[CONTRIBUTION FROM THE EASTERN EXPERIMENT STATION, U. S. BUREAU OF MINES]

Solubility Equilibria of Sodium Sulfate at Temperatures from 150 to 350°.[1] III. Effect of Sodium Hydroxide and Sodium Phosphate

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The present paper is the third in a series presenting the results of an investigation carried out in coöperation with the Joint Research Committee on Boiler Feedwater Studies dealing with the solubility of sodium sulfate in various solutions in the temperature range from 150 to 350°. The first paper[5] gave solubility data for sodium sulfate, in sodium hydroxide-sodium chloride solutions, and the second[6] for sodium sulfate in sodium hydroxide-sodium carbonate solutions. This paper presents data for (1) a design for a new high temperature solubility bomb, (2) the solubility of trisodium phosphate in water and in sodium hydroxide solutions, (3) data for the system sodium sulfate-trisodium phosphate-water, (4) the solid phases in this system, and (5) the effect of sodium hydroxide on the system. These studies involving the phosphate are the most complicated, and perhaps the most interesting, of the three solubility investigations.

High Temperature Solubility Bomb

The bomb originally used in the study of the high temperature solubility equilibria of sodium sulfate has been described in the first paper[5] of this series. As the investigation proceeded several disadvantageous features were found in this equipment. It has been redesigned and the difficulties have been corrected in the bomb shown in Fig. 1. The body is open at both ends to make for easy machining, with the sampler as well as the bottom held in place by studs. The necessary seals are formed by metal-to-metal contact between seats machined at 60° so that no gaskets or material other than the bomb metal comes in contact with the solution. The valve stem is large enough to eliminate sticking and danger of twisting off.

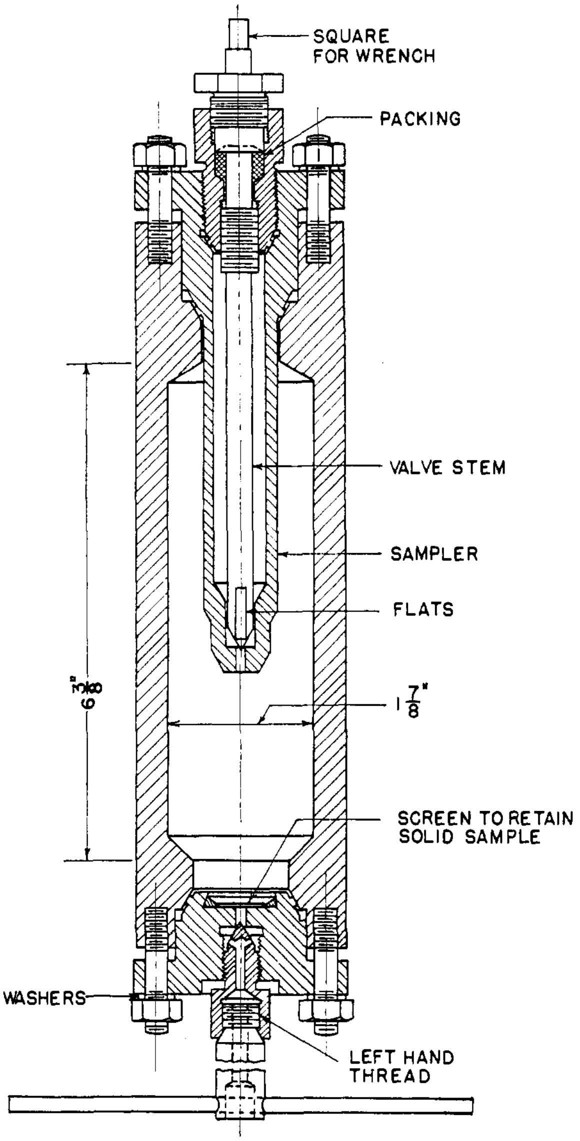

Fig. 1.—Solubility bomb (dimensions in inches): *pressure*, 200 atmospheres or 3000 lb. per sq. in.; *volume*, total with sampler in place 230 cc., below sampler 120 cc., above sampler 110 cc., sampler 18 cc.

The sampler is enclosed in the bomb to ensure sampling at the operating temperature, and the end may be equipped with a filter of carbon or fine wire screen if this is desirable. Crane pack-

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[5] W. C. Schroeder, A. Gabriel and E. P. Partridge, THIS JOURNAL, **57**, 1539-1546 (1935).

