DETERMINATION OF THE VAPOR PRESSURE OF SALT-HYDRATES BY A DISTRIBUTION—CONDUCTIVITY METHOD.

BY ARTHUR A. NOYES AND LEON R. WESTBROOK.

I. Introduction.

In the foregoing article a promising distribution method has been outlined by R. E. Wilson for determining the water vapor pressure of salt-hydrates. In carrying out this method the pair of salt-hydrates is shaken with anhydrous or hydrous *iso*-amyl alcohol till equilibrium is reached, and the alcoholic phase is analyzed for its water content by saturating it with solid potassium thiocyanate and measuring the electrical conductance of the mixture. The interpretation of the results requires also a knowledge of the water-vapor pressure of the water—*iso*-amyl-alcohol mixtures corresponding to definite water contents, and these must be experimentally determined.

The preliminary experiments which led to the inception of this method have been described by Professor Wilson in his article, and, as he has turned his attention to another phase of the investigation (the study of a method for evaluating accurately the vapor pressures of hydrated salts by determining whether they lose or gain weight when placed within an enclosed space in communication with aqueous solutions of sulfuric acid) we have undertaken with his coöperation to perfect the distribution-conductance method. The results of this investigation are described in this article.

II. The Conductance-Composition Diagram for Water—Iso-amyl-alcohol Solutions Saturated with Potassium Thiocyanate.

1. **Description of the Method.**—The general procedure for obtaining the data for constructing the conductance-composition diagram was simply to shake solutions of *iso*-amyl alcohol and water of known composition with solid potassium thiocyanate for 24 hours in a thermostat at 25°, and to measure the conductance of the resulting mixture. Several such mixtures with compositions varying from 0 to 3% of water were so investigated.

The *iso*-amyl alcohol used throughout the work was a commercial product which contained much water and small amounts of other impurities   It was purified by repeated fractionation, the constant-boiling

fraction coming over between 131.1 and 131.6° after several distillations being used. Measurements, made as outlined later, of the conductance of mixtures prepared by shaking several such samples with solid potassium thiocyanate gave the following values for the specific conductance multiplied by 10^6: 34.52, 34.73, 34.30, 34.10, 34.32, 33.78, 34.23; average 34.28. These results show that a practically constant composition was obtained by the process of purification.

The potassium thiocyanate used was obtained by recrystallizing the purest commercial product obtainable and drying the crystals at 110°. The crystals were then ground, the powder dried to constant weight at 110°, and kept in a vacuum desiccator over sulfuric acid.

In making the mixtures of water and *iso*-amyl alcohol, it was found impracticable to weigh small amounts of water directly into the alcohol, even from a weighing pipet, because of the error introduced by evaporation. In order to meet this difficulty and at the same time increase the precision of weighing very small amounts of water, the following method was used. A 250-cc. conical flask provided with a well-ground glass stopper was weighed, about 150 g. of anhydrous *iso*-amyl alcohol was poured in, care being taken not to wet the neck of the flask, and the flask was weighed again; then about 8% as much conductivity water was added, and the exact weight was again determined. The resulting solution served as a standard for making solutions of smaller water content. This was done by weighing some anhydrous *iso*-amyl alcohol in a tared glass-stoppered flask of about 50 cc. capacity, and adding the required amount of the standard solution of water in *iso*-amyl alcohol and weighing again.

The alcohol-water mixtures were rotated in a thermostat at 25° for 24 hours with solid potassium thiocyanate in 40 cc. wide-mouth glass-stoppered specimen bottles, carefully protected from moisture by coating the stoppers with paraffin and covering them with rubber nipples. After the shaking, the bottles were hung up in the thermostat to permit the solid matter to settle. The top of a bottle was then carefully dried, the bottle was opened, a pair of plunge electrodes was introduced into the solution, and after a few minutes the conductance was measured.

The electrodes were 2 platinum plates measuring about 1 cm. $\times$ 2 cm., welded to platinum wires, which in turn were fused into the ends of a Λ-shaped tube. The plates were rigidly supported at a distance 3 mm. apart by 4 small pieces of glass fused on each corner. The lower branches of the Λ tube contained mercury into which dipped 2 copper wires, which passed out through the upper branch, being insulated from each other by wax. The upper branch of the tube passed through a rubber stopper which fitted the bottles in which the solutions were shaken. The elec-

trodes, when not in use, were kept immersed in anhydrous amyl alcohol in a similar bottle, suspended in the thermostat.

