

[CONTRIBUTION FROM THE JARVIS CHEMICAL LABORATORY OF TRINITY COLLEGE]

EQUILIBRIUM IN THE SYSTEM, PHTHALIC ACID-POTASSIUM PHTHALATE-WATER

BY STERLING B. SMITH

RECEIVED JULY 7, 1931

PUBLISHED OCTOBER 5, 1931

Introduction

The use of potassium acid phthalate for the standardization of alkaline solutions in volumetric analysis has been widely adopted. Its use was first suggested by Francis D. Dodge in a paper read before the New York section of the American Chemical Society, January 8, 1904. Some years later the substance of this paper was put in print,¹ advocating the use of both the potassium and the sodium acid salts as volumetric standards. This paper was in theory only and was followed by two papers by Hendrixson² giving experimental evidence that the acid phthalates of potassium and sodium are suitable for this purpose.

In a second article, Dodge,³ after acknowledging Hendrixson's work, makes the following statement. "A saturated solution of potassium acid phthalate on chilling will deposit crystals of a more acid salt, having the formula, $2\text{KHC}_8\text{H}_4\text{O}_4 \cdot \text{C}_8\text{H}_6\text{O}_4$. A contamination of the acid phthalate with this 'tri-phthalate' would be fatal for its use as a standard, but the formation of the latter can be entirely avoided by crystallization at temperatures above 20°C."

No experimental data were given establishing this formula or this maximum temperature. It is, therefore, with the purpose of determining the possibilities of the crystallization of potassium acid phthalate from aqueous solutions that a phase rule investigation of the three component system, phthalic acid, potassium phthalate and water has been made.

Experimental Part

Materials and Methods.—Phthalic acid was prepared by crystallizing sublimed phthalic anhydride from aqueous solution.

Potassium phthalate was prepared by dissolving the best grade of potassium carbonate in water and making the solution exactly neutral to phenolphthalein by the addition of phthalic anhydride, taking care that all the evolved carbon dioxide was removed by boiling. Upon evaporating this neutral solution to a small volume and cooling, long silky needles of the neutral potassium phthalate crystallized from a very viscous sticky solution. The product resulting from this preparation is impossible to separate from mother liquor. It was found that if a small quantity of ethyl alcohol be added to the neutral solution prepared as above, the potassium phthalate will crystallize from a not at all viscous solution. Crystals prepared in this manner were filtered on a Büchner funnel and dried at 110°.

¹ F. D. Dodge, *J. Ind. Eng. Chem.*, **7**, 29 (1915).

² W. S. Hendrixson, *THIS JOURNAL*, **37**, 2352 (1915); **42**, 724 (1920).

³ F. D. Dodge, *ibid.*, **42**, 1655 (1920).

The potassium acid phthalate used in this investigation was obtained from the Eastman Kodak Company. While not a component of the system, this salt appears as one of the solid phases, and its use in the preparation of mixtures is apparent.

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, however, the temperature was maintained constant by the use of ice and a small amount of salt. Temperature variations were not over 0.1° .

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. Attempts to obtain the densities of these solutions had to be abandoned due to the viscosity of the solutions of high potassium phthalate content.

Phthalic acid was determined by transferring the sample to a weighed glass-stoppered Erlenmeyer flask, reweighing, and, after dilution, titrating with standard barium hydroxide, using phenolphthalein as the indicator.

No quantitative method was found for the determination of the phthalate radical. Potassium phthalate was determined by transferring the sample to a weighed porcelain evaporating dish, rapidly weighing, acidifying the solution with sulfuric acid and evaporating to dryness. The sample was then ignited over a Tirrel burner and the last traces of sulfuric acid removed by igniting in a current of ammonia. The resultant potassium sulfate was weighed and potassium phthalate calculated.

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. In some cases the composition of the solid phases was determined by the graphic method of Schreinemakers.⁴ In others, the original mixtures were accurately compounded, and the composition of the solid phases determined by the extrapolation of the tie-line connecting the points on the triangular diagram representing the composition of the original mixtures and the points representing the composition of the solutions after equilibrium had been attained.

Experimental Results.—Isotherms at 0 , 25 , 35 and 60° have been completed. At all these temperatures double salt formation takes place, and at the three lower temperatures two double salts have been found to exist. The solubility isotherms at these three temperatures therefore consist of four intersecting curves, representing isothermally univariant equilibrium between the solutions and one solid phase, and three isothermally invariant points where two solid phases are in equilibrium with the solutions.

At 60° one of the double salts has disappeared and the isotherm consists of but three curves representing isothermally univariant equilibrium and two isothermally invariant points.

