Summary.

Experimental results have been communicated which prove that nickel may be quantitatively separated from salts of arsenic acid in ammoniacal solution by means of the electric current.

The striking and radical difference between the behavior of cobalt and nickel when deposited from such solutions has been pointed out. This interesting property of cobalt is being made the subject of further study in order to determine why arsenic is always deposited with cobalt and not with nickel.

In conclusion the writer wishes to thank Dr. L. W. McCay for very valuable advice and suggestions during the progress of this work.

PRINCETON, N. J.

[CONTRIBUTION OF THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY.]

A STUDY OF THE VAPOR PRESSURE OF AQUEOUS SOLUTIONS OF MANNITE.[1]

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Received July 6, 1920.

Introduction.

The vapor pressure method offers certain advantages for the investigation of the colligative properties of solutions, and, though many efforts have been made to apply it to the study of aqueous solutions, the results have not been entirely successful. The fundamental importance of the knowledge of the vapor pressure of solutions is shown by its frequent use in thermodynamic formulas. In practice 2 methods, known as the dynamic and static methods, have been used. The first depends on the determination of the amount of the solvent required to saturate the same volume of air when in equilibrium with the solvent and solution, respectively, both maintained at the same constant temperature. This method has been used by Ostwald; the Earl of Berkeley[2] and his associates have investigated the various sources of error involved in this method and have made many improvements in the apparatus and details of manipulation. The recent work of Washburn[3] has been essentially an application of the apparatus of Berkeley.

Some time ago Frazer and Lovelace,[4] in spite of the failure of earlier workers, described an apparatus and manipulation by which accurate measurements of vapor pressure of aqueous solution by the static method could be made. Many of the errors which had previously been encoun-

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[1] The experimental part of this article forms the basis of a dissertation submitted by T. H. Rogers to the Johns Hopkins University.

[2] *Proc. Roy. Soc. A.*, **17**, 156 (1906).

[3] Washburn, THIS JOURNAL, **37**, 309 (1915).

[4] Frazer and Lovelace, *ibid.*, **36**, 2439 (1914); *Z. physik. Chem.*, **89**, 155 (1914).

tered in attempting to apply this method were eliminated by making it differential, comparing directly, by means of the Rayleigh manometer, the vapor pressures above the solution and the pure solvent when both were maintained in the same accurately regulated thermostat.

After preliminary work certain improvements were made in the temperature regulation and the method of stirring, and the method was applied to the study of aqueous solutions of mannite. After the elimination of certain other slight sources of error the method was extended to aqueous solutions of potassium chloride.[1]

The present paper is a repetition of the study of mannite solutions in the course of which an additional slight source of error was discovered and eliminated. The work on potassium chloride solutions was also repeated, the results of which will be the subject of a future communication.

Experimental.

Series I.—The apparatus used for this work was that described in the work on potassium chloride solutions.[2] The mannite used was carefully purified and the same sample used throughout. The experimental details were carried out in this series in practically the same manner as in the previous work. The solutions were subjected to a preliminary removal of air by repeatedly exhausting the space above the solution contained in a specially constructed flask as there described, and were further freed from air after they were introduced into the bath. Often the vapor was allowed to expand into an evacuated bulb as many as 25 times before the solution was sufficiently air-free to take observations. The test for air was made by measuring with the McLeod gage the residual pressure after the liter bulb, which contained the vapor from the solution, had been opened to the flask containing phosphorus pentoxide.

To insure equilibrium between liquid and vapor phase before testing, the solution was left open to the vapor bulb for 24 hours with intermittent stirring of the solution. When the test was made, it was observed that while practically all the vapor seemed to be absorbed in perhaps a half hour, a further slow absorption took place for a number of hours. At the end of about 12 hours the reading on the gage became constant and, if the pressure indicated was 0.0005 mm. or less, the test was considered satisfactory and the air present deemed negligible. While this behavior, especially the slowness of the absorption, occasioned surprise, its significance was entirely overlooked during this series.

