

copper. The reaction is apparently a quantitative one, involving 3 atoms of copper, cadmium or zinc, and 2 molecules of trichloro-acetic acid.

As a matter of economy or convenience, chloroform or carbon tetrachloride may be used instead of trichloro-acetic acid, but if this is done the ammoniacal solution should consist of one part of conc. aqueous ammonia and one part of alcohol (denatured will do) in order to increase the solubility of the organic trihalide. The latter may be added in any quantity, though it is well not to add more than will dissolve. If carbon tetrachloride is used it must be free from sulfur compounds, which it is very liable to contain, and which will stain the silver. The action of these reagents on copper is considerably slower than that of the ammonium trichloro-acetate solution.

#### Summary.

Copper can be rapidly and quantitatively removed from a silver cathode by means of an ammoniacal solution of a compound containing a trichloro-methyl or tribromo-methyl group. An ammoniacal solution of ammonium trichloro-acetate is recommended for this purpose, but a solution of chloroform or carbon tetrachloride in ammoniacal aqueous alcohol can also be used.

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### SOME NEW METHODS FOR THE DETERMINATION OF THE VAPOR PRESSURE OF SALT-HYDRATES.

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#### I. Introduction.

The vapor pressures of salt-hydrates have been studied by a large number of investigators. Indeed, as the bibliography presented in the next section indicates, few physico-chemical phenomena have aroused a livelier or more sustained interest.

Both practical and theoretical considerations have united to arouse this interest. Much of the earlier work was done for the express purpose of substantiating van't Hoff's equation and other thermodynamic laws for the case of salt-hydrates. Others have worked with a view to determining the free energy of the compounds. Furthermore, a knowledge of the exact conditions under which salts are efflorescent, stable, or deliquescent, the preparation and preservation of pure hydrates of a given composition, the selection of desiccating agents, and the construction of phase-rule diagrams are important practical considerations which also depend on an accurate knowledge of the vapor pressure of hydrates.

The author desires to express his appreciation of the helpful advice and suggestions of Dr. A. A. Noyes, under whose direction this work was carried on, and his indebtedness to the Carnegie Institution of Washington for the financial assistance by which the research was aided.

## II. Previous Investigations.

Since this paper is to present several new methods for the determination of vapor pressures, it seems desirable to describe briefly the work and methods of previous investigators and later point out wherein they are not satisfactory.

Prior to 1875 the work had little scientific value, owing chiefly to the hazy notions which prevailed as to the nature of the phenomenon. Between 1875 and 1881 several independent investigators discovered and formulated in a more or less general way the fundamental fact that a mixture of two hydrates (or the lowest hydrate and its anhydrous salt) is necessary to produce a monovariant system with a definite vapor pressure for each temperature.<sup>1</sup>

A great variety of methods have been used by different investigators for the determination of the vapor pressures of salt-hydrates. They may be grouped under three heads: static methods, dynamic methods, and indirect methods.

**1. Static Methods.**—The first method employed for the measurement of vapor pressures was to introduce the hydrate into an ordinary barometer tube, and record the lowering of the mercury column after it reached a constant value as the vapor pressure of the hydrate. This method was used by Debray,<sup>2</sup> Lescoeur,<sup>3</sup> Wiedemann,<sup>4</sup> and especially Pareau,<sup>5</sup> all among the earliest investigators.

To Frowein<sup>6</sup> are due several important improvements in the static methods for vapor-pressure determination. He developed an improved form of tensimeter, in which the pair of hydrates was placed in one bulb, conc. sulfuric acid in another, and the two connected by a U-tube filled with olive oil. The whole apparatus was then evacuated and sealed off. The use of the lighter liquid in the manometer had the advantage of giving greater differences in height. Various further improvements and refinements in the procedure and in the liquid used in the U-tube were made by Andreae,<sup>7</sup> Roozeboom,<sup>8</sup> and Schottky.<sup>9</sup> Menzies<sup>10</sup> has very recently obtained quite satisfactory results, using cottonseed oil.

During the last decade, however, the trend of static methods has been toward the

<sup>1</sup> This fixed vapor pressure is generally referred to as the vapor pressure of the higher hydrate of the pair under consideration.

<sup>2</sup> Debray, *Compt. rend.*, **64**, 603 (1867-8); **66**, 194 (1868).

<sup>3</sup> Lescoeur, *Ann. chim. phys.*, [6] **16**, 378 (1889); see also *ibid.*, **21**, 511 (1890).

<sup>4</sup> G. Wiedemann, *J. prakt. Chem.*, [2] **9**, 338 (1874); see also *Pogg. Ann. Jubeband*, **1873**, p. 474.

<sup>5</sup> Pareau, *Wied. Ann.*, **1**, 55 (1877).

<sup>6</sup> C. P. Frowein, *Z. physik. Chem.*, **1**, 5; also 362 (1887).

<sup>7</sup> I. L. Andreae, *ibid.*, **7**, 241 (1891).

<sup>8</sup> Roozeboom, *ibid.*, **4**, 43 (1889).

<sup>9</sup> H. Schottky, *ibid.*, **64**, 433 (1908).

<sup>10</sup> Menzies, *THIS JOURNAL*, **42**, 1951 (1920).

use of mercury rather than oil, with the adoption of many refinements in apparatus and manipulation, especially in the measurement of the height of the mercury columns. Johnston,<sup>1</sup> Bahr,<sup>2</sup> Bolte,<sup>3</sup> and Salvadori,<sup>4</sup> have adopted such refinements in working on hydrates, while Fraser and Lovelace<sup>5</sup> and Tower and Germann<sup>6</sup> have used other very accurate measuring devices to determine the vapor-pressure lowering of solutions.

Other little used static methods involve the direct measurement of the pressures with a very sensitive gage introduced by Mitscherlich<sup>7</sup> and also by Dieterici.<sup>8</sup> Another scheme introduced by Lescoeur<sup>9</sup> consisted in a determination of the dew point of air above the hydrates.

**2. Dynamic Methods.**—A second type of methods for vapor-pressure determination may be classed as dynamic. The first one of this type was developed in the early eighties by Mueller-Erbach,<sup>10</sup> who assumed that the vapor pressures of two substances were proportional to their relative rates at which water vapor passed out of similar flasks containing the hydrates or pure water, when the flasks were placed in a desiccator.

The ordinary dynamic method, first introduced by Tammann,<sup>11</sup> and modified by Partington,<sup>12</sup> consists in passing a measured volume of air slowly through a tube containing the hydrate and calculating the vapor pressure from the loss in weight. Although this type of method, as applied to the vapor pressure of solutions, has recently been brought to a high degree of accuracy by Berkeley, Hartley and Burton,<sup>13</sup> and especially by Washburn,<sup>14</sup> it had never given very satisfactory results with solid hydrates up to the time the investigation here described was carried out. Baxter and Lansing<sup>15</sup> and Menzies<sup>16</sup> have since obtained some very good results by adopting certain important refinements. They have not, however, reported any results on salts which are known to approach equilibrium but slowly.

Two other ingenious dynamic methods have been developed by Johnston<sup>17</sup> and by Smith and Menzies.<sup>18</sup> The latter method has recently been used with success by Derbe and Yngve.<sup>19</sup>

**3. Indirect Methods.**—Under this head may be classed a group of methods in which the vapor pressure of a hydrate is not measured directly, but is determined by

<sup>1</sup> Johnston, *Z. physik. Chem.*, **62**, 347 (1908).

<sup>2</sup> F. Bahr, *Z. anorg. Chem.*, **71**, 88 (1911).

<sup>3</sup> H. Bolte, *Z. physik. Chem.*, **80**, 338 (1912).

<sup>4</sup> R. Salvadori, *Gazz. chim. ital.*, **42**, (a) 458 (1912).

<sup>5</sup> Fraser and Lovelace, *THIS JOURNAL*, **36**, 2439 (1914).

<sup>6</sup> Tower and Germann, *ibid.*, **36**, 2449 (1914); see also *ibid.*, **30**, 1219 (1908).