The curve representing the composition of solutions in equilibrium with solid potassium phthalate is so short that it appears to coincide with the invariant point.

The experimental results are given in the following table. The symbol "P" is used here and in subsequent places to designate the phthalate radical, $C_8H_4O_4$. D. S. stands for the double salt, $K_2P \cdot 4H_2P \cdot 4H_2O$. The

⁴ Schreinemakers, *Z. physik. Chem.*, 11, 76 (1893).

figures representing the composition of the solutions at the isothermally invariant points are the average of several closely agreeing results.

Since the region in which double salt $K_2P \cdot 4H_2P \cdot 4H_2O$ is stable is so small, the composition of this salt could not be accurately determined by either of the previously described methods. In this case, samples of the solid phase were filtered on a Büchner funnel, centrifuged, air-dried for a short while and analyzed. The small amount of mother liquor adhering to the crystals is considered to produce but slight error as the concentration of the solutions in equilibrium with the double salt is not

TABLE I
SOLUBILITY DATA
Temperature, 0°C.

Point in Figs.	% H_2P	% K_2P	Solid phase
A	0.30	...	H_2P
	.89	1.00	H_2P
B	1.55	2.12	H_2P ; D. S.
	1.74	2.79	D. S.
C	2.01	4.01	D. S.; KHP
	1.06	8.33	KHP
	0.40	20.43	KHP
	.19	33.02	KHP
	.11	48.89	KHP
E	.10	60.4	KHP; K_2P
D	...	60.4	K_2P

Temperature, 25°C.

Point in Figs.	% H_2P	% K_2P	Solid phase
F	0.75	...	H_2P
	1.72	1.47	H_2P
	2.61	2.87	H_2P
	3.44	4.12	H_2P
G	3.77	4.80	H_2P ; D. S.
	3.93	5.41	D. S.
H	4.16	6.11	D. S.; KHP
	3.07	7.10	KHP
	2.12	9.99	KHP
	1.25	16.65	KHP
	0.93	20.35	KHP
	.77	23.33	KHP
	.58	28.71	KHP
	.55	30.26	KHP
	.54	31.23	KHP
	.47	35.70	KHP
	.36	39.70	KHP
	.28	48.16	KHP
	.27	60.97	KHP
	J	.17	74.7
I	...	74.8	K_2P

TABLE I (*Concluded*)

Temperature, 35°C.				
Point in Figs.	% H ₂ P	% K ₂ P	Solid phases	
K	0.98	...	H ₂ P	
	2.38	2.06	H ₂ P	
	3.38	3.53	H ₂ P	
	4.74	5.60	H ₂ P	
	5.29	6.35	H ₂ P	
L	5.53	6.64	H ₂ P; D. S.	
M	5.70	7.32	D. S.; KHP	
	5.10	7.43	KHP	
	4.18	8.11	KHP	
	3.48	9.16	KHP	
	3.23	9.76	KHP	
	2.32	13.09	KHP	
	1.28	21.03	KHP	
	0.89	27.07	KHP	
	.51	37.43	KHP	
	.38	48.67	KHP	
	.33	58.59	KHP	
	.26	65.69	KHP	
	.27	68.51	KHP	
	O	.28	75.6	KHP; K ₂ P
	N	..	75.8	K ₂ P
Temperature, 60°C.				
Point in Figs.	% H ₂ P	% K ₂ P	Solid phases	
P	2.58	...	H ₂ P	
	7.68	5.97	H ₂ P	
	11.14	9.64	H ₂ P	
Q	14.61	13.00	H ₂ P; KHP	
	13.19	13.13	KHP	
	8.50	12.59	KHP	
	7.46	13.10	KHP	
	4.94	16.57	KHP	
	2.15	29.66	KHP	
	0.80	49.07	KHP	
	.51	64.17	KHP	
S	.40	79.0	KHP; K ₂ P	
R	..	78.9	K ₂ P	

high. Results of analyses of various samples obtained at 0 and at 25° are as shown in Table II.

These percentages correspond most nearly to formula, $K_2P \cdot 4H_2P \cdot 4H_2O$ or otherwise expressed, $2KHP \cdot 3H_2P \cdot 4H_2O$. The theoretical composition of a salt of this formula is the following: H₂P, 67.88%; K₂P, 24.75%; and H₂O, 7.36%.