Observations.—A careful study was made of the proper conditions for taking observations. In the light of the previous work it was obvious that an essential condition is that the temperature of the room should be

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[1] Lovelace, Frazer and Miller, THIS JOURNAL, 38, 515 (1916).

[2] *Loc. cit.*

fairly constant. As the work progressed, however, it was found unnecessary to provide for any special regulation of the temperature of the room, though it is necessary, of course, to prevent any sudden change. Under these conditions evaporation and condensation at the surface of the solvent and solutions are sufficiently rapid to prevent any disturbance in the pressure of the system caused by the slow fluctuations of the room temperature.

After removal from the bath the solutions were analyzed both by the use of the interferometer and by evaporating a weighed portion to dryness and heating the residue to constant weight at 130°. The results of the 2 methods accorded well.

Table I gives in brief the results of this (preliminary) investigation of the lowerings of mannite solutions of 10 different concentrations. Column 1 gives the concentrations expressed in mols (O = 16) of solute per 1000 g. of solvent. Column 3 gives the lowerings produced in mm. of mercury at the prevailing room temperature. For the sake of comparison, Column 2 gives the lowerings found by Mullikin[1] expressed similarly. His data have been extrapolated over a slight range in order to get values corresponding to the concentrations in Column 1.

Column 4 shows the theoretical lowerings of these solutions as calculated from Raoult's law, and under the same conditions as the values in Columns 2 and 3. Column 5 gives the deviations from Raoult's law of the values found in this series.

TABLE I.

Comparison of the Values Obtained for the Lowering of Mannite Solutions.

M.	Mullikin.	Series I.	Calculated.	Difference.	Series II.
0.0995	0.0287	0.0280	0.0314	0.0034	0.0311
0.1993	0.0587	0.0585	0.0627	0.0042	0.0620
0.2985	0.0906	0.0882	0.0939	0.0057	0.0930
0.3984	0.1188	0.1221	0.1251	0.0030	0.1239
0.4986	0.1538	0.1533	0.1563	0.0030	0.1553
0.5968	..	0.1819	0.1867	0.0048	0.1869
0.6960	..	0.2127	0.2175	0.0048	0.2173
0.7958	..	0.2471	0.2489	0.0018	0.2491
0.8944	..	0.2740	0.2784	0.0044	0.2802
0.9941	..	0.3061	0.3088	0.0027	0.3108

Column 6 gives the values found in Series II (*vide infra*) extrapolated and expressed similarly.

The agreement of the results in Series I with those of Mullikin is fair, though in several cases there is greater deviation than the 0.001 mm. claimed as the accuracy of the method. However, the nearly constant deviation from Raoult's law was suspicious, especially in the concentrations where the best agreement would be expected. In order to make

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[1] R. Mullikin, *Dissertation*, Johns Hopkins Univ., 1916.

certain that the solutions measured were free from air another method of preliminary removal of air was devised. This will be described when the discussion of the results of Series II is taken up. It was found that solutions so prepared gave a lowering from 0.003 to 0.005 mm. greater than those recorded in Series I. Further, when tests for air were made on the solutions of Series II, the readings on the McLeod gage showed negligible air pressure after 20 minutes absorption by the phosphorus pentoxide. This difference in behavior was obviously due to the fact that the solutions of Series I were measured with an air pressure of 0.003–0.005 mm. The gage readings on air tests should have been made after the same length of time, 20 minutes, whereupon the air present would have been discovered. If the pentoxide is kept open for a longer time, adsorption of the residual air takes place slowly, both by the pentoxide and the glass surfaces[1] of the system. The agreement between Mullikin's results and those of Series I is better than might be expected since the solutions in Series I were measured with an air pressure of about 0.004 mm. But this residual amount of air pressure was practically the same in each case since the same methods of preparation of solutions were used and the same criterion adopted for testing the presence of air, the result being that nearly the same amount of air was left in practically every case.