At the beginning the electrodes were platinized and the cell-constant was determined in the usual manner, and was found to have the value 0.08523 (this being the factor by which the conductance of a solution in the bottle must be multiplied to give its specific conductance).

The range of values of the water content covered in this work was 0 to 3%. Although the solubility of water in amyl alcohol is roughly 10%, it was found that when the water content exceeded 2.5 to 3%, the solubility of the potassium thiocyanate became so great as to cause separation of an aqueous phase. When it was desired to determine the composition of mixtures containing more than 2.5% of water, a weighed sample was diluted with a weighed amount of anhydrous *iso*-amyl alcohol sufficient to bring the water content of the resulting solution below 3%, and this solution was shaken with potassium thiocyanate.

2. The Conductance Data.—Table I contains the values of the specific conductance $\times 10^6$ in reciprocal ohms at 25° of the various water—*iso*-amyl-alcohol solutions after they had been saturated with potassium thiocyanate at 25°. These data served for the construction of the composition-conductance diagram which was used later for determining the water content of the solutions in equilibrium with the solid hydrates.

TABLE I.—CONDUCTANCE OF WATER—ISO-AMYL–ALCOHOL SOLUTIONS SATURATED WITH POTASSIUM THIOCYANATE AT 25°.

Water. %	Specific conductance. $\times 10^6$.	Water. %	Specific conductance. $\times 10^6$.
0.00	34.28	1.289	97.65
0.1082	37.55	1.454	115.3
0.1770	41.20	1.500	116.2
0.2319	43.50	1.541	123.1
0.3532	47.75	1.848	149.9
0.3736	48.04	1.915	160.4
0.4809	51.60	2.132	180.7
0.5675	55.76	2.137	182.8
0.7612	67.78	2.561	239.0
0.8822	70.01	2.786	274.5
1.019	82.40	2.944	299.5
1.226	94.58	3.016	317.8
1.288	98.47	.....	......

III. Solubility of Water in Iso-amyl Alcohol.

The method was first used to determine the solubility of water in *iso*-amyl alcohol. Anhydrous alcohol and water (with a specific conductance of 1.7×10^{-6}) were shaken together in a thermostat at 25° for several hours. The water content of the alcohol layer was then determined by diluting it with a known weight of anhydrous *iso*-amyl alcohol, saturating it with potassium thiocyanate, and measuring its conductance, as described above.

Several determinations gave the following values for the weight percentage of water in the alcoholic phase at 25°: 9.902, 9.924, 9.860, 9.840, 9.891; average, 9.884%. This result is about 1% higher than that (9.75–9.78) found by R. E. Wilson as described in the preceding article. This variation is of little moment as far as the vapor–pressure—water–content curve is concerned, however, because the curve is very flat in this vicinity.

IV. Composition of Iso–amyl alcohol—Water Mixtures in Equilibrium with Solid Hydrates.

1. **Description of the Method.**—The second part of the work consisted in obtaining data for a water–content—vapor–pressure diagram. The general procedure employed consisted in preparing a pair of hydrates of known composition, shaking them with anhydrous or hydrous *iso*-amyl alcohol, determining the water-content of the resulting equilibrium mixture by conductivity measurements as described in Section II of this article, and plotting this water-content against the known vapor pressure of the same pair of hydrates.

The hydrates employed were those whose vapor pressures were being accurately determined in this laboratory by R. E. Wilson and R. G. Dickinson by the method described in the preceding article. A few others were included, among which are the hydrates of strontium chloride, whose vapor pressures have since been accurately determined by Baxter and Lansing.[1]

The equilibrium was approached from both sides by shaking the hydrates with solutions of appropriate composition. This was possible, since the composition of the equilibrium mixture could be roughly estimated from the approximately known values of the vapor pressure of the pairs of hydrates under investigation. The solution which was prepared with a water content lower than the estimated equilibrium value will be called the undersaturation mixture, while the other solution prepared with a higher water content will be known as the oversaturation mixture.

Determinations of the water content of the solution in contact with the hydrates were made (by shaking a sample of the solution with solid potassium thiocyanate, and measuring the conductivity) at intervals of about 24 hours. The rate of change in water content or the rate of attaining the equilibrium was thus ascertained. This rate was found to vary very greatly with the different salts used, as the data given in the tables below show.

In cases where the water content exceeded about 2.5%, a weighed portion of the sample was diluted with a weighed amount of anhydrous *iso*-amyl alcohol, and then shaken with thiocyanate. Although the composition-conductance diagram was determined for values of the water

[1] Baxter and Lansing. THIS JOURNAL, 42, 425 (1920).

content up to 3%, it was found that as this percentage is approached the salting-out effect of the thiocyanate varies with the length of shaking, so that unreliable results are obtained.

