[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE TWO-COMPONENT SYSTEM, WATER--ARSENIC PENTOXIDE.[1]

BY ALAN W. C. MENZIES AND PAUL D. POTTER.

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A review of the literature on arsenic acid shows that, up to 1911, there was no close agreement as to the formulas and properties of the hydrated forms of the pentoxide, except in the case of the so-called hemihydrate of the ortho acid. As the methods used in deducing accepted formulas, also, have not been entirely beyond criticism, it was thought desirable that an effort be made to establish the facts with certainty. Work in this direction has led to a closer study of the manner in which rather small quantities of water are associated with arsenic pentoxide at higher temperatures. To facilitate the quantitative determinations, a new method of titration of arsenic acid has been worked out.

Earlier Work.—Balareff,[2] in a recent article on this subject, gives a complete list, here reproduced, of the formulas for the solid hydrates of arsenic pentoxide that have been proposed. The approximate dates of publication by the various authors have been added.

$H_3AsO_4.{}^1/_2HO$ or $As_2O_5.4H_2O$, Geuther (1859).
H_3AsO_4 or $As_2O_5.3H_2O$, Kopp (1856); Bucholz (1802).
$H_4As_2O_7$ or $As_2O_5.2H_2O$, Kopp (1856); Baud (1907).
$H_5As_3O_{10}$ or $3As_2O_5.5H_2O$, Auger (1908).
$H_6As_4O_{13}$ or $2As_2O_5.3H_2O$, Joly (1885); Auger (1902).
$HAsO_3$ or $As_2O_5.H_2O$, Kopp (1856); Joly (1885).

On account of the unsatisfactory character of the methods employed before 1885 and because the field has been well covered since that date, detailed reference to the work of earlier date may be omitted. It should be stated, however, that Geuther's formula for the hemihydrate, $H_3AsO_4.{}^1/_2H_2O$ (often inaccurately called Joly's hydrate) has been frequently verified. For example, Joly,[3] who is the first of the more modern workers, gives the formula of the hydrate that separates when a concentrated solution of arsenic acid is inoculated with the hemihydrate of phosphoric acid as $H_3AsO_4.{}^1/_2H_2O$.

Joly gives, further, two methods of preparation of the supposed hydrate $2As_2O_5.3H_2O$. First, by desiccating the hemihydrate of the ortho acid in a vacuum for two months at room temperature; second, by concentrating solutions of arsenic acid at 110°. Because of a difference between the conclusions of Kopp and Joly, Auger[4] repeated their work. By rather crude analysis he verified the formula $2As_2O_5.3H_2O$ as given by

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[1] Certain of the results described in this paper were reported at the Eighth International Congress of Applied Chemistry under the titles "A New Method of Titration of Arsenic Acid" and "The Retention of Small Quantities of Water by Arsenic Pentoxide at Elevated Temperatures."

[2] *Z. anorg. Chem.*, 71, 73 (1911).

[3] *Compt. rend.*, 101, 1262 (1885).

[4] *Ibid.*, 134, 1059 (1902).

Joly, but found him as well as Kopp in error in respect to the formula $HAsO_3$. He says that what Joly thought to be of that composition was also the hydrate $2As_2O_5.3H_2O$. Auger concludes that this hydrate and the hemihydrate of the ortho acid are the only ones that exist. These two hydrates were obtained by Baud[1] who considered that he isolated also the pyro acid, $H_4As_2O_7$. The latter resulted on desiccating the hemihydrate of the ortho acid over sulfuric acid at about 15°. He supports his claim of the existence of the pyro acid by a thermochemical study.

The fact that Baud obtained a lower hydrate by desiccating over sulfuric acid than was obtained by Auger when using phosphorus pentoxide caused the latter to repeat his own work.[2] As a result, he denied the existence of the pyro acid and changed the formula of the hydrate that he formerly believed to be $2As_2O_5.3H_2O$ to $3As_2O_5.5H_2O$. In regard to this correction he says, "The errors which I mentioned in my first paper" (the error consisted in drying only by means of a porous plate) "prevented the determination of the composition of this hydrate." It is to be noted that, although the error in his earlier work was due to imperfect drying, the later amended formula contains the more water. Balareff,[3] in attacking the question anew, criticizes the work of Auger because the latter did not take all of the precautions necessary for the formation of unmixed preparations. In none of the three groups of experiments made by Balareff were any indications found of the existence of new hydrates. He concluded, in agreement with Auger's amended work, that the only isolible hydrates are $As_2O_5.4H_2O$ and $3As_2O_5.5H_2O$.

Preparation of the Arsenic Acid Employed.

The Hydrate $As_2O_5.4H_2O$.—The material used as a starting point was in part the best preparation of Merck and in part Baker's "Analyzed Arsenic Acid." The solution obtained by dissolving in distilled water was filtered through asbestos and concentrated to a boiling point of about 150°. After cooling, this solution was inoculated with crystals taken from a small portion of the solution that had been caused to crystallize by inoculation with the 1–4 hydrate of phosphoric acid, $P_2O_5.4H_2O$ (Joly's hydrate). After standing over night, about half of the liquid had solidified into a network of needles of the 1–4 hydrate. These were allowed to drain for several hours and the mother liquor again concentrated and inoculated. The second crop was recrystallized after the addition of a little water and solution by fusion before it was combined with the first. After about a kilogram of crystals had been obtained, the whole mass was recrystallized until free of antimony.

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[1] *Compt. rend.*, **145**, 322 (1907).

[2] *Ibid.*, **146**, 585 (1908).

[3] *Loc. cit.*

Freedom from antimony was determined by precipitating the arsenic in a sample of about 5 grams as $MgNH_4AsO_4.6H_2O$ in the presence of tartrate[1] and testing the filtrate for antimony with hydrogen sulfide. Similar tests showed that the mother liquors contained appreciable quantities of antimony.