Series II. Preparation of the Solutions.—In order that the solutions might be made up to a definite concentration it seemed best to have both solvent and solute free from air and mix the two in a vacuum. After several trials a method was found which accomplished this in a satisfactory manner.

The water is introduced into a 500-cc. flask A, Fig. 1, to which is sealed a length of 7 mm. glass tubing. A constriction *a* is drawn near the end of the tube and a short piece of rubber tubing fitted on the end. After boiling the water vigorously for 30–35 minutes, the rubber tube is suddenly pinched shut, at the same time removing the burner. The tube is then quickly sealed off at the constriction. The flask having been previously weighed, by weighing the sealed flask and tip the amount of water contained is determined.

A short length of tubing is sealed to the neck of a 300-cc. flask and another into the bottom, as shown in B, Figs. 1 and 2. An amount of solute corresponding to the weight of water prepared is introduced in the flask. After making a file mark on the tip, the tube of the flask containing the water is joined to one end of the flask B by means of a stout rubber tube, as shown in Fig 2, and the other end is connected to a vacuum pump. The solute is thus freed from air after several hours pumping. Finally the tube connecting to the pump is sealed off at *b* and the solute

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[1] Menzies, THIS JOURNAL, 42, 978 (1920).

and solvent mixed by breaking the tip of the flask A inside the connecting rubber tube. After solution is effected, the rubber tube is pinched shut, the flask A removed and a specially constructed pipet, *p*, Fig. 3, put in its place. A file scratch is made on the other end of the flask now free and connection made to a mercury reservoir as shown. To introduce the solution this tip is broken under the mercury and the end of the pipet placed under the bottom of the tube which, dipping in mercury, leads up into the temperature bath.[1] Under pressure from the reservoir the solution flows out of the flask and bubbles up through the mercury to the reservoir in the bath.

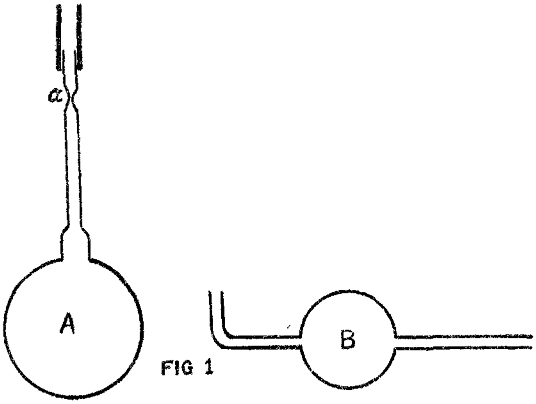

FIG 1

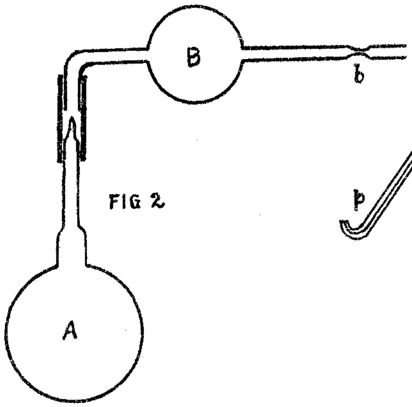

FIG 2

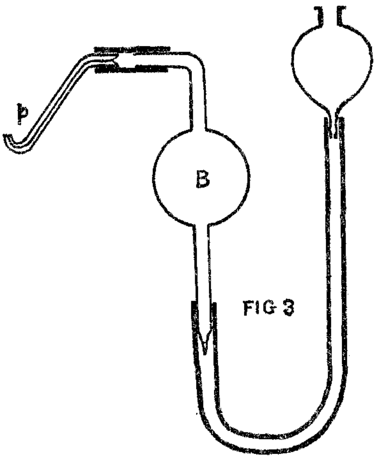

FIG 3

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[1] See Fig. 1, THIS JOURNAL, 38, 517 (1916).

