(1) The powder placed in distilled water and agitated at room temperature became partly converted to needle-like crystals. All the powder was converted to needles upon prolonged agitation at 60°. The product was washed with water, alcohol and ether. Microanalyses gave 59.88% lead and 6.07% nitrogen. Theoretical values for basic lead styphnate are 59.94% lead and 6.00% nitrogen. An exact match of the X-ray diffraction powder pattern of the needles with that of a previously prepared and well-characterized pure sample of the basic salt confirmed that these needles were the basic salt.

(2) The chemically pure normal salt agitated in hot distilled water also formed needles. These needles also gave an X-ray powder pattern matching perfectly with that of the pure basic salt. The microanalyses gave 59.72% lead and 5.63% nitrogen.

(3) When the basic salt was placed in 50% alcohol containing sufficient styphnic acid to yield a *p*H of 4 and was heated to 60°, excellently formed large orange crystals of the normal salt appeared after cooling.

These experiments demonstrate the reversibility of the basic and normal salt chemical changes as well as the change of the gel powder to the basic salt. The yellow crystalline needles of the basic salt, $PbC_6H(NO_2)_3O_2 \cdot Pb(OH)_2$, are usually prepared at *p*H greater than 5 by prolonged agitation and heating of the yellow amorphous basic lead styphnate precipitate[7] in its occurring medium. The basic salt is even more insoluble than the slightly soluble normal salt.

When first formed the jelly had a marked instability, readily reverting to the normal salt on standing in its usual medium of *p*H 3 to 4. However, the dried powder obtained from the jelly, when agitated in warm water which was acidified with nitric acid until a *p*H of 3 to 4 was reached, largely dissolved, thus behaving like the basic salt. The remaining solid appeared needle-like and gave analyses of 59.25% lead and 6.05% nitrogen. These needles, formed at these low *p*H values, are believed to be a slightly impure basic salt.

[7] H. Tauson, U. S. Patent, 2,020,665 (1935).

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The Solubility of Potassium Hexafluorophosphate in Water

BY JAMES N. SARMOUSAKIS AND MANFRED J. D. LOW

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With the exception of the one value (0.432 mole/l. at 22.5°) reported by Lange and Müller,[1] no data for the solubility of potassium hexafluorophosphate, KPF_6, in water are to be found in the chemical literature. The present investigation was undertaken to supply this information in the temperature range 0 to 100°.

Experimental

Materials.—Potassium hexafluorophosphate[2] was recrystallized three times from alkaline aqueous solutions by the method of Woyski.[3] Gravimetric analysis of the recrystallized product, as described below, indicated a content of 100.0% KPF_6.

For the analytical work, nitron (Eastman Kodak Co.) was dissolved in 10% aqueous acetic acid to produce a solution approximately 5% in the reagent. Only solutions which were pale yellow in color were used; dark colored solutions were discarded.

Saturation Procedure.—An excess of potassium hexafluorophosphate was added to distilled water and the mixture stirred. For determinations above 70°, the water was made just basic to litmus with ammonia to avoid hydrolysis of the dissolved salt during the period of equilibration. Samples of the solution were then analyzed. In most cases, attainment of equilibrium at a given temperature was verified by the determination of solubilities in water alone and also in water previously supersaturated with salt. In the thermostats employed for the work, temperatures below 50° were controlled to within ±0.05°, those above 50° to within ±0.1°.

Analysis.—The analytical procedure was that of Lange[1,4,5] with slight modification. Cold nitron acetate reagent was added, dropwise with stirring, to a solution of the sample containing approximately 1 g. in 100 ml. of water at 0° until precipitation appeared complete. A 2 to 3 ml. excess of precipitating agent was then added and the mixture allowed to stand in an ice-bath for at least 4 hours. The precipitate of nitron hexafluorophosphate was collected in a Selas crucible, washed either with cold dilute acetate acid or with cold water and dried at 100 to 110° for at least 4 hours. Drying at higher temperatures usually resulted in darkening of the precipitate.

Results

The averages in wt. % of at least two experimentally determined solubilities at each temperature, *t*, °C., are given in the second column of Table I.