<sup>7</sup> Mitscherlich, "Lehrbuch der Chemie," 4th Ed., p. 565; *J. prakt. Chem.*, [2] **9**, 338 (1874); *J. Chem. Soc.*, **99**, 467 (1911).

<sup>8</sup> Dieterici, *Wied. Ann.*, **42**, 513 (1891); see also *ibid.*, **50**, 47 (1893); **62**, 616 (1897).

<sup>9</sup> Lescoeur, *loc. cit.*

<sup>10</sup> Mueller-Erbach, *Ber.*, **14**, 1093 (1881); see also *Z. physik. Chem.*, **2**, 113, 546 (1888); **4**, 1 (1889); *Wied. Ann.*, **32**, 316 (1888).

<sup>11</sup> G. Tammann, *Ann. chim. phys.*, **63**, 16 (1897); see also *Z. physik. Chem.*, **27**, 323 (1898); *Wied. Ann.*, **33**, 322.

<sup>12</sup> J. R. Partington, *J. Chem. Soc.*, **99**, 466 (1911).

<sup>13</sup> Berkeley, Hartley and Burton, *Phil. Trans.*, (A) **209**, 177 (1909).

<sup>14</sup> Washburn, *THIS JOURNAL*, **37**, 309 (1915).

<sup>15</sup> G. P. Baxter and J. E. Lansing, *ibid.*, **42**, 419 (1920).

<sup>16</sup> Menzies, *loc. cit.*

<sup>17</sup> Johnston, *loc. cit.*

<sup>18</sup> Smith and Menzies, *THIS JOURNAL*, **32**, 907 (1910).

<sup>19</sup> Derbe and Yngve, *ibid.*, **38**, 1439 (1916).

bringing it into equilibrium with some liquid whose aqueous vapor pressure has previously been determined with reference to its water content or some other more easily measured property, such as specific gravity, boiling point, etc.

Thus Mueller-Erbach<sup>1</sup> determined the concentration of sulfuric acid over which a pair of hydrates neither gained nor lost weight. This method was also used by Tammann,<sup>2</sup> Van Bemmelen,<sup>3</sup> and Löwenstein,<sup>4</sup> in the study of silicic acid gels, etc.

Linebarger<sup>5</sup> first suggested obtaining equilibrium by shaking the hydrates with an excess of a liquid in which they were insoluble, but which would dissolve small amounts of water until equilibrium was reached. He used ether as the comparison liquid, worked at its boiling point, and measured the water content by the change in boiling point. Considerably later Foote and Scholes<sup>6</sup> published a large number of results based upon the use of ethyl alcohol as the reference liquid, the water content being determined by density measurements.

### Results.

The vapor-pressure data at 25° for practically all the hydrated salts on which more than one determination has been made are summarized in Table I. Most of the values have been corrected for small variations in temperature or interpolated from curves. For the sake of completeness and comparison the new values presented in this article and in the following article by Noyes and Westbrook are included in the last column of the table.

### III. Factors Governing the Selection of Methods.

The extremely unsatisfactory state of the data now available becomes apparent upon studying the comparative results presented in Table I. With the exception of a few hydrates with fairly high vapor pressures, the average deviations from the mean are well over 10%. This can arise only from unsatisfactory methods of measurement.

Disregarding many obvious errors in principle or practice which invalidate most of the early work, it seems desirable to consider briefly a few of the inherent difficulties and limitations in the various types of methods previously available.

The *static methods* previously described, even with the more recent refinements, appear to give good results in measuring the vapor pressure of pure liquids, but when applied to salt hydrates they are subject to several serious difficulties. *First*, many solid hydrates approach equilibrium with extreme slowness when left undisturbed in a closed space; thus several observers have reported that the vapor pressure appeared to be increasing slowly, even after a period of 3 or 4 months at ordinary temperatures. *Second*, the equilibrium is ordinarily approached from one side only, making it difficult to ascertain how closely equilibrium has been

<sup>1</sup> Mueller-Erbach, *loc. cit.*

<sup>2</sup> G. Tammann, *loc. cit.*

<sup>3</sup> Van Bemmelen, *Z. anorg. Chem.*, **13**, 233 (1897).

<sup>4</sup> Löwenstein, *ibid.*, **63**, 69 (1909).

<sup>5</sup> Linebarger, *Z. physik. Chem.*, **13**, 500 (1894).

<sup>6</sup> Foote and Scholes, *THIS JOURNAL*, **33**, 1309 (1911).

TABLE I.  
The Vapor Pressure of Salt-Hydrates at 25° in Millimeters of Mercury.

Salt.	Hydrate.	Voote and Scholes.	Frowin.	Lescour.	Mneller-Erzbach.	Cohen(C) Andreae(A) Porceau(P)	Baxter(Ba) Bolte(Bo) Menzies(M) Johnston(J)	Wiedmann(W) Partington(P) Schottky(S) Roozeboom(R)	Wilson(W) Dickinson(D) Noyes-Westbrook(N-W)
CuSO <sub>4</sub> .....	3-5	7.0	7.4	8.5	7.3	7.9(P)	7.77(M)	7.68(P)	7.80(W)
	1-3	4.7	..	3.3	4.6	..	..	7.5(S)	(4.7)(W)
	0-1	0.8	..	..	0.5	..	..	..	..
Na <sub>2</sub> SO <sub>4</sub> .....	0-10	18.2	..	19.0	17.6	..	19.20(Ba)	..	19.22(D)
K <sub>2</sub> CO <sub>3</sub> .....	0-1.5	1.1	..	1.5	..	..	..	..	..
ZnSO <sub>4</sub> .....	6-7	13.6	14.6	14.0	12.9	..	..	14.5(W)	..
	1-6	12.8	13.2	..	11.7	..	..	..	13.0(N-W)
	0-1	1.0	..	..	0.5	..	..	..	..
MgSO <sub>4</sub> .....	6-7	11.5	11.5	11.7	..	12.0(C)	12.0(Bo)	18.0(W)	..
	5-6	9.8	..	..	..	..	10.1(Bo)	..	..
	4-5	8.8	..	..	..	..	7.9(Bo)	..	..
	1-4	4.9	..	..	..	..	4.6(Bo)	..	..
	0-1	1.0	..	..	..	..	..	..	..
BaCl <sub>2</sub> .....	1-2	4.8	5.2	6.9	4.9	..	..	5.26(P)	5.8(W)
	0-1	2.5	..	..	2.4	2.9(P)	..	1.1(S)	..
Na <sub>2</sub> HPO <sub>4</sub> .....	7-12	18.0	18.8	18.0	17.6	..	..	..	19.13(D)
	2-7	12.4	..	..	13.6	..	..	..	14.51(D)
	0-2	..	..	..	1.4	..	..	..	9.80(N-W)
SrCl <sub>2</sub> .....	2-6	..	7.5	..	..	8.5(A)	8.37(Ba)	..	..
CaCl <sub>2</sub> .....	4α-6	..	..	..	6.3	..	..	5.1(R)	..
FeSO <sub>4</sub> .....	7-6	..	..	..	..	14.7(C)	..	15.6(W)	..
Ba(OH) <sub>2</sub> .....	8-16	..	..	..	21.1	..	20.8(J)	..	..
	1-8	..	..	9.0	..	..	5.4(J)	..	..

reached. *Third*, the presence of adsorbed (and possibly occluded) gases on the surface of the hydrate (which is usually powdered in order to obtain as rapid a rate of efflorescence as possible) unquestionably causes large errors in certain cases; these gases cannot ordinarily be removed by any pre-treatment without simultaneously dehydrating the crystal. *Fourth*, no entirely satisfactory confining liquid is available. Mercury usually necessitates the accurate measurement of very small distances, while oil is likely to give off gases slowly, and also tends to dissolve and transmit water vapor.