The original samples were free from sulfur, phosphorus, and nitrates. The crystals of the 1-4 hydrate were proven free of trivalent arsenic by their failure to reduce permanganate. A quantitative analysis of these crystals, according to the method described later,[2] showed 94.13 and 94.10% of H_3AsO_4 as against 94.04% calculated for $As_2O_5.4H_2O$ from the atomic weight table of 1912.

The Hydrate $3As_2O_5.5H_2O$.—During the above work it was found, as mentioned by Joly, that the 1-4 hydrate, on standing in the superfused state, frequently deposits a hard white crystallin scale; further, that the scale appears more readily when the liquor is maintained at a temperature of 100°.

In order to find out the conditions under which a pure sample of this hard scale could be prepared, a weighed sample of the 1-4 hydrate was placed in a specially constructed weighed tube so arranged that a current of air, dried over concentrated sulfuric acid, could be passed through it. This tube was inserted into a wide deep test tube which was maintained at 100° in a water bath. Periodic weighings showed that, with the disappearance of the liquid phase, there was practically a cessation of the loss of weight.

This experiment, as well as others that will be mentioned later, showed that this crystallin scale could be satisfactorily prepared by evaporation of a sufficiently pure arsenic acid solution to complete dryness at 100°. Accordingly, a quantity of the pure crystals of the 1-4 hydrate, obtained as described above, was melted and evaporated at 100°. The resulting crystal scale was finely ground in a mortar and the powder heated in dry air at 100° until a weighed sample further treated in the same way showed no loss of weight.

The dry powder was analyzed by the pentasulfide method[3] and yielded the results following: percentage of arsenic pentoxide (1) 88.42, (2) 88.41, (3) 88.68, (4) 88.49; average 88.50. The calculated percentage of arsenic pentoxide in the hydrate $3As_2O_5.5H_2O$ is 88.45. Equally good analyses of this preparation were later[4] made by ignition to arsenic anhydride.

In what follows, this preparation will be referred to as the 3-5 hydrate, in harmony with the naming "1-4 hydrate" for $As_2O_5.4H_2O$ (otherwise called Joly's hydrate or the hemihydrate of the ortho acid).

[1] Cf. *Analytical Chemistry*, Treadwell-Hall, 1st. ed., 2, 184.

[2] Cf. p. 1455.

[3] Cf. *Analytical Chemistry*, Treadwell-Hall, 1st. ed., 2, 183.

[4] Cf. Table IX, below.

Measurement of Temperature and of Mass.

Temperatures below 0° were measured with a pentane thermometer graduated in degrees; between 0° and 100°, with a mercury thermometer graduated in tenth degrees; above 100° with a mercury thermometer graduated in degrees. These thermometers were compared with a platinum resistance thermometer with the same dispositions as used by Smith and Menzies[1] and the readings given have been corrected accordingly; so that, below 0°, it is believed that the temperature measurement was accurate to ±1, between 0° and 100° to ±0.1 and above 100° to ±1.

The weights used were calibrated by the method of Kohlrausch. Corrections of the weighings to vacuum were omitted, as tares were uniformly employed, and the differences in density of the solids weighed are such as not to give rise to errors greater than 1 part in 3000.

A New Method of Titration of Arsenic Acid.

It is well known that arsenic acid, when titrated with sodium hydroxide, appears to act as a dibasic or as a monobasic acid according as the indicator is phenolphthalein or methyl orange, the latter indicator being the more sensitive towards hydroxyl ion. In neither case, however, is the end point as sharp as could be desired; so that an accuracy of 1 part in 300 can be attained only by the help of good light, a comparison tint, patience and practice. In these circumstances, and as many titrations of arsenic acid were in prospect, it seemed desirable to cast about for possible improvements in the method.

Since both the too early appearance and the indistinctness of the secondary end point are due to the feebleness of the ionization $H_2AsO_4' \longrightarrow H^{\cdot} + HAsO_4''$, it was evident that matters could be improved by replacing the acid $H^{\cdot} — HAsO_4''$ by a strong acid such as hydrochloric. Reference to the literature showed that $BaHAsO_4$ is very little soluble, so that such replacement promised to be fairly complete if sufficient barium chloride were added to the solution. Other circumstances favoring the use of this precipitant were the high degree of ionization of barium hydroxide and the obvious impossibility of a concentration of $HAsO_4''$ ion approaching that required to yield a $H^{\cdot}$ ion concentration that should prejudice the turning pink of phenolphthalein.

Preliminary experiments, in which a solution of barium chloride was first added to the arsenic acid, having shown a marked sharpening of the end point with phenolphthalein, plans were made for a more careful study of the best conditions for titration. For this purpose, two solutions were prepared; one containing 37.010 grams of arsenic acid (H_3AsO_4) per liter, and the other containing enough barium chloride to yield a solution

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[1] THIS JOURNAL, 32, 1422 (1910).

saturated with respect to $BaCl_2.2H_2O$ at a temperature a trifle below that of the room. Of the latter solution, 10 cc. is a little more than is necessary to form $BaHAsO_4$ with the arsenic acid in 50 cc. of the former solution. The following data were obtained using a sodium hydroxide solution with a normality factor of 0.6513 as determined against Iceland spar weighed in air:

TABLE I.

No.	Cc. H_3AsO_4 solution.	Cc. $BaCl_2$ solution.	Total volume in cc.	Cc. NaOH solution.
I	50	10	250	39.99
II	50	10	250	39.96
III	50	30	250	39.95
IV	50	30	250	39.97
V	50	30	250	39.94
VI	50	30	250	39.95
VII	50	30	250	44.14
VII*a*	50	15	250	39.95
VII*b*	50	15	250	39.99

The calculated number of cubic centimeters of the above alkali which should be required for 50 cc. of the arsenic acid solution regarded as a dibasic acid is 39.95.

The end points of the titrations in experiments I and II were far inferior in sharpness to those in experiments III–VI, VII (*a*) and (*b*), in which latter groups, according to the principle of the solubility product, the precipitation process was more complete by reason of the very much higher concentration of $Ba^{\cdot\cdot}$ ion furnished by the excess of barium chloride beyond the required 10 cc. Little difference in sharpness of end point could be distinguished between III–VI and VII (*a*) and (*b*).