[6] W. C. Schroeder, A. A. Berk and Alton Gabriel, *ibid.*, **58**, 843-849 (1936).

ing, Style No. 250, has been cut from its case, shredded and used for packing the valve stem. In the initial run with this material the bomb was held at the operating temperature for periods from twenty-four to forty-eight hours, to bake out the oil, then the packing nut was tightened down and the sample taken. After the oil had once been removed it was necessary to tighten the nut only occasionally between solubility determinations.

The bomb has a total volume of approximately 230 cc. with the sampler in place, 120 cc. below the sampler, and 110 above, allowing ample volume for expansion of the solution at the high temperatures with sufficient solution in the bomb to ensure a liquid sample. The sampler holds about 18 cc.

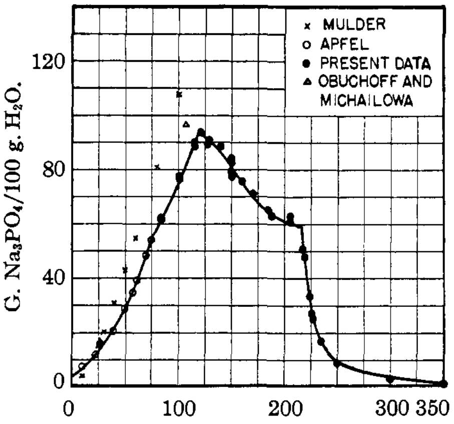

Fig. 2.—Solubility of sodium phosphate in water.

The drain plug and screen shown at the bottom of the bomb make it possible to blow out the solution leaving a solid sample that may be cooled to room temperature out of contact with water. This prevents rehydration and change in crystallographic form. It should be noted, however, that this procedure leaves the bomb filled with steam at atmospheric pressure which may condense to give a small amount of liquid in the solid. The wrench handle which opens the drain plug is hollow and the solution blows through it to the outside of the thermostat. This method of removing water from the solid has been used at pressures up to 160 atmospheres (2400 lb. per sq. in.), and while the solution leaves with considerable violence, no real danger or difficulty has been experienced. The wrenches for opening the valve stem and drain plug should be long enough so that they can be inserted from the outside of the thermostat, a procedure which will both protect the operator and eliminate temperature changes before sampling. The operation of the bomb was essentially as described in the first paper of this series.[5]

Solubility of Sodium Phosphate in Water and Sodium Hydroxide Solutions

Mulder[7] and Apfel[8] have shown that the solubility of trisodium phosphate in water increases rapidly with temperature from 0 to above 100°. Above 25° Mulder's values as shown in Fig. 2 are progressively higher with temperature than those given by Apfel. Since two determinations by the present authors made at 83 and 101° are in good agreement with results of Apfel, it seems reasonable to conclude that his values are probably more accurate throughout most of the temperature range. Figure 2 also shows two values recently reported by Obuchoff and Michailowa[9] for the solubility of trisodium phosphate at 25 and 105°. The point at 25° agrees with the results of Mulder and Apfel, but at 105° the value is slightly higher than that obtained in this investigation. Obuchoff and Michailowa also give values for the solubility of trisodium phosphate in sodium chloride solutions at 25 and 105°.

The curve shown in Fig. 2 indicates at least four solid phases. Apfel thought that $Na_3PO_4 \cdot 12H_2O$ existed from 0 to 40°, $Na_3PO_4 \cdot 10H_2O$ from 50 to 60°, and $Na_3PO_4 \cdot 8H_2O$ from 70 to 75°. Figure 2 indicates a change in the phase at approximately 75° that may correspond to a decrease in water content from 10 to 8 molecules, but the slopes of the curves for the two phases are so nearly alike that it is impossible to establish accurately the point for this transition. The temperature of this phase change was not studied further, since this investigation was concerned primarily with the range above 150°.

The solid phase from 120 to 215° contains 1 molecule of water, and trisodium phosphate exists in the anhydrous condition above 215°. Considerable trouble was encountered in establishing the position of the curve from 120 to

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(7) G. J. Mulder, "Schukundige Verhandelingen en Onderzoekingen, Vol. III, Pt. 2, Bijdragen tot de geschiedenis van Het Scherkungig Gebonden Water," Rotterdam, 1864; also "Solubilities of Inorganic and Organic Compounds," Seidell, Vol. I, second edition, D. Van Nostrand Co., New York, p. 662.

(8) O. Apfel, Dissertation, Technischen Hochschule, Darmstadt, 1911: also "Solubilities of Inorganic and Organic Compounds," Vol. II, second edition, p. 1432.

(9) A. P. Obuchoff and M. N. Michailowa, *J. App. Chem. U. S. S. R.*, 8, 1149–1157 (1935).

215°, due to difficulty in reaching equilibrium. Saturation in this temperature range was not obtained in twenty-four hours, even with constant rotation of the bombs, and it was necessary to run samples from forty-eight to ninety hours as well as to approach equilibrium from both the high- and low-temperature side.