The principal objections to the ordinary *dynamic methods* are similar to those for the static methods—the extremely slow rate at which many solid hydrates approach equilibrium at ordinary temperatures, and the fact that equilibrium can ordinarily be approached from one side only. This makes it almost impossible to be sure that the air has taken up the equilibrium amount of water vapor in any reasonable length of time. The results reported by most observers using this method are very discordant; and Foote and Scholes found it to be quite unsatisfactory. It should be pointed out, however, that Baxter and Lansing's very recent paper presents many important refinements and improvements in this method, although no results have yet been published on hydrates which are known to be slow in approaching equilibrium.

If the dynamic methods could readily be modified to approach equilibrium from both sides, they would be on a much firmer basis. This would involve many difficulties, however, and a method of this kind has only been used by Johnston<sup>1</sup> for special cases where he desired only approximate results at comparatively high temperatures, where the rates of approaching equilibrium are much more rapid.

The *indirect methods* of shaking up with some anhydrous solvent offer the very obvious advantages of permitting the equilibrium to be approached from both sides and of reaching equilibrium much more rapidly than in the case of solid-gas systems. However, both of the solvents previously used, ethyl ether and ethyl alcohol, have serious disadvantages. Ether takes up such small amounts of water that its accurate determination is difficult; and the ethyl alcohol suffers from the opposite defect of taking up so much water that the hydrated salts are likely to dissolve in it to a considerable extent (thus disturbing the vapor-pressure calibration), and the amount of water taken from or given to the hydrate before equilibrium is reached is likely to be rather large.

If, however, a solvent intermediate in properties between those previously used could be selected, this type of method would appear to be extremely promising. Once the vapor-pressure—water-content curve was accurately determined for the solvent and a rapid method developed

<sup>1</sup> Johnston, *loc. cit.*

for the determination of the water content in any equilibrium mixture, the method could be applied in a very short time to the determination of the vapor pressures of a large number of salts.

For these reasons it seemed advisable to endeavor to improve the *indirect* type of methods, whose possibilities have certainly not been exhausted, rather than follow the more beaten track of the various *direct* methods with their recognized defects. The plan of attack involved the selection of the most suitable solvent, the development of a rapid and accurate method for determining its water content, and finally the establishment of the vapor-pressure—water-content curve for the chosen solvent.

#### IV. Methods Involving Equilibrium with Mixtures of Water and Iso-amyl Alcohol.

**1. Selection of Solvent.**—For the reasons outlined previously a satisfactory solvent for use in the indirect method should dissolve a moderate, but not a large, amount of water. After a careful consideration of the possibilities, *iso*-amyl alcohol was selected as the liquid best suited for the purposes in hand. It has been found to dissolve about 9.8% of water at 25°. The sample used throughout this investigation was Kahlbaum's pure *iso*-amyl alcohol, b. p. 131.1°–131.5°.<sup>1</sup>

**2. Determination of Water in Iso-amyl Alcohol.**—Having selected a suitable solvent, the next problem was to find a rapid method of determining the water content of the *iso*-amyl alcohol after it had been equilibrated with a given hydrate.

Several methods have been proposed and tried for accurately determining small amounts of water in organic solvents. Diels<sup>2</sup> determined the water in methyl amine by adding methyl amine chloride, quantitative precipitation being obtained. Zerewitinoff<sup>3</sup> treated the material to be analyzed with an alkyl magnesium halide, and determined volumetrically the methane evolved. Berthelot<sup>4</sup> suggested that water might be determined by adding calcium carbide, and absorbing the acetylene evolved in ammoniacal silver nitrate, titrating the excess of silver. Weaver<sup>5</sup> advocated the use of cuprous chloride instead of silver nitrate. Danne<sup>6</sup> suggested measuring the acetylene volumetrically. A number of other men have modified this method slightly, the most

<sup>1</sup> This material probably contained some of the optically active form of the alcohol, though unfortunately its rotatory power was not determined. In view of the practical identity of all the known physical properties of the two forms, such a variation in composition would almost certainly not affect the results obtained in this investigation. A few runs were made with a sample carefully fractionated within the same boiling-point limits from an impure product, and identical results were obtained.

<sup>2</sup> Diels, *Ber.*, **32**, 697 (1889).

<sup>3</sup> Zerewitinoff, *Z. anal. Chem.*, **50**, 680 (1911). See also *C. A.*, **6**, 203 (1911).

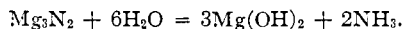
<sup>4</sup> Berthelot, *Compt. rend.*, **129**, 361 (1889).

<sup>5</sup> Weaver, *THIS JOURNAL*, **36**, 2462 (1914).

<sup>6</sup> Danne, *Paper*, Soc. Chem. Industry of Victoria, 1900. See also *Chem. Eng.*, **6**, 163 (1912).

important among them being Chavastelon,<sup>1</sup> Masson,<sup>2</sup> and West.<sup>3</sup> The latter gives a good description and bibliography of the methods which involve the use of calcium carbide.

Mr. N. Balyozian of this laboratory tried out several of the older methods and found that they did not give the requisite degree of accuracy in the case of the small amounts of water which he wished to determine. After considerable experimentation he devised a new procedure which gave better satisfaction. It consisted in dropping magnesium nitride into the alcohol-water mixture, which reacted according to the equation



The ammonia evolved was driven off by heat, absorbed in water, and titrated with standard hydrochloric acid. The method as finally perfected gave good results, but it required careful manipulation, and took about an hour for a single determination. The magnesium nitride was also rather difficult to prepare and handle. It was therefore thought that a still better method might be devised.

The author tried out several new possibilities for this determination which, though not entirely successful for the purpose in hand, are of enough interest to merit brief mention. One method depended on the decomposition of barium amylate (formed by boiling barium oxide with anhydrous *iso*-amyl alcohol) at room temperature according to the reaction  $\text{Ba}(\text{OC}_5\text{H}_{11})_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{C}_5\text{H}_{11}\text{OH} + \text{Ba}(\text{OH})_2$  (insoluble). This method was abandoned for several reasons, chief among which were the low solubility of the amylate, the seeming instability of its solutions, and manipulative difficulties in determining either the barium hydroxide or the excess of the amylate.

Still another attempt consisted in adding to the solution of unknown water content a weighed amount of water, and then determining the temperature at which the cloudiness (due to the formation of a water phase) appeared and disappeared. By reference to the curve of solubility of water against temperature, as determined by Fontain,<sup>4</sup> it is then possible to determine the amount of water present in the original solution. This method was abandoned because it was found impossible to determine this temperature with a sufficient degree of accuracy.

**3. Colorimetric Method with Cobalt Chloride.**—This rather interesting method, which is applicable to a number of other cases, takes advantage of the fact that the color of cobalt chloride solutions changes from blue in absolute amyl alcohol to pink in amyl alcohol saturated with water. The procedure used consisted in preparing a series of standard solutions containing known amounts of water in *iso*-amyl alcohol by mixing anhydrous amyl alcohol with various amounts of amyl alcohol saturated with water. To 10 cc. of each of these solutions in test-tubes was added exactly 2.5 cc. of a clear saturated solution of anhydrous cobalt chloride (previously heated in a stream of dry hydrogen chloride) in anhydrous amyl alcohol. This gave a series of color standards ranging from blue to pink, each corresponding to a known water content. The standard cobalt chloride solution could then be added to the *iso*-amyl alcohol solutions of unknown water content, and the latter determined by matching the color thus produced with that of the standard solutions.

This method proved to be more accurate than might have been expected, because of the fact that most of the change from blue to pink takes place (at room temperature) while the water content varies from 30 to 60% of saturation. This range of sharp color

<sup>1</sup> Chavastelon, *Compt. rend.*, **125**, 245 (1897); **132**, 1489 (1901).

<sup>2</sup> Masson, *Chem. News*, **103**, 37 (1911).

<sup>3</sup> West, *J. Ind. Eng. Chem.*, **8**, 32 (1916).