TABLE I

SOLUBILITY OF POTASSIUM HEXAFLUOROPHOSPHATE IN WATER

t, °C.	Wt. % Exptl.	 Calcd.	Dev., %
0	3.560	3.551	0.3
4.5	4.242	4.223	.4
10.5	5.270	5.255	.3
16.2	6.400	6.389	.2
20.2	7.30	7.28	.3
25	8.35	8.45	−1.2
30	9.69	9.80	−1.1
35	11.15	11.27	−1.1
40	12.85	12.87	−0.2
45	14.82	14.58	1.6
50	16.48	16.42	0.4
55	18.22	18.35	− .7
60	20.29	20.38	− .4
65	22.49	22.49	.0
70	24.61	24.69	− .3
75	27.29	26.94	1.3
80	29.38	29.23	0.5
85	31.96	31.57	1.2
90	34.03	33.91	0.4
95	35.88	36.27	−1.1
100	38.30	38.62	−0.8

The equation

$$\log_{10} (1/N) = -14.83906 + 1831.26/T - 4.34237 \log_{10} T$$

where N is the mole fraction of the solute and T is the absolute temperature, was obtained as a fit to the

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[1] W. Lange and E. Müller, *Ber.*, **63**, 1058 (1930).

[2] The donation of a supply of this salt by the Ozark–Mahoning Company, Tulsa, Oklahoma, is gratefully acknowledged.

[3] M. M. Woyski, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1953, p. 111.

[4] W. Lange, *Ber.*, **61**, 799 (1928).

[5] W. Lange and G. von Krueger, *ibid.*, **65**, 1253 (1932).

data by the method of least squares. Wt. % solubilities computed from this equation are given in column 3 of Table I; the % deviations of the experimental values from those calculated are recorded in column 4.

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Solvent Extraction Separation of Cobalt and Nickel with Thiocyanate and the Preparation of Nickel-free Cobalt Salts[1]

BY RODMAN A. SHARP AND GEOFFREY WILKINSON[2]

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In the course of a spallation study on cobalt,[3] it was necessary to prepare very pure cobalt metal foil targets for cyclotron bombardments. The best reagent grade cobalt salts available[4] contained about 0.25% alkali salts and 0.15% nickel as principal impurities. The alkali impurities were removed in the electrolytic process used to produce the foils but the nickel impurity persisted and interfered with the spallation experiments. No convenient procedure appears to be in the literature for the preparation of comparatively large quantities of nickel-free cobalt, although the converse can be achieved readily since cobalt forms an anionic complex with chloride which can be retained on an ion-exchange column.

As early as 1879 Vogel[5] reported the extraction of a cobalt thiocyanate complex into a 1:1 mixture of amyl acetate and ethyl ether. Subsequent study by many investigators[6-8] established the thiocyanate extraction as a standard colorimetric procedure for determining cobalt. Sandell[9] showed that nickel in considerable excess did not interfere in the colorimetric determination of cobalt with thiocyanate in an acetone–water medium due to the feeble color of the nickel–thiocyanate complex. He also found no interference from 100-fold excesses of nickel in the colorimetric extraction procedure.

Although the above observations were no guarantee that nickel was not extracting under the specified conditions, preliminary experiments with Ni^{57} tracer showed that the distribution coefficient for nickel from aqueous thiocyanate solutions into various organic solvents was indeed low. Further experiments were done using Ni^{57} and Co^{60} tracers and a variety of solvents to find the optimum conditions for removing traces of nickel from cobalt salts.

Experimental

Materials.—Mallinckrodt Analytical Reagent Grade salts were used throughout. The ethyl acetate, ethyl ether, isoamyl alcohol and *n*-butyl alcohol were Merck and Co. reagent grade. The butyl acetate was Eastman Kodak Co. White Label material, while the methyl isobutyl ketone (hexone), methyl *n*-amyl ketone and tributyl phosphate were obtained from Commercial Solvents Corporation.

