

from the data of Starck and Bodenstein¹⁴ is 36,860 calories, which corresponds to 1.59 volts. If the ionization potential corresponds to the reaction $I_2 = I^+ + I + \Theta$, then the ionization potential of the atom should be $10.0 - 1.6 = 8.4$ volts, which agrees well with the value of Found, but is slightly higher than that of Compton and Smyth. Series relations for the spectrum of iodine are not known, so that it is impossible to calculate a theoretical value; 8.4 volts would correspond to a wave length of 1472 Å. In view of the relatively low heat of dissociation of iodine, the above equation probably corresponds to the principal ionization potential of iodine.

Summary

1. The theory of the luminous discharge proposed by Gibson and Noyes is discussed with reference to its applicability to the luminous discharge in an electronegative gas such as iodine.

2. The most probable value of the ionization potential of iodine as determined in the experiments described is 10.0 ± 0.2 volts. This gives 8.4 volts as the ionization potential of the atom, which would correspond to a wave length of 1472 Å. It is impossible to verify this from the spectroscopic data now available.

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THE DISSOCIATION PRESSURES OF CERTAIN SALT HYDRATES BY THE GAS-CURRENT SATURATION METHOD

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Numerous methods, both direct and indirect, have been devised for the measurement of the dissociation pressures of salt hydrates. Some of these are more ingenious than accurate; others involve apparatus so elaborate that few experimenters would be inclined to adopt them, if other, less troublesome methods could be found to serve the same purpose.

The static methods, involving the use of the tensimeter, require the greatest care in the elimination of sources of error—in particular, the removal of adsorbed moisture from the walls of the instrument, and in the elimination of parallax in determining the difference in level in the two arms of the tensimeter while it is immersed in a thermostat. Furthermore, in the case of those salts which are slow to reach equilibrium with the gaseous phase, a determination by such a method is very time-consuming. Likewise, the dew-point method, originated by Lescoeur,¹

¹⁴ Starck and Bodenstein, *Z. Elektrochem.*, **16**, 961 (1910).

¹ Lescoeur, *Ann. chim. phys.*, [6] **16**, 394 (1889).

attracts one by its directness; yet, in the majority of cases, it is too crude for any but approximate results.

The indirect methods in general consist in equilibrating, at a given temperature, the pair of hydrates (or the hydrate and the anhydrous salt) with some organic solvent, and determining the water content of the resultant solution. The vapor pressure of water in the solution, which must equal the dissociation pressure of the hydrates, is found by reference to a curve, established by separate experiments, expressing the change of vapor pressure of water in the solution with the water content.

Ether, ethyl and *iso*-amyl alcohols have been employed as reference liquids, and the water content has been variously determined by measurements of the boiling point, density, or conductivity of the liquid.² These interesting methods are doubtless open to modification and extension. In general, however, their applicability is limited to those substances, of which the solubilities in the pure reference liquid are so slight as to escape detection. The mixture of substances, after being shaken with the liquid, should settle, leaving above a clear solution of water in the reference liquid. Many salt hydrates appear to act in just this way, but in some cases—even of common substances—such methods are found to be inapplicable.

An indirect method of general application, which has been employed by a number of investigators, is that in which the hydrate pair is allowed to approach equilibrium through the gaseous phase with an aqueous solution—such as one of sulfuric acid—of which the vapor pressure has previously been determined with reference to percentage composition. When a solution is found over which the mixture of the hydrates tends neither to gain nor to lose weight, the vapor pressures of solution and hydrates of course are equal. It should be emphasized, however, that no such method will be reliable unless equilibrium either is actually attained, or else approached very closely on each side; for if one attempts to locate the equilibrium point by a study of the *rate* of approach thereto, the result is dependent on the accidental conditions of the experiment, such as fineness of solid particles, size of vessels, stirring—in a word, all the influences which affect the rates of evaporation, diffusion, and absorption.

In choosing a method of general applicability and reasonable accuracy for the measurement of the dissociation pressures of a series of salt hydrates, whereby a determination could be carried out in a day or less, the considerations above mentioned were borne in mind, and led to the adoption of the gas-current saturation method, which was first used by Tammann,³ and through various modifications has been developed by a number of other investigators, working both with solutions and with solid

² See, for example, (a) R. E. Wilson, *THIS JOURNAL*, **43**, 704 (1921). (b) Noyes and Westbrook, *ibid.*, **43**, 726 (1921). (c) Linebarger, *Z. physik. Chem.*, **13**, 500 (1894).

³ Tammann, *Wied. Ann.*, **33**, 322 (1888).

hydrates. Very good results have been obtained in this way by Baxter and Lansing⁴ and also by Menzies.⁵ Menzies' procedure differed from that of Baxter and Lansing in that it was a differential method: the weight of water taken up in the passage of a given volume of air through a tube containing the hydrate mixture was compared with the weight taken up when the same volume of air was passed through a saturator containing pure water. The vapor pressure of water being known at the experimental temperature, the dissociation pressure of the hydrate pair could be calculated. It is important in this method that there be no pressure drop in the saturators containing the hydrate mixture and pure water, respectively; hence, the necessity of employing water saturators of special design. Washburn's apparatus,⁶ for use in determining the vapor-pressure lowering of solutions, is perhaps the most elaborate of this type, but is not suitable for use with solid hydrates.

