

If  $\alpha = 1/2$ , expression (29) can be integrated in series after replacing  $x$  by its equivalent in  $\xi$  and expanding the exponential function in a power series. Upon integration one obtains the following:

$$f = \frac{1}{R} \left\{ R - \log(1 + 2R) + \sum_{i=1}^{\infty} \frac{(-2)^i}{i(i+1)!} \left[ \frac{1}{(1+2R)^i} - 1 \right] \right\} \quad (33)$$

For other values of  $\alpha$ ,  $f$  can be determined numerically for particular values of  $R$  by means of the trapezoidal rule or some other approximate method.

In Figs. 2 and 3 are plotted values of  $f$  as a function of the average composition  $\bar{x}$  for various values of  $\alpha$ . It is seen that regardless of whether  $\alpha$  is greater or less than unity, the fraction of halogen left after treating a copolymer with zinc is less than it would be for a true copolymer of the same average composition. This is a natural consequence of the fact that the actual copolymers tend to resemble a mixture of polymers of extreme compositions. The curves for  $\alpha = 1, 2$ , and  $1/2$  were calculated by use of equations (28), (32) and (33). The other curves were drawn through points for  $\bar{x} = 0.25, 0.50$  and  $0.75$ , the corresponding values of  $f$  having been calculated by means of the trapezoidal rule using at least ten intervals for each numerical integration.

#### Discussion

Qualitative support for the theory presented here has already been obtained by Staudinger and Schneiders<sup>4</sup> as well as by Fikentscher and Hengstenberg.<sup>5</sup> Quantitative evidence in support of

the theory is not yet available, but Professor C. S. Marvel and co-workers in the organic chemistry division of this Laboratory are now working on that problem. Preliminary results on copolymers of vinyl chloride and vinyl acetate are in agreement with the theory both as to rates of polymerization and as to removal of chlorine by means of zinc.

An important point to be recognized is that the average composition of a copolymer is not by itself sufficient to specify the properties of the polymer. This follows because a copolymer with a certain composition might consist of anything between a true copolymer and a mixture of polymers of extreme compositions, depending upon the value of  $\alpha$ . It is to be expected that a true copolymer will be more uniform in its behavior than will a mixture of polymers.

The author is indebted to Professor C. S. Marvel for helpful discussions and for experimental information.

#### Summary

The structure of copolymers is considered theoretically and it is deduced that an ordinary copolymer consists of a mixture of polymers subject to a composition distribution function. It is found convenient to define a "true copolymer" as distinguished from an ordinary copolymer. The intramolecular distribution of monomer units within the polymer chains is also considered together with its effect on quantitative chemical experiments on the substances.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TRINITY COLLEGE]

## Ternary Systems. VII. Sodium Phthalate, Sodium Carbonate and Water

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Phase rule studies of the solubilities in ternary systems involving the phthalates of the alkali metals have been carried on in this laboratory for several years. As a further step along this line, this investigation has been undertaken.

#### Experimental Part

**Materials and Methods.**—The sodium phthalate used was prepared by neutralizing phthalic acid with sodium

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

carbonate and recrystallizing the product from water. Sodium carbonate decahydrate was prepared by recrystallization of reagent grade sodium carbonate from aqueous solution at zero degrees. Sodium carbonate heptahydrate was prepared by placing a saturated solution of reagent grade sodium carbonate in a water-bath kept at a temperature between 32 and 35.37° and allowing isothermal evaporation to take place. Sodium carbonate monohydrate was prepared by grinding purified sodium carbonate decahydrate to a fine powder and allowing the salt to stand in the atmosphere for about one week, occasionally grinding the lumps formed.

These hydrates, while not components of the system,

appear as solid phases and were used to prepare mixtures for analysis.

Solubilities were determined by analyzing solutions obtained by rotating mixtures of these three components in an electrically controlled thermostat until equilibrium was established. A minimum of twenty-four hours was allowed. Temperature variations did not exceed  $0.05^\circ$ . The equilibrium mixtures were allowed to settle and samples for analysis removed from the clear supernatant liquid by means of a pipet.

Sodium carbonate was determined by adding an excess of standard sulfuric acid, boiling off the carbon dioxide, and titrating the excess acid with standard base. Total sodium was determined by acidifying with sulfuric acid and evaporating to dryness in a silica dish. Excess sulfuric acid was removed by ignition in a current of ammonia. Neutral sodium sulfate was weighed and the weight of sodium phthalate calculated. Water was determined by difference.

