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The System Cadmium Oxalate, Potassium Oxalate and Water at 20 to 30°

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The purpose of this research was to determine what compounds can exist in equilibrium with solutions containing cadmium and potassium oxalates at 20 to 30°. Souchay and Lenssen[1] prepared the compound $K_2Cd(C_2O_4)_2 \cdot 2H_2O$, and the corresponding sodium and ammonium compounds. Schaefer[2] reported the formation of three complex salts from cadmium and ammonium oxalates in the proportions of 1:4, 1:6 and 1:8, respectively. Scholder, Gadenne and Niemann[3] prepared the salt $(NH_4)_2Cd_3(C_2O_4)_4 \cdot xH_2O$. In this investigation two complex salts were found to exist in equilibrium with saturated solutions containing an excess of potassium oxalate, namely, the compounds $K_2Cd(C_2O_4)_2 \cdot 3H_2O$ (or $K_2Cd(C_2O_4)_2 \cdot 4H_2O$) and $K_2Cd_3(C_2O_4)_4 \cdot xH_2O$ where x is uncertain.

Cadmium oxalate was prepared by slow precipitation from C. P. cadmium chloride and potassium oxalate. A complex salt was prepared by dissolving some cadmium oxalate in a hot 15 to 25% solution of potassium oxalate and allowing it to cool, when the complex salt crystallized out. The quantity of cadmium oxalate was adjusted so that the solution would contain more than 7% potassium oxalate at the end. This complex salt proved to be the compound $K_2Cd(C_2O_4)_2 \cdot 3H_2O$. Solubility experiments with this compound and with cadmium oxalate indicated the existence of a second complex salt capable of existing in equilibrium with solutions containing between 2.3 and 7.1% of potassium oxalate. By slow addition of cadmium chloride solution to a 7% potassium oxalate solution the second complex salt was precipitated. The precipitation was discontinued when the potassium oxalate content of the solution had been reduced to about 3%.

Mixtures consisting of a potassium oxalate solution and either cadmium oxalate or the appropriate complex salt were sealed in Pyrex tubes and rotated for two days or more. The solution was then separated from the wet solid phase in a manner previously described[4] and both were analyzed. Cadmium was determined electrolytically and oxalate by titration with permanganate. Many of the mixtures were made in duplicate and the analyses performed after different times of rotation. It was important that the proper solid phase be introduced at the start because otherwise the approach to equilibrium was very slow.

In most of the experiments the solutions were saturated at 25°. However, the solubilities of cadmium oxalate and the complex salts in potassium oxalate solutions is small, and the variation with temperature between 20 and 30° (and with concentration) was less than the experimental error; therefore, some of the solutions were saturated at 30° and some at temperatures between 20 and 25°.

The results are given in Table I and Fig. 1. The small values for the concentration of cadmium

(1) Souchay and Lenssen, *Ann.*, **103**, 316 (1857).
(2) Schaefer, *Z. anorg. Chem.*, **45**, 293 (1905).
(3) Scholder, Gadenne and Niemann, *Ber.*, **60**, 1489 (1927).
(4) Tarbutton and Vosburgh, THIS JOURNAL, **54**, 4539 (1932).

oxalate in the saturated solutions are omitted from the table. They were of the order of 0.15% and subject to a large relative error. In the last column of Table I the letter A stands for cadmium oxalate, $CdC_2O_4 \cdot 3H_2O$, B for the compound $K_2Cd_3(C_2O_4)_4 \cdot xH_2O$, C for the compound $K_2Cd(C_2O_4)_2 \cdot yH_2O$ and D for hydrated potassium oxalate. The percentage of water in the dry solid in the fourth column of Table I was found by algebraic extrapolation with the assumption of the formulas $K_2Cd_3(C_2O_4)_4 \cdot xH_2O$ and $K_2Cd(C_2O_4)_2 \cdot yH_2O$.