In the present work, the method of Baxter and Lansing, slightly modified, was adopted as a reasonably accurate and very convenient procedure, whereby a series of hydrates may be studied. In brief, the method

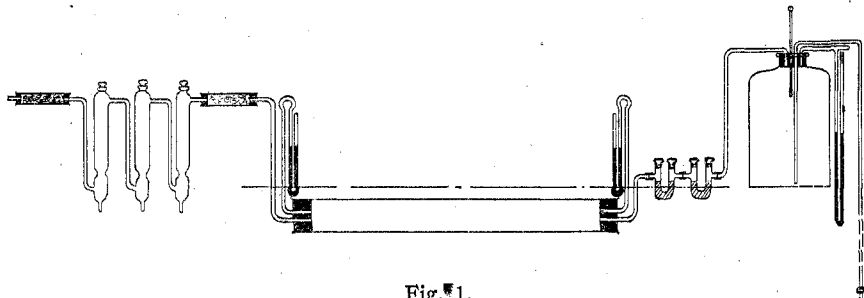


Fig. 1.

consists in drawing a measured amount of dry air, free from carbon dioxide, through an intimate mixture of the pair of hydrates and collecting the water vapor thus taken up by the air in weighed U-tubes containing phosphorus pentoxide. The accompanying figure shows the apparatus employed.

The air was first filtered by a tube containing glass wool, and then passed in turn through towers containing calcium oxide, or better, fused potassium hydroxide, and sulfuric acid. Another tube of glass wool was inserted between the towers and the saturator containing the hydrate mixture, in order to reduce the danger of acid spray being carried over into the saturator.

These saturators consisted of long, wide glass tubes, the outside diameters of which were, respectively, 45 and 50 mm. The lengths of the columns of solid in the tubes varied from 30 to 50 cm. The tubes were tightly closed by means of rubber stoppers, the inner surfaces of which were lightly coated with paraffin. A coating of paraffin

⁴ Baxter and Lansing, *THIS JOURNAL*, **42**, 419 (1920).

⁵ Menzies, *ibid.*, **42**, 1951 (1920).

⁶ Washburn, *ibid.*, **37**, 309 (1915).

was also applied to the outside of the tube where it joined the stopper. Ground joints could of course be used for the same purpose, but the rubber stoppers employed gave an air- and water-tight joint. The tubes were filled with an intimate mixture of the two finely-powdered hydrates (or the hydrate and the anhydrous salt)⁷ together with a plentiful addition of clean glass beads. The moist air leaving the saturator then passed through two tubes containing phosphorus pentoxide, mixed with glass beads, and finally into the aspirator bottle. The apparatus was set up in triplicate, so that three determinations could be carried on simultaneously.

From a knowledge of the volume of air (reduced to the dry basis) drawn through the apparatus, of the total pressure in the tube containing the salt-hydrate mixture, and of the weight of water obtained, the partial pressure of the water vapor in the tube may be calculated.⁸

There are at least three sources of difficulty in the present method which may give rise to discordant results. These difficulties are encountered, first, in the determination of the total pressure in the tube containing the hydrate mixture—a pressure which is not constant, depending as it does on barometric changes; second, in the determination of the actual volume of air, reduced to the dry basis, drawn through the apparatus—a procedure which requires the measurement of fairly large volumes of a gas; third, in the accurate weighing of the usually rather small quantities of water. A few words with regard to each of these factors may not be out of place here.

In the method of Baxter and Lansing, the total pressure is taken as the average total internal pressure in the aspirator bottle, which in turn is equal to the average barometric pressure during the run minus the average value of the water manometer (converted into mm. of mercury) attached to the aspirator bottle. Now, this is nearly but not quite the same as the average total pressure in the tube containing the hydrates, for the reason that the phosphorus pentoxide tubes interposed between the tube and the aspirator bottle offer an appreciable resistance to the flow of air. Consequently, in the present experiments it seemed advisable to determine the total pressure in the hydrate tube directly; and manometers, filled with Nujol of known specific gravity, were inserted at each end of the hydrate tube for this purpose. The total pressure in the tube thus becomes equal to the average barometric pressure during the run minus the average value of the oil-manometer readings. It had been anticipated that with a tube of such length (35 to 50 cm.), filled with salt and glass beads, a considerable difference in level of the oil-manometers at the entrance and at the exit of the tube, respectively, would be noticed; but this did not prove to be the case, as the oil-manometer readings rarely differed by as much as

⁷ It is essential, of course, that both solid phases be present in order that equilibrium be established.