The wet residues were partially dried between sheets of filter paper as rapidly as possible and analyzed by the same procedures. Their composition was determined by the graphic method of Schreinemakers.<sup>2</sup>

In some cases the original mixtures were accurately compounded and the composition of the solid phases determined by extrapolation of the tie lines. In making up the original mixtures, wherever possible the salts were used which exist as solid phases when equilibrium is reached.

**Experimental Part.**—Isotherms at  $25^\circ$ ,  $30^\circ$ ,  $33^\circ$  and  $40^\circ$  have been completed. No evidence of compound formation or solid solution between the carbonate and phthalate has been found at these temperatures. Sodium phthalate forms one hydrate and sodium carbonate three. The composition of the hydrate of sodium phthalate has been shown by Foote and Smith<sup>3</sup> to be  $2\text{Na}_2\text{C}_8\text{H}_4\text{O}_4 \cdot 7\text{H}_2\text{O}$ . The hydrates of sodium carbonate found were the decahydrate, the heptahydrate and the monohydrate. These are in accord with the results of Wells and McAdam<sup>4</sup> in their investigation of the binary system sodium carbonate and water. Hill and Miller<sup>5</sup> also report finding these, and only these, three hydrates in their study of the system, sodium carbonate, potassium carbonate and water. No evidence was found of the existence of the trihydrate of sodium carbonate as reported by J. W. Bain.<sup>6</sup>

Experimental results are given in Table I. The symbol "P" is used here as in previous work to designate the phthalate radical,  $\text{C}_8\text{H}_4\text{O}_4$ .

At temperatures below  $26.6^\circ$  the only solid phases which occur are sodium phthalate and the decahydrate of sodium carbonate. In the  $25^\circ$  isotherm the solubility curve consists of two branches intersecting at an isothermally invariant point. Between  $26.6$  and  $31.5^\circ$  an additional solid phase appears, sodium carbonate heptahydrate. The  $30^\circ$  isotherm therefore consists of three solubility curves and two isothermally invariant points.

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

(3) Foote and Smith, *THIS JOURNAL*, **46**, 84 (1924).

(4) Wells and McAdam, *ibid.*, **29**, 721 (1907).

(5) Hill and Miller, *ibid.*, **49**, 669 (1927).

(6) J. W. Bain, *ibid.*, **49**, 2734 (1927).

At temperatures above  $32^\circ$ ,<sup>4</sup> the transition temperature of sodium carbonate decahydrate to heptahydrate in aqueous solution, the decahydrate cannot be present. Above  $31.5^\circ$  the monohydrate of sodium carbonate makes its appearance. Consequently the  $33^\circ$  isotherm also consists of three intersecting curves and two isothermally invariant points. The transition temperature of sodium carbonate heptahydrate to monohydrate in aqueous solution has been found to be  $35.37^\circ$ <sup>4</sup>; hence at  $40^\circ$  the heptahydrate has disappeared and the isotherm consists once again of two intersecting curves and one isothermally invariant point.

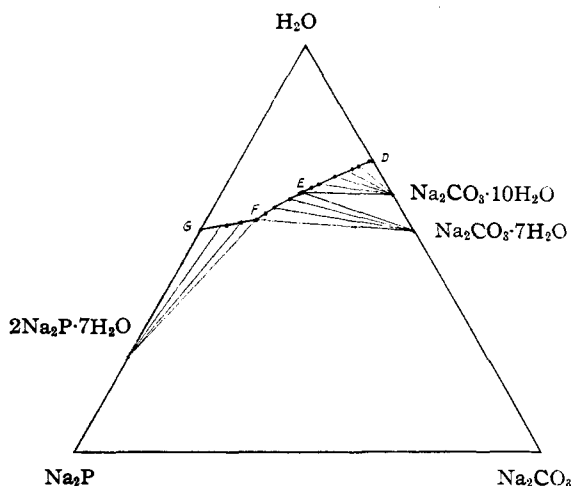


Fig. 1.—At temperature,  $30^\circ$ .