<sup>4</sup> Fontain, *Z. physik. Chem.*, **73**, 212 (1910). See also "Landolt-Börnstein," **1912**, p. 589.



change can, moreover, be shifted at will merely by changing the temperature, so that to get an accurate determination of the water content in an unknown sample it is only necessary to find the temperature at which it has the intermediate pinkish-purple color, and match it with the adjacent standards at this temperature. The temperature which gives the sharpest color change for different water contents was found to be as follows:

TABLE II.

Degree of saturation of amyl alcohol solutions with water (before addition of $\text{CoCl}_2$ solution). %	Kind of bath to use.
0 to 10	Freezing mixture
10 to 30	Ice-water
30 to 60	Room temperature
60 to 80	Water, 60° to 75°
80 to 100	Boiling water

This shift in the color change with temperature was to be expected, since the salt tends to give off water as the temperature increases, while the amyl alcohol tends to dissolve more and more water, thereby lowering the vapor pressure of a given amount in solution. It is planned to study this interesting change in a quantitative way, using a spectrophotometer.

A modified colorimetric procedure using a titration method instead of a set of standards has also been used with success as an undergraduate laboratory experiment in physical chemistry.

While the accuracy of these methods is better than that of most colorimetric determinations, and might be further improved by using a colorimeter, it seems doubtful if the water content could at best be determined within 0.2% which would correspond to an error of 2% or more in the vapor-pressure measurements. This was not considered sufficiently precise for the contemplated vapor-pressure work.

**4. Conductivity Method with Cobalt Chloride.**—The next method tried was based on the belief that the conductivity of salts dissolved in amyl alcohol would vary considerably with the water content of the alcohol. Some work of Harry C. Jones<sup>1</sup> confirmed this, and, although he gave no data on the conductivity of salts in *iso*-amyl alcohol solution, his work did indicate what salts could be expected to give the greatest difference in conductivity for a given difference in water content. His results, supplemented by some preliminary determinations in this laboratory, showed that cobalt chloride gave a greater range than any of the other common salts, the increase in conductivity between a solution in absolute alcohol and one in water-saturated alcohol being about 10-fold. Most of the work was accordingly done with this salt.

The general plan in mind was to add a measured quantity of a standard solution of cobalt chloride in absolute *iso*-amyl alcohol to a measured amount of the amyl alcohol with unknown water content, and determine the conductivity of the resulting mixture in an appropriate cell.

In working out the details of a satisfactory method several important factors had to be considered. The ratio between the amount of standard cobalt chloride solution and of the unknown solution used should be very small, so that the water content of the final mixture will vary over the widest possible range and thus be very sensitive to small changes in the unknown.

Dilute solutions of cobalt chloride were found to give the greatest percentage variation in conductivity for a given change in water content, but more concentrated

<sup>1</sup> H. C. Jones, *Z. physik. Chem.*, **69**, 389 (1909). See also *Am. Chem. J.*, **41**, 433 (1909); see also several other articles in *Am. Chem. J.*, 1907-11.

solutions were easier to measure and less susceptible to impurities. The cell must be small in volume, easily cleaned, and have an extremely small cell constant.

With these and other factors in mind, the following procedure was found after considerable experimentation to be the most satisfactory. While this method was not finally adopted for the vapor-pressure determinations, it was used in determining the solubility of water in *iso*-amyl alcohol, and the results obtained on the conductivity of various salts appear to be of enough importance to justify its description.

The *standard solution* was prepared as follows. 40 g. of Merck's pure cobalt chloride containing a trace of nickel was powdered, partially dehydrated over sulfuric acid and then heated in a stream of dry hydrogen chloride (to prevent hydrolysis) to 400-500°. It was then allowed to cool, and dry nitrogen was passed through until the issuing gas gave no test for hydrochloric acid. The anhydrous cobalt chloride was then quickly introduced into a liter of pure anhydrous *iso*-amyl alcohol and allowed to stand, with frequent shaking, for 24 hours. The resulting deep blue solution was filtered in an atmosphere of dry air and diluted with  $\frac{1}{10}$  of its volume of the anhydrous alcohol, in order to prevent precipitation if the solution should become cold. By determining the chloride content (as AgCl) this solution was found to contain 14.70 g. or 0.2262 equivalent of cobalt chloride per liter (at 25°).

The cell (see Fig. 1) was constructed so as to give a very small cell constant and yet a small volume. The electrodes consisted of 2 concentric platinum cylinders 5 cm. long, 1 cm. and 1.2 cm. in diameter, respectively, this giving a uniform distance of about 1 mm. between the electrodes. The leads of platinum wire were welded on, and the 2 cylinders fastened rigidly in position at top and bottom by fusing on a cross of fusible glass, as indicated in Fig. 1, which shows clearly the essential details of the construction. The bottom of the stopper was protected as far as possible from the action of the alcohol vapor by a shield of platinum foil. The suction Tube A came to a depth such that the alcohol never filled the cell, but was always at the same level whenever any of the solution showed in the tube above the stopper. The construction of the cell was thus very simple, and its operation quite satisfactory. The electrodes were platinumized by the customary method.

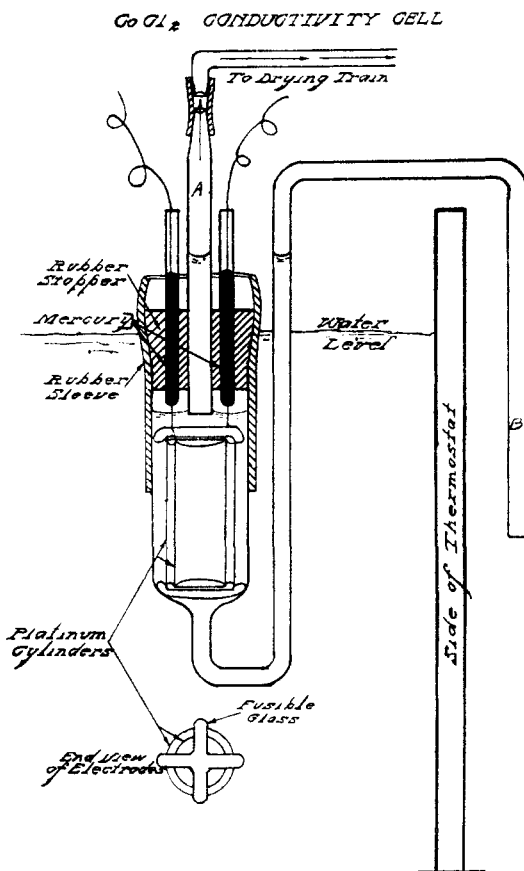


Fig. 1.

The *cell-constant* was found to be 0.005930 by standardization with carefully purified sodium chloride substantially according to the directions of Kohlrausch.<sup>1</sup> This value is certainly correct within a few tenths of 1%.

The *conductivity measuring apparatus* used was a slide wire bridge of the roller type. It was standardized by the method of Strouhal and Barus, and the resistance by comparison with a standard box. The alternating current was provided by a small induction coil, and it gave a very good minimum for all alcohol solutions having resistances between 200 and 5000 ohms. The best minimum for aqueous solutions in the same cell was in a considerably lower range, about 40 to 1000 ohms.

