[CONTRIBUTION FROM THE BUREAU OF SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE SOLUBILITY AND FREEZING-POINT CURVES OF HYDRATED AND ANHYDROUS ORTHOPHOSPHORIC ACID

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The existence of a hydrate of phosphoric acid was first described by Joly[1] who prepared a crystalline acid having the composition $2H_3PO_4.H_2O$. In a study of the hydrates of the phosphoric acids Giran[2] also concluded that only one hydrate of orthophosphoric exists, but Smith and Menzies[3] the following year announced the discovery of a new hydrate having the composition $10H_3PO_4.H_2O$.

In the course of an investigation on the purification of volatilized phosphoric acid by crystallization, efforts were made by the authors in collaboration with C. B. Durgin of the Federal Phosphorus Company to prepare the different crystal forms of the acid with a view to studying the most efficient method of applying crystallization to the purification of phosphoric acid. Crystals corresponding to the anhydrous acid and also the semihydrate were very readily prepared from both volatilized and the ordinary C. P. acid, but no crystals were obtained which corresponded to the decihydrate described by Smith and Menzies.

A study was then undertaken of the equilibrium relations between crystalline phosphoric acid and water at different temperatures. The procedure followed was similar to that outlined by Smith and Menzies but the results obtained, which form the subject matter of this paper, likewise gave no positive indication of the existence of a decihydrate of orthophosphoric acid.

Preparation of Crystalline Phosphoric Acid

The starting material used in this work consisted of crystals of anhydrous phosphoric acid. These were prepared by maintaining the ordinary C. P. acid in an open vessel at a temperature of about 95° until it reached a specific gravity of approximately d_4^{25} 1.85. The solution was then cooled below 40°, inoculated with a crystal of orthophosphoric acid, allowed to stand until crystallization was complete and the mother liquor then separated from the crystals by centrifuging in a porcelain-lined centrifuge. The crystals recovered in this way were then melted at a temperature of about 50°, sufficient water was added to bring to a specific gravity of d_4^{25} 1.85, the solution inoculated as before and the process repeated thrice. The crystals were finally dried by allowing them to stand for several months over phosphorus pentoxide.

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[1] Joly, *Compt. rend.*, **100**, 447 (1885).

[2] Giran, *ibid.*, **146**, 1270 (1908); *Ann. chim. phys.*, [8] **14**, 565 (1908).

[3] Smith and Menzies, THIS JOURNAL, **31**, 1183 (1909).

Crystals of the semihydrate were prepared by adding the proper amount of water to a weighed portion of fused, anhydrous phosphoric acid, cooling below 29° and inoculating with a crystal of the hydrate.

The purity of the crystals prepared in this way and their freedom from absorbed moisture were shown (1) by analysis, (2) by the sharpness of their melting points and (3) by their rate of formation.

Method of Analysis.—The analysis of high-grade phosphoric acid was found to be made most conveniently and accurately by titrating with standard sodium hydroxide solution until the color given by phenolphthalein as indicator exactly matched that of another solution of similar volume which contained approximately the same quantity of indicator and of phosphoric acid in the form of disodium phosphate.

TABLE I

MELTING POINTS OF THE CRYSTAL FORMS OF PHOSPHORIC ACID

Crystal Composition	Observers					
	Thomsen[a]	Berthelot[b]	Joly[c]	Girand[d]	Smith and Menzies[e]	Authors
H_3PO_4	38.6°	41.75°	..	..	42.30°	42.35°
$2H_3PO_4.H_2O$	..	...	27.0	29.0	29.35	29.32

[a] Thomson, *Ber.*, **7**, 997 (1874).

[b] Berthelot, *Ann. chim. phys.*, [5] **14**, 441 (1878).

[c] Ref. 1.

[d] Ref. 2.

[e] Ref. 3.

Melting Point.—In Table I are given the melting points of phosphoric acid crystals as reported by different investigators. The results show that the values obtained for the crystals used in this investigation agree closely with those reported by Smith and Menzies but differ considerably from those given by the other observers.

