[Contribution from the Department of Chemistry of Duke University]

The System Nickel Oxalate, Potassium Oxalate and Water at 30°

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A complex oxalate with the formula $K_2Ni(C_2O_4)_2 \cdot 6H_2O$ was reported by Rammelsberg,[1] and an analogous sodium salt, $Na_2Ni(C_2O_4)_2 \cdot 8H_2O$, by Dodson,[2] but no satisfactory study of the system nickel oxalate, potassium oxalate and water by the phase rule method seems to have been made. Deakin, Scott and Steele[3] made some determinations of the solubility of nickel oxalate in potassium oxalate solutions. They found the approach to equilibrium very slow, and obtained evidence of the formation of solid solutions of nickel and potassium oxalates.

Experimental.—Nickel sulfate was treated to remove cobalt by the method used by Deakin, Scott and Steele.[3] Potassium oxalate was recrystallized. Nickel oxalate was prepared by adding a solution of nickel sulfate to a solution of oxalic acid at a slow rate with mechanical stirring. Samples of the complex salt were prepared by dissolving nickel oxalate in saturated potassium oxalate solutions at an elevated temperature, filtering and allowing to crystallize at room temperature.

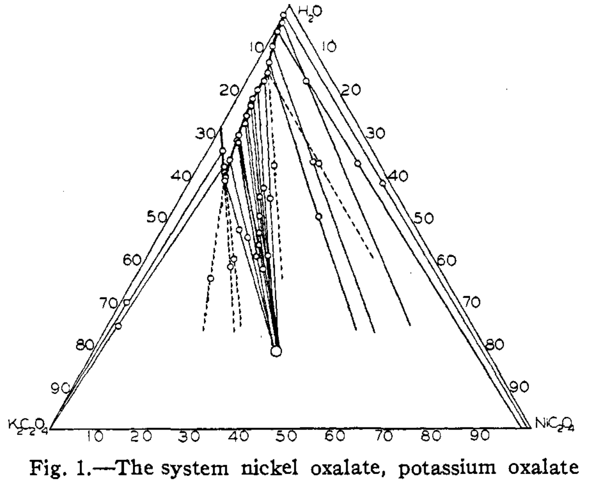

Fig. 1.—The system nickel oxalate, potassium oxalate and water at 30°. The large circle represents the theoretical composition of the compound $K_2Ni(C_2O_4)_2 \cdot 4H_2O$.

The experiments consisted in solubility determinations in which both the saturated solutions and wet solid phases were analyzed. The procedure was essentially as described in a previous paper[4] except as mentioned below. For solutions containing more than 12.4% of potassium oxalate, the samples were prepared as follows. A portion of either nickel oxalate or the complex salt was dissolved completely in a potassium oxalate solution by heating. The solution was allowed to cool in the Pyrex tube in which the sample was to be brought to equilibrium. In some of the experiments seeds were added. Seeding was found desirable, as otherwise erratic results were frequent. The excess complex salt was allowed to crystallize while the tube was rotated mechanically. The crystals were slow in forming, even after seeding. All samples were rotated for at least a week and some for much longer times. When the right solid phase was present, a week's rotation undoubtedly was sufficient, as the results were independent of the time of rotation.

For the more dilute potassium oxalate solutions (less than 12.4% potassium oxalate) the solid phase was nickel oxalate prepared either as described above or by slow addition of a nickel sulfate solution to a large excess of a potassium oxalate solution. Samples prepared by the second method were brought to equilibrium with solutions of about the same concentration as those from which they had been precipitated. The nickel oxalate was not dissolved completely and reprecipitated as in the more concentrated solutions.

The temperature was maintained at 30 ± 0.1° for at least a day previous to sampling, in either an oil-bath or an air-bath.

In the analysis of the samples,[5] the oxalate content was determined by titration with permanganate and the nickel content either by means of dimethylglyoxime or by cyanide titration.[6] Both methods for nickel were checked by the analysis of known samples to which potassium oxalate had been added. For some of the samples it was found necessary to evaporate to fumes with sulfuric acid to destroy the oxalate before titration with cyanide. The results are given in Table I and Fig. 1. In the fifth column of Table I the letter A represents solid solutions of nickel oxalate and potassium oxalate, B the complex salt, $K_2Ni(C_2O_4)_2 \cdot xH_2O$, and C potassium oxalate, possibly containing nickel oxalate in solid solution. In Fig. 1 the larger circle represents the theoretical composition of the compound $K_2Ni(C_2O_4)_2 \cdot 4H_2O$.

