solution and compensating plates have different dispersions. To correct for such gain or loss of fringes plots were made[4] of the compensator plate reading *versus* concentration of each solute, at closely spaced values of concentration, and the necessary correction determined from the graph. The refractive indices are all relative to the refractive index of water for which an average of literature values, $n^{20} = 1.334468$ at $\lambda = 5461$ Å., was selected. The refractive indices of potassium ferrocyanide and ferricyanide were determined with a Bausch and Lomb immersion refractometer at $\lambda = 5893$ Å., $n^{20}\text{D} = 1.333221$ for pure water.

Densities were measured with a modified Ostwald pycnometer. The probable error in the refractive indices is about 1×10^{-5} and in the molar refractions about ±2% (chlorides) or ±4% (fluorides).

Acknowledgment.—The authors wish to acknowledge the generous support of this work by the Atomic Energy Commission through Contract AT(11-1)-151.

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The Lead Styphnate Jelly[1]

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RECEIVED SEPTEMBER 9, 1955

During the course of investigations to determine a method of preparation of the pure, explosive normal lead salt of styphnic acid (2,4,6-trinitroresorcinol) we noted that a jelly may result from solutions of soluble styphnate and a lead salt mixed at room temperatures. We undertook preliminary studies of the nature of this jelly both because of its possible chemical and physical relationship to the desired salt and to determine other useful characteristics of this novel heavy metal–organic jelly of potentially explosive constitution. We noted that Miles[2] employed lead nitrate and magnesium styphnate; however, solutions of lead acetate and styphnic acid formed a jelly.[3] Using resorcinol or its mono- or dinitro derivatives in place of styphnic acid, we found no jellies under comparable conditions. Salts of zinc and magnesium did not form jellies with styphnic acid solutions.

We found that the jelly was translucent and slightly yellow when freshly prepared, and became more opaque and yellow on standing. It was made sufficiently rigid to permit slicing or the inversion of its container without textural change. Agitation converted the jelly to a gelatinous precipitate which did not regain its original rigidity.

We observed that by mixing at room temperatures, saturated solutions of lead acetate trihydrate and styphnic acid formed the jelly directly. The addition of molar lead nitrate to a solution of styphnic acid saturated at 20° did not form the jelly until the addition of base sufficient to bring the *p*H to 2.8. As the *p*H of the styphnate solution was raised, the yield of gel became greater, with an increasing proportion of gelatinous precipitate mixed with the jelly. With styphnate solutions of *p*H greater than 5.5, addition of the lead nitrate did not cause the formation of the jelly, giving way to a more granular, yellow precipitate. In every instance observed, hardening of the jelly caused a sharp drop in *p*H.

We found the sequence of addition and the concentration of reagents to be critical. For example, the jelly was produced by the dropwise addition of 2 *M* sodium hydroxide to a solution of a rapidly agitated, saturated solution of styphnic acid containing more than a quarter equivalent of lead nitrate. Sufficient base was added to bring the *p*H to 3.7. However, when a 0.1 *M* lead nitrate solution was added dropwise to a rapidly agitated, saturated solution of styphnic acid which was previously brought to a *p*H of 3.7 by addition of sodium hydroxide, crystals precipitated without any apparent preliminary gelation. Furthermore, when two equivalents of 1 *M* lead nitrate were added rapidly to an unagitated styphnic acid solution at *p*H 3.7, the jelly was obtained again.

The jelly, prepared by a special method, gave way to fibrous crystals on standing, Miles reported. He analyzed the crystals for PbO and loss of water and found them to be a normal salt of lead styphnate which was able to lose two moles of water. These fibers spontaneously decomposed to the common monohydrate[4] of the normal salt of lead styphnate, $PbC_6H(NO_2)_3O_2\cdot H_2O$, usually called normal lead styphnate. This normal salt was also obtained directly by allowing the usual preparation of the jelly to stand at room temperature. Purer preparations of the normal salt are prepared by crystallization from hot solutions of *p*H 2 to 5 with or without the temporary jelly formation.[5]

Our attempts to isolate the dried component of the jelly by freeze–drying techniques have only yielded crystals of the impure normal salt. We suspected that shrinking and washing the jelly to remove possible reactants might keep the component of the jelly in its occurring chemical form. We obtained a yellow powder by shrinking the jelly with 1,4-dioxane, washing it briefly with water and alcohol, and drying it with ether. Under the microscope the powder appeared amorphous and gave an X-ray diffraction powder pattern lacking the many orientation planes of the normal and basic[6] lead styphnates.

Several analyses of the powders showed a variation in content of Pb, C, N and in loss of water of successive preparations, with no indication of a stoichiometric relation. The minimum lead obtained was 52.3% in contrast to 43.1% for the fibrous crystals of Miles. The amount of lead in the powder increased toward 60% with increased *p*H of the jelly's preparation medium. X-Ray powder patterns of successive preparations were not comparable, none showing strong orientation. The slight solubility and chemical sensitivity of the powder sharply limited the investigation of its solution properties.

Attempts to crystallize the gel component from the powder resulted in the following observations.

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[1] A contribution from the Institute of Science & Technology, University of Arkansas, Fayetteville, Arkansas. Studies supported by U. S. Navy Bureau of Ordnance, Contract NOrd 10,417.

[2] F. D. Miles, *J. Chem. Soc.*, 2532 (1931).

[3] F. M. Garfield, U. S. Patent 2,295,104 (1942).

[4] A. Stettbacher, *Nitrocellulose*, **8**, 3 (1937).

[5] S. D. Erlich, B. M. Franz and J. W. Wilkinson, U. S. Patent 2,150,653 (1939); W. Brun, *ibid.*, 2,202,647 (1940).

[6] W. Brun, *ibid.*, 1,942,274 (1934); 2,137,234 (1948); 2,275,169 (1942); A. L. Hitchens, Jr., and F. M. Garfield, *ibid.*, 2,265,230 (1941).

(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

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RECEIVED AUGUST 1, 1955

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.	Wt. % 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).