⁸ Menzies [THIS JOURNAL, 42, 979 (1920)] has pointed out that water vapor in air at ordinary temperatures closely follows Dalton's law.

a millimeter of oil. In the case of the phosphorus pentoxide tubes, however, the pressure drop was very noticeable, due to the fact that the contents of the tube soon began to assume a sirupy consistency at the point where the water vapor entered, and the interstices between the glass beads became partially clogged. The greater part of the drop in pressure of the air passing through the apparatus occurred in the purifying and drying towers at the entrance, especially in the driers containing sulfuric acid.

The determination of the average barometric pressure over an interval of about 18 hours—the normal length of one of the runs—offered difficulty at first, for it was not feasible to take readings of the mercurial barometer over the entire interval. An adequate solution of this difficulty was found, however, by referring to a barograph record.⁹ When the readings of this instrument were corrected to sea level, they were found to vary rarely as much as a millimeter—usually not over 0.5 mm.—from the corrected mercurial barometer readings taken at the same time in this Laboratory. Readings from the barograph record were taken every 2 hours during a run, and the corrected average of these values was used in calculating the “average total pressure in the tube,” as given in Table I.

The volume of the air drawn through the apparatus was determined by measuring the water drawn from the aspirator bottle, and reducing this volume to a dry-gas basis at standard temperature and pressure. The volume of the water run out was usually about 6 liters, at times as much as 7 to 8 liters. Reason indicated, and experiment showed, that the slower the rate of flow, the greater the likelihood that equilibrium would be attained between gas and solid in the passage of the air through the tube. This point is considered below. It is sufficient here to state that at the slow rate of flow employed—never more than $\frac{1}{3}$ liter per hour—the duration of the run was necessarily long, and hence the temperature of the water in the bottle at the end of the experiment was invariably different from that at the beginning. Although the percentage error involved usually is not very great, it is not negligible if the temperature change exceeds a degree or two; hence, a uniform practice was made of correcting the volume of the water collected, as measured in standardized flasks and burets, for the shrinkage due to fall of temperature over the period of the run. This shrinkage, of course, results in more air being drawn into the aspirator than would have been the case if the temperature were constant; and conversely, if the temperature of the water in the aspirator rises during the run, less air is drawn over, and a negative correction is called for.

At the conclusion of a run the stopcocks on the aspirator were closed,

⁹ The record of the Harvard Observatory was referred to, where an exceptionally good instrument is maintained.

and the water manometer, the thermometer and the barometer (corrected to 0° and sea level) were read. The volume of water, measured and corrected as above mentioned, thus represents the volume of moist air in the aspirator at the observed temperature, and at a pressure equal to the atmospheric minus the manometer correction. From these data the volume of dry air at standard conditions may be calculated.

A sample calculation may help to make the matter clear. In the first determination listed in Table I for barium chloride dihydrate, the saturator contained an intimate mixture of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 1\text{H}_2\text{O}$ and glass beads.

Volume of water collected from aspirator, 6000. cc. Temp. of water at start, 26.2°; at end 20.5°. (1.0 cc. of water at 20.5° becomes 1.00138 cc. at 26.2°.) Vol. of filled aspirator bottle, 8470 cc. Shrinkage, (8470) \times (0.00138) = 11.7 cc. Corrected vol. of moist air drawn into aspirator, 6012 cc.

H_2O manometer reading at end, 286.0 mm. of H_2O = 21.0 mm. Hg. Temp. of moist air in aspirator at end = 22.25°. Aqueous tension at 22.25° = 19.9 mm. of Hg. Final barometer reading (corr.) = 763.5 mm. of Hg. Vol. dry air at 0° and 760 mm. drawn through = (6012) $\left(\frac{763.5 - 21.0 - 19.9}{760} \right) \left(\frac{273.1}{295.35} \right)$ = 5286 cc.

Wt. of water = gain in wt. of P_2O_5 tube = 0.0315 g. Calc. vol. of water vapor at 0° and 760 mm. contained in air drawn through = (0.0315) $\left(\frac{22410}{18.016} \right)$ = 39.18 cc. Av. barometer during run (corr.) = 758.7 mm. of Hg. Av. oil-manometer reading = 209 mm. of oil = 13.5 mm. of Hg. Av. total press. in saturator = 745.2 mm. of Hg. Decomposition pressure is $\left(\frac{39.18}{5286 + 39.18} \right)$ (745.2) = 5.48 mm.

Another precaution adopted was to avoid as far as possible evaporation of the water collected from the aspirator bottle, only a very small vent being allowed for the escape of air in the lower bottle, into which the water was siphoned.

In the matter of weighing the water taken up by the air in its passage through the hydrate tube, all the usual precautions of careful weighing of glass vessels, with the use of a counterpoise, were observed; and a maximum error of 0.2 mg. may be fairly assumed for these weights. It is evident that one limit to the applicability and accuracy of this method lies here; for with salt hydrates of low vapor pressure, such as copper sulfate pentahydrate or barium chloride dihydrate, it readily can be calculated that to obtain a weight of at least 0.1 g. of water 15 or 20 liters of air would be required (at 25°), with a consequent increase to inconvenient length in the time required for a determination.