Table I gives the experimental values obtained for the solubility of trisodium phosphate above 83°. The tests at each temperature represent duplicate solubility determinations and practically all of the variation is due to difficulty in attaining true equilibrium.

TABLE I

SOLUBILITY OF SODIUM PHOSPHATE IN WATER FROM 83 TO 350°

Temp., °C.	G. Na_3PO_4/ 100 g. H_2O	Hours in thermostat
83	61.1	39
	62.2	39
101	78.4	43
	76.8	43
115	88.6	48
	90.3	48
	89.8	48
121	93.2	86
129	91.1	45
	89.3	45
139	88.2	39
	88.7	39
	88.8	39
150	83.9	16
	79.8	16
	83.1	44
	78.9	44
	82.2	44
	84.1	18
	78.6	18
159	76.0	66
169	71.9	47
	70.2	47
185	66.2	48
	65.0	48
187	63.1	67
	62.0	67
204	62.0	71
	60.8	71
214	50.0	90
	50.8	90
216	48.8	65
	47.6	65
225	25.2	15
	33.7	15
	27.3	18
	27.8	18
235	17.9	17
250	8.6	17
	8.6	17
	8.5	17
300	2.4	18
350	0.15	19

The low solubility of the anhydrous trisodium phosphate above 250° is of considerable interest and indicates that this salt may be crystallized from the solution in a pure state at high temperature.

Examination with the petrographic microscope shows that trisodium phosphate monohydrate is hexagonal rhombohedral, many of the rhombs being modified presumably by the scalenohedron. Twinning lamellae are common, as in calcite. The material is uniaxial positive, and the refractive indices for white light determined by the immersion method are $\omega = 1.498$, and $\epsilon = 1.525$. Figure 3 is a photomicrograph of the monohydrate crystals.

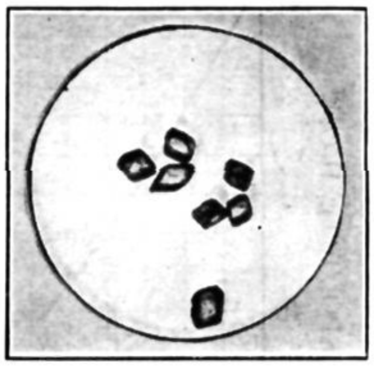

Fig. 3.—Photomicrograph (10 ×) of hexagonal rhombohedrons of $Na_3PO_4 \cdot H_2O$ formed at 160°.

Anhydrous trisodium phosphate forms colorless monoclinic crystals that are made up in their simplest form of orthopinacoid (100–$\bar{1}$00), prism, and base pinacoid (001–00$\bar{1}$). As observed perpendicular to 100-plane, the crystals are rectangular tablets with beveled edges on the longest dimensions. This view shows parallel extinction, the slower component vibrating across the crystal. It yields a symmetrical obtuse interference figure indicating that the acute bisectrix is parallel to *b* and that the plane of the optic axes lies approximately across the crystal. Twinning parallel to 100 is very common, and penetration twins are often seen. Sections observed perpendicular to 001 are roughly hexagonal and show parallel extinction. As viewed perpendicular to *b* (010-plane produced) the crystal shows a prism terminated by the "base" pinacoid (001–00$\bar{1}$). This view shows oblique extinction, the slower component forming an angle of about 10° with the *c*-axis. Crystals lying on prism faces show low birefringence, no definite extinction and yield an interference figure denoting an optic axis nearly normal to the face. Since the optic axes are symmetrically placed on the prism faces, the acute bisectrix parallels *b*. Anhydrous trisodium phosphate is optically positive and $2V$ is large. The axial plane is parallel to X; $b = Z = B_{x_a}$; $Y \wedge c = \pm 10°$ and $r > v$ distinct. The refractive indices are $\alpha = 1.493$; $\beta = 1.499$; $\gamma = 1.508$. Figure 4 is a photomicrograph of anhydrous trisodium phosphate.

Fig. 4.—Photomicrograph (12 ×) of monoclinic Na_3PO_4 formed at 250°.

The solubility of sodium phosphate in sodium hydroxide solutions is shown in Fig. 5, and the data are given in Table II. At 150° the addition of the sodium hydroxide causes a rapid decrease in solubility, at 250° only a very slow decrease and at 350° a slight increase. It should be noted that the monohydrate is the stable phase at 150°, while the anhydrous salt is in equilibrium with the solution at the two higher temperatures.

