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-1-

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TOPICAL REPORT

on

THE SOLUBILITY OF SODIUM PHOSPHATE IN SODIUM HYDROXIDE SOLUTIONS

by

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-3-

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THE SOLUBILITY OF SODIUM PHOSPHATE IN SODIUM HYDROXIDE SOLUTIONS

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ABSTRACT

Data are presented on the solubility of trisodium phosphate in 10 to 50 per cent sodium hydroxide solutions at temperatures ranging from 25° to 100°C.

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-4-

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TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION.	5
SUMMARY	6
EXPERIMENTAL RESULTS.	6
APPENDIX I.	13
Description of Apparatus	13
Operating Procedure.	13
Preparation of Caustic Soda Solution	14
Method of Sampling	14
Method of Analysis	15
APPENDIX II	17
Solubility Data.	17

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INTRODUCTION

This investigation was carried out in conjunction with the development of a process for recovering thorium and uranium from monazite sand concentrates. The details of this process are described in reports BMI-243 and BMI-243A, dated September 15, 1950.

When monazite is reacted with a solution of caustic soda, the metal phosphates in the sand are converted to metal hydroxides and trisodium phosphate. The metal hydroxides are separated from the solution by filtration under conditions (diluted solution and elevated temperature) such that the trisodium phosphate and excess sodium hydroxide remain in solution. Since a large excess of sodium hydroxide is used for the reaction, it is desirable to recover it as free as possible from phosphate so that it can be recycled. This may be accomplished by crystallizing the trisodium phosphate from a concentrated sodium hydroxide solution.

In the course of working out the extraction procedures for monazite, phosphate determinations were made on the sodium hydroxide solutions from which the trisodium phosphate had been removed at about 25°C. These separations were not made under completely controlled conditions, and there were unexpected variations in solubility. Hence, it became desirable to make more precise determinations of the solubility of trisodium phosphate at several concentrations of sodium hydroxide and at several temperatures.

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SUMMARY

By use of the equipment and techniques described in the Appendix, the solubilities of trisodium phosphate in sodium hydroxide solutions were determined at 25°, 50°, 75°, and 100°C. over a range of sodium hydroxide concentrations from 10 to 50 per cent. At sodium hydroxide concentrations above about 36 per cent by weight, the sodium phosphate solubilities are about 1.3 per cent, or lower, and nearly the same at all temperatures. They decrease as the sodium hydroxide concentration increases, to about 0.2 per cent at 50 per cent sodium hydroxide concentration. At 75 and 100°C. the sodium phosphate solubility increases in a regular manner as the sodium hydroxide concentration decreases. However, at 50 and 25°C., maxima occur at concentrations of about 28 and 36 per cent sodium hydroxide, respectively, and minima at about 24 per cent.

These results show that trisodium phosphate can be most satisfactorily removed from sodium hydroxide solutions at 40 per cent sodium hydroxide concentration, or higher, the temperature being practically immaterial, or it can be removed satisfactorily from 15 to 30 per cent sodium hydroxide at 25°C.

EXPERIMENTAL RESULTS

The literature on solubility of trisodium phosphate in the presence of sodium hydroxide was inadequate for present purposes. Seidel⁽¹⁾

(1) Seidel, "Solubility of Inorganic and Metallo-Organic Compounds", Third Ed., Vol. 1, page 1287 (D. Van Nostrand - 1940).

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gives solubilities at two concentrations of sodium hydroxide at temperatures of 150°, 250°, and 350°C. Also, the solubility in water only is given at numerous temperatures from 0° to 350°C. Seidel⁽¹⁾ also gives a number of points for the system NaOH, H₃PO₄, and H₂O at 25°C. All but four points, however, involve the acid salts rather than trisodium phosphate.

The results of the present study are best shown graphically (Figures 1, 2, and 3). At 75° and 100°C., the curves are perfectly regular, the solubilities of trisodium phosphate increasing with decreasing sodium hydroxide concentration. Above about 30 per cent sodium hydroxide, the curves nearly coincide. However, there may be a break in reality, though it was not detected, since the crystals above about 30 per cent sodium hydroxide were chunky and heavy while, at lower concentrations, the crystals were needle-like.

