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THE SOLUBILITIES OF ORTHOPHOSPHORIC ACID AND ITS HYDRATES. A NEW HYDRATE.

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Our purpose was to make a systematic attempt to ascertain what hydrates of orthophosphoric acid exist. Only one, the semihydrate, Joly's hydrate,[1] $2H_3PO_4.H_2O$, has been heretofore described. When our work was begun (April, 1908), no such study had previously been made. Before its completion (in August, 1908), however, Giran[2] published the results of a search made with the same object. But his method was not sufficiently refined, and he failed to discover any new hydrate. His work and its results will be discussed after our own have been given.

Among the methods available were: (1) that of measuring or comparing (at constant temperature) the vapor pressures of water over specimens having different degrees of hydration and, (2) that of making a series of measurements of concentrations of saturated solutions in stable equilibrium with the solid phase at a series of temperatures. The former method has been applied with success to the hydrates of many salts, such as the series, $CuSO_4.5H_2O$; $CuSO_4.3H_2O$; $CuSO_4.H_2O$ (Lescoeur[3]). In the case of phosphoric acid and Joly's hydrate, however, we found (see below) that, at temperatures at which the solid hydrates exist, the vapor pressures were so low and equilibrium was reached so slowly, that the method was inapplicable. Measurements of the solubility of the acid

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

[2] Giran, *Ibid.*, **146**, 270 (June, 1908); *Ann. chim. phys.* [8], **14**, 565.

[3] *Compt. rend.*, **102**, 1466 (1886); *Ann. chim. phys.* [6], **21**, 511 (1890).

and its known hydrate have not previously been made, but no difficulty was found in applying this method. By means of it, satisfactory solubility curves of orthophosphoric acid, of Joly's hydrate, and of a new hydrate of intermediate composition ($10H_3PO_4.H_2O$) were secured. The data show also that only these two hydrates exist.

The Preparation of the Materials.—The starting material was Kahlbaum's pure "crystallized orthophosphoric acid." The specimens were composed of a mass of crystals covered with a small amount of a liquid. The crystals proved to be Joly's hydrate ($2H_3PO_4.H_2O$), and after being freed from the adhering solution, were used in determining the solubilities of this substance. It may be noted, in passing, that this hydrate crystallizes spontaneously, and rather easily, from a solution of the pure acid of suitable concentration (between 78 and 94 per cent.) and that no noteworthy supercooling occurs.

The solid orthophosphoric acid was prepared by melting Joly's hydrate in a platinum basin, and driving off water by heating, until a concentration between 96 and 100 per cent. was reached. To avoid formation of pyrophosphoric acid, the temperature was kept below 120°. The anhydrous acid crystallizes with much greater difficulty than does Joly's hydrate, and the solution may be kept in a supercooled condition for a considerable time. Crystallization was brought about by cooling the liquid with a freezing mixture and stirring vigorously, or more promptly by inoculating with crystals of arsenic acid. To insure purity, the material was tested for hydrochloric, nitric, sulphuric, and metaphosphoric acids, and all were found to be absent. It was shown to be free also from heavy metals (including arsenic) and from metals of the alkaline earths. It did not decolorize a dilute solution of potassium permanganate.

Both the acid and its hydrates are very hygroscopic.

Methods Used in Determining the Solubilities.—The solubility vessel consisted of a wide, stout test-tube 10 cm. long and 2.5 cm. wide. It was fitted with a doubly bored rubber stopper, through which passed two short tubes. One of these was wide enough to admit the pipette, by means of which samples of the solution were withdrawn for analysis. The tube was opened only when a sample was to be taken. The other tube, 10 cm. in length, formed the bearing of the stirrer, which fitted it as tightly as was consistent with free rotation, and carried a glass shoulder ground to fit the upper end of the bearing-tube. The closeness of the fit was essential to the exclusion of moisture carried by the air. The stirrer was a glass rod twisted in a worm-shape at the end. The worm reached to the bottom of the tube and kept the whole mass in continual agitation. For each measurement about 1.5 cc. of the liquid were withdrawn by a bent pipette, which could be suspended and weighed on the balance.