Only in the case of nickel sulfate heptahydrate, and then only when the temperature of the room was lower than usual, was there danger of condensation of moisture occurring in the tube connecting the hydrate tube with the phosphorus pentoxide tubes. Nevertheless, this connection was made as short as possible, so that a minimum length of tubing was exposed to the air of the room.

The moist air always entered the glass-stoppered absorption tube at the same side to prevent loss of water by evaporation; and a guard tube, also containing phosphorus pentoxide, was interposed between the absorption tube and the aspirator, to prevent gain of water by backward diffusion.

The objection has been raised to this method, that in those cases in which equilibrium between the solid and gaseous phases is found by static methods to be slowly attained, it seemed very improbable that time enough would be allowed in any such method as the present for equilibrium to be established; but the data here presented for such hydrates as $\text{CuSO}_4 \cdot 5\text{-}3\text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot 6\text{-}2\text{H}_2\text{O}$ do not support this objection, for values have been obtained which agree with the reliable results of experimenters using other methods. It is also true, however, that unless the precautions are adopted of employing a saturator of large dimensions, and of employing a slow current of air, equilibrium in such cases will not be obtained. Thus, a U-tube about 1 cm. in diameter, containing a column 90 cm. long of $\text{CuSO}_4 \cdot 5\text{-}3\text{H}_2\text{O}$ and glass beads, was not sufficient to saturate the air very slowly drawn through it; whereas a tube half as long and 5.0 cm. in diameter gave correct results. A similar experience is reported by Menzies.¹⁰ Obviously, the time necessary for the attainment of equilibrium will be much greater when diffusion alone is relied upon to bring the air into contact with the salt hydrate mixture, or even when the air space is mechanically stirred to assist this process, than when the air is drawn through the finely powdered material.

Still another objection has been brought forward¹¹ to the gas-current saturation method, which is entirely groundless: namely, that equilibrium by this method would be difficult to approach from both sides. All that need be done to accomplish this result is to employ solutions of sulfuric acid in the towers, through which the air passes first, of such concentration that the effluent air will contain either slightly more or slightly less than the amount it will contain when at equilibrium with the hydrate pair.¹² It is important, of course, that there be present an ample supply of both solid phases in the saturator, so that the excess of moisture will be removed, or the deficiency of moisture be supplied, in the passage of the air through the mixed solids.

The temperature of these experiments was 25.00° , maintained in a very large water thermostat, which was controlled by a large mercury regulator and heating lamp in the usual manner. The 110-volt a. c. circuit which supplied to the heating lamp of the thermostat also passed through a small transformer, which in turn supplied current to operate the relay controlling the heating circuit. Temperature control was accurate within

¹⁰ Ref. 5, p. 1953.

¹¹ Ref. 2a, p. 709.

¹² Professor G. P. Baxter of Harvard University has privately communicated the fact that this procedure has been tried and gives very satisfactory results.

a few hundredths of a degree, as established by comparison of the bath thermometer with 2 standard thermometers. In certain cases, for example, with sodium sulfate, close control of temperature is essential for obtaining accurate and concordant results. Thus at 25°, a variation of 0.1° corresponds to a change of about 0.14 mm. in the decomposition pressure of the decahydrate.

The following hydrate pairs were studied: $\text{CuSO}_4 \cdot 5-3\text{H}_2\text{O}$; $\text{Na}_2\text{SO}_4 \cdot 10-0\text{H}_2\text{O}$; $\text{BaCl}_2 \cdot 2-1\text{H}_2\text{O}$; $\text{SrCl}_2 \cdot 6-2\text{H}_2\text{O}$; $\text{MgSO}_4 \cdot 7-6\text{H}_2\text{O}$; $\text{ZnSO}_4 \cdot 7-6\text{H}_2\text{O}$; $\text{FeSO}_4 \cdot 7-6\text{H}_2\text{O}$; $\text{CoSO}_4 \cdot 7-6\text{H}_2\text{O}$; $\text{NiSO}_4 \cdot 7-6\text{H}_2\text{O}$. Of these hydrate pairs, the first four were chosen in order to check the method against the recent results of Baxter and Lansing,⁴ of Menzies,⁵ and of R. E. Wilson,^{2a} each of whom made use of somewhat different methods. In the case of copper sulfate and of sodium sulfate the agreement is quite satisfactory; the value obtained with strontium chloride is a little higher than that of Baxter and Lansing, possibly because the capacity of their saturator was considerably less than that used in the present work. Cupric sulfate and barium chloride were investigated, furthermore, as furnishing a very severe test of the applicability of the method to substances with low dissociation pressures, which are likewise slow to reach equilibrium with the gaseous phase. The vitriol series was last studied, as a means of determining the effect of change of cation in a group of substances otherwise identical in composition.