In the last column of Table I are given values for the percentage of water in the complex salt, calculated by algebraic extrapolation on the assumption of the formula $K_2Ni(C_2O_4)_2 \cdot xH_2O$. The theoretical value for $x = 4$ is 18.7% water and that for $x = 6$ is 25.7%. The results may be divided roughly into two groups, one indicating four and the other six molecules of water. In nearly all of the results that indicate six molecules, the percentage of nickel oxalate in solution is a little larger than that in comparable results indi-

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(1) Rammelsberg, *Ann. Physik*, **95**, 198 (1855).

(2) Dodson, *Proc. Chem. Soc.*, **27**, 260 (1911).

(3) Deakin, Scott and Steele, *Z. physik. Chem.*, **69**, 129 (1909).

(4) Vosburgh, Newlin, Puette, Peck and Dick, This Journal, **58**, 2079 (1936).

(5) The authors are indebted to Mr. Herbert A. Pohl for making some of the analyses.

(6) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley & Sons, Inc., New York, 1929, p. 320.

TABLE I

COMPOSITION OF SATURATED SOLUTIONS AND WET SOLID PHASES

Weight per cent					
Solution		Wet solid			
$K_2C_2O_4$	NiC_2O_4	$K_2C_2O_4$	NiC_2O_4	Solid phase	Dry solid H_2O, %
2.26	0.08	1.76	40.34	A	..
3.77	.55	5.42	12.52	A	..
5.67	.57	4.42	32.84	A	..
8.40	1.38	13.48	23.26	A	..
11.08	2.55	18.82	30.95	A	..
12.44	3.53	12.45	24.79	A + B	..
12.44	3.53	21.88	15.82	A + B	..
14.22	3.80	26.79	18.81	B	20.3
16.74	3.28	26.67	16.27	B	17.6
18.77	3.48	30.41	21.68	B	28.5
18.78	3.39	34.05	24.93	B	17.6
19.95	3.84	28.46	16.57	B	20.2
20.50	3.77	29.62	17.66	B	19.3
20.62	3.87	31.71	21.98	B	25.2
22.12	4.02	30.95	18.82	B	21.6
23.24	4.55	32.94	20.78	B	18.2
25.82	4.67	36.54	25.56	B	19.4
26.83	4.93	36.21	22.74	B	14.7
26.94	5.13	35.83	25.55	B	24.5
26.98	5.13	33.53	20.07	B	24.1
27.11	5.20	34.42	21.91	B	23.8
30.55	5.85	35.87	18.69	B	16.5
34.08	7.39	36.84	16.01	B	16.8
33.03	6.64	41.24	18.19	B + C	..
33.31	6.81	47.91	15.80	B + C	..
33.57	6.37	43.00	18.44	B + C	..
31.07	3.34	68.80	1.30	C	..
32.51	5.56	73.19	2.22	C	..

cating four molecules. This suggests that the solid phases having the larger percentages of water were metastable and leads to the conclusion that the stable solid phase at 30° is the tetrahydrate. However, the variability in the calculated percentage of water could have been caused by a small variation in the ratio of nickel oxalate to potassium oxalate in the solid phase, and the conclusion as to the amount of water in the dry solid is uncertain.

In the experiments corresponding to the two tie-lines that approach the nickel oxalate corner of Fig. 1, the solid phase introduced was nickel oxalate prepared from nickel sulfate and oxalic acid. Since nickel oxalate is a hydrated salt, the direction of the lines indicates the presence of potassium oxalate in the solid phase, probably in solid solution. Other similar experiments gave similar results. The time allowed was insufficient for the establishment of equilibrium in the solid phases in these experiments.

Samples of nickel oxalate precipitated from potassium oxalate solutions were contaminated with potassium oxalate, the amount of contamination varying with the concentration of the solution. Portions of these precipitates were washed with water, dried at 110° and analyzed. The results are given in Table II.

TABLE II

COMPOSITION OF NICKEL OXALATE PRECIPITATED FROM POTASSIUM OXALATE SOLUTIONS

$K_2C_2O_4$, concn., %	[a]	3	5	7	10
Ni in ppt., %	31.83	29.37	26.74	23.44	20.26
C_2O_4 in ppt., %	46.67	47.88	49.20	50.80	51.50

[a] Precipitated from oxalic acid solution.

The conclusion of Deakin, Scott and Steele that solid solutions are formed of potassium oxalate in nickel oxalate is confirmed.

Summary

Solid solutions of nickel oxalate and potassium oxalate can exist in equilibrium at 30° with aqueous solutions containing less than 12.5% of potassium oxalate and saturated with the nickel salt. From 12.5% to saturation with potassium oxalate the stable solid phase is the complex salt $K_2Ni(C_2O_4)_2 \cdot xH_2O$ in which x is probably four.

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