The course of the titrations I–VI was somewhat as follows: the first drops of alkali added to the solution of arsenic acid, barium chloride, and phenolphthalein caused a local pink coloration and an amorphous curdy precipitate, both of which disappeared on stirring. After sufficient alkali had been added to neutralize the primary hydrogen, the redissolving of the curdy precipitate, which is probably tertiary barium arsenate, became slower. Since secondary barium arsenate, $BaHAsO_4$, is highly insoluble, the solution at this stage is obviously supersaturated with respect to this salt. This can be shown very clearly when, for example, half as much alkali has been added as would be necessary to neutralize the arsenic acid regarded as tribasic; for, at this stage, if the walls of the beaker be scratched below the surface of the clear solution, a copious crystallin white precipitate results that makes the liquor appear silky when stirred. This precipitate increases in quantity until the end point is reached at 39.9 cc.

When care was taken to stir the liquid only very gently and to avoid scratching the walls of the beaker, results like that shown in experiment

VII could occasionally be obtained. In such cases, the formation of insoluble $BaHAsO_4$ had apparently been delayed until more than 39.9 cc. of alkali had been run in. In order to test this point, a few titrations were carried out otherwise, as before, but with a total volume of 500 cc. instead of 250 cc. This dilution, by reducing the concentration of both $Ba^{\cdot\cdot}$ and $HAsO_4''$ to about one-half, should reduce the degree of supersaturation with respect to $BaHAsO_4$ to about one-fourth. Under these conditions it was easy to avoid the precipitation of any $BaHAsO_4$ as the following examples show:

TABLE II.

No.	Cc. H_3AsO_4 sol.	Cc. $BaCl_2$ sol.	Total volume in cc.	Cc. NaOH sol.
VIII	50	30	500	59.99
IX	50	30	500	59.81
X	50	10	500	40.08

In experiment X, crystals of $BaHAsO_4$ were added as seed after about 30 cc. of alkali had been run in.

The end points in experiments VIII and IX, it is interesting to note, lie quite close to that calculated for a tribasic acid (59.92). It is perfectly possible to obtain a good end point as for a tribasic acid even at the dilution of 250 cc., provided that about 58 cc. of alkali is run in rapidly. In this way, the stage at which the ion $HAsO_4''$ is at high concentration, namely when about 40 cc. of alkali have been added, is passed over very rapidly. If stirring is avoided also, much of the arsenic, which, at this stage, would be present as $HAsO_4''$ if opportunity for equilibrium were allowed, is actually present as insoluble $Ba_3(AsO_4)_2$, locally precipitated. After 58 cc. of alkali have been added, stirring is unlikely to yield a precipitate of $BaHAsO_4$, for the $HAsO_4''$ ion is now again at low concentration; and the well stirred white liquor may be turned pink at the end point by the addition of a single drop of alkali. For solutions of which the arsenic acid content is not known approximately beforehand, however, titration as for the tertiary end point is plainly too uncertain to be serviceable for scientific work.

It should, perhaps, be pointed out that once the crystallin $BaHAsO_4$ has formed, the solution remains permanently pink for any additions of alkali beyond 39.9 cc.; for, as long as this salt is present, the (fixed) concentration of its ion $HAsO_4''$ governs the concentration of the hydrogen ion possible, and this is sufficiently low to admit of a high enough concentration of hydroxyl ion to affect phenolphthalein.

The Best Procedure.—A sufficiently large sample of arsenic acid should be used to require, as a dibasic acid, between 30 and 40 cc. of normal alkali. Fifteen cc. of saturated barium chloride solution are added, the liquid diluted to 250 cc., boiled 15 minutes to remove carbon dioxide cooled, and titrated with phenolphthalein as indicator. The alkali which may profitably contain barium hydroxide to insure absence of soluble carbonate, is added with stirring until the locally formed precipitate becomes slow in redissolving. The walls of the vessel are now, if necessary, scratched below the surface of the clear solution until the liquid, on stirring, appears lustrous with fine crystals, after which the titration is completed as usual. The lustrous crystals and final pink color make the titration resemble that of the Zimmerman-Reinhardt method for iron.

The degree of concordance between duplicate determinations is well shown by the results of the analyses made in the solubility measurements described below (see Tables V and VI). The two members of nineteen duplicate pairs of analyses there tabulated differ from each other, on the average, by 1 part in 1500.

Instead of basing the calculation of results upon the acidimetric factor of the alkali employed, it may, perhaps, be more convenient to determin the titer of the alkali against solutions containing known weights of arsenic acid. Such solutions may be prepared in any one of three ways: (1) by oxidizing known weights of pure arsenious oxide by nitric acid, evaporating off the excess of the reagent below 200° and subsequent dilution; (2) by synthesis from the 3–5 hydrate, the method of preparation of which has been given above; or (3) by synthesis from arsenic pentoxide prepared as indicated below (cf. Expt. XVIII).

In view of the satisfactory character of the end point of this titration, of the possibility of easy synthetical preparation of solutions of arsenic acid of accurately known concentration, and of the opportunity of simply relating this alkalimetric solution, through arsenious acid, to oxidimetric solutions, it appears likely that this titration could be profitably employed for the original standardization of alkalies. The subject will receive further investigation with this in view.

Application of the Solubility Method.

As the solubility method has not hitherto been utilized in the study of the two-component system, water–arsenic anhydride, the application of this powerful method presented itself as an appropriate means of attacking the problem, the more so as making possible a comparison with phosphoric acid.[1]

Measurement of Solubility.—The solubility vessel consisted of a wide, stout test tube fitted with a doubly bored rubber stopper through which passed two short glass tubes. One of these, of 10 mm. bore and located near the edge of the stopper, was closed with a small rubber plug and only opened when a sample of the liquor was being drawn. The other tube passed through the center of the stopper and formed the bearing of the stirrer which fitted as tightly as was consistent with free rotation

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[1] Cf. Smith and Menzies, THIS JOURNAL, 31, 1183 (1909).

