

[CONTRIBUTION FROM THE JARVIS CHEMICAL LABORATORY OF TRINITY COLLEGE]

## Equilibrium in the System, Sodium Phthalate, Phthalic Acid and Water<sup>1</sup>

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### Introduction

The use of potassium and sodium acid phthalates as standards in volumetric analysis has been recommended by Dodge<sup>1a</sup> and by Hendrixson.<sup>2</sup> Little or no experimental evidence of the crystallizability of these salts from aqueous solution was presented in any of these papers. A phase rule study of the ternary system, potassium phthalate, phthalic acid and water has been made by Smith.<sup>3</sup> It is for the purpose of establishing the solubility relations in the system, sodium phthalate, phthalic acid and water, that a phase rule study of this system has been made.

### Experimental Part

**Methods and Materials.**—Phthalic acid was prepared by crystallizing from water sublimed phthalic anhydride obtained from the Eastman Kodak Co. Sodium phthalate was prepared by neutralizing an equivalent weight of phthalic acid, prepared as above with an equivalent weight of pure sodium carbonate. The solution was boiled to drive off all carbon dioxide, evaporated to a small volume, and inoculated with a crystal of sodium phthalate. The crystals of sodium phthalate so obtained were filtered on a Büchner funnel and dried in the air. The composition of this hydrated salt has been shown by Foote and Smith<sup>4</sup> to be  $2\text{Na}_2\text{C}_8\text{H}_4\text{O}_4 \cdot 7\text{H}_2\text{O}$ . Sodium acid phthalate was prepared by adding an equivalent weight of phthalic acid to slightly more than one-half the equivalent weight of pure sodium carbonate in solution, boiling off the carbon dioxide, and evaporating to the point of crystallization. This salt, while not a component of the system, appears as one of the solid phases and is used to prepare mixtures for analysis.

Solubilities were determined by analyzing solutions obtained by rotating for a minimum of twenty-four hours mixtures of the three components in glass stoppered tubes in an electrically controlled thermostat. At zero degrees the temperature was maintained constant by the use of ice and a small amount of salt. Temperature variations were within  $\pm 0.1^\circ$ . When equilibrium was reached, the mixture was allowed to settle, and samples for analysis were removed from the clear supernatant liquid by means of a pipet. To prevent the entrance of solid phase into the pipet, a small plug of cotton was placed in a short length of rubber tubing slipped over the end of the pipet.

Phthalic acid was determined by titration with alkali. Sodium phthalate was determined by conversion into sodium sulfate with sulfuric acid, and removing the excess of acid by ignition in a current of ammonia. Water was determined by difference.

In making up the original mixtures, wherever possible the salts were used which exist as solid phases when equilibrium is reached. The composition of the solid phases was determined by the analysis of wet residues according to Schreinemakers.<sup>5</sup>

(1) The material for this paper was taken from a thesis of Mr. William A. Sturm presented to the Graduate Committee of Trinity College in partial fulfillment of the requirements for the Master of Science degree.

(1a) Dodge, *J. Ind. Eng. Chem.*, **7**, 29 (1915); *THIS JOURNAL*, **42**, 1655 (1920).

(2) Hendrixson, *ibid.*, **37**, 2352 (1915); **42**, 724 (1920).

(3) Smith, *ibid.*, **53**, 3711 (1931).

(4) Foote and Smith, *ibid.*, **46**, 84 (1924).

(5) Schreinemakers, *Z. physik. Chem.*, **11**, 76 (1893).

**Experimental Results.**—Isotherms at 0, 25, 35 and 50° have been completed. Double salt formation takes place at all these temperatures. The solubility isotherms at these temperatures therefore consist of three intersecting curves, representing isothermally univariant equilibrium between the solutions and one solid phase, and two isothermally invariant points where two solid phases are in equilibrium with the solutions.

Experimental results are given in the following table. The symbol "P" is used here and in subsequent places to designate the phthalate radical,  $C_8H_4O_4$ . The figures representing the composition of the solutions at the isothermally invariant points are the average of several closely agreeing results.