At 25°C., the solubility curve is very different. There seems to be a region where the solubility depends on which form of the solid phase (chunky or needle-like crystals) is present. Near 36 per cent sodium hydroxide, both forms may be present. Above 36 per cent sodium hydroxide, there appears to be a continuation of the solubility curve of needle-like crystals, though these crystals are probably unstable above 36 per cent sodium hydroxide. Above 36 per cent sodium hydroxide, the trisodium phosphate solubility is about the same as at 75° and 100°C.

At 50°C., a similar situation prevails, namely, that above 36 per cent sodium hydroxide the sodium phosphate solubility is about the same as at 25°, 75°, and 100°C., but below 36 per cent sodium hydroxide,

(1) Seidel, "Solubility of Inorganic and Metallo-Organic Compounds", Third Ed., Vol. 1, page 1290 (D. Van Nostrand - 1940).

FIGURE 1. SOLUBILITY OF TRISODIUM PHOSPHATE IN SODIUM HYDROXIDE SOLUTIONS AT 25 C

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FIGURE 2 SOLUBILITY OF TRISODIUM PHOSPHATE IN SODIUM HYDROXIDE SOLUTIONS AT 50°C

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FIGURE 3. SOLUBILITY OF Na_3PO_4 IN NaOH AT 75 C AND 100 C

there is a region of instability where both types of crystals may be present. This is preceded by a region where only the needle-like crystals exist. This portion of the solubility curve contains a minimum.

The compositions of the crystals were not determined, the graphs being drawn as though the phases had been pure trisodium phosphate.

The numerical values, from which the curves were constructed, are given in Appendix II.

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-12-

SECRET

APPENDIX

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APPENDIX I

Description of Apparatus

On account of the corrosive effect of hot and/or concentrated sodium hydroxide solutions on glass, stainless steel apparatus was used for the solubility determinations. The equilibrium vessel was a cylinder 6.3 cm. in diameter and 15 cm. deep. While in a thermostatically controlled bath, the vessel was closed with a rubber stopper bearing (1) a metal-stem thermometer; (2) a stainless steel tube, 0.63 cm. in diameter, connected at the bottom to a porous stainless steel filtering disk, 5.3 cm. in diameter; and (3) a glass tube for pressurizing the vessel to withdraw samples. Both the metal tube and the glass tube were fitted with short lengths of rubber tubing closed by screw clamps.

Operating Procedure

The operating procedure was as follows: (1) the desired weight of saturated sodium hydroxide solution was siphoned into the cylinder from its stainless steel storage vessel; (2) water was added to give the desired concentration of sodium hydroxide; (3) the cylinder was then heated on a hot plate and the contents stirred mechanically with a stainless steel stirrer; (4) an excess of either $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ or partly dehydrated phosphate (approximately $\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$, obtained by several hours' heating of the dodecahydrate on a steam bath) was added; (5) the temperature was raised to 100-110°, 90-100°, 80-90°, or 70-80°C. for the 100°, 75°, 50°, or 25°C. determinations, respectively, and maintained

for one-half to one hour; (6) the stirring was discontinued, the stirrer removed, and the stopper placed in position, with the filter disk raised to a position just beneath the stopper, but not immersed in the solution; (7) the rubber tubes, with clamps, were placed over the glass and metal tubes and the assembly placed in a thermostat; (8) the bath temperature was controlled to $\pm 0.10^{\circ}\text{C}.$; (9) there was no provision for agitation of the solution while in the thermostat; (10) the assembly was left in the thermostat for 18-24 hours; and (11) an analytical sample was taken as described below.

Preparation of Caustic Soda Solution

The caustic soda solution was prepared by dissolving 1500 grams of solid sodium hydroxide in about 1300 ml. of CO_2 -free distilled water, allowing the solution to cool, then filtering it with suction directly into a two-liter, stainless steel Erlenmeyer flask, through a porous, stainless steel filter disk of the same type used in the sample vessel. Although the effect of sodium carbonate was not completely eliminated, since the solutions were handled briefly in air, and since sodium carbonate has a slight solubility in an unsaturated solution of sodium hydroxide, the amount of sodium carbonate present was only 0.2 to 0.3 per cent.