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. The rotary stirrer consisted of a glass rod twisted for the last two inches of its length into a helix, the tip of which reached within 1 mm. of the bottom of the tube thus preventing, by its lifting power, permanent sedimentation of even a portion of the solid phase.

Whenever the crystals, of which the solubility was being determined, were large enough to permit of the obtaining of a clear mother liquor by allowing the whole to stand a short time after saturation, the samples for analysis were drawn from near the surface of the liquor without filtration. For purposes of weighing, the 2 cc. pipet that was used for withdrawing samples was bent through 90° at a point above the bulb.

Filtration.—The 3–5 hydrate invariably gave a liquor that was milky white with minute crystals, necessitating filtration at the temperature of saturation. By way of a filter that could be introduced readily into the solubility tube and thus used at its temperature, a felt of asbestos fibers was supported in an inverted position by granules of broken glass contained in a 10 mm. length of common glass tubing connected through a glass capillary tube to a test tube into which the clear liquor could be drawn by suction. On account of the very marked tendency towards supersaturation, no trouble was experienced with any of the liquors crystallizing in the capillary. The filter was easily washed and dried, and was therefore used repeatedly. As with concentrated phosphoric acid solutions, paper filters are here inadmissible.

Thermostats.—For the determinations above 100°, the solubility tube above described was placed in a mechanically stirred oil bath, which was kept at a temperature constant to ±1° by hand. Between 0° and 100°, constant temperature was obtained by means of a bath, holding about 60 liters of water, regulated automatically to a constancy of ±0.1°. For determining the melting point of the 1–4 hydrate, regulation was made sensitive to ±0.01°. Below 0°, the solubility apparatus was immersed in a salt and ice freezing mixture, or in a mixture of solid carbon dioxide and alcohol contained in a large Dewar tube. Here again the temperature was kept constant to ±1° by hand.

In the last case, it was not desirable to take the temperature of the bathing liquid, since its volume was small and its temperature fluctuation greater than that of the contents of the solubility vessel. The solid rod used as the stirrer in the solubility apparatus was therefore replaced by a short tube to which a glass helix was sealed in such a way that a thermometer could be placed inside the tube and helix. The thermometer was fastened to the top of the tube by means of a rubber connection and allowed to rotate, except when readings were being made. This arrangement brought the bulb of the thermometer in the center of the agitated liquid.

Solubilities Determined.—Data for the concentration of the solution in equilibrium with the various solid phases, ice, 1–4 hydrate, and 3–5 hydrate were obtained and will be found, expressed in terms of grams of H_3AsO_4 per hundred grams of solution, in tabular form under these heads, and in graphic form in Fig. 1. No hydrates other than these were encountered in equilibrium with solutions in the temperature range —37° to +141°.

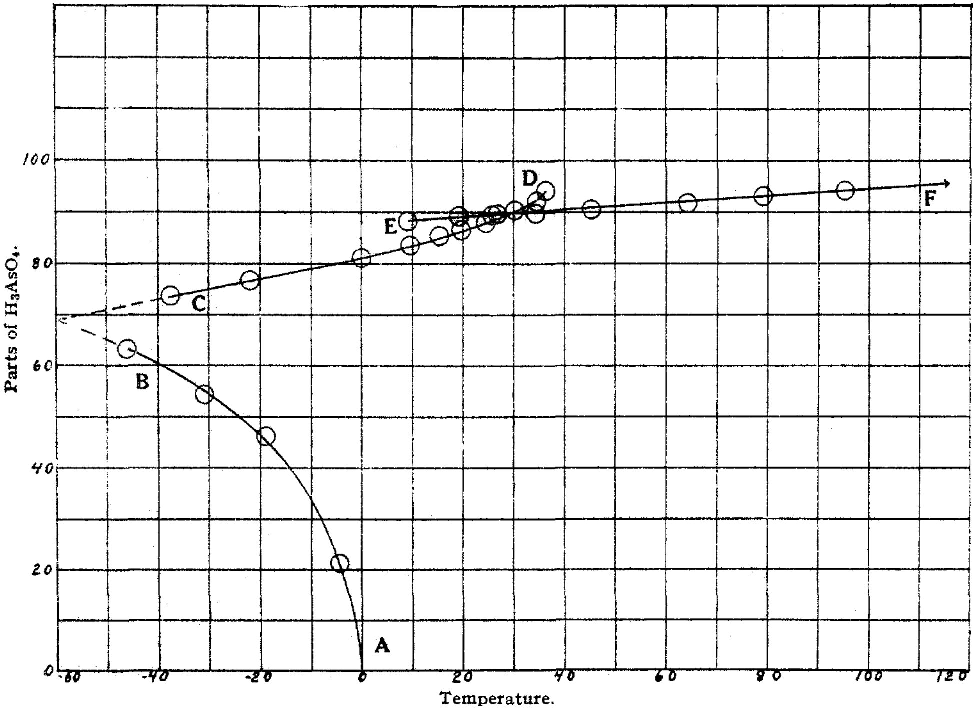

FIG. 1.

Solid Phase Ice.—The method was similar to the freezing point method for molecular weight determination. A solution of suitably chosen concentration was somewhat undercooled and inoculated with ice. The analyses of successive samples of solutions drawn without the necessity of filtration showed that equilibrium was reached within 1 hour. Analysis of each sample was made in duplicate by the volumetric method above described.

TABLE III.

Temperature.	Per cent H_3AsO_4.	Temperature.	Per cent H_3AsO_4.
— 4.2	21.10	—30.8	54.43
"	21.09	"	54.42
—18.8	46.29	—46.0	63.46
"	46.15	"	63.37

These data are represented by the curve AB in the figure.