The possibility that the hydrates investigated were considerably soluble in water-alcohol solutions necessitated a determination of this solubility in order to ascertain whether it was of such a magnitude as to affect the conductance, which is assumed to be wholly due to the dissolved thiocyanate. For this purpose the conductance of a portion of the equilibrium mixture was measured, and compared with the conductance of a solution of pure alcohol and conductivity water of the same composition. The difference between these values could then be ascribed to the presence of dissolved salt. The following results, obtained with hydrates of copper sulfate and disodium hydrogen phosphate show that the conductance due to the dissolved salt is negligible.

	Conductance.
Equilibrium mixture (containing 2.5% of water) from $CuSO_4.$- 5–3 H_2O	0.08×10^{-6}
Mixture of amyl alcohol and water containing 2.5% of water..	0.02×10^{-6}
Equilibrium mixture (containing 5% of water) from $Na_2HPO_4.$- 12–7 H_2O	0.20×10^{-6}
Mixture of amyl alcohol and water containing 5% of water...	0.03×10^{-6}

2. Preparation of the Salt Hydrates.—The salt-hydrates with which the alcohol-water solutions were rotated were in most cases prepared by finely powdering the crystallized salt with the maximum water content, and heating this in a crucible at 110° till it contained a percentage of water intermediate between those of the two hydrates to be investigated, as shown by a determination of the water content made by igniting a sample of the preparation at a temperature sufficient to dehydrate it competely. Thus the hydrates of disodium orthophosphate were ignited to sodium pyrophosphate. When the salt-hydrate was prepared otherwise than by the method just described, this is indicated in the tables below by foot-notes.

The attainment of equilibrium proved to be so extremely slow with certain hydrates (those of zinc and copper sulfates) that only rough estimates of the water content corresponding to equilibrium could be made. It seems probable that a more rapid rate might be realized by preparing separately each of the two hydrates of the pair under investigation and grinding them intimately together, as was done by Baxter and Lansing in their recent investigation. It was planned to try this method, but the time available did not permit giving it a fair trial.

3. The Water-content Data.—Table II, which is for the most part self-explanatory, shows in detail the results obtained with the three hydrates of disodium orthophosphate. The initial percentage of water in the salt-hydrate rotated with the solution and the initial composition of

TABLE II.—WATER CONTENT OF WATER—ISO-AMYL-ALCOHOL SOLUTIONS SHAKEN WITH VARIOUS SALT-HYDRATES.

HYDRATES: $Na_2HPO_4.12-7\ H_2O$.

Over-saturation mixture at the start:

$Na_2HPO_4.10.0\ H_2O$. 50 g.; iso-amyl alcohol 160 g.; water, 8 g.

Under-saturation mixture at the start:

$Na_2HPO_4.7.6\ H_2O$,[a] 50 g.; iso-amyl alcohol 150 g.; water, 14.2 g.

Hours of shaking.	Percentage of water.	
	Under-saturated mixture.	Over-saturated mixture.
0	4.8	8.7
24	5.04	5.12
54	5.00	5.00
78	5.00	5.02
198	5.006	5.008
∞	**5.005** ± 0.005	

[a] Prepared by exposing to dry air the preceding preparation (with 10.0 H_2O).

HYDRATES: $Na_2HPO_4.7-2\ H_2O$.

Under-saturation mixture at the start:

$Na_2HPO_4.6.0\ H_2O$, 40 g.; iso-amyl alcohol, 110 g.; alcohol-water mixture (8% H_2O), 50 g.

Over-saturation mixture at the start:

$Na_2HPO_4.3.0\ H_2O$, 30 g.; iso-amyl alcohol, 45 g.; alcohol-water mixture (8% H_2O), 75 g.

0	2.5	5.0
40	2.98	3.03
64	3.00	3.02
112	3.003	3.031
212	3.009	.....
312	3.024	3.036
∞	**3.02** ± 0.01	

HYDRATES: $Na_2HPO_4.2-0\ H_2O$

Under-saturation mixture at the start:

$Na_2HPO_4.1.9\ H_2O$, 40 g.; iso-amyl alcohol, 160 g.; alcohol-water mixture (8% H_2O), 40 g.

Over-saturation mixture at the start:

$Na_2HPO_4.1.0\ H_2O$, 40 g.; iso-amyl alcohol, 120 g.; alcohol-water mixture (8% H_2O), 40 g.