The *determination of the composition-conductivity curve* was carried out as follows: To a weighed amount (about 22 g.) of pure absolute *iso*-amyl alcohol in a small, well-stoppered bottle was added a weighed amount of conductivity water (with a specific conductance of  $1.4 \times 10^{-6}$ ) from a small weighing pipet. This solution was well shaken, and 25 cc. was pipetted into a small Erlenmeyer flask. To this was immediately added 5 cc. of the standard solution of cobalt chloride in absolute *iso*-amyl alcohol. Both pipets were carefully standardized with water at 25°. The resulting mixture was again stoppered and shaken, after which 3 successive 4-cc. portions were used to

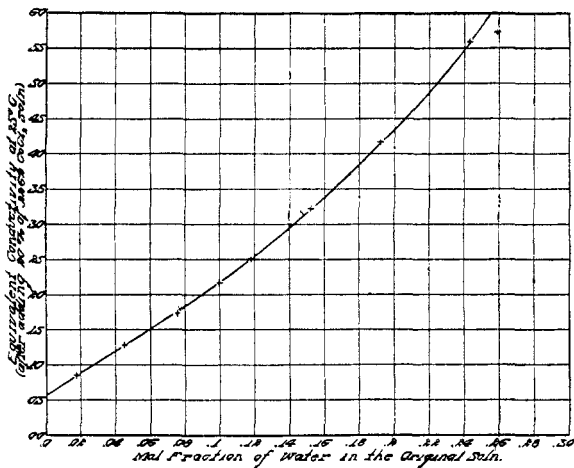


Fig. 2.—Composition conductivity curve for *iso*-amyl—alcohol-water solution after adding  $\frac{1}{8}$  of their volume of 0.2262  $N$   $\text{CoCl}_2$  solution.

rinse out the cell. The remainder of the solution was next sucked in (through Tube B) until the liquid just appeared above the stopper in Tube A. (Tube A leads to the mouth through a drying tower containing soda lime and calcium chloride.) As soon as it came to the temperature of the thermostat an approximate bridge setting was determined. The switch was then opened for a couple of minutes before the final setting was made, in order to eliminate any error due to the heating effect of the current. Each reading was made with at least 2 different resistances in one side of the bridge, and very close check readings were obtained.

The results of the series of measurements are tabulated in Table III and shown graphically in Fig. 2.

The equivalent conductance  $\lambda$  was calculated from the measured conductance  $h$  by the equation

<sup>1</sup> Kohlrausch, "Leitvermogen der Electrolyte," see THIS JOURNAL, 33, 785 (1911).

$$\lambda = h \times \frac{\text{Cell-constant}}{\text{Equiv. CoCl}_2 \text{ per cc.}} = h \times \frac{0.005930}{(5/30) \times 0.0002262} = h \times 157.3.$$

All the points except No. 9 (see below) are very close to a smooth curve. In fact, for mol fractions *less than* 0.075, a straight line relationship exists between the mol-fraction  $x$  and the equivalent conductance  $\lambda$  of the solutions, whose equation is

$$x = 0.650 (\lambda - 0.0580).$$

It will be noted that it was impossible to use this method for solutions containing above 6.5% H<sub>2</sub>O, in spite of the fact that the solubility of water is over 3.5% higher. When more concentrated solutions were used, however, a water phase separated out partly due to the salting-out effect, but primarily to the fact that the water phase which separated dissolved most of the cobalt chloride, thus giving it an abnormally low vapor pressure.

By the aid of this curve it is obvious that the determination of the mol fraction of water in any amyl alcohol solution containing less than 6.5% of water is rendered very simple and far more accurate than by any previous method. It is indeed remarkable that a change of 6% in the water content of a solution makes a change of 1000% in a physical property which is as easily and accurately measured as its conductivity. This fact has been used to good advantage in this case and might readily be applied elsewhere under similar circumstances.

TABLE III.—DATA FOR COMPOSITION-CONDUCTIVITY CURVE.

	Water in 25 cc. G.	Alcohol in 25 cc. G.	H <sub>2</sub> O by weight, %	Mol. frac. H <sub>2</sub> O.	Conductivity.	
					10 <sup>6</sup> × measured conductance.	Equivalent conductance.
1.....	0	0	0	0	363.4	0.0572
2.....	0	0	0	0	363.2	0.0571
3.....	0.2033	21.081	0.955	0.04503	808.9	0.1272
4.....	0.3812	22.832	1.642	0.07548	1105.7	0.1739
5.....	0.6372	23.258	2.667	0.11814	1592.0	0.2504
6.....	0.8258	22.488	3.542	0.1522	2053.0	0.3229
7.....	1.0619	21.840	4.637	0.1921	2659.0	0.4183
8.....	1.3889	21.170	6.157	0.2429	3551.0	0.5586
9.....	1.5750	22.059	6.664	0.2588	3620.0	0.5694
10.....	0.0829	22.987	0.359	0.01733	546.0	0.0859
11.....	0.4867	21.535	2.210	0.09950	1381.0	0.2172

This method was also used to determine the solubility of water in amyl alcohol with the following results.

TABLE IV.—DETERMINATION OF THE PERCENTAGE BY WEIGHT OF WATER IN *iso*-AMYL ALCOHOL SOLUTIONS SATURATED AT 25°.

	Determination No. 1.	Determination No. 2.
Wt. saturated alcohol, g.....	2.7474	2.5266
Wt. absolute alcohol, g.....	19.691	22.777
Measured conductance × 10 <sup>6</sup> .....	913.5	815.3
Equivalent conductance.....	0.1437	0.1282
% H <sub>2</sub> O in the mixture (from curve).....	1.193	0.969
Same corrected for cond. of impurities.....	1.198	0.974
% H <sub>2</sub> O by wt. in saturated solution.....	9.78	9.75
Mol fraction of H <sub>2</sub> O in saturated solution.....	0.347	0.346

These values agree quite well with the best previous work, that of Fontain,<sup>1</sup> who reports a value of 9.72% at 25°.

<sup>1</sup> Fontain, *Z. physik. Chem.*, 73, 212 (1910).

When, however, the attempt was made to apply this method to the determination of the water content of alcohol which had been shaken with a hydrate, a new and serious difficulty arose, due to the fact that contamination with small amounts of the other salts made appreciable variation in the conductivity of the solutions. Some preliminary experiments with an ordinary conductivity cell had seemed to show that the solubility of most neutral inorganic salts was too small to have any effect, but later and more careful measurements with the more sensitive new cell gave the series of results shown in Table IV.

These measurements showed clearly that the factor of contamination is a serious one. Not only would the hydrate which was shaken with the alcohol dissolve to some extent, but any slight impurities in the hydrate, especially the alkali halides, would also dissolve to give conductivities which are small, indeed, but of the same order of magnitude as those measured after the addition of the cobalt chloride. It also appears that the composition-conductivity curve should be corrected by about 0.5 of 1% on account of the conductivity of impurities in the conductivity water.

TABLE V.—DATA ON CONTAMINATION.

Solution measured.	Spec. cond. × 10 <sup>8</sup> at 25°.
25 cc. a. a. + 5 cc. CoCl <sub>2</sub> solution.....	215.0
25 cc. a. a. + 6.157% H <sub>2</sub> O + 5 cc. CoCl <sub>2</sub> solution.....	2100.0
A. a. alone.....	8.2 <sup>a</sup>
A. a. + 2% conductivity water.....	11.2 <sup>a</sup>
A. a. + 5% conductivity water.....	16.0 <sup>a</sup>
A. a. saturated with conductivity water.....	5.9 <sup>a</sup>
A. a. + 5% tap water.....	40.0 <sup>a</sup>
A. a. saturated with tap water.....	11.7
A. a. shaken with CuSO <sub>4</sub> ·5H <sub>2</sub> O (C. P.).....	27.1 <sup>a</sup>
A. a. + Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O (C. P.).....	10.5 <sup>a</sup>
A. a. + NaCl + H <sub>2</sub> O.....	323.0
Conductivity water alone.....	140.0

A. a. refers to pure absolute *iso*-amyl alcohol.

<sup>a</sup> In the case of these solutions, the conductivity dropped off steadily for 10 or 20 minutes after they came to the temperature of the thermostat. The values at the start were from 20 to 40% higher than the final constant ones which are recorded in the table. This phenomenon was probably due to the absorption by the electrodes of some impurities present in the alcohol, since alcohol which had been shaken with the conductivity water showed no such decrease, the impurities presumably having been shaken out into the water phase. This did not cause any trouble with the CoCl<sub>2</sub> solutions, probably because the salt concentration was constant in all measurements.

The fact, which may at first sight appear rather anomalous, that 2 and 5% of the conductivity water increased the conductivity of the solution, whereas a saturated solution containing 9.75% of water had a less conductivity than even the anhydrous alcohol, is due to the fact that impurities in the conductivity water were in the first two cases simply added to those in the alcohol, thus giving a higher conductivity, whereas in the preparation of a saturated solution the conducting impurities are largely removed by the excess of the aqueous phase.