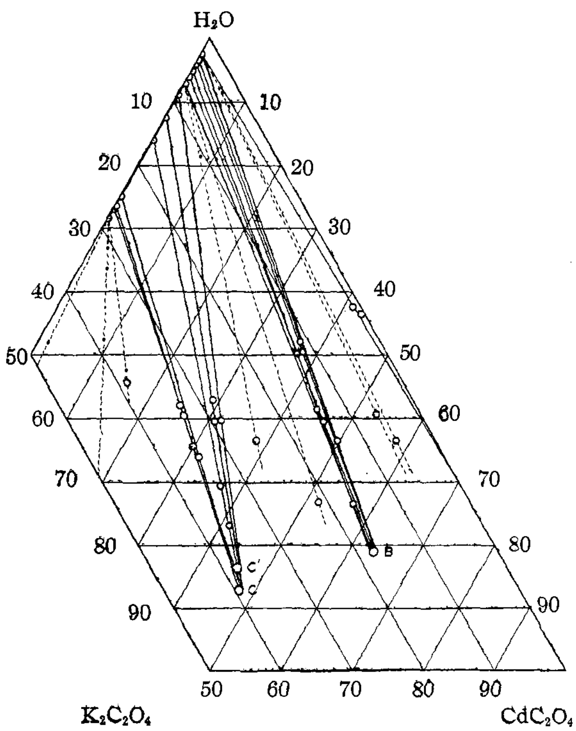

Fig. 1.—The system cadmium oxalate, potassium oxalate and water at 20 to 30°. Point B represents the composition calculated from the formula $K_2Cd_3(C_2O_4)_4 \cdot 10H_2O$ and points C and C′ the compositions calculated from the formulas $K_2Cd(C_2O_4)_2 \cdot 3H_2O$ and $K_2Cd(C_2O_4)_2 \cdot 4H_2O$.

The percentage of water found by algebraic extrapolation for both compounds is uncertain. For compound C the first three values are subject to the largest extrapolation error, and if these three are neglected the average lies between 12.85%, which is the theoretical value for $y = 3$ and 16.43% for $y = 4$. Of the two, the value $y = 3$ is more probable because positive errors in the determination of cadmium would lead to a high value for y, and a check of the method of determining cadmium on known samples gave somewhat high results.

TABLE I

COMPOSITION OF SATURATED SOLUTIONS AND SOLID PHASES

Solution $K_2C_2O_4$ wt. %	Wet solid $K_2C_2O_4$ wt. %	Wet solid CdC_2O_4 wt. %	Dry solid H_2O wt. %	Solid
2.28	0.46	43.16	..	A
2.25	1.05	41.35	..	A
2.31	5.54	57.90	..	A + B
2.24	6.20	53.06	..	A + B
2.35	13.82	49.64	34	B
3.10	11.17	36.73	31	B
3.87	11.60	37.80	31	B
3.80	15.96	53.57	2	B
4.67	12.24	37.19	18	B
4.89	12.51	37.34	18	B
4.89	14.11	44.40	9	B
5.77	11.64	33.83	27	B
5.86	14.13	46.32	13	B
6.87	16.60	56.82	17	B
7.11	25.18	38.26	..	B + C
7.06	21.35	51.75	..	B + C
8.59	28.50	31.77	22.2	C
12.29	27.95	29.00	22.1	C
12.39	29.46	30.91	17.9	C
15.73	33.73	36.77	15.2	C
15.87	35.67	41.19	16.7	C
24.75	34.51	31.52	12.7	C
26.25	34.48	29.79	13.1	C
26.66	33.05	24.81	14.6	C
26.79	33.44	26.09	14.6	C
28.20	50.30	18.98	..	C + D
28.37	38.68	15.57	..	C + D
28.73	77.66	3.53	..	C + D

Summary

The compound $K_2Cd_3(C_2O_4)_4 \cdot xH_2O$ in which x is uncertain but may be as high as 10 can exist in equilibrium with solutions containing between 2.3 and 7.1% of potassium oxalate. The compound $K_2Cd(C_2O_4)_2 \cdot yH_2O$, in which y is probably 3, can exist in equilibrium with solutions from 7.1% of potassium oxalate to saturation. At temperatures of 20 to 30° the solubility of both compounds is small.

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