The materials used were of the highest analytical quality obtainable, recrystallized wherever it appeared advisable, and analyzed for water content by heating to constant weight at the proper temperature. In the case of ferrous sulfate this heating was cautiously done in a current of dry hydrogen. Care must be taken to avoid decomposition of the less stable anhydrous salts by overheating. In each case the hydrate mixture was made up by intimately grinding approximately 90% of the higher hydrate with 10% of the lower, which was prepared from the higher by heating in an oven at the required temperature, or by air-drying in the case of the hydrates with sufficiently high decomposition pressures.

The following table gives the more important experimental data and the results calculated therefrom.

TABLE I
EXPERIMENTAL DATA AND RESULTS

Length and diam. of column. Cm.	Av. bar. (corr.) Mm.	Av. oil manometer Mm. Hg.	Av. total press. in saturator Mm. Hg.	Final bar. (corr.) Mm.	H ₂ O manometer Mm. Hg.	Final total press. in aspirator Mm.	Aqueous tension Mm. Hg.	Calc. vol. of dry air at 0°, 760 mm. Hg. Cc.	Wt. H ₂ O G.	Dissociation press. of hydrate Mm. Hg.
$\text{Cu SO}_4 \cdot 5-3\text{H}_2\text{O}$										
30 × 5.0	747.3	13.2	734.1	748.8	13.6	735.2	21.9	5180	0.0447	7.80
	751.8	13.2	738.6	753.2	13.5	739.7	21.4	5223	0.0446	7.77
40 × 5.0	757.9	13.2	744.7	760.6	16.5	744.1	24.1	5173	0.0440	7.80
	760.2	13.2	747.0	761.2	15.1	746.1	25.6	5118	0.0431	7.75
Mean										7.78

TABLE I (Continued)

Length and diam. of column. Cm.	Av. bar. (corr.) Mm.	Av. oil man. ome-ter Mm. Hg.	Av. total press. in sat-urator Mm. Hg.	Final bar. (corr.) Mm.	H ₂ O man. ome-ter Mm. Hg.	Final total press. in as-pirator Mm.	Aqueous ten-sion Mm. Hg.	Calc. vol. of dry air at 0°, 760 mm. Cc.	Wt. H ₂ O G.	Dissocia-tion press. of hydrate Mm. Hg.	
Na₂SO₄·10-0H₂O											
45 × 5.0	754.4	13.0	741.4	754.3	13.3	741.0	20.9	6991	0.1492	19.18	
	755.9	13.0	742.9	753.5	13.1	740.4	22.2	5211	0.1110	19.18	
	762.4	13.0	749.4	763.3	15.2	748.1	20.5	5267	0.1109	19.13	
	761.0	12.9	748.1	757.1	18.8	738.3	19.1	5306	0.1121	19.16	
	754.7	12.9	741.8	757.6	14.4	743.2	19.9	5396	0.1150	19.16	
	761.8	12.9	748.9	763.8	15.4	748.4	21.4	5317	0.1123	19.18	
	764.1	12.9	751.2	764.6	14.7	749.9	23.8	5306	0.1115	19.14	
											Mean 19.16
BaCl₂·2-1H₂O											
35 × 5.0	758.7	13.5	745.2	763.5	21.0	742.5	19.9	5286	0.0315	5.48	
	764.3	13.5	750.8	764.9	17.9	747.0	22.1	5263	0.0312	5.50	
	761.7	13.5	748.2	757.7	21.4	736.3	21.6	5196	0.0305	5.43	
	754.1	13.5	740.6	752.1	21.6	730.5	21.2	5194	0.0314	5.53	
	766.1	13.5	752.6	763.8	21.8	742.0	24.5	5202	0.0314	5.61	
	763.0	13.5	749.5	768.5	24.0	744.5	18.9	5507	0.0327	5.49	
	764.3	13.4	750.9	765.6	20.0	745.6	25.8	5226	0.0309	5.49	
	761.2	13.5	747.7	758.8	17.7	741.1	25.1	5217	0.0308	5.45	
										Mean 5.50	
SrCl₂·6-2H₂O											
32 × 5.0	756.2	12.9	743.3	758.4	14.1	744.3	22.0	5241	0.0488	8.51	
	766.3	12.9	753.4	764.7	14.4	750.3	21.5	5298	0.0487	8.52	
	757.7	12.9	744.8	754.2	14.4	739.8	24.1	5169	0.0478	8.47	
	761.3	9.4	751.9	759.7	10.9	748.8	18.8	5552	0.0512	8.53	
	761.8	9.4	752.4	763.9	10.9	753.0	20.4	5793	0.0531	8.49	
	754.5	9.4	745.1	757.2	11.5	745.7	18.9	5295	0.0495	8.57	
											Mean 8.52
MgSO₄·7-6H₂O											
29 × 5.0	759.2	9.4	749.8	761.5	16.4	745.1	25.7	5177	0.0701	12.42	
	757.7	9.4	748.3	753.6	15.0	738.6	24.7	5160	0.0699	12.40	
	753.9	9.4	744.5	753.7	15.2	738.5	27.9	5090	0.0703	12.58	
	758.7	9.4	749.3	763.4	17.9	745.5	24.3	5213	0.0711	12.51	
	764.3	9.4	754.9	764.4	15.7	748.7	22.7	5265	0.0717	12.58	
	761.7	9.4	752.3	756.9	15.1	741.8	22.5	5216	0.0708	12.50	
	763.3	9.4	753.9	764.8	13.3	751.5	25.2	5228	0.0708	12.49	
	766.1	9.4	756.7	768.5	17.4	751.1	25.5	5235	0.0710	12.56	
	766.1	9.4	756.7	763.8	13.6	750.2	24.1	5246	0.0709	12.51	
	763.0	9.4	753.6	769.0	10.5	758.5	20.9	5298	0.0712	12.39	
	764.3	9.4	754.9	765.3	15.1	750.2	26.8	5182	0.0696	12.41	
											Mean 12.50
	ZnSO₄·7-6H₂O										
50 × 4.5	759.7	12.5	747.2	755.4	15.3	740.1	20.6	6117	0.1029	15.32	
	754.1	12.5	741.6	754.9	15.7	739.2	21.5	5217	0.0884	15.31	
	761.7	12.5	749.2	761.9	30.6	731.3	23.5	5057	0.0849	15.33	
	762.8	12.5	750.3	763.9	29.8	734.1	24.3	5024	0.0842	15.33	
	762.6	12.5	750.1	763.7	27.3	736.4	19.5	5208	0.0876	15.38	
	761.3	12.4	748.9	759.7	28.1	731.6	19.0	5159	0.0866	15.32	
	763.9	12.5	741.4	752.2	27.9	724.3	18.5	5115	0.0870	15.36	
											Mean 15.34