While this difficulty might possibly be obviated by determining the conductivity of the alcohol both before and after the addition of the cobalt chloride solution, this would complicate the method and the validity of the resulting correction would be very doubtful.

**5. Conductivity Method with Potassium Thiocyanate.**—In view of the foregoing difficulties, it appeared necessary to search further for a salt which would give much higher conductivities than cobalt chloride, and yet give a reasonably high variation with change in the water content. A large number of salts were tried out with this end in view. Table V shows the results for all salts which were found to be reasonably soluble. The procedure consisted in adding a given number of cc. of a saturated solution of the salt in the absolute alcohol, first to 25 cc. of the absolute alcohol, and then to 25 cc. of alcohol containing about 3.3% of water, and then determining the conductivity of each mixture. These results are only rough values, of interest chiefly for the purpose of comparison.

TABLE VI.—DATA ON POSSIBLE SUBSTITUTES FOR COBALT CHLORIDE.

Cc.	Saturated solution of	Values of $\bar{\chi} \times 10^4$ .		
		Sat. sol. + 25 cc. A.a.	Sat. sol. + 25 cc. A.a. + 3.3% H <sub>2</sub> O.	Ratio.
5.....	CoCl <sub>2</sub>	210	1,130	5.4
5.....	CaCl <sub>2</sub>	780	3,100	4.0
5.....	Ca(NO <sub>3</sub> ) <sub>2</sub>	3,100	4,800	1.5
5.....	KBr	780	1,600	2.1
5.....	KI (unstable)	.....	.....	.....
5.....	KCNS	1,700	2,400	1.4
5.....	LiCl	8,300	13,600	1.6
1.....	LiBr	6,500	12,000	1.85
2.....	LiBr	1,300	22,000	1.7
3.....	LiBr	19,500	31,000	1.6
4.....	LiBr	26,000	39,000	1.5
5.....	LiBr	32,500	47,000	1.45
5.....	LiI (unstable)	53,000	78,000	1.5

A glance at the table shows that, as a rule, the higher the conductivity which a salt gives, the smaller is the ratio of the conductivities for two different water contents; hence, the more completely the error due to contamination is eliminated, the less is the degree of accuracy in determining the water content by measuring the conductivity. The best possibility is evidently lithium bromide, using 5 cc. of a solution about half saturated with the salt (a saturated solution being undesirable because of its great viscosity). This gives conductivities about 50 times as great as cobalt chloride, thus eliminating the errors due to contamination, and at the same time it gives a fairly satisfactory ratio of conductivities. The iodides are unavailable because they decompose on standing in the alcohol.

Fortunately, however, another line of procedure presented itself. Presumably, an increase in the water content of amyl alcohol increases two factors, *viz.*, the *conductivity* of a given amount of salt, and the *solubility* of the salt (in the case of salts which are more soluble in water than in alcohol). Thus far the methods tried had benefitted by only one factor, *viz.*, the increase in conductivity, because a fixed amount of salt was used. If, however, the solutions of unknown water content were *saturated* with some salt, both factors would tend to increase the ratio of conductivities for a given change in water content, as well as having the advantage of higher conductivities. The method has the further advantage that it does away with all necessity for the use of pipets in measuring the solutions. It therefore eliminates at once the greatest two sources of error in the cobalt chloride method.

In selecting the best salts for use in saturating the solutions the choice was limited to those which do not form hydrates; for otherwise the excess of the solid phase would tend to absorb water from, or give it up to, the alcohol solution, and establish a new

equilibrium with different water content. This eliminates all the most desirable salts at once. The substance must also be soluble enough to give a fairly high conductivity, and yet not so high as to make the solution very viscous or to exert too great a salting-out effect. These and other considerations seemed to eliminate all but two possibilities, potassium bromide and potassium thiocyanate. When tried out these salts gave the following results:

TABLE VII.  
Spec. Cond.  $\times 10^3$  at 25°.

Solution.	Spec. Cond. $\times 10^3$ at 25°.	
	Sat. with KBr.	Sat. with KCNS.
Pure amyl alcohol . . . . .	3,600	5,250
With 3% H <sub>2</sub> O . . . . .	.....	13,000
Sat. with H <sub>2</sub> O . . . . .	4,750	36,500

This shows that potassium thiocyanate has a surprisingly large range of conductivity, and one which is sufficiently high to eliminate all error due to contamination. Although its "salting-out effect" is so large that a water phase forms when the original water content of the alcohol is much above 3%, most hydrates fortunately give solutions falling within this range, and solutions with higher water-content can readily be analyzed by adding to them a known weight of anhydrous alcohol before adding the potassium thiocyanate.

Some experiments were made to determine the rate at which the potassium thiocyanate saturates a solution of *iso*-amyl alcohol with which it is well shaken. When a few g. of the powdered material was added to 40 cc. of the alcohol, extrapolation of the rate curve indicated that 99.9% saturation was reached after 15 minutes' shaking.

Other preliminary experiments indicated the entire practicability of the thiocyanate conductivity method for the accurate determination of the water content of the *iso*-amyl alcohol. However, before the method could be used for the determination of the vapor pressures of hydrates it was necessary to establish the vapor-pressure—water-content curve for amyl alcohol solutions. Unfortunately, this curve cannot be readily determined by any of the customary methods because of the presence of both substances in the gas phase, which makes it difficult to determine the water vapor pressure separately.

It therefore appeared that the most feasible method of establishing the curve was to determine the water content resulting from shaking pure *iso*-amyl alcohol with materials of known vapor pressure. For the higher vapor pressures it is possible to use certain salt solutions whose vapor pressures are very accurately known. In such cases correction must be made for the vapor pressure lowering due to the amyl alcohol which dissolves in the aqueous phase. Raoult's law may be safely assumed for calculating this correction term, since the solubility of *iso*-amyl alcohol in pure water is only 0.25% by weight corresponding to a mol fraction of 0.005.

From the lower vapor pressures, however, no satisfactory reference substances were available. Sulfuric acid solutions could not be used because of the solubility of the acid in the alcohol. Salt-hydrates would be ideal for the purpose but the data in the literature were not sufficiently reliable for the purpose.<sup>1</sup> It therefore seemed necessary to develop another

<sup>1</sup> Baxter has since then published accurate values for the vapor pressures of Na<sub>2</sub>SO<sub>4</sub>·10-H<sub>2</sub>O and SrCl<sub>2</sub>·6-2H<sub>2</sub>O, which are suitable for this purpose.

method, which, even if it should prove more elaborate and time-consuming, would enable the vapor pressure of a few salt-hydrates to be accurately determined for reference purposes. The author therefore turned his attention to this phase of the problem, with the results described in the following section, while the final perfection and use of the thiocyanate conductivity method was undertaken by Mr. L. R. Westbrook of this Laboratory, under the direction of Prof. A. A. Noyes. The results of the latter research are presented in a separate article immediately following this one.

#### V. Method Involving Equilibrium of the Salt-Hydrates with Aqueous Solutions of Sulfuric Acid.

1. **Description of the Method.**—Aqueous solutions of sulfuric acid are recognized to be of great value as reference liquids for vapor-pressure and humidity-control work. Their vapor pressures are known with great accuracy over a wide range of compositions and temperatures, and their variations in density afford a rapid and accurate method of determining their water content. It therefore seemed desirable to develop some method of comparing a few hydrates with sulfuric acid solutions, varying the strength of acid until a given pair of hydrates placed in a desiccator above the acid neither gained nor lost weight.

In order to obviate the necessity of removing the hydrate from the desiccator for the weighings, a small, sensitive horn-pan balance was put into the desiccator and provision made for adding weights to the pan by an outside mechanism. Shallow aluminum pans were substituted for horn on account of the hygroscopicity of the latter. A small toy electric fan was inserted into the desiccator just above the scale pan to speed up the diffusion of water vapor to and from the salt. This was found to make a surprising increase—between 10- and 20-fold—in the rate of approaching equilibrium. After the fan was introduced it was found that the use of an ordinary vacuum from a Richards pump did not further accelerate the rate and its use was accordingly discontinued.