Solid Phase, 1-4 Hydrate.—The remarkable degree to which the 1-4 hydrate forms supersaturated solutions was frequently observed. In no case did this hydrate separate spontaneously. Saturated solutions were obtained by inoculating and stirring solutions that were somewhat supersaturated at the desired temperature. It was found that equilibrium usually resulted on stirring for 2 hours, though it was generally convenient to continue stirring much longer. The only determinations which caused any difficulty were those between 29° and 36°. Examination of Fig. 1 shows that above 29.5° the 3-5 hydrate is more stable than the 1-4 hydrate. In consequence of this, the friction of the crystals of the 1-4 hydrate against each other frequently caused a separation of the 3-5 hydrate above this temperature. It is evident from the figure that the cryohydric point must lie close to —60°.

TABLE IV.

Temperature.	Per cent H_3AsO_4.	Temperature.	Per cent H_3AsO_4.
—37.3	73.70	19.80	86.65
"	73.77	"	86.63
—21.8	76.55	24.63	87.92
"	76.59	"	87.94
0.00	81.19	30.14	90.32
"	81.00	"	90.50
9.78	83.77	34.81	92.57
"	83.62	"	92.64
15.49	85.68	36.22	94.10
"	85.50	"	94.13

These data are shown graphically by the curve CD in the figure.

Melting Point of the 1-4 Hydrate.—The crystals used were obtained by repeatedly melting a mass of about 500 grams and draining off any liquor that remained after seeding and allowing to stand over night. The accepted product analyzed 94.13% and 94.10% H_3AsO_4 as against 94.04 calculated.

Just as in the case of the "one-tenth" hydrate of orthophosphoric acid,[1] the process of fusion of this hydrate, in specimens approximately 1 gram in weight, is extremely slow when carried out in a bath but little hotter than the melting point. In consequence of this, it was necessary to make long observations on the melting point and during these periods there was the constant danger of formation of the more stable 3-5 hydrate. So far as could be determined, the 3-5 hydrate forms at this temperature only from the liquid state. In order to afford little opportunity for its formation in contact with the 1-4 hydrate, crystals of the latter were sealed in constricted ("hour-glass") tubes in such a way that the liquefied hydrate would drain away as fast as formed. These tubes were placed

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[1] Cf. Smith and Menzies, *loc. cit.*

in the thermostat and the temperature raised by successive increments of 0.05°. It was found that crystals could be kept 24 hours at 36.11,° although, generally, the 3–5 hydrate had formed in the liquor drained off. At 36.16° crystals only partially melted in 7 hours, and no 3–5 hydrate formed, but they were entirely gone on standing over night, and the 3–5 hydrate had developed. The melting point of the 1–4 hydrate may therefore be taken as 36.14° ± 0.05. For these experiments, an accuracy of temperature measurement to hundredths was attained by employing as a standardizing point the transition point sodium sulfate decahydrate ⇄ anhydrous sodium sulfate.[1]

Solid Phase, 3–5 Hydrate.—As the 1–4 hydrate was considerably easier of preparation, the solubilities of the 3–5 hydrate were determined by inoculating a superfused mass of the former. By inoculation in this case is meant the addition of so large a number of fine crystals that the mass was somewhat viscous because of them. As a confirmation of accuracy, saturation was, in several cases, attained from less concentrated instead of from supersaturated solutions.[2] Table V contains the solubility data for the 3–5 hydrate. The straight line EF in Fig. 1, represents these data graphically with the exception of the determination at 141°, which lies on EF produced straight, and has been omitted to avoid a reduction of scale.

TABLE V.

Temperature.	Per cent H_3AsO_4.	Temperature.	Per cent H_3AsO_4.
9.21°	88.26	45.48°	90.53
"	88.28	"	90.39
19.30	89.23	64.15	91.94
"	89.26	"	91.95
25.28	89.49	74.85	92.01
"	89.45	"	92.08
26.80	89.71	79.15	93.23
"	89.79	"	93.10
34.35	89.77	99.25	94.35
"	89.76	"	94.35
35.28	89.91	141.0	96.87
"	89.94	"	96.96
45.23	90.51	...	...
"	90.45	...	...

At 67.4° it was found that equilibrium resulted in 2 hours. At lower temperatures the time required was longer so that it was found convenient to make but one determination per day, thus allowing the first period of stirring to continue about 24 hours, which was sufficiently long

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[1] Cf. Richards, *Z. physik. Chem.*, **26**, 690 (1898); Dickinson and Mueller, Bur. Standards, *Bull.* [4] **3**, 655 (1907).

[2] Cf. Hulett, THIS JOURNAL, **27**, 49 (1905).

to produce saturation at 19.3°. At 9.2°, however, the time required was very much longer.

Persistence of Supersaturation.—The solution employed at 9.2° was freshly prepared by fusing a quantity of moist 1–4 hydrate and had an initial concentration of about 94%. This was very richly inoculated, in the manner mentioned, and stirred in a way to avoid grinding.[1] The analyses of samples withdrawn periodically, however, showed that saturation was not attained at this temperature until after 27 days' continuous stirring. The results of these analyses are tabulated below (Table VI) and represented graphically in Fig. 2. Slight irregularities on the curve are attributable to variations in the rate of stirring, which, however, was at all times sufficiently vigorous to keep the contents of the solubility tube in active agitation.