Method of Sampling

When the equilibrium solution in the thermostat was to be sampled, the stainless steel filter was lowered into the solution by sliding its support tube further down through the rubber stopper. The glass tube in

the rubber stopper was connected to a source of air pressure (1-1.5 pounds) for the filtration. A glass sample tube was attached to the steel tube of the filter with rubber tubing. For the determinations at 75° and 100°C., this connecting tube was heated by a resistance wire winding. The first 10-ml. portion of solution, possibly containing water condensed inside the filter disk during the period when it was above the solution, was discarded and approximately another 10-ml. portion was collected in a tared tube. This was closed and weighed, as soon as the desired amount of sample had been collected. The sample was washed into a volumetric flask and diluted to 500 ml. Portions of 25 or 50 ml. of this solution were taken for analysis.

Method of Analysis

Analysis for sodium hydroxide, sodium carbonate, and trisodium phosphate was made by the volumetric method of McKinney and Amorosi⁽¹⁾. By this method, a titration was conducted with 0.5N hydrochloric acid at first, then with 0.02N acid near the end point, to a pH of 9.0. This gave a value equivalent to all the sodium hydroxide, one-half of the sodium carbonate, and one-third of the trisodium phosphate. The solution was further titrated to pH 5; this titration gave the sum of one half of the carbonate and one-third of the trisodium phosphate. Excess acid was added and the solution was boiled to remove CO₂. The solution was cooled and the pH was adjusted to 9.0 by titration with sodium hydroxide of known carbonate content. Finally, titration with 0.02N acid to pH 5

(1) McKinney and Amorosi, Ind. Eng. Chem., Anal. Ed., 16, 315 (1944).

gave the equivalent of one-third of the trisodium phosphate after correcting for the carbonate in the alkali. The end points of the titrations were determined by comparison of the solutions being analyzed with Clark and Lubs buffer solutions of pH 9.0 and 5.0, in the presence of both methyl red and o-cresolphthalein indicators.

APPENDIX II

Solubility Data

The percentage by weight values for sodium hydroxide concentration and trisodium phosphate content from which the solubility curves were constructed are given in Table I, pages 18 and 19.

TABLE 1. SOLUBILITY OF TRISODIUM PHOSPHATE IN SODIUM HYDROXIDE SOLUTIONS

At 25°C.		At 50°C.	
NaOH, Per Cent	Na ₃ PO ₄ , Per Cent	NaOH, Per Cent	Na ₃ PO ₄ , Per Cent
48.21	0.296	50.74	0.298
47.95	0.443	43.05	0.405
38.18	0.792	39.45	0.645
36.43	1.050	37.32	0.958
36.24	1.310	34.36	0.569
36.18	1.290	31.35	2.360
35.87	1.340	30.11	2.350
35.80	1.340	29.90	2.090
35.75	1.140	28.60	2.330
35.71	1.730	27.58	2.320
35.35	1.400	27.06	3.190
35.01	1.800	26.93	3.190
34.71	1.180	26.54	2.990
34.54	1.050	26.45	2.910
34.52	1.250	26.30	3.020
34.49	1.360	25.55	2.980
32.67	0.859	25.54	2.630
32.40	0.791	25.40	2.610
31.29	0.671	24.80	2.360
28.85	0.470	24.66	2.440
27.08	0.332	24.63	2.450
24.50	0.313	23.27	2.290
22.02	0.346	20.98	2.250
19.48	0.382	18.88	2.200
17.30	0.457	15.94	2.770
14.51	0.541	12.73	3.320
12.03	0.720		
9.66	0.986		
6.63	1.680		
At 75°C.		At 100°C.	
52.02	0.273	50.33	0.353
45.93	0.314	45.07	0.432
41.82	0.532	40.54	0.724
37.44	0.853	37.98	0.913
34.34	1.430	36.86	1.040
33.34	1.110	34.82	1.440
31.70	2.590	32.37	2.270
30.27	3.090	29.92	3.290

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-19-

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TABLE 1. (CONTINUED)

At 75°C.		At 100°C.	
NaOH, Per Cent	Na ₃ PO ₄ , Per Cent	NaOH, Per Cent	Na ₃ PO ₄ , Per Cent
26.26	5.640	28.76	3.890
25.39	6.390	25.13	6.870
22.13	7.860	23.89	7.940
20.79	9.560	23.73	8.360
20.56	10.210	21.28	9.810
19.73	11.120	21.13	11.220
15.78	14.610	17.93	15.880
13.46	16.890	16.92	16.860
9.50	20.370	14.25	21.560

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