[Contribution from the Department of Chemistry, Yale University]

EQUILIBRIUM IN THE SYSTEM, SODIUM PHTHALATE-SODIUM SULFATE-WATER

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In several industries at the present time, sodium phthalate is obtained as a by-product in considerable quantities and its conversion into phthalic acid has become desirable. This can be done very readily by acidifying a solution of the sodium salt with sulfuric acid and precipitating the relatively insoluble phthalic acid. To accomplish this conversion under the most favorable conditions, it is necessary to determine the equilibrium conditions at several temperatures in the four-component system, sodium phthalate, sulfuric acid and water. As a first step in this problem, the ternary system sodium phthalate, sodium sulfate and water has been investigated.

The method of investigation adopted has been to determine the solubility curves at the temperatures 0°, 25° and 35° of mixtures containing sodium phthalate and sodium sulfate in varying proportions. At the same time, the solid phases in equilibrium with the solutions have been determined. Double salt formation does not occur in the system, and at temperatures where the solid salts do not change their degrees of hydration in the presence of solutions containing the other, a solubility isotherm consists of two intersecting curves, each with one of the sodium salts as the solid phase. At the univariant point where the two curves intersect, the solution, saturated with the two salts, has a fixed composition. This type of isotherm exists above 32.38°, the transition temperature of sodium sulfate decahydrate, and below 23°. Above 32.38°, the solid phases are anhydrous sodium sulfate along one curve and sodium phthalate along the other. Below 23°, the solid phases are sodium sulfate decahydrate and sodium phthalate. At 23.0°, a transition temperature exists at which the three salts mentioned, solution and vapor are in equilibrium. Between this temperature and the transition temperature, 32.38°, a solubility isotherm consists of three curves instead of two, and the solid phases may be the decahydrate, anhydrous sodium sulfate or sodium phthalate, depending on the concentrations. The three curves intersect at two univariant points; at one, the solid phases sodium phthalate and anhydrous sodium sulfate exist, and at the other, the latter salt and its decahydrate.

Experimental Part

Sodium phthalate was obtained by neutralizing phthalic acid with sodium carbonate and recrystallizing the product from water. It tends to form somewhat viscous, supersaturated solutions but crystallizes readily when inoculated. The crystals were filtered off on a Büchner funnel and dried in the air. The water of crystallization has not been previously determined with certainty. In the literature it is stated to crystallize with two and with three molecules of water. A number of analyses of the hydrate were made during the investigation, either by determining sodium as sulfate or by loss in weight when the salt was heated at 120°. Different samples showed 23.02, 23.07, 23.48, 23.04, 23.02, 23.61 and 23.03% of water of crystallization. This corresponds closely to the somewhat unusual formula[1] $2Na_2P.7H_2O$, in which the calculated percentage of water is 23.09. For the salt $Na_2P.3H_2O$, the calculated percentage is 20.46.

TABLE I

SOLUBILITY DATA

Solution		Wet Residue				
Na_2SO_4 %	Na_2P %	Na_2SO_4 %	Na_2P %	Solid phases	Corresponding point in diagrams	Figs.
				$T = 0°$		
None	40.56	...	...	$2Na_2P.7H_2O$	A	1,4
0.59	40.29	6.68	64.02	$Na_2SO_4.10H_2O$ and $2Na_2P.7H_2O$	X	1,4
.42	40.28	...	...			
.68	40.01	29.53	22.17			
.63	25.83	42.21	1.45	$Na_2SO_4.10H_2O$	D	1,4
4.48	none	...	...			
				$T = 25°$		
None	43.79	...	...	$2Na_2P.7H_2O$	B	2,4
3.52	40.63	...	...			
4.39	39.98	50.34	34.70	Na_2SO_4 and $2Na_2P.7H_2O$	M	2,4
4.74	39.85	23.36	52.87			
5.48	37.99	84.39	6.79	Na_2SO_4	R	2
8.69[a]	30.88[a]	83.88	3.74			
12.62[a]	24.62[a]	81.09	4.07			
20.91[a]	13.67[a]	...	...			
6.26	35.69	47.48	4.04	Na_2SO_4 and $Na_2SO_4.10H_2O$	N	2,4
6.35	35.55	44.13	5.63			
6.36	35.31	41.59	5.04			
6.32	35.10	60.32	5.19			
6.39	34.06	41.51	3.32	$Na_2SO_4.10H_2O$	E	2,4
7.59	27.52	...	...			
9.67	21.09	...	...			
11.12	17.47	...	...			
13.61	12.35	...	...			
14.78	10.14	...	...			
16.53	7.39	...	...			
17.35	6.18	...	...			
21.75[2]	none	...	...			
				$T = 35°$		
None	46.06	...	...	$2Na_2P.7H_2O$	C	3,4
3.30	43.11	55.25	30.03	$2Na_2P.7H_2O$ and Na_2SO_4	Y	3,4
3.31	43.26	62.49	22.80			
3.21	43.39	4.86	71.65			
9.67	28.64	92.03	2.39	Na_2SO_4	G	3,4
22.38	11.25	...	...			
33.10	none	...	...			