The bath was a large one, holding about three hundred liters, and its temperature was maintained by means of electric incandescent lamps. The automatic regulation of the temperature was secured by means of a large tube of mercury and an electric appliance devised by Mr. T. B. Freas in this laboratory. The whole device[1] works in such a way that the instrument may quickly be adjusted to give any required temperature, and this temperature is thereafter maintained with an exactness of ±0.005° in spite of all variations in the temperature of the room. The constancy of the temperature was verified by means of a Beckmann thermometer.

The actual temperatures, with the exception of the two lowest, were ascertained by means of a thermometer made by Götze, with a scale reading from +2° to +60°, divided into tenths of a degree. This thermometer, and another used for the low temperatures, were compared several times, during the progress of the work, with a normal thermometer made by Baudin, of Paris, and provided with a certificate of the *Bureau International des Poids et Mesures*. Corrections were applied for the barometric height and for the depth of the immersed bulb. The actual temperatures have, therefore, an accuracy of ±0.01°.

Most of the samples withdrawn by the pipette were analyzed by titration with normal alkali. As indicators, both methyl orange and phenolphthaleïn were used in succession with each sample. With the first, one mole of sodium hydroxide was required for each mole of phosphoric acid. After the second had been added, an additional mole of the alkali was required. The two end-points could be determined with precision, and the double measurement rendered the results more accurate. In some cases the orthophosphoric acid was determined gravimetrically as magnesium pyrophosphate in the usual way. The two methods were compared and found to give closely agreeing results with the same solution. The exactness with which all the points lie upon a smooth curve further demonstrates the sufficient accuracy of the method.

Agitation of the crystals with the liquid for two hours was found to be necessary and sufficient for the attainment of equilibrium. The time allowed was therefore never shorter than this, although it was often much longer.

The Solubilities Observed.—The following table gives the temperatures and corresponding solubilities. The latter are expressed as parts by weight of orthophosphoric acid (H_3PO_4) in one hundred parts of the solution.

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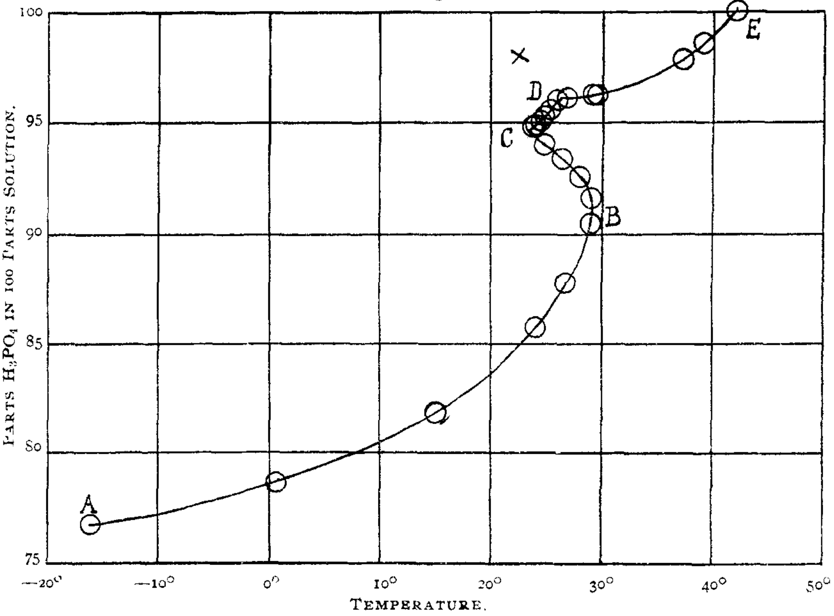
[1] Mr. Freas will shortly publish a description of the apparatus, and all details are therefore omitted here.

Solid phase.	Temperature.	Solubility.	Remarks.
Joly's hydrate, $2H_3PO_4.H_2O$	—16.3	76.7	
	+ 0.5	78.7	
	14.95	81.7	
	24.03	85.7	
	27.00	87.7	
	29.15	90.5	
	29.35	91.6	m. p.
	28.50	92.5	Retroflex part of curve
	27.00	93.4	
	25.41	94.1	
New hydrate, $10H_3PO_4.H_2O$	24.11	94.78	
	24.38	94.80	
	24.40	94.84	
	24.81	94.95	
	25.41	95.26	
	25.85	95.54	
H_3PO_4	26.23	95.90	
	27.02	95.98	
	29.42	96.15	
	29.77	96.11	
	37.65	97.80	
	39.35	98.48	
	42.30	100.00	m. p.