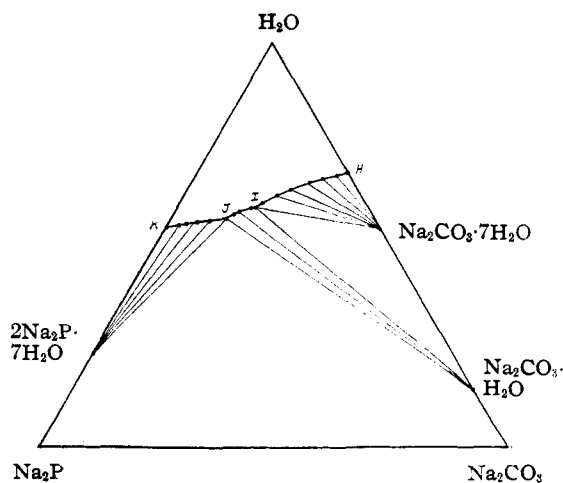


Fig. 2.—At temperature,  $33^\circ$ .

The transition temperature of sodium carbonate monohydrate to the anhydrous salt in aqueous solution has been found to be  $149^\circ$ .<sup>7</sup> The

(7) Seyer and Todd, *Trans. Roy. Soc. Can.*, **23**, 67 (1929).

anhydrous salt, therefore, does not appear in this investigation.

**The Transition Points.**—The addition of sodium phthalate to the saturated solution of

sodium carbonate decahydrate, like the addition of any soluble substance, lowers the temperature of transition of that salt to the heptahydrate. There must, however, be a limiting temperature

TABLE I  
SOLUBILITY DATA  
Original complex or wet residue  
%  $\text{Na}_2\text{CO}_3$  %  $\text{Na}_2\text{P}$   
At 25°

Point in Fig.	Solution % $\text{Na}_2\text{CO}_3$	% $\text{Na}_2\text{P}$	Original complex or wet residue % $\text{Na}_2\text{CO}_3$	% $\text{Na}_2\text{P}$	Solid phases
	22.50	...			$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
	18.13	7.95	34.65	1.56	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
	16.54	10.35	34.52	1.73	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
	13.96	15.66	33.57	3.49	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
	11.25	21.84	34.39	2.43	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
	9.72	25.96	33.99	3.16	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
	9.27	27.54	32.74	4.66	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
	8.13	31.47	30.48	8.23	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
	{ 7.31	35.22	27.29	15.20	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ $2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
	{ 7.31	35.19	5.97	58.20	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ $2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
	4.67	38.40	1.33	65.54	$2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
	3.25	39.90	0.93	67.34	$2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
	...	43.88			$2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
Temperature, 30°					
D	28.31	...			$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
	27.76	0.84	36.53	0.04	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
	25.81	3.88	35.24	0.28	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
	24.83	5.39	35.73	0.06	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
	22.11	9.98	35.29	1.05	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
	19.72	14.19	34.95	1.46	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
	18.64	16.41	35.62	0.07	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
E	{ 17.32	18.99	35.55	3.49	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
	{ 17.32	18.94	36.85	4.35	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
	16.93	19.65	35.88	7.21	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
	15.25	22.61	36.97	7.43	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
	12.99	26.92	36.42	7.53	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
	11.73	29.58	36.01	8.51	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
F	{ 10.68	32.25	28.27	20.33	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ $2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
	{ 10.74	32.27	11.34	48.88	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ $2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
	8.04	35.69	0.82	74.34	$2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
	5.11	39.08	0.43	75.59	$2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
G	...	45.27			$2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
Temperature, 33°					
H	31.96	...			$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
	29.85	2.55	41.12	0.00	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
	27.81	5.90	40.31	1.19	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
	25.18	9.10	39.87	3.24	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
	21.90	14.17	39.22	3.93	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
	19.72	17.67	41.92	2.81	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
	17.28	21.69	37.69	5.63	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$
I	{ 16.25	24.07	26.00	17.00	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
	{ 16.50	24.17	26.00	20.00	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
	15.80	24.76	25.00	21.00	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
	13.69	27.99	26.00	23.00	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
	12.75	29.52	54.46	11.57	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
J	{ 11.65	31.57	50.30	14.78	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ $2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
	{ 11.70	31.55	4.26	61.39	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ $2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
	8.32	35.34	2.67	63.36	$2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
	5.96	38.21	2.04	64.03	$2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
	3.66	41.01	1.17	65.32	$2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
	2.33	42.56	0.81	65.49	$2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$
K	...	45.43			$2\text{Na}_2\text{P} \cdot 7\text{H}_2\text{O}$