It was later found that the presence of the fan motor in the desiccator caused fluctuations in temperature, and the fan was therefore driven on a shaft through the top of the desiccator, and provision was made for the complete immersion of the desiccator in the thermostat.

The construction of the final apparatus is shown clearly in Fig. 3.

The procedure used in determining the vapor pressure of a hydrate with this apparatus was as follows. A hydrate of known composition was weighed, ground very finely, and partially dehydrated by heating until it consisted of about 50% of each of the pair of hydrates, the composition of the mixture being determined by its weight. About 6 or 8 g. of the mixture were then spread out on one scale pan, and counter-balanced with weights. The balance was kept near mid-position by add-



ing, from time to time, small weights, or some dry quartz sand, to one or the other pan, sliding it in through a bent glass tube inserted through *b*. The gain or loss in weight while the hydrate was in the desiccator was not sufficient to change its composition appreciably from that at the beginning.

The fan was rotated for about an hour to bring about equilibrium conditions, and then a scale reading recorded. Another hour's rotation was in general sufficient to show whether the salt was gaining or losing, and

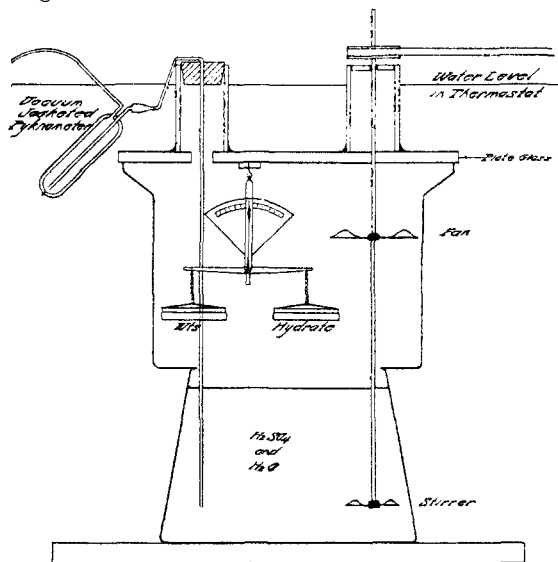


Fig. 3.—Desiccator and equipment for vapor-pressure determinations.

the strength of the acid was then changed by adding water or stronger acid, as the case might be.

When a point was reached where the salt gained only very slightly, but steadily, after rotating the fan overnight, the density of the acid was determined. This was done either by immersing the plummet of a Westphal balance in the acid through the sampling hole, or preferably by sucking out a sample into a carefully calibrated vacuum-jacketed pyc-

nometer such as that shown in Fig. 3, using the ordinary precautions to prevent the formation of bubbles and attain constant temperature before adjusting the meniscus and weighing.

The strength of the acid was then slowly changed until the salt reversed the direction of its change in weight, when another density determination was made. The density was usually taken at several points near equilibrium, instead of at only those two which were absolutely necessary. The composition of the acid was also roughly kept track of by noting the amounts of water or acid added.

<sup>1</sup> Domke, *Z. anorg. Chem.*, **43**, 125 (1905). See also Landolt-Börnstein, 1912, p. 265.

independent investigators. Their results were calculated to the same temperature by thermodynamical methods and plotted on a large scale in a recent article by the writer.<sup>1</sup> Table VIII gives enough points from the best representative curve for 25° to permit its reconstruction on a large scale. The agreement between results was very good over the entire middle range of concentrations, and the curve is a straight line between 35 and 56% sulfuric acid.

TABLE VIII.—BEST VALUES FROM VAPOR-PRESSURE CURVES FOR SULFURIC ACID. Solutions at 25°.

H <sub>2</sub> SO <sub>4</sub> . %.	Rel. V. P. in %.	Abs. V. P. in mm. Hg.	H <sub>2</sub> SO <sub>4</sub> . %.	Rel. V. P. in %.	Abs. V. P. in mm. Hg.
0	100	23.70	45	46.8	11.09
5	98.5	23.34	50	36.8	8.72
10	96.1	22.78	55	26.8	6.35
15	92.9	22.02	60	17.2	4.08
20	88.5	20.98	65	9.8	2.32
25	82.9	19.64	70	5.2	1.23
30	75.6	17.92	75	2.3	0.55
35	66.8	15.83	80	0.8	0.19
40	56.8	13.46			

Using the above method and apparatus, it was found surprisingly easy to make very accurate determinations of the limits of vapor pressure between which the salt lost and gained in weight. The closeness of the limits depended largely on the rate at which the salt gains or loses its water of crystallization. Na<sub>2</sub>HPO<sub>4</sub>.12-7H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub>.10-0H<sub>2</sub>O showed a remarkably sharp change between fairly rapid gaining and losing. CuSO<sub>4</sub>.5-3H<sub>2</sub>O is somewhat slower, while CuSO<sub>4</sub>.3-1H<sub>2</sub>O and especially BaCl<sub>2</sub>.2-1 H<sub>2</sub>O are rather unsatisfactory and harder to determine with accuracy.

While this method was designed only to determine the vapor pressure of a few "standard" salts to be used in the indirect conductivity method, it has given such satisfactory results that it may, with some refinement of the balance, be adopted for the determination of most of the salts which come quickly to equilibrium, in addition to those which, on account of solubility in amyl alcohol, cannot be determined by the other method. Although the method takes 2 or 3 weeks for a determination, it requires very little attention; and the results are less open to question than those obtained by any other known method, since it definitely approaches equilibrium from both sides, and refers *directly* to sulfuric acid solutions whose vapor pressures and densities are known with great accuracy, not only at 25°, but also at other temperatures. The rate of approaching equilibrium would probably be much greater at 50°. There is no need for special purification of the hydrates.

<sup>1</sup> Wilson, *J. Ind. Eng. Chem.*, 13, 326 (1921).

TABLE IX.—THE VAPOR PRESSURE OF  $\text{CuSO}_4 \cdot 5\text{-}3\text{H}_2\text{O}$  AT  $25^\circ$ .  
 (Exact Composition,  $\text{CuSO}_4 \cdot 3.88 \text{H}_2\text{O}$ .)

$\text{H}_2\text{SO}_4^a$ in sol. %	$p_{\text{H}_2\text{O}}$ in $\text{H}_2\text{SO}_4$ sol. Mm.	Interval in hours.	Increase in scale reading.	Change in mg. per day.
52.16	7.69	2	-0.2	-0.48
		2	-0.1	-0.24
		18	-0.7	-0.20
52.02	7.76	6	-0.1	-0.08
		17	-0.3	-0.08
		6	-0.2	-0.16
		1.5	-0.1	-0.32
51.91	7.81	20	+0.3	+0.08
		16	+0.1	+0.03
		7	0.0	0.00
		24	0.0	0.00
		16	+0.1	+0.30
51.89	7.82	6	+0.1	+0.08
		10	+0.1	+0.30
		24	+0.2	+0.04

Most probable vapor pressure of the hydrates:  $7.80 \pm 0.03^b$  mm.

<sup>a</sup> Found by density determinations.

<sup>b</sup> These values following the  $\pm$  signs are not "probable errors" in the usual sense, but they show the limits within which the vapor pressure almost certainly lies, as far as can be judged from the changes in weight. They do not take account of possible errors in the vapor pressure of the sulfuric acid solutions.

 TABLE X.—THE VAPOR PRESSURE OF  $\text{BaCl}_2 \cdot 2\text{-}1\text{H}_2\text{O}$  AT  $25^\circ$ .  
 (Exact Composition  $\text{BaCl}_2 \cdot 1.31\text{H}_2\text{O}$ .)