[a] Supersaturated with respect to $Na_2SO_4.10H_2O$.

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[1] The symbol P is used throughout this article to represent the phthalate radical $C_8H_4O_4$.

[2] Richards and Yngve, THIS JOURNAL, 40, 164 (1918).

The solubility determinations at 25° and 35° were carried out in an ordinary thermostat. At 0°, ice was used. The heating effect of the surroundings was overcome by adding a little salt to the bath and the temperature was kept constant within 0.1° with little trouble. The mixtures were shaken in glass-stoppered bottles, made tight by dipping the stoppers in paraffin. Samples for analysis were drawn off through filters of glass wool directly into weighed specimen tubes and aliquot parts used for analysis. The solid residue was partly dried as rapidly as possible and the moist residue analyzed. The composition of the dry residue was obtained by the Schreinemakers graphic method.[3] Sulfate was determined gravimetrically by the usual barium sulfate precipitation. Total sodium was determined by acidifying with sulfuric acid and evaporating to dryness. The excess of sulfuric acid was removed by ignition in a current of ammonia gas, and neutral sodium sulfate was weighed. The amounts of sodium sulfate and phthalate could then be calculated. At least two solubility determinations were made at every univariant point, using samples in which the proportions of the two solid phases varied widely. The solubilities of sodium phthalate in water at the three temperatures are the average of several closely agreeing results at each temperature. The solubilities of sodium sulfate are taken from the literature.

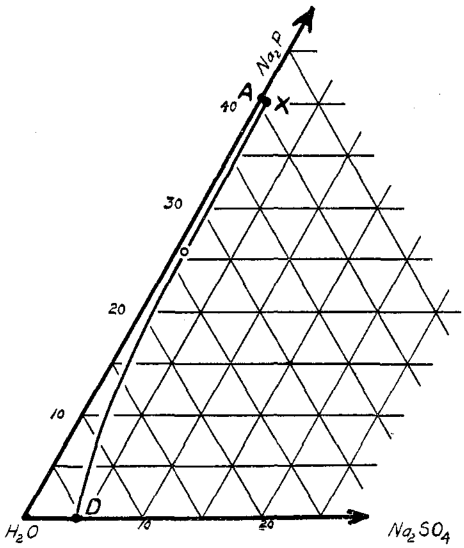

Fig. 1.—Temperature = 0°

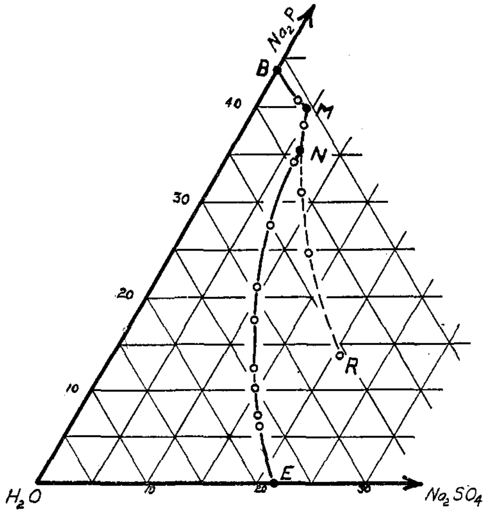

Fig. 2.—Temperature = 25°

The results obtained are given in the preceding tables. In all cases the percentages represent the parts in 100 parts of solution.

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[3] Schreinemakers, *Z. physik. Chem.*, **11**, 76 (1893).

The results given in Table I when plotted by the Schreinemakers method lead to the compositions of the solids whose formulas are given.