The error in the measurements of concentration is less than 1 in 1000.

Notes on the Solubility Curve, Fig. 1.—The ascending curve *A B* is the solubility curve of Joly's hydrate. *B* is the melting point of this hy-

Fig. 1.



drate (29.35°). At this point the solution contains the same percentage of phosphoric acid as does the solid hydrate. The retroflex portion *B C* contains the melting points of Joly's hydrate depressed by the presence of increasing proportions of phosphoric acid. *C* is the eutectic point of the two hydrates (23.5°). *C D* is the solubility curve of the new hydrate. *D* is another quadruple point (26.2°), at which the new hydrate and anhydrous phosphoric acid can coexist as solid phases, together with solution and vapor. *D E* is the solubility curve of H_3PO_4. *E* is the melting point of the latter, 42.30°. The melting points of Joly's hydrate and of orthophosphoric acid were determined, apart from the solubility measurements. Large quantities of the carefully purified solids were used. They were placed in a thermostat, the temperature of which was raised by very gradual stages of at least two hours duration, at first one-tenth of a degree at a time, and later more slowly still. The temperatures at which the last crystals melted were taken.

Measurements of Previous Observers.—Joly[1] gives the melting point of his hydrate as 27°. We find 29.35°, and at this temperature the solution has the exact composition of the hydrate (91.6 per cent. H_3PO_4 and 8.4 per cent. Aq = $2H_3PO_4.H_2O$). This is, therefore, the melting point.

The melting point of orthophosphoric acid has been found difficult of determination on account of its depression by hygroscopically absorbed water. It is given by Thomsen[2] as 38.6°, by Berthelot[3] as 41.75°. We find 42.30°, and in view of the constant presence of moisture and its effect on this melting point, it is evident that the true melting point cannot be lower than this. The fact that this point lies on the curve given by our other measurements shows that the true melting point cannot be far above it.

Giran,[1] whose papers were referred to in the opening paragraph, attempted to find out what hydrates are formed by each of the three phosphoric acids by determining the temperatures of beginning solidification (or freezing) of mixtures of water with each acid. On account of the inevitable supercooling, his curves could not be the same as ours. They probably approach supersaturation curves, *i. e.*, curves which contain the temperatures at which crystallization begins in supercooled solutions in the absence of inoculation. He does not publish the numerical data, but in the *Ann. chim. phys.* he gives a diagram. The curve for orthophosphoric acid begins at Berthelot's melting point of the pure acid. It presents two temperature minima, the positions of which he gives at +22.5° and —81°, and a single maximum at +29°. He con-

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[1] *Loc. cit.*

[2] *Ber.*, 7, 997 (1874).

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

cludes that only one hydrate (Joly's) exists, and that 29° is its melting point. This is 2° higher than the temperature given by Joly, and is close to that found by us (29.35°). His minimum at −81° probably represents the cryohydric point. A small × in our diagram (Fig. 1) shows the position of his minimum at +22.5° with 98 per cent. H_3PO_4. This does not coincide with either of our transition points. His curve for Joly's hydrate lies fairly close to ours, because, as remarked before, this hydrate crystallizes easily with little supercooling. On the other hand, the part of his curve containing the points at which anhydrous phosphoric acid separates is very much displaced in consequence of the marked supercooling required before crystallization of this substance begins. For this reason the intersection giving his 22.5° point is thrown far above our points. Apparently, there are also considerable errors in the retroflex portion of his curve for Joly's hydrate, since the corresponding portion of our curve does not run toward his 22.5° point at all. Considering the nature of Giran's method, however, it is surprising that the divergence from our results is not greater.

Although the solubilities of phosphoric acid have not previously been determined, Huskinson[1] mentions some facts bearing on the subject. He found that crystals which had separated from an old specimen of phosphoric acid of sp. gr. 1.750 (= 88.8 per cent.), induced crystallization in acids of sp. gr. 1.66 (= 82 per cent.) to 1.75 at "ordinary temperatures," but did not do so in acids of higher or lower sp. gr. The crystals were apparently Joly's hydrate and his "ordinary temperatures" evidently did not range below 13°, as otherwise he would have obtained crystals from less concentrated solutions. He also found that when he concentrated his acid to a point above sp. gr. 1.75, he obtained crystals, after long standing *in vacuo*, which differed from the first kind; these were evidently H_3PO_4. In such solutions, crystals of the first kind (Joly's hydrate) induced no crystallization. These observations are clearly in harmony with the results of our work.