The Transition Temperature.—Since this double salt is present in the 35° isotherm and has disappeared at 60°, it is apparent that there must be between these two temperatures a transition temperature, a maxi-

TABLE II
ANALYSIS OF DOUBLE SALT

	% H ₂ P	% K ₂ P	% H ₂ O
	66.89	25.07	8.04
	66.98	25.84	7.18
	67.37	25.52	7.11
	67.43	25.61	6.96
	66.84	25.59	7.57
	66.88	25.65	7.47
	66.13	26.47	7.40
	67.97	25.50	6.53
	68.60	25.10	6.30
	70.61	23.14	6.25
	70.73	22.99	6.28
Average	67.86	25.13	7.01

imum temperature above which this double salt cannot exist in stable equilibrium with saturated solution. At this temperature, a true invariant point, three solid phases, H₂P, KHP and K₂P·4H₂P·4H₂O, must be in stable equilibrium with the saturated solution. This temperature was determined by means of a time-temperature cooling curve. A solution saturated at 60° with phthalic acid and potassium acid phthalate and containing an excess of these two salts as solid phases was placed in a Dewar flask and allowed to cool slowly and with shaking. After each few degrees drop in temperature, the mixture was inoculated with the second double salt. The temperature fell slowly until 36.32° had been reached, when it suddenly rose to a constant value of 36.66° (corr.), representing a supercooling of 0.34°. A duplicate cooling curve gave a value of 36.68° (corr.) after a supercooling of 0.6°.

Unfortunately the solution in equilibrium with the three solid phases could not be removed and analyzed as the heat change is so small that if sufficient liquid phase for analysis were present, no break was obtained in the cooling curve. It was only when the mixture was of a sloppy consistency that a break was obtained. In order to determine the composition of the solution at the transition temperature, an excess of the three solid phases with water was placed in a glass-stoppered tube and rotated in a thermostat at 36.67°. When equilibrium was attained, the solution was analyzed in the usual manner. Analyses of duplicate solutions are as given in Table III.

TABLE III
COMPOSITION OF SOLUTION AT THE TRANSITION TEMPERATURE

% H ₂ P	6.14	6.18
% K ₂ P	7.65	7.66

It is true that if the transition temperature were not exactly 36.67°, this analysis would not represent the composition of the solution at the

true invariant point but at one of the isothermally invariant points. Inasmuch as these two points are extremely close at 35° and approach each

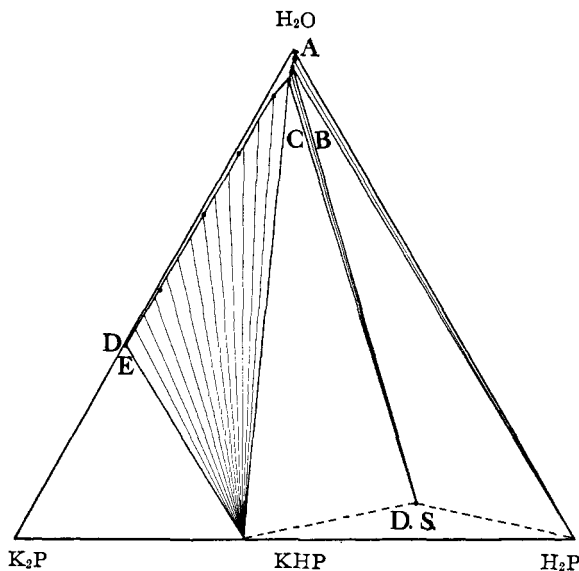


Fig. 1.—Temperature, 0° .

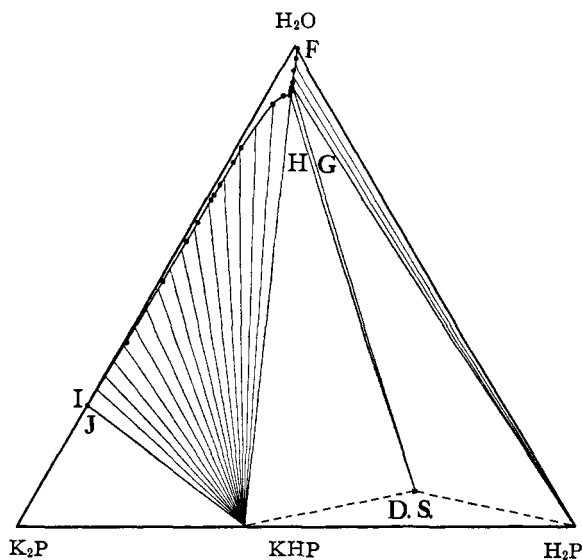


Fig. 2.—Temperature, 25° .

other as the transition temperature is approached, it is believed that any error from this source cannot be large.

Discussion of Results

In order that a salt shall be crystallizable from water at any given temperature, it is necessary that a straight line on the triangular diagram for that temperature, drawn from the apex, representing pure water, to that point on the diagram representing the composition of the pure salt in question, pass through or cut the line representing the composition of all solutions in stable equilibrium with the salt in question as the solid phase.