TABLE I  
SOLUBILITY DATA  
Temperature, 0°

Point in figs.	Solution		Solid phases	Wet residues		
	% $H_2P$	% $Na_2P$		% $H_2P$	% $Na_2P$	
A	0.30	...	$H_2P$			
	1.68	1.93	$H_2P$			
	B	2.70	3.88	$H_2P$ ; $2NaHP \cdot H_2O$		
		1.63	6.60	$2NaHP \cdot H_2O$		
		0.50	19.26	$2NaHP \cdot H_2O$		
		.28	27.20	$2NaHP \cdot H_2O$		
C	.16	36.20	$2NaHP \cdot H_2O$			
	.16	40.74	$2NaHP \cdot H_2O$ ; $2Na_2P \cdot 7H_2O$			
D	..	40.73	$2Na_2P \cdot 7H_2O$			

Temperature, 25°					
Point in figs.	Solution		Solid phases	Wet residues	
	% $H_2P$	% $Na_2P$		% $H_2P$	% $Na_2P$
E	0.68	...	$H_2P$		
	1.98	1.67	$H_2P$		
	3.51	3.94	$H_2P$	99.63	...
F	4.48	5.52	$H_2P$ ; $2NaHP \cdot H_2O$	52.64	78.28
	2.82	7.58	$2NaHP \cdot H_2O$		
	1.85	10.85	$2NaHP \cdot H_2O$	41.50	50.67
	1.41	13.87	$2NaHP \cdot H_2O$		
	0.82	20.17	$2NaHP \cdot H_2O$		
	.56	26.04	$2NaHP \cdot H_2O$	40.89	53.32
	.48	29.22	$2NaHP \cdot H_2O$		
	.33	35.78	$2NaHP \cdot H_2O$		
	.31	37.20	$2NaHP \cdot H_2O$		
	.31	41.30	$2NaHP \cdot H_2O$		
.28	42.46	$2NaHP \cdot H_2O$	38.40	51.58	
G	.28	44.04	$2NaHP \cdot H_2O$ ; $2Na_2P \cdot 7H_2O$	4.63	20.49
H	..	43.81	$2Na_2P \cdot 7H_2O$	71.66	62.57

Temperature, 35°			
Point in figs.	Solution		Solid phases
	% $H_2P$	% $Na_2P$	
I	0.98	..	$H_2P$
	1.93	1.07	$H_2P$
	4.31	4.15	$H_2P$
	5.51	5.88	$H_2P$
J	5.83	6.38	$H_2P$ ; $2NaHP \cdot H_2O$

TABLE I (Concluded)

Point in figs.	Solution		Solid phases
	% H <sub>2</sub> P	% Na <sub>2</sub> P	
	5.32	6.60	2NaHP·H <sub>2</sub> O
	4.72	6.78	2NaHP·H <sub>2</sub> O
	3.27	9.56	2NaHP·H <sub>2</sub> O
	1.23	19.26	2NaHP·H <sub>2</sub> O
	1.08	20.84	2NaHP·H <sub>2</sub> O
	0.51	31.81	2NaHP·H <sub>2</sub> O
	.39	42.03	2NaHP·H <sub>2</sub> O
K	.34	45.90	2NaHP·H <sub>2</sub> O; 2Na <sub>2</sub> P·7H <sub>2</sub> O
L	..	45.66	2Na <sub>2</sub> P·7H <sub>2</sub> O

Temperature, 50°

Point in figs.	Solution		Solid phases
	% H <sub>2</sub> P	% Na <sub>2</sub> P	
M	1.75	..	H <sub>2</sub> P
	5.27	4.30	H <sub>2</sub> P
N	8.69	8.35	H <sub>2</sub> P; 2NaHP·H <sub>2</sub> O
	6.82	8.47	2NaHP·H <sub>2</sub> O
	5.91	9.19	2NaHP·H <sub>2</sub> O
	4.13	12.17	2NaHP·H <sub>2</sub> O
	1.68	22.20	2NaHP·H <sub>2</sub> O
	0.86	33.75	2NaHP·H <sub>2</sub> O
	.60	44.58	2NaHP·H <sub>2</sub> O
O	.55	50.93	2NaHP·H <sub>2</sub> O; 2Na <sub>2</sub> P·7H <sub>2</sub> O
P	..	50.60	2Na <sub>2</sub> P·7H <sub>2</sub> O