0	1.6	2.0
27	1.785	.....
51	1.787	2.10
99	1.788	2.05
152	....	1.995
197	....	1.892
220	....	1.870
244[a]	....	1.867
292	....	1.793
∞	**1.79** ± 0.01	

[a] Because of the slow rate of change and the nearly constant value for the water content in this series, it was thought that perhaps the anhydrous salt present had been coated over with a layer of hydrate. and was therefore ineffective. Consequently 10 g. of anhydrous disodium orthophosphate was introduced just before starting the last shaking.

the solution itself are shown in each case in the headings of the table. The first few determinations of the water content were made more roughly than those near the end of a series when equilibrium was practically attained. What is regarded as the best value of the water-content is given at the foot of each table opposite the time ∞. To this best value is attached with a $\doteq$ sign a quantity which indicates, not the "probable error" in the usual conventional sense, but the limits between which the true value almost certainly lies, as far as can be judged from a consideration of the results from the under saturated and oversaturated side.

The results for these three hydrates are typical of all those studied—varying from the 12–7 pair which approach equilibrium quite rapidly, to the 2–0 pair which are very sluggish. Detailed results are therefore omitted for the other hydrates studied, the final results and probable deviation being given in Table III.

V. The Vapor–pressure—Water–content Diagram.

Table III contains the best values derived above of the percentages of water in the water—*iso*–amyl–alcohol solutions in equilibrium with the various pairs of salt-hydrates, and also the vapor pressures at 25° of these pairs of hydrates, as determined by Wilson (W),[1] Dickinson (D),[1] Baxter and Lansing (B),[2] and Menzies (M).[3]

TABLE III.—SUMMARY OF THE VALUES OF VAPOR PRESSURE AND THE WATER CONTENT OF THE EQUILIBRIUM MIXTURE.

Hydrates.	Percentage of water.	Vapor pressure in mm.
Water[a]	9.88 $\doteq$ 0.05	23.58 (W)
$Na_2SO_4.10$–0 H_2O	5.095 $\doteq$ 0.005	$\begin{cases} 19.22 \text{ (D)} \\ 19.20 \text{ (B)} \end{cases}$
$Na_2HPO_4.12$–7 H_2O	5.005 $\doteq$ 0.005	19.13 (D)
$Na_2HPO_4.7$–2 H_2O	3.02 $\doteq$ 0.01	14.50 (D)
$ZnSO_4.6$–1 H_2O	2.55 $\doteq$ 0.05	....
$Na_2HPO_4.2$–0 H_2O	1.79 $\doteq$ 0.01	....
$SrCl_2.6$–2 H_2O	1.475 $\doteq$ 0.005	8.37 (B)
$CuSO_4.5$–3 H_2O	1.3 $\doteq$ 0.2	$\begin{cases} 7.80 \text{ (W)} \\ 7.77 \text{ (M)} \end{cases}$

[a] Saturated with *iso*-amyl alcohol.

The results are represented diagrammatically in Fig. 1. It will be seen that the graph passing through the points forms a smooth curve, and that in the case where a control is made possible by independent measurements (those of Dickinson and Baxter and Lansing on $Na_2SO_4.10$–0 H_2O and of Dickinson on $Na_2HPO_4.12$–7 H_2O), there is satisfactory agreement between them. (The water-content value in the mixture in equilibrium with $CuSO_4.5$–3 H_2O is too inexact to make the small divergence of the point representing it from the curve significant.) The diagram (or better,

[1] See the preceding article.
[2] Baxter and Lansing, THIS JOURNAL, **42,** 425 (1920).
[3] Menzies, *ibid.*, **42,** 1954 (1920).

one plotted on a larger scale with the aid of the data given in Table III) can therefore be employed with the expectation that it will give an accuracy of about 0.1 mm. in the vapor-pressure value.