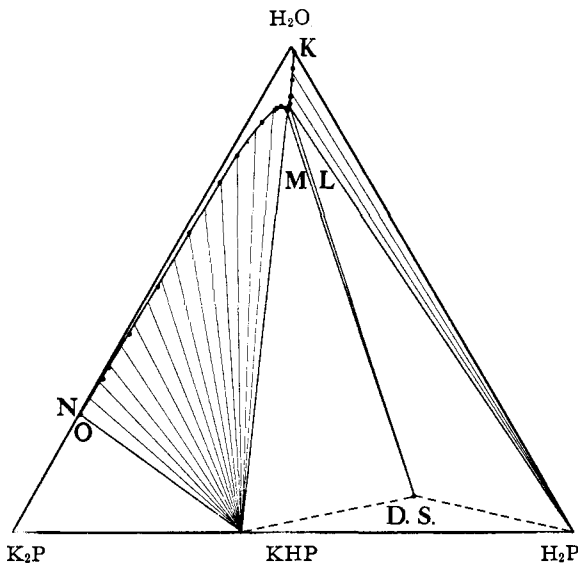


Fig. 3.—Temperature, 35°.

Careful observation of Figs. 1 and 2 shows that such a line in the 0° isotherm does not cross the line representing the composition of all solutions in equilibrium with solid potassium acid phthalate, and at 25° passes directly through the isothermally invariant point at one end of this line. At 35°, this line passes just inside the isothermally invariant point and at 60° it is well to the left of the isothermally invariant point, in both cases cutting the line representing the composition of all solutions in stable equilibrium with solid potassium acid phthalate.

This shows that potassium acid phthalate cannot be recrystallized from aqueous solution at 0°. At 25° potassium acid phthalate could be recrystallized from water if it were already pure or if the impurity were potassium phthalate. If the impurity were phthalic acid or the double salt, $K_2P \cdot 4H_2P \cdot 4H_2O$, further crystallization would not improve the quality of the product as this double salt would separate from solution along with the biphthalate. At 35°, and at higher temperatures, potassium acid phthalate can be purified by repeated crystallization from water.

It will be noticed that the composition of the second double salt, $K_2P \cdot 4H_2P \cdot 4H_2O$ or $2KHP \cdot 3H_2P \cdot 4H_2O$, found in this investigation does not agree with that found by Dodge,³ namely, $2KHP \cdot H_2P$. No evidence of any salt of this composition was obtained in this investigation. A complete phase rule study of the system was not made by Dodge, and no experimental evidence was given in support of his formula. It is apparent from the preceding discussion that potassium acid phthalate crystallized from aqueous solution at low temperatures would be contaminated with double salt, $K_2P \cdot 4H_2P \cdot 4H_2O$. It is suggested that the material analyzed by Dodge was a mixture of potassium acid phthalate and the second double salt in such proportion as to correspond to the molecular ratio, $2KHP : 1H_2P$.

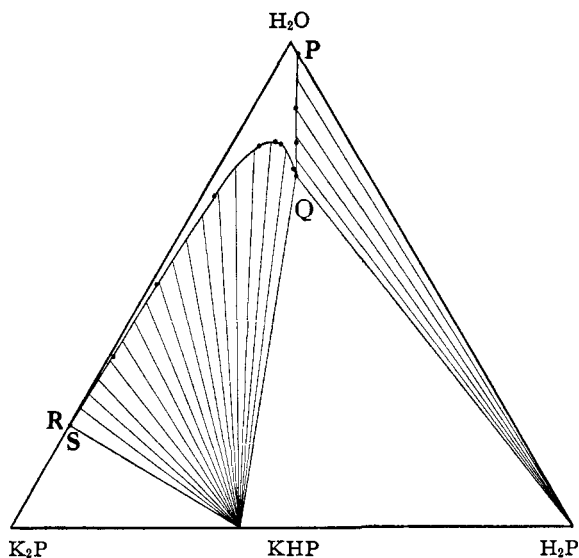


Fig. 4.—Temperature, 60°.

Summary

1. The solubility relations in the ternary system, phthalic acid, potassium phthalate and water at 0, 25, 35 and 60° have been determined.
2. A new double salt has been found and its composition established, $K_2P \cdot 4H_2P \cdot 4H_2O$.
3. The transition temperature above which this double salt does not exist in stable equilibrium with saturated solution has been found to be 36.67°.
4. It has been shown that potassium acid phthalate should be recrystallized from aqueous solution at temperatures not lower than 35°.

HARTFORD, CONNECTICUT