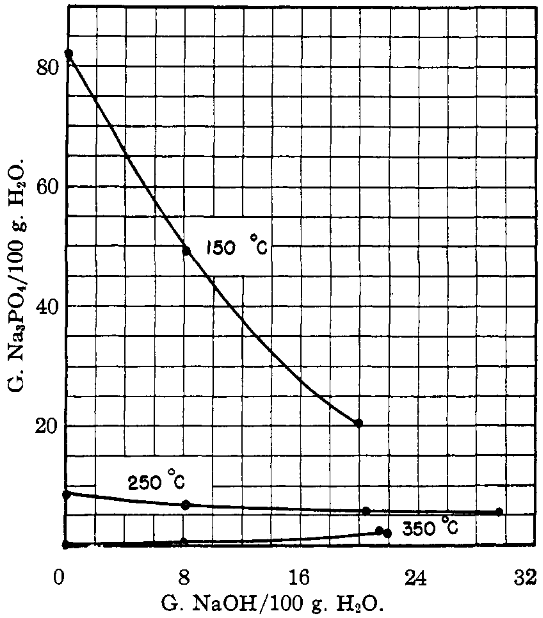

Fig. 5.—Solubility of sodium phosphate in solutions of sodium hydroxide at 150, 250 and 350°.

TABLE II

SOLUBILITY OF SODIUM PHOSPHATE IN SODIUM HYDROXIDE SOLUTIONS FROM 150 TO 350°

Temp., °C.	G./100 g. H_2O	
	NaOH	Na_3PO_4
150	Water	82
	8.2	49.0
	20.0	20.6
250	Water	8.6
	8.2	7.0
	20.6	5.5
	29.5	5.7
350	Water	0.15
	8.0	0.44
	21.9	2.0
	21.3	2.2

Sodium Sulfate-Sodium Phosphate-Water from 150 to 350°

The isotherms for the system involving the three components, sodium sulfate-sodium phosphate-water, at 50° intervals from 150 to 350° are shown in Fig. 6. The data for this system are given in Table III.

TABLE III

SODIUM SULFATE-SODIUM PHOSPHATE-WATER SYSTEM FROM 150 TO 350°

G. Na_3PO_4/100 g. H_2O	G. Na_2SO_4/100 g. H_2O
150°	
3.1	41.5
6.1	40.6
9.0	39.8
11.9	39.1
15.4	38.4
21.4	37.2
30.5	34.6
40.6	31.2
51.7	27.3[a]
57.4	24.9[a]
60.8	21.8[a]
65.9	20.2[a]
70.9	17.7[a]
69.7	13.5[a]
67.4	12.6[a]
69.4	6.6[a]
70.7	2.9[a]
74.9	1.8[a]
76.5	3.3[a]
80.0	3.0[a]
79.8	0.9[a]
200°	
2.9	44.6
5.8	44.9
10.0	45.6
15.1	46.2
22.2	47.2
17.9	45.8
17.8	44.9
20.1	43.6
20.5	43.8
19.3	37.8
20.3	37.3
22.5	29.2
23.7	27.0
23.9	25.4
26.4	21.2
28.4	19.5
29.3	16.0
29.5	16.1
30.9	14.2
35.4	7.6
34.6	7.6
48.9	3.0[a]
56.0	0.5[a]
250°	
2.9	46.6
6.0	47.4
8.1	48.9
8.0	48.5
8.5	48.5
9.3	45.9
8.4	42.7[b]
8.5	38.8
8.3	35.6
8.0	27.3
7.6	25.6
7.8	19.9
7.6	16.3
7.4	11.9
7.6	10.7
7.4	8.5
7.8	6.7
8.8	4.1[b]
8.1	2.7
8.5	2.2
9.5	1.1
8.3	0.5
8.6	Trace
300°	
2.0	30.7
4.9	36.8
3.5	25.2
2.7	17.8
1.8	6.9
1.7	2.8
3.7	2.4[c]
1.9	1.4
350°	
0.14	2.02
.11	1.01
.21	0.10

[a] Values not plotted on Fig. 5. [b] Possible leak in sampler. [c] Value not in agreement with other results.

At 150° the addition of trisodium phosphate to a solution saturated with sodium sulfate causes an almost linear decrease in the solubility of the sulfate. No solid phase other than sodium sulfate appears at this temperature within the range of phosphate concentrations represented in Fig. 6. The system was, however, investigated to about 80 g. of trisodium phosphate per 100 g. of water, and there is evidence of two new solid phases, one at 60 and one at 70 g. of trisodium phosphate per 100 g. of water. Somewhat above 70 g. per 100 g. of water, trisodium phosphate monohydrate appears as the stable solid phase. Above 45 g. of trisodium phosphate per 100 g. of water the data secured are not consistent enough to plot in Fig. 6, but the values are recorded in Table III. Although the experiments were run for a period of twenty hours, it is not believed that equilibrium conditions were reached with sodium phosphate concentrations above 45 g. per 100 g. of water.