Preparation and Analysis of the New Hydrate—the Decihydrate, $10H_3PO_4.H_2O$.—The diagram showed the exact conditions required for the preparation of the new hydrate. The phosphoric acid was concentrated to 96 per cent. and was kept in the bath at 24.38°. A glass stirrer, the fine point of which scraped against the wall of the bottle, was installed, and crystallization began within a few hours. It continued until the mother liquor had been reduced in concentration to 94.8 per cent. The fact that the concentration thus reduced itself to that proper to the existing temperature (giving an additional solubility point, included in the table), and then remained stationary, indicated that the crystals were composed of the required substance. A second quantity was prepared

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[1] *Pharmaceutical J.*, **1884**, 644.

in the same way, except that crystallization was induced by inoculation from the first lot, and stirring was omitted.

At first the crystals intended for analysis were freed from the mother liquor in a centrifuge and transferred rapidly to stoppered tubes. But satisfactory analyses were not obtained. The necessity of absolutely excluding all contact with moist air, at least during the humid months of summer, was shown by our analysis of crystals of anhydrous phosphoric acid handled in the same way. Only 99.27 per cent. of the acid was found. An air-tight box, with glass sides and rubber gloves projecting into the interior, was therefore prepared. Shallow vessels containing phosphoric anhydride were placed in the box, along with the materials and the weighing tubes. After sufficient time for drying the atmosphere had elapsed, portions of the larger crystals were wiped with absorbent cotton and transferred to the tubes. To test the efficiency of the plan, the box was opened and, on the following day, the whole operation of closing, drying, and transferring was repeated. The last of the following analyses was made with one of the second series of samples, and showed that constant results were obtainable.

	Calc. per cent. H_3PO_4.	Found.
$12H_3PO_4,H_2O$	99.495	98.00
$10H_3PO_4,H_2O$	98.195	98.18
$9H_3PO_4,H_2O$	98.00	98.09
$8H_3PO_4,H_2O$	97.75	98.13
	Average,	98.10

Incomplete removal of the mother liquor was obviously the only unavoidable source of error, and hence the proportion of phosphoric acid found is slightly below the theory for $10H_3PO_4.H_2O$.

A few substances, such as Staudinger's $K_5H_4(PO_4)_3.H_2O$,[1] are known which contain proportions of water of hydration approaching in smallness that in the present hydrate. Probably, however, many more exist. In preparative chemistry, when a case like this occurs, the presence of the water, if detected at all, is likely to be attributed to incomplete drying.

Properties of the Decihydrate, $10H_3PO_4.H_2O$.—The hydrate forms large, clear prisms, very similar in appearance to those of the anhydrous acid and of Joly's hydrate.

When heated, the hydrate might be expected to behave as some hydrates do (*e. g.*, $Na_2SO_4.10H_2O$), and melt at, or close to, the temperature of the transition point *D* (26.2°). It might, however, resemble the large number of hydrates (*e. g.*, $CaCl_2.6H_2O$) which exhibit delayed transformation. In point of fact it shows delayed transformation in very

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[1] *Z. anorg. Chem.*, **5**, 383.

pronounced fashion. A specimen (about 0.5 g.), when heated slowly (1° per 5 min.), underwent no obvious change at 26° and melted very gradually. It remained altogether 1½ hours above 30° and twelve minutes above 42.3° before the whole specimen had melted. This behavior indicates that it should be possible to follow the solubility curve upward, into the metastable region. We hope shortly to take up the investigation of the upward course of the curve, to attempt to study the crystalline forms of the acid and its hydrates, and to explore the case of arsenic acid.