$\text{H}_2\text{SO}_4$ in sol. %	$p_{\text{H}_2\text{O}}$ in $\text{H}_2\text{SO}_4$ sol. Mm.	Interval in hours.	Increase in scale reading.	Changes mg. per day.
57.00	...	2	-0.3	-0.72
56.65 <sup>a</sup>	5.58	2	-0.2	-0.48
		3	-0.1	-0.16
		10	-0.5	-0.24
56.11 <sup>a</sup>	5.83	4	0.0	0.00
		16	-0.2	-0.06
		4	+0.1	+0.12
		10	+0.1	+0.04
		12	+0.2	+0.08
		3	0.0	0.00
56.08	5.84	4	0.0	0.00
		16	+0.1	+0.03
		6	0.0	0.00
55.93 <sup>a</sup>	5.91	5	+0.1	+0.10
		10	+0.1	+0.03
		7	0.0	0.00
		22	+0.1	+0.02

Most probable vapor pressure of the hydrates:  $5.8 \pm 0.1$  mm.

<sup>a</sup> Found by density determinations.

TABLE XI.—THE VAPOR PRESSURE OF  $\text{Na}_2\text{HPO}_4 \cdot 12\text{-}7\text{H}_2\text{O}$  AT  $25^\circ$ .  
(Exact Composition  $\text{Na}_2\text{HPO}_4 \cdot 10.6\text{H}_2\text{O}$ .)

$\text{H}_2\text{SO}_4$ in sol. %. C.	$p_{\text{H}_2\text{O}}$ in $\text{H}_2\text{SO}_4$ Mm.	Interval in minutes.	Increase in scale reading.	Change in mg. per hour.
26.74	19.09	40	-1.2	-1.8
		20	-0.4	-1.2
		30	-0.9	-1.8
26.61	19.12	43	-0.7	-1.0
		40	0.0	0.0
		43	-0.4	-0.6
		40	-0.5	-0.7
		20	-0.3	-0.9
26.63	19.13	40	-1.2	-1.8
		25	+0.2	+0.4
		20	-0.1	-0.3
		20	+0.1	+0.3
26.59	19.14	30	-0.4	-0.8
		45	+0.5	+1.0
		15	+1.4	+1.9
		135	+1.8	+0.8
		60	+1.8	+1.8
		50	+2.1	+2.5

*Most probable vapor pressure of the hydrates:* 19.13  $\pm$  0.01 mm.

TABLE XII.—THE VAPOR PRESSURE OF  $\text{Na}_2\text{HPO}_4 \cdot 7\text{-}2\text{H}_2\text{O}$  AT  $25^\circ$ .

$\text{H}_2\text{SO}_4$ in sol. %. C.	$p_{\text{H}_2\text{O}}$ in $\text{H}_2\text{SO}_4$ sol. Mm.	Interval in minutes.	Increase in scale reading.	Change in mg. per hour.
37.87	14.47	75	-0.05	-0.04
		105	-0.05	-0.03
		60	-0.4	-0.4
37.85	14.48	60	-0.1	-0.1
		120	-0.3	-0.15
		30	+0.2	+0.4
		135	0.0	0.0
		375	+1.3	+0.2
37.80	14.50	65	0.0	0.0
		200	+0.6	+0.2
		65	-0.3	-0.3
		120	0.0	0.0
		45	-0.1	-0.1
37.71	14.51	45	+0.2	+0.2
		630	0.0	0.0
		125	-0.3	-0.1
		160	-0.5	-0.2
		100	+1.6	+1.0
37.63	14.58	110	+0.6	+0.3
		310	0.0	0.0
		900	+2.5	+0.1
		45	+0.1	+0.1
		60	+0.1	+0.1
		60	+0.2	+0.2
		60	+0.4	+0.4

*Most probable vapor pressure of the hydrates:* 14.51  $\pm$  0.04 mm.

2. **Measurements by the Author.**—The first vapor pressure measured was that of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . This was first done before the apparatus was finally perfected, and later checked within 0.02 mm. with the new apparatus and freshly prepared hydrates. The results of this second determination are given in Table IX. The series is short because the proper strength of acid was already approximately known.

The second determination was with  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ . This was also done by an earlier form of apparatus and has not been checked as yet. Much greater difficulty was experienced in establishing the equilibrium point in this case; and the final value (about 4.7 mm.) cannot be regarded as definitely established.

The third hydrate was selected with the view of studying an unfavorable case, *i. e.*, one in which the rate of loss of weight would be slow.  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  was accordingly chosen because it has a low vapor pressure, a high molecular weight, and loses only one molecule of water at a

TABLE XIII.—THE VAPOR PRESSURE OF  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  AT  $25^\circ$ .

$\text{H}_2\text{SO}_4$ in sol. %	$\rho_{\text{H}_2\text{O}}$ in $\text{H}_2\text{SO}_4$ . Mm.	Interval in minutes.	Increase in scale reading.	Change in mg. per hour.
26.48	19.18	35	-2.1	-3.6
		45	-5.0	-5.4
		30	-3.9	-7.8
		50	-1.8	-2.2
26.42	19.20	80	-1.8	-1.4
		55	-0.2	-0.2
		50	-0.4	-0.4
		180	-0.3	-0.1
		60	-0.2	-0.2
26.39	19.21	30	+0.6	+1.2
		20	+0.5	+1.5
		20	-0.7	-2.1
		30	-0.1	-0.2
		25	+0.1	+0.2
		30	0.0	0.0
26.34	19.22	60	0.0	0.0
		80	-0.2	-0.2
		50	-0.2	-0.2
		70	+0.2	+0.2
26.26	19.25	25	+0.8	+1.9
		20	+0.1	+0.3
		15	+0.4	+1.6
		20	+0.2	+0.6
		155	+0.5	+0.2
26.11	19.30	50	+2.4	+2.9
		30	+1.0	+2.0
		40	+0.8	+1.2
		45	+3.0	+4.0

Most probable vapor pressure of the hydrates:  $19.22 \pm 0.02$  mm.

time. All who have tried this salt testify to the extreme difficulty of reaching equilibrium. As the results in Table X indicate, it was not possible to bring the limits nearly as close together as with the  $\text{CuSO}_4 \cdot 5-3 \text{H}_2\text{O}$ . From this table of values several preliminary observations, which add nothing of interest, have been omitted.

**3. Measurements by R. G. Dickinson.**—The following measurements on a number of other salt-hydrates were made in this laboratory by R. G. Dickinson, who has kindly authorized their inclusion in this article.

### VI. Summary.

1. The methods used by previous investigators in the determination of the vapor pressure of salt-hydrates are described in some detail and their defects pointed out. In Table I of this article are summarized most of the existing data for  $25^\circ$  for hydrates on which more than a single determination has been made.

2. Reasons are advanced for choosing a new type of indirect method involving the establishment of equilibrium between the hydrates and a solution of water in amyl alcohol, followed by a determination of the water content of the resulting mixture.

3. Three new quantitative methods are presented for determining the water content of *iso*-amyl alcohol solutions: (*a*) colorimetric comparison of standard cobalt chloride solutions; (*b*) determination of the conductivity of standard cobalt chloride solutions; (*c*) determination of the conductivity of saturated potassium thiocyanate solutions. The last method is the one preferred.

4. Data are presented on the color and conductivity of cobalt chloride solutions in amyl alcohol as a function of the temperature and water content; approximate values are also given for the conductivity of a large number of other salts in anhydrous and hydrous amyl alcohol.

5. The solubility of water in *iso*-amyl alcohol was determined to be 9.77% at  $25^\circ$ .

6. In order to establish the vapor-pressure—water-content curve for *iso*-amyl alcohol solutions, it was necessary to determine with especial accuracy the aqueous-vapor pressures of a few hydrated salts. For this purpose the salts were placed in a small balance inside a desiccator equipped with a fan and stirrer and containing sulfuric acid solution, the strength of which was varied until the concentration was found at which the salt neither gained nor lost in weight. This method was found to be very satisfactory for salts which gained or lost water with fair rapidity.

7. By this method the vapor pressures of 5 pairs of salt-hydrates were determined, partly by the writer and partly by Dr. R. G. Dickinson. The values so obtained are summarized in the last column of Table I, making possible a comparison with the results of previous investigators.