FeSO ₄ ·7-6H ₂ O										
48 × 5.0	761.0	9.5	751.5	760.8	14.9	745.9	24.8	5200	0.0830	14.63
	760.5	9.5	751.0	763.1	17.8	745.3	22.0	5251	0.0830	14.49
	759.7	9.5	750.2	756.0	17.6	738.4	21.0	5222	0.0828	14.51
	754.4	9.5	744.9	755.6	17.4	738.2	21.8	5204	0.0834	14.56
	759.2	9.5	749.7	763.3	17.7	745.6	23.0	6108	0.0976	14.62
	763.3	4.6	758.7	765.0	6.9	758.1	23.2	5860	0.0920	14.54
										Mean
NiSO ₄ ·7-6H ₂ O										
50 × 4.5	764.3	12.5	751.8	765.2	21.3	743.9	21.6	5257	0.1192	20.63
	761.7	12.5	749.2	757.9	18.4	739.5	21.2	5228	0.1186	20.57
	756.2	12.5	743.7	757.3	29.3	728.0	22.5	5114	0.1179	20.74
	763.3	12.5	750.8	765.4	36.7	728.7	24.4	5084	0.1154	20.62
	765.8	12.5	753.3	762.7	25.6	737.1	24.5	5142	0.1163	20.62
	765.5	12.5	753.0	767.0	17.3	749.7	26.3	5152	0.1177	20.81
	764.0	12.5	751.5	765.6	29.3	736.3	25.1	5123	0.1171	20.78
	761.2	12.4	748.8	758.5	30.0	728.5	24.5	5068	0.1160	20.74
										Mean
CoSO ₄ ·7-6H ₂ O										
48 × 4.5	761.7	9.4	752.3	759.8	11.4	748.4	24.1	5293	0.0963	16.65
	758.7	9.4	749.3	756.4	30.0	726.4	25.1	5134	0.0933	16.55
	757.9	9.4	748.5	760.3	22.6	737.7	25.0	5266	0.0955	16.52
	760.2	9.4	750.8	761.2	26.8	734.4	26.2	5112	0.0926	16.55
	760.5	9.4	751.1	761.1	11.7	749.4	24.1	5274	0.0962	16.67
	759.2	9.4	749.8	758.6	11.4	747.2	24.4	6151	0.1113	16.51
	764.8	9.4	755.4	764.9	30.4	734.5	24.7	5097	0.0921	16.61
										Mean

Table II summarizes the results given above and compares them as far as possible with the results of other experimenters, the values appearing in decreasing order of magnitude. In some cases the values can be assigned only approximately, either because of variation in the results of the original experimenter with changing experimental conditions—