**The Double Salt.**—The composition of the double salt, 2NaHP·H<sub>2</sub>O, was established both graphically and by analysis. The extrapolated tie lines at each temperature intersected at points representing approximately this composition. To verify this formula, a sample of sodium acid phthalate was crystallized five times from aqueous solution at 50°. The moist crystals were dried to constant weight in a desiccator over anhydrous sodium acid phthalate and then analyzed. Water was determined by loss in weight when samples were heated to 110°. Other analyses were made by determining the sodium acid phthalate content and obtaining the water by difference. Different samples showed 4.97, 4.81, 4.76, 4.80, 4.82, 4.71, 4.40, 4.64 and 4.72% of water. For the composition 2NaHP·H<sub>2</sub>O the calculated percentage is 4.57. This formula agrees with that given by Dodge.<sup>6</sup>

### Discussion of Results

An inspection of Fig. 2 shows that a straight line drawn from the apex of the triangle representing pure water to the point within the triangle representing the composition 2NaHP·H<sub>2</sub>O passes directly through the isothermally invariant point "F." This may be interpreted to mean that sodium acid phthalate cannot be recrystallized from water at 25° if the impurity be phthalic acid. If the impurity were sodium phthalate re-

(6) Dodge, *J. Ind. Eng. Chem.*, **7**, 29 (1915).

crystallization would result in purification. By comparison of Figs. 1, 2, 3 and 4 it is observed that the isothermally invariant point representing

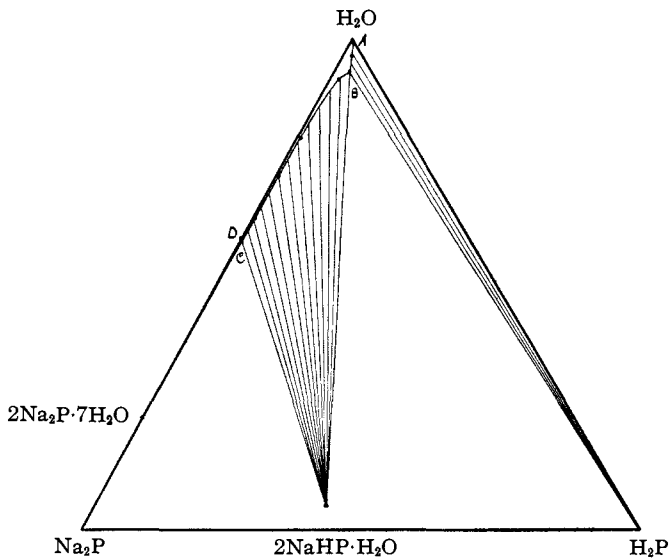


Fig. 1.—Temperature, 0°.

the composition of all solutions in equilibrium with solid phthalic acid and solid sodium acid phthalate, moves to the right of this reference line at temperatures above 25° and to the left at lower temperatures. This

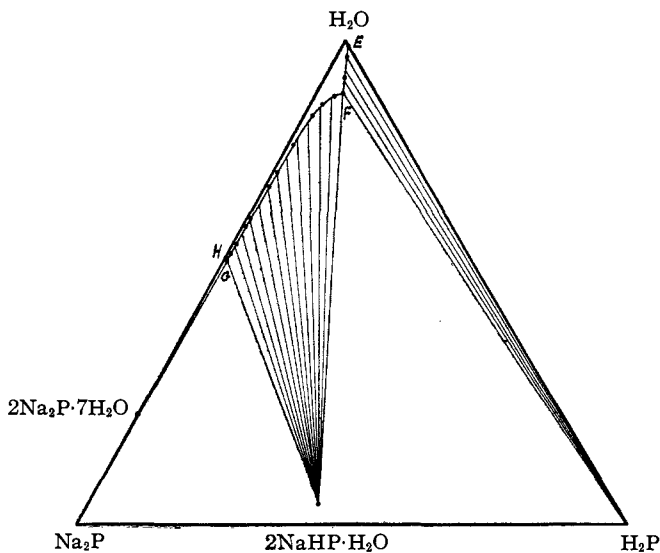


Fig. 2.—Temperature, 25°.

means that at the higher temperatures the danger of small amounts of phthalic acid contaminating the final product is lessened. A temperature