TABLE I (Concluded)

Solution		Original complex or wet residue		Solid phases
% Na <sub>2</sub> CO <sub>3</sub>	% Na <sub>2</sub> P	% Na <sub>2</sub> CO <sub>3</sub>	% Na <sub>2</sub> P	
		Temperature, 40°		
32.84	...			Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O
28.47	5.26	35.00	5.00	Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O
20.01	17.34	28.00	15.00	Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O
15.77	24.11	26.03	20.02	Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O
11.80	30.59	20.00	27.00	Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O
8.33	37.13	15.00	34.00	Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O 2Na <sub>2</sub> P·7H <sub>2</sub> O
				Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O 2Na <sub>2</sub> P·7H <sub>2</sub> O
8.32	37.21	10.07	43.37	Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O 2Na <sub>2</sub> P·7H <sub>2</sub> O
7.17	38.49	5.00	50.00	2Na <sub>2</sub> P·7H <sub>2</sub> O
3.27	43.23	3.00	46.00	2Na <sub>2</sub> P·7H <sub>2</sub> O
...	47.06			2Na <sub>2</sub> P·7H <sub>2</sub> O

below which the decahydrate and heptahydrate of sodium carbonate cannot exist in stable equilibrium with the solution, due to the fact that the solution becomes saturated with sodium phthalate. This temperature at which the solution is in equilibrium with the three solid phases, sodium carbonate decahydrate, sodium carbonate heptahydrate and sodium phthalate, is a true invariant point.

Similarly the addition of sodium phthalate lowers the transition temperature of the heptahydrate to the monohydrate. A second true invariant point exists where the solution is in equilibrium with the three solid phases, sodium carbonate heptahydrate, sodium carbonate monohydrate and sodium phthalate.

These transition temperatures were determined experimentally by mixing the three solid salts in excess with the saturated solution in a vacuum

TABLE II

COMPOSITION AND TEMPERATURE OF SOLUTIONS AT TRUE INVARIANT POINTS AT ATMOSPHERIC PRESSURE

Solid Phases: Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O, Na<sub>2</sub>CO<sub>3</sub>·7H<sub>2</sub>O, 2Na<sub>2</sub>P·7H<sub>2</sub>O

Equilibrium reached on	Temp., °C.	%Na <sub>2</sub> CO <sub>3</sub>	%Na <sub>2</sub> P
Falling temperature	26.60	8.72	33.98
Falling temperature	26.61		
Rising temperature	26.60	8.72	33.86
Rising temperature	26.60		
Average	26.60	8.72	33.92

Solid Phases: Na<sub>2</sub>CO<sub>3</sub>·7H<sub>2</sub>O, Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O, 2Na<sub>2</sub>P·7H<sub>2</sub>O

Falling temperature	31.52	11.79	31.06
Falling temperature	31.50		
Rising temperature	31.50	11.80	30.98
Rising temperature	31.50		
Average	31.50	11.80	31.02

jacketed flask and allowing the mixture to come to equilibrium with constant shaking. The experimental results were obtained by approaching the equilibrium temperature from both sides. A thermometer graduated in tenths of a degree and calibrated by comparison with a Bureau of Standards certified thermometer was used. The results obtained, together with the composition of the saturated solution, are given in Table II.

### Summary

1. The solubility relations in the ternary system sodium phthalate, sodium carbonate and water at 25, 30, 33 and 40° have been determined.

2. No compound formation or solid solution between phthalate and carbonate was observed at these temperatures.

3. One hydrate of sodium phthalate, 2Na<sub>2</sub>C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>·7H<sub>2</sub>O, and three hydrates of sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O, Na<sub>2</sub>CO<sub>3</sub>·7H<sub>2</sub>O and Na<sub>2</sub>CO<sub>3</sub>·H<sub>2</sub>O, were present as solid phases in this investigation.

4. The transition temperature at the quintuple point, where the solid phases are sodium carbonate decahydrate, sodium carbonate heptahydrate and sodium phthalate, has been found to be 26.60°.

5. The transition temperature at the quintuple point, where the solid phases are sodium carbonate heptahydrate, sodium carbonate monohydrate and sodium phthalate, has been found to be 31.50°.

6. The composition of the solutions at the quintuple points has been determined.

HARTFORD, CONN.

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