	BaCl ₂ 2-1H ₂ O	SrCl ₂ 6-2H ₂ O	CuSO ₄ 5-3H ₂ O	Na ₂ SO ₄ 10-0H ₂ O	MgSO ₄ 7-6H ₂ O	ZnSO ₄ 7-6H ₂ O	FeSO ₄ 7-6H ₂ O	CoSO ₄ 7-6H ₂ O	NiSO ₄ 7-6H ₂ O
Present									
Paper	5.50	8.52	7.78	19.16	12.50	15.34	14.56	16.58	20.69
	5.8 ^{2a}	8.4 ¹³	8.5 ¹⁸	19.22 ^{2a}	18.9 ²²	15.1 ²²	13.3 ²²	17.3 ²²	19.3 ²²
					to	to	to	to	to
					20.3	15.5	16.5	18.1	21.4
	5.26 ²¹	8.37 ⁴	7.9 ²⁰	19.20 ⁴	11-12 ¹⁴	14.6 ¹⁷	14.5 ¹⁵
	7.80 ^{2a}	19.0 ¹⁸	11-12 ¹⁵
	7.77 ⁵
	7.68 ²¹
.....									
	5.2 ¹⁷	7.5 ¹⁷	7.4 ¹⁷	18.2 ¹⁶	11.7 ¹⁸	14.0 ¹⁸
	4.8 ¹⁶	...	7.3 ¹⁹	17.6 ¹⁹	11.6 ¹⁷	13.6 ¹⁶
	4.7 ¹⁹	...	7.0 ¹⁶	..	11.5 ¹⁸	12.9 ¹⁹

See footnotes for Table on page 352.

as in the data of Wiedemann—or because of necessarily long extrapolation on experimental curves, in order to obtain the value at 25°—as in the data of Cohen and Bolte. The wide variations seen clearly testify to the unsatisfactory state of the data to be found in the literature at the present time. All the values below the dotted line are unquestionably too low, while some of those above the line are too high.

A study of the preceding table indicates that the gas-current saturation method gives results in good agreement with the most reliable of available data as obtained by other methods.

Discussion.—The relationships which may exist between the composition of a salt hydrate and the magnitude of its decomposition pressure at a given temperature is by no means clear, although some attempts to connect the stability and the composition of these substances have been made. Thus, recently, G. L. Clark and Buckner,²³ considering the results of their own work, in addition to that of Ephraim,²⁴ upon both ammines and hydrates, summarize in part as follows:

“The strength of secondary valence forces as judged by the number of groups bound and the stability runs as a parallel phenomenon to the following properties: (1) with constant molecular group and anion to decreasing atomic volume, ionic radius, and percentage of total volume occupied by the cation; (2) with constant molecular group, anion and cation to higher valence, and hence stray field, of the cation; (3) with constant molecular group and cation to increasing atomic or radical volume, ionic radius and percentage of total volume occupied by the anion; (4) hence to increasing difference in volume between anion and cation; and (5) with constant anion and cation to decreasing volume of the ammine molecule and to increasing values of the entropy-like ratio of critical pressure to critical temperature.”

In corroboration of Rule 3 above, the authors point out that the halides of cobalt form hydrates and ammines, the stability of which increases from the fluoride to the iodide; that is, with increasing atomic volume of the anion, stability increases.

Now, a comparison of the stability of a series of hydrates as judged by their dissociation temperatures measured at a given pressure, or by their dissociation pressures measured at a given temperature, may lead to contradictory results, dependent upon the pressure or the temperature chosen,

¹³ Andreae, *Z. physik. Chem.*, **7**, 241 (1891).

¹⁴ Bolte, *ibid.*, **80**, 338 (1912).

¹⁵ Cohen, *Arch. néerland.*, [2] **5**, 295 (1900).

¹⁶ Foote and Scholes, *THIS JOURNAL*, **33**, 1309 (1911).

¹⁷ Frowein, *Z. physik. Chem.*, **1**, 5, 362 (1887).

¹⁸ Lescoeur, *Ann. chim. phys.*, [6] **21**, 511 (1890).

¹⁹ Mueller-Erzbach, *Wied. Ann.*, **32**, 313 (1887).

²⁰ Pareau, *Wied. Ann.*, **1**, 55 (1877).

²¹ Partington, *J. Chem. Soc.*, **99**, 466 (1911).

²² Wiedemann, *J. prakt. Chem.*, [2] **9**, 338 (1874); *Pogg. Ann. Jubelbd.*, **1873**, 474.

²³ Clark and Buckner, *THIS JOURNAL*, **44**, 242 (1922).

²⁴ Ephraim, *Ber.*, **45** to **54** (1913-1921).

which is usually a perfectly arbitrary one, such as 760 mm. or 25°. As a matter of fact, the pressure-temperature curves for the several substances under comparison may cross one another, and the order of stability, therefore, will differ on either side of such an intersection. This condition, for example, was encountered by Wiedemann²⁵ in the case of the sulfates of iron, cobalt, nickel, magnesium and zinc. His P - T curves, plotted for temperatures ranging from 10° to 85°, show a number of intersections: thus at 20° the order of decreasing dissociation pressure in the series of sulfates is as follows: nickel, cobalt, iron, magnesium, zinc; at 25° the order is: nickel, magnesium, cobalt, iron, zinc; while at 70° the order becomes: iron, cobalt, nickel, magnesium, zinc. While there is reason to believe that some of Wiedemann's values are of doubtful accuracy, the results just mentioned indicate that the order of relative stability of a series of hydrates may vary with changing experimental conditions.