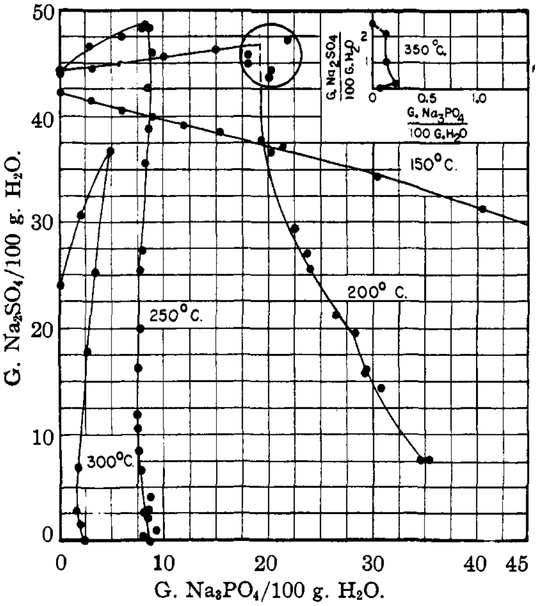

Fig. 6.—Sodium sulfate–sodium phosphate–water at 150, 200, 250, 300 and 350°.

At 200° increase in the sodium phosphate concentration caused a slight increase in the solubility of the sodium sulfate forming the solid phase on the first branch of this curve. On the second branch, the concentration of sodium sulfate decreases rapidly with increase in sodium phosphate concentration. The data for the 200° curve are given in Table III and include values above 35 g. of sodium phosphate per 100 g. of water that are not plotted in Fig. 6.

The sodium sulfate branch of the 250° curve shows a marked increase in solubility as sodium phosphate is added. The next branch is almost vertical and may include several solid phases, but there is no definite indication of any appreciable portion in equilibrium with anhydrous trisodium phosphate. The vertical branch has been studied intensively and it has been found that heating periods of more than forty hours are required to ensure equilibrium.

The solubility curve at 300° is very similar to the one at 250°. The increase in the solubility of the sodium sulfate with addition of sodium phosphate is, however, much greater. At 350° the initial solubility of both the sodium sulfate and the sodium phosphate is very low. The curve may have a sodium sulfate phase showing a rapid increase in solubility as the sodium phosphate increases but no actual points were obtained on this branch. The remainder of the curve is similar to those obtained at 250 and 300°.

Identification of Solid Phases

The chemical composition of the solid phase in contact with the solutions at 200 and 250° has been calculated from the weighed amounts of solid charged into the bomb and the amount of these solids found in the solution at the end of the determination. A detailed explanation of this method of calculation and the method of plotting used in Fig. 7 will be found in the second paper of this series.[6] Chemical analysis and petrographic examination indicated that all the solid phases, with the exception of $Na_3PO_4 \cdot H_2O$, were anhydrous at these temperatures and the calculation of the solid composition is based on this fact.

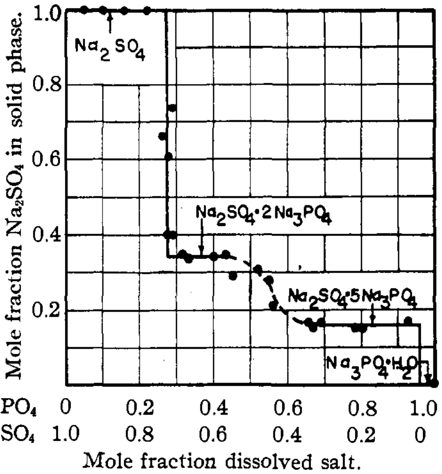

Fig. 7.—Composition of the solid phases in the sodium sulfate–sodium phosphate–water system at 200°.

The first branch of the solid composition curve for 200° in Fig. 7 indicates equilibrium with sodium sulfate. The points on the vertical branch of the curve represent equilibrium with two solid phases, Na_2SO_4 and $Na_2SO_4 \cdot 2Na_3PO_4$, and should correspond to an invariant point on the curve in Fig. 6. This is not the case, and these samples fall instead within the circle shown in Fig. 6, probably indicating the difficulty in reaching invariant equilibrium since some of these samples were run for about ninety hours. Figure 7 indicates that no appreciable amount of solid solution can be formed between Na_2SO_4 and $Na_2SO_4 \cdot 2Na_3PO_4$.