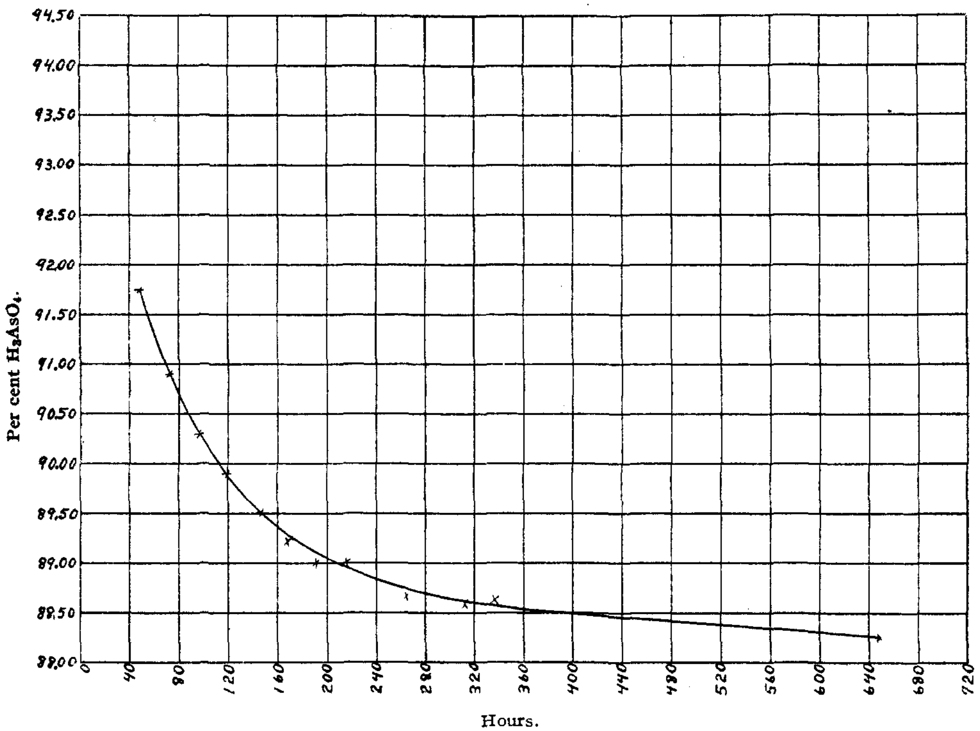

FIG. 2.

Similar determinations were attempted at 0°, but it was found that absolutely no measurable change of concentration took place in 48 hours in a highly supersaturated solution, even although the mass was thick with fine crystals, and the experiment was, in consequence, abandoned.

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[1] Cf. Hulett, *loc. cit.*

TABLE VI.

Hrs. stirring.	Per cent H_3AsO_4 in solution.	Hrs. stirring.	Per cent H_3AsO_4 in solution.
48	91.75	264	88.62
..	91.71	..	88.71
72	90.88	312	88.63
96	90.28	..	88.52
120	89.84	336	88.63
147	89.45	..	88.63
168	89.20	648	88.26
192	89.05	..	88.26
216	89.02	816	88.31
..	...	..	88.44

Viscosity.—In order to endeavor to turn to some good account the apparent extreme sluggishness of reaction of these solutions, viscosity measurements were made upon a solution of a concentration of 90.54%, at 30°. The solution in the viscosimeter was brought to this temperature in some cases from 0° and in other cases from above 60° in the hope that any difference of molecular complexity existing at these widely different temperatures might persist long enough to make itself evident in differences of viscosity at 30°. No difference of viscosity was found beyond the limit of experimental error.

Rounded Solubility Results.—The table below exhibits the above results

TABLE VII.

Solid phase.	Temperature.	Solubility.	Temperature.	Solubility.
Ice	—5°	23.0	—35°	57.8
	—10	33.6	—40	60.5
	—15	41.1	—45	62.9
	—20	46.2	—50	65.1
	—25	50.7	—55	67.1
	—30	54.5	..	..
$As_2O_5.4H_2O$	—55	69.9	—5	80.0
	—50	70.9	0	81.0
	—45	71.9	+5	82.1
	—40	72.9	10	83.3
	—35	73.9	15	84.7
	—30	74.9	20	86.3
	—25	75.9	25	88.0
	—20	76.9	30	90.1
	—15	77.9	35	92.8
	—10	78.9	..	..
$3As_2O_5.5H_2O$	+10	88.4	80	93.2
	20	89.1	90	39.8
	30	89.8	100	94.4
	40	90.5	110	95.0
	50	91.2	120	95.6
	60	91.9	130	96.2
	70	92.6	140	96.8

as rounded graphically for every 5 or 10°, parts of H_3AsO_4 in 100 parts solution being tabulated against temperature.

Dehydration of the Hydrate $3As_2O_5.5H_2O$.

A part of Auger's summary of one of his articles[1] on the hydrates of arsenic pentoxide reads as follows: "It remains still, for the completion of this work, to study the dehydration of the hydrate $3As_2O_5.5H_2O$ at temperatures between 150° and 180°. I have proved in my first work and verified anew that from 180° to 440° the dehydration is complete, and that at 440° the anhydride begins to lose oxygen. One sees that the temperatures remaining to be explored (about 30°) may contain hydrates between $3As_2O_5.5H_2O$ and As_2O_5." From this it would appear that arsenic oxide can be prepared in the anhydrous form by igniting any of its hydrates to constant weight at any temperature above 180°. As it was desired to obtain a small sample of anhydrous pentoxide, a portion of the 3–5 hydrate was ignited under Auger's conditions in a porcelain boat in a current of dry air. When a weighing was made at 6 hours, it was found that most of the water had been expelled; and a second weighing at 8 hours appeared to indicate that dehydration was complete, for the small further loss of weight of the sample was within the ordinary limits of analytical error. Further heating for 24 hours showed, however, that the boat was really losing about 0.2 mg. per hour. The rate of loss was not affected by stirring the contents of the boat with a weighed-in stirrer. A water tube added to the train showed no gain of arsenic, while a tube, containing sulfuric acid of concentration identical with that used for drying, gained in weight precisely what was lost by the boat.

It is well known that the last traces of water are removed from certain substances with great difficulty even at elevated temperatures. As the quantity of water remaining in this instance was by no means so insignificant as to be difficult to determin accurately, this case seemed to offer a favorable opportunity for further study with a view to throwing light on the manner in which such small quantities of water are associated with the anhydrous material. A study of the loss of water from the 3–5 hydrate offered opportunity, also, to any lower hydrates of bringing their existence to light. A number of experiments in dehydration were therefore undertaken, the results of which are described below. The starting material was in all cases the 3–5 hydrate, prepared as described above, and in the form of very fine powder.