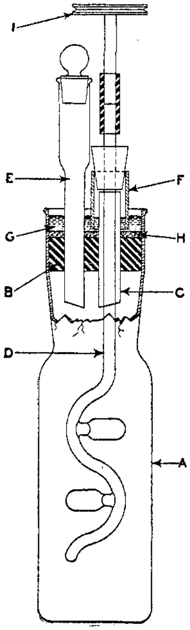

Fig. 1.

Rate of Crystallization.—The rate of crystallization of fused phosphoric acid was determined in a horizontal Pyrex glass tube of 3 mm. internal diameter and 10 cm. long which was terminated at each end with a vertical side-arm closed with a stopcock. The values found for the rate of crystallization of the anhydrous and hydrated acids amounted to 33.3 cm. and 2.6 cm. per minute, respectively, at 20°.

Experimental Part

The apparatus used in determining the solubility of the acid is represented in Fig. 1.

The vessel A in which the acid was placed was made of Pyrex glass and was provided with a two-holed stopper B. Through one hole was passed the tube C which served as a bearing for the stirrer D. The stoppered tube E which passed through the other hole served as an opening through which material could be added or withdrawn from the vessel. To the stirrer was attached the glass ring F which dipped below the surface of the mercury G in the compartment above the stopper. In this way the contents of the vessel were completely sealed from contact with the outside air without interfering with the free rotation of the stirrer. The stopper B was fitted into the vessel A rather loosely so that it could be easily removed when desired. Leakage of mercury into the vessel was avoided by covering the stopper with a layer of paraffin H. The stirrer was attached rather loosely with rubber tubing to the axis of the pulley I and became automatically disconnected without breaking when the growth of crystals at any time interfered with its rotations.

Samples of the saturated solution were withdrawn by means of a 1cc. pipet and quickly transferred to a small weighing bottle. Constant temperatures were maintained by use of a Freas constant-temperature water-bath. The thermometers used were tested at the Bureau of Standards. Agitation of the solution in contact with the solid phase was maintained for at least three days and duplicate samples were withdrawn on successive days to insure that equilibrium conditions had been reached. The results given in Table II represent the mean of closely agreeing results obtained by us working independently.

Table II

Solubility of Orthophosphoric Acid in Water

Temperature °C.	G. of H_3PO_4 per 100 g. of satd. soln.	Solid phase	Temperature °C.	G. of H_3PO_4 per 100 g. of satd. soln.	Solid phase
−85.0[a]	62.5	Ice + $2H_3PO_4.H_2O$	28.28	92.72	$2H_3PO_4.H_2O$
−57.0	67.5	$2H_3PO_4.H_2O$	27.36	93.33	$2H_3PO_4.H_2O$
−43.0	70.0	$2H_3PO_4.H_2O$	26.08	93.74	$2H_3PO_4.H_2O$
−29.0	72.5	$2H_3PO_4.H_2O$	23.50[b]	94.75	$2H_3PO_4.H_2O$ + H_3PO_4
−17.5	75.0	$2H_3PO_4.H_2O$	25.88	95.22	H_3PO_4
0	78.75	$2H_3PO_4.H_2O$	27.30	95.56	H_3PO_4
18.92	84.07	$2H_3PO_4.H_2O$	28.38	95.86	H_3PO_4
23.41	85.93	$2H_3PO_4.H_2O$	29.90	96.18	H_3PO_4
25.24	87.05	$2H_3PO_4.H_2O$	31.96	96.80	H_3PO_4
27.30	88.51	$2H_3PO_4.H_2O$	34.06	97.40	H_3PO_4
28.75	90.00	$2H_3PO_4.H_2O$	36.15	98.00	H_3PO_4
29.32	91.60	M. p. of hydr. cryst.	40.02	99.27	H_3PO_4
28.80	92.30	$2H_3PO_4.H_2O$	42.35	100.00	M. p. of anhyd. cryst.