The Co^{60} tracer was high specific activity processed material obtained from Oak Ridge National Laboratory. The Ni^{57} tracer was prepared by bombarding 100 mg. cobalt foils with 45 Mev. protons in the internal circulating beam of the Harvard synchrocyclotron. The Ni^{57} activity was recovered by dissolving the cobalt foil in nitric acid containing 1 mg. of nickel carrier and removing the cobalt by extracting it into ethyl acetate from a solution 0.5 *M* in HNO_3 and 5 *M* in KSCN. The Ni^{57} tracer was purified by recovering it from the aqueous phase by precipitation with NaOH and by successive precipitations from acetic acid–acetate buffer with dimethylglyoxime. The nickel dimethylglyoxime precipitate was destroyed finally with HNO_3 and evaporated with H_2SO_4 to give the final tracer solution.

The Na^{22} tracer was prepared by bombarding 20 mg. of aluminum foils with 60 Mev. protons, dissolving the aluminum in HCl containing sodium carrier and precipitating the aluminum with NH_4OH. Evaporating the supernate with concd. HNO_3 gave Na^{22} as the nitrate.

Analyses.—Cobalt and nickel concentrations in the stock solutions were determined by adding H_2SO_4 to an aliquot of the concentrate, evaporating to dryness, and weighing the anhydrous sulfates. Thiocyanate concentrations were determined by titrating aliquots of the stock solutions against silver nitrate with ferric ion indicator.

Apparatus and Procedure.—Ten-ml. portions of aqueous solution were equilibrated with an equal volume of organic solvent by shaking for 30 seconds once every five minutes over a period of 30 minutes. The solutions were contained in four-ounce polyethylene bottles and were held at constant temperature (±0.5°). After equilibration, 4-ml. aliquots of the two phases were pipetted into 5-ml. glass vials and counted in a well-type NaI (Tl) scintillation counter. After subtracting background to obtain net activities, the distributing coefficient K_d was calculated as K_d = (net activity of organic phase aliquot)/(net activity of inorganic phase aliquot). The errors in the K_d values were less than 3% for $0.01 < K_d < 100$. Beyond these limits errors increased due to small interphase contaminations.

Results and Discussion

To allow economical purification of cobalt salts, cobalt and thiocyanate concentrations were chosen to allow the maximum cobalt concentration consistent with complete extraction. With trace amounts of cobalt, there was little point in using aqueous phases more than 2 *M* in thiocyanate as the K_d for cobalt increased only slowly beyond this point. In concentrated cobalt solutions, thiocyanate was consumed in complexing and about 13 moles SCN^-/mole Co over and above the 2 *M* value were needed for complete extraction. At 0° 0.35 *M* $Co(NO_3)_2 \cdot 6H_2O$ with 5 *M* NaSCN gave the maximum cobalt concentration which was 99% extractable without precipitation in the aqueous phase. Slightly higher concentrations were possible with NH_4SCN.

Using NaSCN, thirteen solvents were tested with Ni^{57} tracer (see Table I). Diisobutyl ketone, dichlorodiethyl ether, 2-ethylhexanol and dichlorodiisopropyl ether gave precipitates under the stated conditions. Ethyl ether gave three phases as is observed in the ethyl ether extraction of high concentrations of iron from HCl solutions. In this case the middle phase was rich in cobalt and the bottom one rich in nickel. The three solvents giving the lowest K_d for nickel were hexone,

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[1] This work was supported by the Atomic Energy Commission.

[2] Chemistry Department, Imperial College of Science and Technology, London, England.

[3] R. A. Sharp, R. M. Diamond and G. Wilkinson, *Phys. Rev.*, in press.

[4] Mallinckrodt Chemical Works, St. Louis, Mo.

[5] H. W. Vogel, *Ber.*, **12**, 2314 (1879).

[6] H. Ditz, *Chem. Ztg.*, **25**, 109 (1901.)

[7] R. S. Young and A. J. Hall, *Ind. Eng. Chem., Anal. Ed.*, **18**, 265 (1946).

[8] E. B. Sandell and R. W. Perlich, *ibid.*, **11**, 309 (1939).

[9] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1950, p. 282.