$Na_2SO_4 \cdot 2Na_3PO_4$ exists along the solid line as shown in Fig. 7 and on the second branch of the 200° curve shown in Fig. 6. $Na_2SO_4 5 \cdot Na_3PO_4$ exists on the second horizontal line shown in Fig. 7. The position of the curve between these two solid phases can only be estimated from the data now available and for that reason it has been dotted. In Fig. 7 a short branch has been assumed to exist in equilibrium with $Na_3PO_4 \cdot H_2O$, although this is not absolutely necessary on the basis of the values that have been collected.

The solid composition curve for 250° is shown in Fig. 8. A short sodium sulfate branch is followed by three points on the vertical branch indicating an invariant point, which is in good agreement with the 250° curve shown in Fig. 6. The new solid phase appears to be $Na_2SO_4 \cdot 2Na_3PO_4$. The remainder of the curve has been dotted to indicate that the values are not sufficiently precise to establish the exact composition of the solid phases.

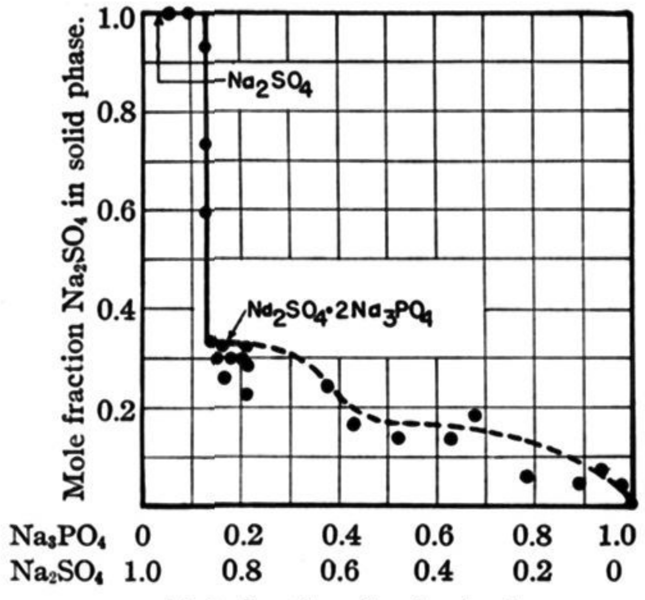

Fig. 8.—Composition of the solid phases in the sodium sulfate–sodium phosphate–water system at 250°.

All of the double salts that form from 150 to 350° are believed to be anhydrous. Chemical analysis of the solids resulting from the tests indicated an average water content of about 4%, the value being quite independent of the temperature at which the determination had been run. This water corresponds roughly to the amount of steam that would condense in the bomb and be taken up by the solid during cooling.

Examination with the petrographic microscope shows that the salt $Na_2SO_4 \cdot 2Na_3PO_4$ exists as a stable solid phase in contact with the correct solution compositions from 150 to 300°. The crystals are well-formed isometric octahedra. The index of refraction ranges from 1.477 to 1.488, due presumably to the temperature of formation and to the capacity of the salt to form a solid solution of limited miscibility with Na_3PO_4 or with other double salts. Figure 9 is a picture of the octahedral $Na_2SO_4 \cdot 2Na_3PO_4$ salt.

Fig. 9.—Photomicrograph (9 ×) of octahedral $Na_2SO_4 \cdot 2Na_3PO_4$ formed at 200°.

At 250° the index of the isotropic phase ($Na_2SO_4 \cdot 2Na_3PO_4$) ranges from 1.480 to 1.488. Further increase in Na_3PO_4 forms an anisotropic salt, presumably of the composition $Na_2SO_4 \cdot 5Na_3PO_4$. This salt appears to form solid solutions with $Na_2SO_4 \cdot 2Na_3PO_4$ and Na_3PO_4. The crystals are pseudo-octahedral but made up of monoclinic or triclinic lamellae, twinned parallel to a plane of symmetry of the octahedron. The lamellae show an extinction angle of about 10°. The crystals are biaxial negative, with $2V$ about 35–40° and $v > r$ is distinct. The refractive indices are approximately $\alpha = 1.491$; $\beta = 1.495$; $\gamma = 1.496$.

Effect of Sodium Hydroxide on the System

Table IV gives the data for the effect of sodium hydroxide, in concentrations up to approximately 20 g. per 100 g. of water, on the sodium sulfate–sodium phosphate–water system at 150, 250, and 350°.

At 150° the addition of sodium hydroxide to the sodium sulfate–sodium phosphate solution produces a marked lowering in the solubility of the sodium sulfate. The values shown in the table all represent equilibrium with solid sodium sulfate; further addition of sodium hydroxide will cause the formation of a new solid phase. Essentially this means that the sodium hydroxide also lowers the sodium phosphate concentration necessary to form a double salt.

