monohydrate in Ammonium Oxalate Solutions at 25° C

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In the course of an investigation on the separation of traces of calcium by precipitation with strontium oxalate as a collector, it was soon found that one of the chief sources of error was the unexpectedly high blank obtained from the ammonium oxalate solution. The solubility of calcium oxalate in ammonium oxalate solutions does not seem to have been determined. Calculation of the solubility from the solubility product may give erroneous results on account of complex formation, this being the case with regard to magnesium oxalate. A determination of the solubility seems therefore to be warranted. *Experimental.* Calcium oxalate monohydrate was prepared in two different ways: Preparation A was precipitated in an excess of calcium, Preparation B in an excess of ammonium oxalate. The precipitation was performed at room temperature and the resulting very finegrained precipitate recrystallized from slightly acidic solution by heating for 24 h at 100° C (Kolthoff and Sandell¹, Mc Comas and Rieman²). The preparations were kept under water. No significant difference in the solubilities of these two preparations in either water or ammonium oxalate solutions was obtained.

About 0.25 g of the preparation was added to 250 ml of solution and stirred for

1-2 h at $25.0 \pm 0.1^\circ$ C. Preliminary experiments showed, in agreement with Mc Comas and Rieman's² statement as to the dissolution velocity of calcium oxalate in water, that the solution equilibrium is rapidly established and no change is obtained after 1 hour. The solution was sucked off through a porcelain filter stick; the first portion of the filtrate was rejected. 200 ml of the solution were evaporated to dryness in a platinum dish and the ammonium oxalate removed by heating. The residue was dissolved in dilute hydrochloric acid, evaporated to dryness and again dissolved in 10.0 ml 0.3 M hydrochloric acid. When determining the solubility in water, only 100 ml of the filtrate were taken for analysis and the final volume was 25.0 ml.

The calcium concentration of the solutions was determined by flame spectrography of the 4227 Å line according to Lundegårdh³; the sensitivity of the modification used was such that a density of 0.1 on the photographic plate was obtained from a solution, $2 \cdot 10^{-5}$ M in calcium. No blank was obtained from the reagents which had been specially purified.

Discussion of the results. The results are given in Table 1. The solubility in water is the mean value of 6 determinations with a standard deviation of $\pm 0.4\%$. Every value for the solubility in ammonium oxalate solutions is the mean of 4 determinations with a standard deviation of $\pm 4.3\%$.

The solubility in water ($4.90 \cdot 10^{-5}$ M) is in good agreement with the earlier results of Kohlrausch⁴ ($4.85 \cdot 10^{-5}$ M) and Pedersen⁵ ($4.84 \cdot 10^{-5}$ M). From this solubility the thermodynamic solubility

Table 1. The solubility at 25° C of calcium oxalate monohydrate in ammonium oxalate solutions and in water.

Ammonium oxalate, molarity	Ionic strength	Square of mean activity coefficient	Solubility of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, molarity $\times 10^6$	calculated	found
0	$1.96 \cdot 10^{-4}$	0.88	—	—	49.0
0.001	0.003	0.62	3.4	5.9	
0.003	0.009	0.46	1.5	4.2	
0.01	0.03	0.28	0.76	3.8	
0.03	0.09	0.16	0.44	4.3	
0.1	0.3	0.060	0.35	5.3	
0.3	0.9	0.027	0.26	8.8	

product was calculated to be $2.12 \cdot 10^{-9}$, using the mean activity coefficient calculated from the formula

$$-\log \gamma = 0.5 z^2 \sqrt{\mu} / (1 + \sqrt{\mu})$$

The activity coefficients used for calculating the solubility in the oxalate solutions having an ionic strength of 0.003–0.09 were interpolated from tables published by Kielland⁶; for an ionic strength of 0.3–0.9, they have been calculated from Mc Comas and Rieman's² values on the solubility of calcium oxalate monohydrate in sodium chloride solutions.

The considerable differences between observed and calculated values indicate complex formation. Minimum solubility occurs at an oxalate concentration of about 0.01 *M* but the solubility differences in the concentration range 0.001–0.1 *M* ammonium oxalate are not large; 5 micro-moles per litre, *i. e.* 0.2 mg Ca per litre, may be accepted as an approximate mean.

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Tetragonal Tungsten Bronzes of Degenerated Perovskite Type

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The existence of isomorphous tetragonal sodium and lithium tungsten bronzes, Me_xWO_3 , of previously unknown structural type was reported in a recent paper from this Institute¹. This note will present an account of the determination of the crystal structure of these compounds.

The investigation was based on powder and single crystal photographs of the sodium compound, the preparation examined having the composition $\text{Na}_{0.10}\text{WO}_3$. The radiation used was Cu-K. The lattice constants of the tetragonal unit cell, as obtained from the powder photographs are (referred to the wave-length of Cu-K α radiation equal to 1.5418 Å):

$$a = 5.248 \text{ Å}, c = 3.895 \text{ Å}, V = 107.3 \text{ Å}^3$$

The observed density of 7.25 corresponds to a cell content of 2 formula units of $\text{Na}_{0.10}\text{WO}_3$.

The Laue symmetry was found from Weissenberg photographs to be 4/*mmm*. The only systematic absences are *h**k*0 reflections with *h* + *k* odd, which unequivocally suggests *P*4/*mmm* as the most probable space-group.

A striking feature of the diffraction pattern is the decisive significance of the *l* index for the intensities of the reflections. In rough outline the following regularities could be observed:

for reflections *hkl* (*h* + *k* even): *hk*0 (strong), *hk*1 (strong), *hk*2 (medium), *hk*3 (weak), *hk*4 (not visible), *hk*5 (weak, only β reflections observed);
for reflections *hkl* (*h* + *k* odd): *hk*0 (absent), *hk*1 (medium), *hk*2 (medium), *hk*3 (medium), *hk*4 (medium).