[a] Eutectic point of ice and the semihydrate.

[b] Eutectic point of the semihydrate and anhydrous orthophosphoric acid.

The solubility of the anhydrous acid, represented by the portion AB of the curve in Fig. 2, was determined by starting with anhydrous crystals at a temperature near their melting point and then successively lowering the temperature and adding sufficient water to give a solution in contact with the crystals. The mixture became solid at the point B on adding a hydrated crystal, showing that the transition point of anhydrous into hydrated acid had been passed.

The solubility of the hydrated acid as represented by the curve CDE was similarly determined by starting near the melting point of the crystals and successively lowering the temperature, adding in one series of experiments sufficient anhydrous acid and in another sufficient water to give a solution in contact with hydrated crystals. Below a temperature of 19° the points on the curve were determined by observing the temperature at which crystals began to form in solutions of known concentrations, care being taken to prevent supercooling by inoculating with a small hydrated crystal. The desired temperatures were secured first with freezing mixture, then with liquid ammonia and finally with solid carbon dioxide. Owing to the viscosity of the solutions at low temperatures the lower points in the solubility and freezing-point curves could not be determined with very great accuracy. The results indicate, however, a eutectic at approximately —85° which is in fair agreement with the value of —81° reported by Giran.[2]

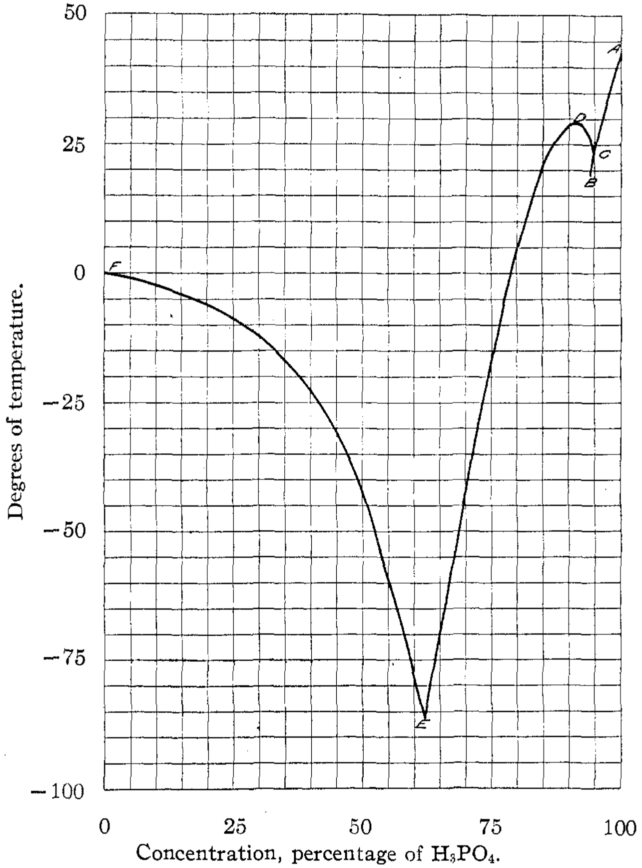

Fig. 2.—Solubility and freezing-point curves of orthophosphoric acid.

In Fig. 3 the curve obtained by Smith and Menzies is superimposed on the corresponding portion of the curve shown in Fig. 2. It is seen that the two curves coincide at certain points but not at others. The curve plotted from the results of this investigation shows no break at 26.3° such as occurs on the curve given by Smith and Menzies and no evidence has therefore been obtained which indicates the existence of a decihydrate of orthophosphoric acid.