TABLE IV

Na_2SO_4–Na_3PO_4–NaOH–H_2O FROM 150 TO 350°

G./100 g. H_2O		
NaOH	Na_3PO_4	Na_2SO_4
	150°	
7.8	3.0	28.7
7.9	6.0	28.4
8.0	8.6	28.1
7.6	14.7	27.7
19.1	2.9	16.0
19.8	5.9	15.9
19.5	8.7	15.9
19.8	12.2	15.9
	250°	
8.1	1.5	37.7
8.0	3.0	39.1
8.1	3.7	39.3
7.9	3.8	39.5
8.1	3.8	39.4
8.2	4.0	34.1
8.4	3.5	25.0
8.4	3.4	18.0
8.4	3.3	11.0
8.3	2.7	2.6
8.4	4.9	0.2
20.0	2.7	32.8
19.8	2.8	32.8
20.0	2.9	31.8
20.6	2.7	26.1[a]
20.5	2.7	18.0
20.7	2.7	11.0
20.6	2.7	5.6[a]
	350°	
8.0	0.6	21.0[a]
8.0	.6	21.0[a]
8.0	.4	20.0[a]
8.0	.4	13.8[a]
8.0	.3	5.7[a]
8.4	.3	3.9
8.0	.3	1.9[a]
21.0	1.9	54.3[a]
21.0	2.6	55.4[a]
21.0	2.7	56.6[a]
21.0	3.1	53.3[a]
21.3	2.2	46.6
21.0	1.8	31.6[a]
21.0	1.4	20.3[a]
21.0	1.2	12.3[a]
21.0	1.0	4.3[a]
21.0	1.4	0.7

[a] Calculated from initial concentrations.

At 250° the sodium hydroxide reduces the amount of sodium sulfate dissolved in the solution for those samples that are in equilibrium with this solid phase. It also causes the formation of the compound $Na_2SO_4 \cdot 2Na_3PO_4$ at lower sodium phosphate concentrations. With no sodium hydroxide this double salt forms at 8.5 g. of sodium phosphate; with about 8.2 g. of sodium hydroxide it forms at 4 g. of sodium phosphate, and with about 20.3 g. of sodium hydroxide it forms at 3 g. of sodium phosphate.

At 350° there is an increase in the solubility of both the sodium sulfate and sodium phosphate with increasing concentrations of sodium hydroxide.

In general, the effect of the sodium hydroxide on the sodium sulfate–sodium phosphate–water system is about as would be predicted from the known effect of sodium hydroxide on the solubility of sodium sulfate and sodium phosphate.

Phosphate determinations throughout all of this work were made by a colorimetric method using aminonaphthol-sulfonic acid.[10] The method was checked against a gravimetric procedure on seven samples, and the maximum error was about 2% of the phosphate present; in general, however, the error was less than 1%. Hydroxide was determined by titration to the methyl red end-point and a deduction of 2 equivalents made for each mole of phosphate present. Sulfate was determined in the usual way by precipitating as barium sulfate, igniting, and weighing, care being taken to avoid adsorption of phosphate in so far as possible.

Merck chemically pure trisodium phosphate containing 12 molecules of water was weighed directly into the bombs for most of the solubility determinations. The actual phosphate content of this material was determined by analysis. When a very high concentration of sodium phosphate was needed in solution the duodecahydrate was dried at 120° to give approximately the monohydrate or was recrystallized at 250° to give anhydrous trisodium phosphate.

Acknowledgment.—The authors wish to acknowledge the valuable suggestions and review of this paper by Dr. Everett P. Partridge of Hall Laboratories, Inc.

Conclusions

1. Data have been presented for the solubility of sodium phosphate in water up to 350°. Above 120° the solubility decreases rapidly with increase in temperature, and approaches zero at 350°. From 120 to 215° the solution is in equilibrium with the monohydrate. Above 215°, anhydrous trisodium phosphate exists as the solid phase. The solubility curve shows that it is readily possible to prepare anhydrous trisodium phosphate by crystallization at high temperature.

2. Sodium hydroxide in concentrations up to 20 g. per 100 g. of water has been found to decrease sharply the solubility of trisodium phosphate at 150°, to decrease slightly its solubility at 250°, and to cause a small increase at 350°.

3. Curves and data are presented for the system sodium sulfate–sodium phosphate–water at 150, 200, 250, 300, and 350°. Two double salts have been found at 200°, $Na_2SO_4 \cdot 2Na_3PO_4$ and $Na_2SO_4 \cdot 5Na_3PO_4$. At 250°, $Na_2SO_4 \cdot 2Na_3PO_4$ forms solid solutions with sodium phosphate or with other double salts of sodium sulfate and sodium phosphate.