Forms of Apparatus.—A Freas electric air oven was employed in maintaining temperatures as high as 230° constant locally to within 1°. Perfectly regular currents of air were obtained by the regulated inflow into a suitable air reservoir of filtered water at constant pressure. Dry air was obtained by passing ordinary air in bubbles not larger than 2 mm. in

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[1] *Compt. rend.*, **146**, 585 (1908).

diameter through a length of 50 cm. of concentrated sulfuric acid contained in an almost horizontal tube. Phosphorus pentoxide was avoided on account of its impurities. Air of known low humidity was obtained by using diluted sulfuric acid in similar tubes immersed in a thermostat. Air of known high humidity was obtained by passing ordinary air over moist cotton wicks contained in a chamber surrounded by the vapor of a boiling liquid, such as carbon tetrachloride. After passing over the wicks, the humid air was conducted to the Freas oven through a glass tube maintained above 100° by means of a winding of electrically heated resistence wire jacketed by asbestos. The material under investigation was contained either in glass tubes or in porcelain crucibles. Air currents of known humidity could be circulated through a vacuum desiccator, containing many crucibles, within the chamber of the air-oven. Connections were entirely of glass.

Dehydration Experiments. XI.—A quantity of 2.4723 grams of the 3–5 hydrate, when heated in a glass tube for 293 hours at 155° in a current of dry air, reached "constant" weight while still containing 1.05% of water. By "constant" weight is here meant that the rate or loss of weight for the last 100 hours of heating was 0.00005 gram per hour. The temperature was then raised successively to 170°, 187°, 208° and 238°, when the water remaining at "constancy" was 0.85%, 0.77%, 0.54% and 0.42%, respectively. The table below indicates, (2) the total number of hours of heating at each temperature, (3) the actual weight of material remaining, (4) the percentage of water remaining in the material, (5) the final rate of loss per hour, (6) the number of hours of final heating used in estimating (5).

TABLE VIII.

(1)	(2) Hours.	(3) Grams.	(4) Per cent.	(5) Grams.	(6) Hours.
25	0	2.4723	11.55	......	..
155	293	2.2101	1.05	0.00005	100
170	99.3	2.2056	0.85	0.00001	86
187	138.8	2.2037	0.77	0.00001	72
208	219.5	2.1987	0.54	0.0000	96
238	235.0	2.1961	0.42	0.000004	119

It was shown that the losses of weight occurring corresponded exactly with the gains of weight of a water absorption tube.

XII.—The experiment at 170° was confirmed by repeating with three portions of the starting material in as many crucibles in ordinary winter air of humidity of the order of 10 mm. aqueous tension. After 547 hours heating at 170° in such air, the average percentage of water remaining was 0.74.

XIII.—Air of 20 mm. humidity when passed over the residue in one of the crucibles from experiment XII at 170° caused no apparent change in weight. Twenty-five mg. of the starting material were then added to the residue in this crucible, in order to induce, by inoculation, the initiation of rehydration at 20 mm. humidity. After 45 hours at 170°, however, in a current of air of this humidity, the added material had arrived at the same degree of dehydration as the rest of the contents of the crucible.

XIV.—A sample of the starting material, when heated at 170° in a current of air of 20 mm. aqueous pressure, became, in 133.3 hours, further dehydrated than the samples subjected to the dehydrating process for longer periods in drier air in experiment XII. The heating was continued for 55 hours longer without further perceptible loss. The percentage of water remaining was 0.72, slightly lower than that remaining at this temperature in experiments XI and XII, pointing to a somewhat higher efficiency in desiccation of the more humid air. It was proved that an empty porcelain crucible did not lose weight when similarly treated.

XV to XVII.—Experiments, in all respects confirmatory of the results at 170°, were made at 210°, the details of which may be omitted. It was established that in a rather humid atmosphere such dehydration is accomplished in 2.5 hours as required 25 hours in ordinary air at the same temperature. As an example of the course of the dehydration of the 3–5 hydrate at 210° in ordinary air, the following results may be quoted:

TABLE IX.

Hours heating at 210°.	Percentage of water remaining			
	Crucible 1.	Crucible 2.	Crucible 3.	Crucible 4.
0	11.55	11.55	11.55	11.55
12.7	0.43	0.41	0.46	0.41
21.5	0.34	0.38	0.38	0.35
30.2	0.21	0.27	0.25	0.26
39.0	0.21	0.21	0.22	0.21
46.5	0.14	0.17	0.19	0.17
53.0	0.06	0.03	0.11	0.07
69.7	0.06	0.03	0.08	0.07

It will be seen that whereas, according to the pentasulfide method of analysis (p. 1454), the starting material should lose 11.50% of water, the average amount actually lost is here 11.49%, which may be regarded as a very satisfactory degree of concordance. The results of these experiments, which were confirmed by four others not quoted, also throw doubt on the accuracy of the analyses made by Balareff[1] by ignition for 3 hours at 200°. His analyses were probably in error by 0.5% rather than by 0.09%, as claimed.

XVIII.—It was shown that at a temperature of 300° in ordinary air, the anhydrous arsenic pentoxide obtained as in the experiments just

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[1] *Loc. cit.*

quoted slowly loses weight, due, probably, to volatilization or decomposition. In 317 hours, four samples showed an average loss of 0.57% of their mass.

XIX.—Air of 300 mm. aqueous pressure, when passed over the residues left on drying to constant weight (for 547 hours) in ordinary air in experiment XII, produced a very marked further dehydration as shown even at their first weighing after 44 hours. It is noteworthy, however, that the content of water remaining in the various samples was not identical within the limits of error of experiment after 245 hours of this treatment. Empty crucibles, similarly treated, remained of constant weight. The error of experiment, as shown by subsequent conversion of the residues to anhydrous pentoxide, in no case exceeded 0.05% of the quantities weighed. This is evidence that no compound of arsenic had been volatilized by the steam. The lack of precise identity in behavior of different samples is covered by the explanation offered below.