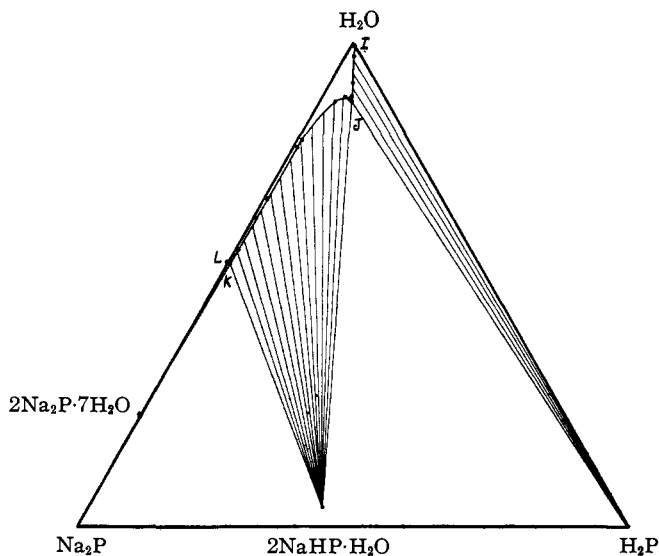


Fig. 3.—Temperature,  $35^\circ$ .

as high as  $50^\circ$  is advisable, therefore, when recrystallizing this salt from aqueous solution. It should be remembered, however, that a sufficient amount of phthalic acid as an impurity would result in a saturated solution

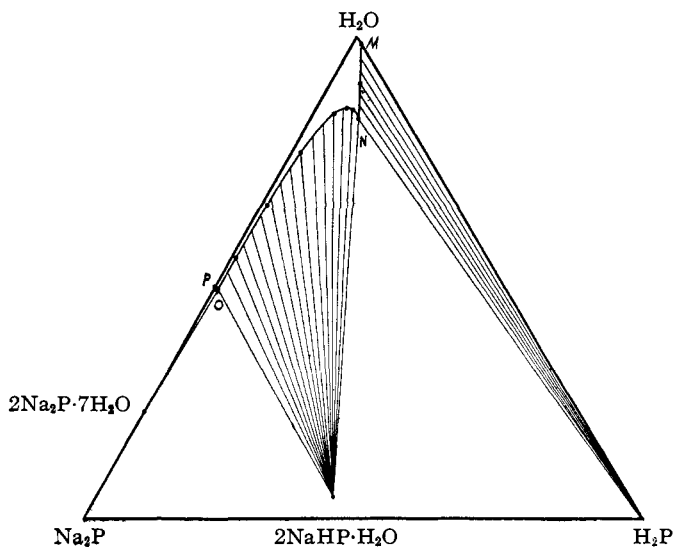


Fig. 4.—Temperature,  $50^\circ$ .

of composition corresponding to that of the isothermally invariant point even at this temperature, and that crystallization would result in the separation of both phthalic acid and sodium acid phthalate, rendering the product useless as a volumetric standard. An impurity of sodium phthalate, on the other hand, will do no harm to the final product as the composition of the solution will move to the left and away from this isothermally invariant point. It is for this reason that an amount of sodium carbonate slightly in excess of the calculated quantity is used in the preparation of sodium acid phthalate.

### Summary

1. The solubility relations in the ternary system, sodium phthalate, phthalic acid and water at 0, 25, 35 and 50° have been determined.
2. Double salt formation has been found to take place at all of these temperatures.
3. The composition of this double salt has been shown to be  $2\text{NaHC}_3\text{H}_4\text{O}_4 \cdot \text{H}_2\text{O}$ .
4. It has been pointed out that sodium acid phthalate should be recrystallized from aqueous solution at temperatures not lower than 50°.
5. It is recommended that in the preparation of sodium acid phthalate for use as a volumetric standard an amount of alkali be used which is slightly in excess of the calculated quantity.

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## Interfacial Tension of Mercury in Contact with Organic Liquids

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A study of the literature shows comparatively great discrepancies in the recorded values for the interfacial tension of mercury against different liquids, but fails to disclose the cause of these discrepancies. Impurities present in the materials used or difference in methods employed might account for the variations observed. Harkins and Grafton<sup>1a</sup> using the drop weight method obtained a value of 375 dynes/cm. for water against mercury, while Burdon and Oliphant<sup>2</sup> using the sessile drop method obtained a value of 427 dynes/cm. for the same system. It will be noted that the first mentioned method is a dynamic method; the second a static method.

(1) The material presented in this paper is from a portion of a dissertation submitted by H. Brown to the graduate school of the University of Michigan, in partial fulfilment of the degree of Doctor of Philosophy, 1932.

(1a) Harkins and Grafton, *THIS JOURNAL*, **42**, 2534 (1920).

(2) Burdon and Oliphant, *Trans. Faraday Soc.*, **23**, 205 (1927).