4. Data are presented to show the effect of sodium hydroxide on the sodium sulfate–sodium phosphate–water system at temperatures of 150, 250, and 350°. At 150 and 250° sodium hy-

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(10) C. H. Fiske and J. T. Subbarow, *J. Biol. Chem.*, **66**, 375–400 (1925).

droxide decreases the solubility of all the solid phases. At 350° the solubilities of the various phases are increased markedly.

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Solubility Equilibria of Sodium Sulfate at Temperatures from 150 to 350°.[1] IV. Comparison of Evaporation and Equilibrium Solubility Values

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The first three papers of this series have presented data for the solubility of sodium sulfate in solutions containing sodium hydroxide, sodium chloride, sodium carbonate and sodium phosphate at temperatures above 100°.[5-7] The utility of this information should be increased materially by the determination of the degree of accuracy with which the equilibrium values can be applied to a system undergoing evaporation. In this paper comparison is made between the amount of sodium sulfate in a solution from which steam is being removed, and the amount of sodium sulfate present in the same solution at equilibrium. The test temperatures were approximately 200, 250, 300 and 350°.

Evaporation Bomb and Test Procedure.—The equipment used in these evaporation tests is shown in Fig. 1. It consisted of a nickel bomb equipped with four samplers for taking solution samples, two of which are indicated in the drawing. Heat for evaporation was supplied by a heater inserted into a tube in the bottom. The bomb body proper was enclosed in an air thermostat. The ends of the samplers protruded from the thermostat, permitting the use of the flat gasket of rubber composition shown in the diagram, without danger from carbonization.

In operation of the bomb it was charged with the desired solution, about 75% saturated with sodium sulfate and containing 300 to 350 g. of water. This solution was heated to the boiling point and put into the bomb which previously had been heated to 100°; the bomb was immediately put into the thermostat and brought up to temperature, preventing any possible crystallization of sodium sulfate from the solution before evaporation was begun. With a constant rate of heat input to the heater steam was led off through the needle valve to maintain constant pressure. The first sample was taken after removal of 3 to 5 g. of water more than the amount necessary to produce saturation and the other samples were taken at various subsequent periods during the evaporation. After the last sampling, the remaining solution was blown out through the drain plug shown in the side of the bomb or evaporation was continued to dryness.

The temperature could be maintained easily within 2° of any desired value. In all of the runs the rate of energy input to the hot tube in the bottom of the bomb was

TABLE I

COMPARISON OF EVAPORATION AND EQUILIBRIUM SOLUBILITY VALUES FOR SODIUM SULFATE IN WATER: SOLID PHASE, SODIUM SULFATE

Run	Sample	Temp., °C.	Pressure[a] lb./sq. in.	Na_2SO_4, g./100 g. H_2O		Scale thickness, inch[c]
				Evapn.	Soly.[b]	
4	1	197	200	46.3	44.5	0.11
	2	197	200	44.8	44.5	
	3	196	205	45.0	44.5	
	4	196	200	44.0	44.5	
18	1	201	210	46.0	44.5	.09
	2	201	205	45.6	44.5	
	3	200	200	45.4	44.5	
	4	199	200	44.8	44.5	
20	1	224	330	2.02[d]	45.5	.14
	2	224	320	45.5	45.5	
	3	225	330	45.2	45.5	
19	1	228	360	47.7	45.7	.08
	2	226	360	45.0	45.5	
	3	225	350	44.7	45.5	
2	1	272	820	36.7	38.0	.18
	2	273	820	36.0	38.0	
	3	272	815	35.8	38.0	
	4	272	820	35.3	38.0	
3	1	310	1400	17.6	18.2	.09
	2	310	1400	17.8	18.2	
	3	309	1400	17.3	18.2	
	4	309	1400	18.1	18.2	
14	1	347	2325	2.6	2.8	.006
	2	347	2300	2.7	2.8	
	3	347	2325	2.9	2.8	

[a] Read from gage attached to bomb. [b] Value from solubility curves. [c] Approximate maximum thickness. [d] Sample in error.

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[5] W. C. Schroeder, Alton Gabriel and Everett P. Partridge, THIS JOURNAL, **57**, 1539–1546 (1935).

[6] W. C. Schroeder, A. A. Berk and Alton Gabriel, *ibid.*, **58**, 843–849 (1936).

[7] W. C. Schroeder, A. A. Berk and Alton Gabriel, *ibid.*, **59**, 1783 (1937).