XX.—Air of 300 mm. humidity was shown to cause more rapid and complete desiccation of the starting material at 170° than less humid air. Here again, ultimate conversion at 250° to arsenic pentoxide showed that nothing but water had been lost.

Discussion of Dehydration Experiments.

In order to obtain further knowledge as to the way in which the small quantities of water under consideration are held by the arsenic anhydride, a number of further experiments suggest themselves. Some of these have been begun and others will be undertaken in the near future, both with this substance and with others, although the examples given indicate the time consuming character of experiments of this type. The results already obtained, however, demonstrate sufficiently well that a more humid atmosphere may, under certain circumstances, be more efficient in desiccating than an atmosphere less humid. It may not, perhaps, be premature to suggest the trial of a humid atmosphere for the dehydration of substances for atomic weight work.[1]

In regard to the manner in which the small quantities of water are retained, the experiments quoted seem sufficient to show:

(1) The water is not superficial adsorbed water, for this would be increased and not decreased in quantity by using a high aqueous pressure in the drying air.

(2) The water is not contained in cavities. Analysis of the starting material, $3As_2O_5.5H_2O$, showed that even this contains only negligible quantities of water beyond that demanded by the formula. In order that the anhydrous pentoxide should retain 0.72% of included water,

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[1] It will be recalled, for example, that Richards was unable to prepare cupric sulfate with less than 0.12% of water by drying even at 400°. Cf. *Proc. Am. Acad.*, 26, 252 (1891).

about 2% of its weight would require to be made up of a saturated solution of arsenic acid. It may be recalled that, as a general method of obtaining an *anhydrous* residue free from cavity water, Richards[1] has recommended this very process of expelling water of hydration from a hydrated compound.

(3) It seems unlikely that the water could be present as water of hydration or constitution, for this would demand the existence of a large number of hydrates of compositions such as $12As_2O_5.H_2O$.

(4) The water may be present in solid solution or otherwise in the interior of granules from which its escape is prevented more or less effectively by the presence of an anhydrous or little hydrous shell or rind. It will be recalled that Baker and Adlam[2] have shown that hydrated substances such as barium chloride dihydrate are pervious to water vapor, while anhydrous substances such as potassium chlorate are not. If the—at best very low—degree of hydration of the impervious shell is controlled jointly by the water concentrations within and without, it is evident that humid air may desiccate the entire material further and more quickly than dry air.[3]

Summary.

1. Only two compounds of arsenic pentoxide and water appear to be isolible, the 1–4 hydrate and the 3–5 hydrate. Satisfactory methods of preparing each of these hydrates have been described.
2. All uncertainty as to the formula of the 3–5 hydrate has been removed.
3. A new volumetric method of determining free arsenic acid has been worked out.
4. The solubility curves of the above two hydrates have been determined, as well as the curve of depression of the freezing point of water by arsenic acid.
5. The melting point of the 1–4 hydrate of arsenic acid has been established.
6. A case of exceptionally slow removal by seeding of supersaturation has been described.
7. The retention of small quantities of water by arsenic pentoxide at elevated temperatures has been investigated and discussed.
8. The correct conditions for the analysis of the hydrates of arsenic pentoxide by igniting to the anhydride have been determined.
9. It has been shown that water vapor is sometimes an aid in dehydration.

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[1] *Proc. Am. Phil. Soc.*, **42**, 28 (1903).

[2] *J. Chem. Soc.*, **99**, 507 (1911).

[3] Industrial chemists may be reminded that an atmosphere of wet steam is used in drying such a wood as oak.

This investigation was carried out in the Kent Chemical Laboratory of the University of Chicago.

OBERLIN COLLEGE,
OBERLIN, OHIO.
415 PARK STREET,
MADISON, WISCONSIN.

THE SPECIFIC HEATS OF CRYSTALLIZED SALTS.

BY FREDERICK GRAY JACKSON.

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The physical structure of double salts and salts containing water of crystallization has long been a subject of discussion. It was hoped that some light might be thrown on this subject by a study of their specific heats at various temperature ranges. These figures would also be of considerable value in other calculations of a thermodynamic nature, and very little work had been done at temperatures below 0°. Accordingly the research was undertaken.

The various sulfates of copper were chosen for this work because of the number of possible salts that could be made, their permanence, purity, and ease of analysis. Baker & Adamson's analyzed chemicals were used throughout the work, but were always checked by analyses made on the sample actually used. The double salts were made by crystallizing them out at about 30° from saturated solutions of the calculated amounts of the single salts. To these a little sulfuric acid was added to prevent the formation of basic salts. The crystals were crushed and washed with distilled water four times, dried in a centrifuge, and then powdered and air dried to constant weight. Electrolytic determination of the per cent of copper was in each case within the limit of accuracy of the method. Anhydrous copper sulfate was made from the pure hydrated salt by grinding and drying for several days at 250° on a sand bath with stirring until constant weight, very nearly that calculated, was attained. The salt was bottled hot and used with minimum exposure. The other salts could be bought in a high state of purity. These were checked only by drying tests to find the amount of included water, which was in all cases negligible. Details of the analyses will be given later.

The specific heats of the single salts used have been determined at short temperature ranges between +15° and +100° by various experimenters of half a century ago. Regnault[1] in 1841, Pape[2] in 1864, Kopp[3] in 1864, and Schüller[4] in 1869, worked on them as part of a comprehensive study of the specific heat of compounds. While their determinations were of the greatest importance at that time, and were undoubtedly performed with the greatest accuracy then obtainable, they cannot be too closely

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[1] Regnault, *Ann. chim.*, [3] **1**, 129 (1841).

[2] Pape, *Pogg. Ann.*, **122**, 408 (1864).

[3] Kopp, *Ann. Suppl.*, [3] **1**, 289 (1864–5).

[4] Schüller, *Pogg. Ann.*, **136**, 70, 235 (1869).