The Measurement of Vapor Pressures.—To ascertain whether the vapor pressures of the hydrates of orthophosphoric acid could be measured readily, two experiments were made with the semi-hydrate (Joly's). The moist crystals of the hydrate were placed in one bulb of a tensimeter. The pressure observed was, therefore, that of the saturated solution of this hydrate. Phosphorus pentoxide was placed in the other bulb, and the vapor pressure of the solution of the hydrate was thus measured against that of metaphosphoric acid in contact with phosphorus pentoxide. As the pressure was very small, a mineral oil of sp. gr. 0.92 was employed as the manometric liquid. Still further to magnify the effect, the manometer was supported on a clinostat so that its position approached the horizontal. The inclination was 1 in 8. The apparatus was evacuated with a pump, leaving a residual pressure of air on each side of less than 1 mm. Although the mere motion of the manometer liquid brought about a difference in pressure of the residual air, the size of the bulbs and tubes were such that, with 1 mm. original pressure, the error due to this effect was negligible.

The tensimeters were kept in the constant temperature bath described above. One of them was disturbed during the experiments, but the other was observed regularly for 1993 hours. At the end of that time the oil column, which moved with exceeding slowness, had not yet come quite to rest, and the system was evidently not yet in equilibrium. The maximum pressure reached was equal to 0.85 mm. of mercury. The temperature was 24.99°, with a limit of variation of ±0.01° throughout the whole period.

Although the plan of using an oil, and placing the manometer in an inclined position, can probably be used successfully for measuring accurately very small differences of vapor pressure, yet the slowness with which, in this instance, equilibrium was approached rendered the whole method inapplicable to our purpose.

Some measurements of the vapor pressures of solutions of phosphoric acid have previously been made by Dieterici.[1] Of the cases he examined, the one nearest to ours (86.3 per cent. H_3PO_4 at 24.99°) was that of

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[1] *Wied. Ann.*, **50**, 61.

79.6 per cent. H_3PO_4 at 0°, when the pressure was found to be 0.636 mm. of mercury.

Conclusions.

1. The solubilities of phosphoric acid and its hydrates were measured with exactness from —16.3° to 42.30° (m. p. of H_3PO_4).
2. The melting point of Joly's hydrate (29.35° ± 0.01) and of orthophosphoric acid (42.30° ± 0.01) were redetermined.
3. A new hydrate, $10H_3PO_4.H_2O$, was discovered.
4. The vapor pressure of a saturated solution of Joly's hydrate at 24.99° ± 0.01 reached 0.85 mm.

[Contributions from the Laboratories of General and Physical Chemistry of the University of Chicago.]

THE ELECTRICAL CONDUCTIVITY AND VISCOSITY OF CONCENTRATED SOLUTIONS OF ORTHOPHOSPHORIC ACID.

By Alexander Smith and Alan W. C. Menzies.

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With increasing concentrations of sulphuric acid, the specific electrical conductivity (at 18°) of an aqueous solution of the acid rises and at 30 per cent. a maximum is attained. As the concentration rises still further, the specific conductivity falls, reaching a minimum at 84 per cent. (the composition of the monohydrate, $H_2SO_4.H_2O$). Beyond this point the conductivity rises to 92 per cent. and finally falls rapidly as 100 per cent. is approached.[1] It will be noted that of the three hydrates revealed by a study of the freezing points of sulphuric acid,[2] namely, those with $4H_2O$, $2H_2O$, and H_2O, only one influences the conductivity. It seemed worth while to learn whether the specific conductivity of phosphoric acid solutions was similarly related to one or both of the hydrates. Kohlrausch and Holborn (p. 157) give the conductivity of phosphoric acid at 18° at concentrations from 10 to 87 per cent. At the time,[3] no measurements had been made beyond the latter concentration. The compositions of the hydrates lie in this unexplored region, namely, the semihydrate ($2H_3PO_4.H_2O$) at 91.58 per cent. and the decihydrate[4] ($10H_3PO_4.H_2O$) at 98.195 per cent.[4]

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[1] Kohlrausch and Holborn, *Leitverm. d. Elektrolyte* (1898), p. 156.

[2] Meyerhoffer, *Physikalisch-Chemische Tabellen*, 567.

[3] This was in August, 1908. Phillips (*J. Chem. Soc. Lond.*, **95**, 64 (1909)) has since published a series from 1.4 per cent. to 100 per cent. at 0°. But his series includes only three observations within the region in question, namely, at 92.07, 93.52, and 100.03 per cent., respectively. These three measurements, although they reveal no irregularity in the curve, are not sufficient by themselves to demonstrate the absence of a maximum.

[4] Preceding paper. Smith and Menzies, This Journal, **31**, 1186.