The vapor pressures of the two pairs of hydrates, $Na_2HPO_4.2-0 \ H_2O$ and $ZnSO_4.6-1 \ H_2O$, for which the percentages of water (2.55 and 1.79) in the alcoholic equilibrium mixture have been determined, but for which
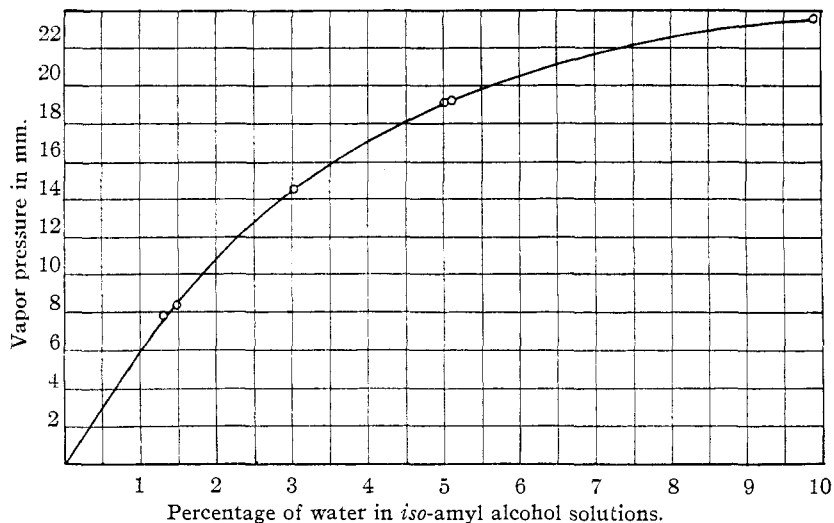

Fig. 1.

accurate vapor pressures are not available, may be obtained from the diagram by interpolation. These vapor pressures are thus found to be *9.8* mm. for $Na_2HPO_4.2-0 \ H_2O$, and *13.0* mm. for $ZnSO_4.6-1 \ H_2O$.

Finally, attention may be called to the vapor–pressure—water–content diagram itself as probably typical of the behavior of two components of limited but considerable miscibility. It will be seen that the vapor pressure of the water (the component present in small proportion) increases at first rapidly, and through a considerable interval not very far from proportionally to its concentration (as Henry's law requires) and that it increases much more slowly as saturation is approached.

VI. Summary.

In this article is described in detail a new method for the determination of the water-vapor pressure of salt-hydrates. This method consists in agitating them with anhydrous or partially hydrated *iso*-amyl alcohol till equilibrium is established and analyzing the alcoholic phase for its water content by saturating it with solid potassium thiocyanate and measuring the electrical conductance of the mixture.

The development of the method into a practically useful form involved (1) the determination of the conductance of *iso*-amyl alcohol solutions of

known water content saturated with potassium thiocyanate, and (2) the determination of the water content in *iso*-amyl-alcohol solutions which had been brought into equilibrium with pairs of hydrates of accurately known vapor pressure.

The results of the conductance—water-content determinations are given in Table I, and those of the vapor–pressure—water–content measurements are summarized in Table III. A vapor-pressure—composition diagram for the water–*iso*-amyl-alcohol mixtures is shown in Fig. 1, which is probably typical for liquids of limited but considerable miscibility.

CAMBRIDGE 39, MASS.

THE ACTION OF SODIUM SULFIDE ON FERRIC OXIDE.

BY J. C. WITT.

Received January 14, 1921.

The color produced by the action of alkaline sulfides on compounds of iron and certain other metals has been noted by several investigators. De Koninck and Ledent[1] observed that when solutions of nickel, cobalt, or iron salts were treated with an excess of sodium sulfide, the mixture became dark, but remained clear and would pass unchanged through the finest filter papers. In the case of iron salts the color gradually changed to a bright green, resembling chrome sulfate or potassium manganate. The authors did not comment on the cause of the color. A number of years later, de Koninck[2] recommended the reaction as a test for iron. He stated that it was as delicate as the ferrocyanide reaction and could be used equally well with the ferrous or ferric ion. In very dilute solutions, the color changed from brown to green. In the presence of sodium chloride or sulfate, the formation of the green substance was retarded and then disappeared more quickly. The effect of the presence of zinc, aluminum, magnesium and cadmium was discussed. De Koninck was of the opinion that oxidation and reduction were not concerned in the change from brown to green but that the color was due to colloidal iron sulfide.

Konschegg and Malfatti[3] have studied the reaction between potassium sulfide and iron salts. They believe the color is not due to colloidal substances, but to the solution of some higher sulfide of iron in the alkali. They state that on dialysis the potassium is removed, leaving behind a black or brownish-black solution of iron sulfide. Szilard[4] has prepared what he terms heterogeneous colloidal hydrates, by treating the hydroxide of a metal with the salt of the same, or of a different metal. He has studied the hydroxides of uranium, thorium, zirconium. lead, yttrium,

[1] De Koninck and Ledent, *Z. angew. Chem.*, **1891**, p. 202.

[2] De Koninck, *Bull. soc. chim. Belg.*, **19**, 181; *J. Chem. Soc.*. **90**, 397 (1906).

[3] Konschegg and Malfatti, *Z. anal. Chem.*, **45**, 747 (1906).

[4] Szilard, *J. chim. phys.*, **5**, 636 (1907).