Furthermore, generalizations concerning the strength of secondary valence forces, as applied to hydrates, based solely on the *number* of groups bound seem open to many exceptions. The present state of the literature is no doubt in part responsible for this, as a brief survey of the field will demonstrate. For example, hydrates of cadmium sulfate have been reported, containing 1, $1\frac{1}{3}$, $2\frac{1}{2}$, $2\frac{2}{3}$, 7, 9, and $14\frac{1}{2}$ molecules²⁶ of water per molecule of anhydrous salt; similarly, for cupric sulfate, besides the $5\text{H}_2\text{O}$, $3\text{H}_2\text{O}$, and $1\text{H}_2\text{O}$, we find listed hydrates with 2, $3\frac{1}{2}$, 6, 7, and $9\text{H}_2\text{O}$, all of which *supposedly* are capable of existence under the proper conditions; chromic sulfate has a list of a dozen different compounds, etc. If we are to judge secondary valence strength solely by the number of molecular groups which under certain conditions may be bound, we shall find much conflicting evidence. In the light of the rules quoted above, why, for example, should gallium chloride, GaCl_3 , and indium trichloride, InCl_3 , be anhydrous, and thallic chloride, TlCl_3 , be capable of forming 3 or 4 different hydrates?²⁷ Although in general it seems to be true that with a given cation and anion, the higher the valence, the more molecules of water may be bound, we find in the case of ferrous and ferric nitrates that both are capable of holding a maximum of $9\text{H}_2\text{O}$; stannous nitrate forms a compound, $\text{Sn}(\text{NO}_3)_2 \cdot 20\text{H}_2\text{O}$, while stannic nitrate is anhydrous. The list could be greatly extended. It seems apparent, after a tabulation of the hydrates of the sulfates, chlorides, and nitrates of the elements, as re-

²⁵ Ref. 22. The curves mentioned will be found at the end of the volume.

²⁶ See Hoffmann, "Lexikon der anorganischen Verbindungen," J. A. Barth 1912-1914.

²⁷ The rules referred to would lead us to expect least stability in the case of the hydrates of thallic chloride, greatest stability in the case of the hydrates of gallium chloride; since with decreasing atomic volume of the cation the strength of secondary valence forces should increase. Conceivably, of course, hydrates of gallium and indium may be capable of existence, but as yet have not been described,

corded in the literature, that while doubtless such factors as valence and atomic or radical volume have an effect upon the number of molecular groups held, they alone do not determine this number in many cases. Before one may fairly judge of the influence of these factors, however, much more experimental work remains to be done, in the formation of new compounds, and in the refutation of many assumed compounds which now find place in the literature.

Summary

1. Measurements of the dissociation pressures of 9 pairs of salt hydrates, $\text{BaCl}_2 \cdot 2-1\text{H}_2\text{O}$; $\text{SrCl}_2 \cdot 6-2\text{H}_2\text{O}$; $\text{CuSO}_4 \cdot 5-3\text{H}_2\text{O}$; $\text{Na}_2\text{SO}_4 \cdot 10-0\text{H}_2\text{O}$; $\text{MgSO}_4 \cdot 7-6\text{H}_2\text{O}$; $\text{ZnSO}_4 \cdot 7-6\text{H}_2\text{O}$; $\text{FeSO}_4 \cdot 7-6\text{H}_2\text{O}$; $\text{CoSO}_4 \cdot 7-6\text{H}_2\text{O}$; and $\text{NiSO}_4 \cdot 7-6\text{H}_2\text{O}$ —have been made by the gas-current saturation method at 25° , and the results compared with those obtained by other experimenters using the same or different procedures.

2. It is found contrary to the experience of some investigators, and supporting the experience in particular of Menzies, and of Baxter and Lansing, that the method gives reliable results when due precautions are taken, particularly with regard to the size of the saturator containing the salt-hydrate mixture, the method of measuring the total internal pressure, the intimate mixing of the two solid phases, the rate of flow of the current of air through the apparatus, and the weighing of the water taken up by the air.

3. The objection raised to this method, that sufficient time for the attainment of equilibrium is not allowed, is shown to be without foundation, in view of the results obtained with salt hydrates of low dissociation pressures; and the possibility of approaching equilibrium from both sides is pointed out.

4. No certain relationship has been found to hold between the composition of analogous salt hydrates and their dissociation pressures measured at a given temperature, although the influence of such factors as atomic volume and valence is admitted. Exception is taken to the generalizations advanced by Clark and Buckner, connecting the composition of amines and hydrates with their stability, in view of the numerous exceptions offered in the literature. It is pointed out that much further work would be necessary, both in the formation of new molecular compounds, as well as in the refutation of numerous assumed compounds at present recorded, before we may hope to establish this relationship definitely.