The addition of sodium phthalate to the saturated solution of Glauber's salt, like the addition of any soluble substance, lowers the transition temperature of the salt. There must, however, be a limiting temperature below which the anhydrous salt and the decahydrate cannot exist in stable equilibrium with the solution, due to the fact that the solution becomes saturated with sodium phthalate. This is the transition temperature mentioned above at which the three salts, solution and vapor are in equilibrium. The solubility results showed that this temperature lies slightly below 25°. It was determined by mixing the three solid salts in excess with the saturated solution in a vacuum-jacketed flask and allowing the mixture to come to equilibrium while it was constantly shaken. The same transition temperature, 23.0°, was obtained when the original mixtures were at temperatures several degrees above and below this temperature. Starting above 23°, heat is absorbed by the dehydration of the decahydrate, and the temperature falls. Starting below 23°, sodium sulfate takes on its water of crystallization and the temperature rises. The results obtained for the composition of the solution at the transition temperature are given below.

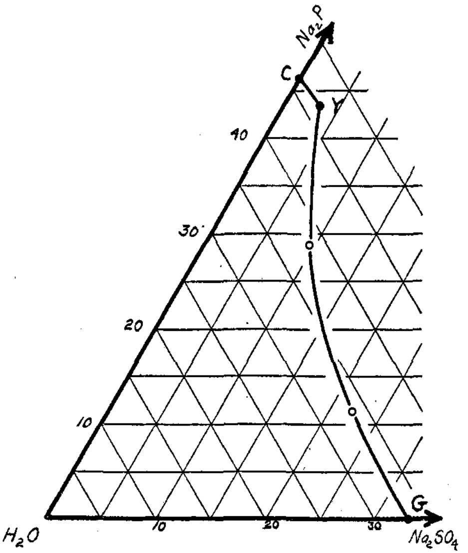

Fig. 3.—Temperature = 35°

TABLE II

COMPOSITION OF SOLUTION AT TRANSITION TEMPERATURE (23.0°)

Solid phases: Na_2SO_4, $Na_2SO_4.10H_2O$, $2Na_2P.7H_2O$.

Na_2SO_4 %	Na_2P %	Equilibrium reached on	Corresponding point in diagram
4.99	39.12	Falling temp.	O, Fig. 4
4.92	39.06	Rising temp.	

It is impracticable to show all of the solubility results and the transition temperature as projections on the base of a triangular diagram, which is the method commonly used. This is due to the decreasing solubility of sodium sulfate above its transition temperature, causing the solubility curves at 25° and 35° to intersect and confuse the diagram. The curves for each temperature are therefore shown in Figs. 1–3, and a space diagram

(Fig. 4) with temperature plotted as ordinate, gives the relation of the different curves to each other and to the transition temperature, O. The three curves radiating from O in this figure show the approximate position of the univariant solubility curves, when two solid phases are present. Thus, the curve OZ gives the composition of solutions saturated with anhydrous sodium sulfate and the decahydrate between the transition temperature at O and the transition temperature of the pure decahydrate at Z.

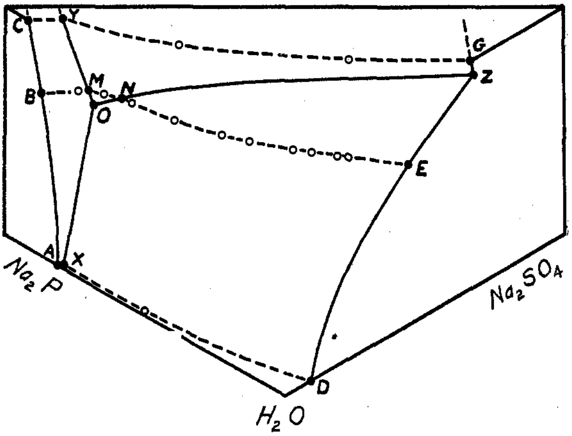

Fig. 4

Work on the four-component system mentioned at the beginning of this article is in progress.

Summary

1. The solubility relations of the system, sodium phthalate-sodium sulfate-water, at 0°, 25° and 35° have been determined.
2. The transition temperature at the quintuple point, where the solid phases are anhydrous sodium sulfate, the decahydrate and hydrated sodium phthalate, has been found to be 23°.
3. When crystallized from water solution at room temperature, sodium phthalate has the formula, $2Na_2C_8H_4O_4.7H_2O$.

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