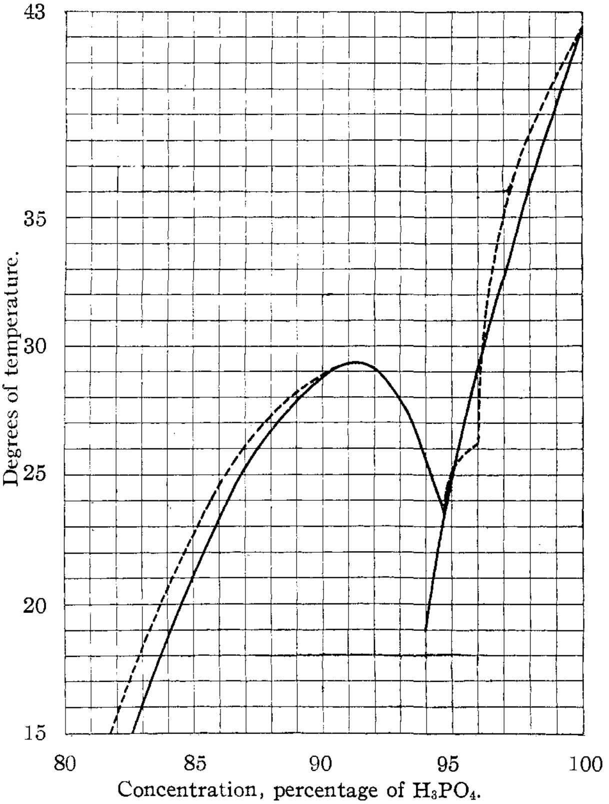

Fig. 3.—Solubility curves of hydrated and anhydrous orthophosphoric acid; —— as determined by the authors; - - - as determined by Smith and Menzies.

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Summary

The solubility and freezing-point curves of orthophosphoric acid were determined for all concentrations of the acid in water. The results obtained give no evidence in support of the existence of a decihydrate of the acid as claimed by Smith and Menzies.

The melting points of the semihydrate and anhydrous crystals were found to be 29.32° and 42.35°, respectively; and their rates of crystallization, respectively, 2.6 cm. and 33.3 cm. per minute at 20°.

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NOTES

Preparation of Nitric Oxide from Sodium Nitrite.—The usual method of preparing nitric oxide by the action of nitric acid on copper is rather tedious in operation and gives a product contaminated with nitrogen dioxide or nitrous oxide unless the concentration of the acid and the conditions are carefully controlled. The gas may be generated rapidly and in nearly pure condition by dropping concd. sulfuric acid into a flask or distilling bulb containing sodium nitrite covered with two or three times its weight of water. The nitrous acid liberated decomposes almost quantitatively according to the equation, $3HNO_2 = HNO_3 + 2NO + H_2O$.

A small amount of nitrogen dioxide which the gas contains may be removed by passing it through a wash bottle containing concd. sulfuric acid or by collecting it over water.

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The Solubility of Urea in Water.—While working with concentrated aqueous solutions of urea at various temperatures, it was found that the solubility of urea as recorded in Seidell's "Solubilities of Inorganic and Organic Compounds,"[1] is considerably too low. Upon examining the original reference,[2] it was found that the results were expressed as "per cent. gram molecules, that is, to the number of gram molecules of solute in 100 gram molecules of solution." In recalculating these results for Seidell's book, this expression had been misconstrued, the data being calculated as moles of solute in 100 moles of solvent, instead of solution.[3] We have recalculated Speyers' data and have also determined the solubility of urea in water at various temperatures.

Our method consisted in heating about 300–400 cc. of urea solution in a water-bath in the presence of solid urea[4] to a temperature a few degrees above that at which the solubility was to be determined. The solution

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[1] W. Seidell, "Solubilities of Inorganic and Organic Compounds," D. Van Nostrand Co., New York, N. Y., 2nd ed., **1919**, p. 737.

[2] Speyers, *Am. J. Sci.*, [IV] **14**, 293 (1902).

[3] Speyers determined the solubilities of a number of carbon compounds in various solvents; we find that the same error has been made in recalculating the solubility data for Seidell's book.

[4] Synthetic urea purified by two recrystallizations from water was used.