Solutions prepared and introduced in this manner require only a few vapor expansions in the bath in order to remove the air completely. The use of rubber tubing for a connection in the apparatus cannot be conveniently avoided and no trouble from leakage was experienced after a good grade of antimony rubber tubing had been selected and care taken to wire the end. Absolutely complete removal of air in the preparation of a solution was not attempted, as there is always some air taken up in introducing, due to the slight amount of air trapped by the mercury column on the walls of the tubes leading up into the bath. The flask in which the water was boiled was steamed out thoroughly before using. After this a sample of water which had been boiled in the flask for 35 minutes was compared in the interferometer with a sample of conductivity water. The difference in density was found to be very slight and certainly not enough impurities were present to effect a lowering of the vapor pressure. In this work either conductivity water or distilled water, which compared favorably in the interferometer with conductivity water, was used throughout.

Observations.—The readings were taken under conditions as described in Series I. Frequently observations were attempted before the solutions were air-free, as in this way the rate of the removal of air could be followed. Hence these preliminary readings were not reliable and no results are recorded here unless the solutions had been shown to have less than 0.0004 mm. residual air pressure. The exact reading of the McLeod gage is unsatisfactory at this slight pressure, but it is safe to say that the maximum air pressure of a solution considered air-free was as small as this amount, while generally it was much less. At the time of making readings the residual air was certainly less, for the solution and solvent were subjected to a fresh vapor expansion just before observations were made.

Constant readings can be obtained within 15 minutes after opening a solution to an evacuated bulb. If appreciable air were present in the solution the deflection would not be constant, due to air coming out of the solution gradually. This phenomenon was actually observed in many preliminary observations on solutions known to contain air, when the readings would gradually drop. When the solution is once freed from air no trouble is experienced in getting a series of concordant measurements.

The observations were continued until at least 5 consecutive concordant sets were obtained. In these final measurements as recorded here no values have been discarded unless the data were unreliable for obvious reasons, such as the loss of the zero point, or a change in bath temperature. A few non-concordant values are bracketed. Some readings were taken while the solutions were being stirred at a variable speed and the deflections were found to be independent of the rate of stirring, so that practically all of the observations were made with constant speed stirring. The arrangement mentioned was such that the rate of stirring was changed over a wide range several times each minute, thus effectually preventing surface concentration.

The zero point of the measurement is given by the setting of the manometer when the limbs of this instrument are open to one another. This reading was always taken before and after each reading of the deflection. Sometimes due to the slight unsteadiness of the telescope mounting, the zero value was not checked. In such cases the deflection was taken again. If the 2 values checked, these 2 deflections together with the included zero point, were used to compute the lowering.

To calculate the lowering, the scale deflection, s, the distance between the points of the manometer, d, and the distance from the mirror on the manometer to the scale D, must be known. The lowering, h, is given by the expression[1] $h = d/2D\ s$ or, $h = ks$. This involves the assumption that $\sin \theta = {}^1/_2 \tan 2\theta$, where θ is the angle of tilt of the manometer. This assumption is found not to introduce an appreciable error in the case of the most concentrated solution investigated here. The value of d for the manometer was redetermined and the length, D, was frequently checked. The value of h thus calculated is the height of a column of mercury at room temperature, about 24°. This is corrected to the height of a column of mercury at 0°, which is the lowering $p_0 - p_1$.

Analysis.—After taking due precaution to keep the solution as near as possible to the original concentration in removing it from the bath, the exact concentration was determined. The Rayleigh-Zeiss interferometer served admirably for this purpose. With a 20 mm. cell a solution can be compared with a standard with as great an accuracy as that with which the standard can be prepared. By making a rough analysis and then preparing a standard of very nearly the concentration of the solution being analyzed the interferometer serves practically as a zero instrument. Often as a check the weighed portion of a solution was evaporated to dryness and the residue dried to a constant weight at 130°. These results accorded well with those from the interferometer method. No trouble was experienced in getting a constant weight of the mannite residue, a difficulty mentioned by Flügel.[2] The molar concentration was thus easily determined with an accuracy of 2×10^{-4} weight molar, which corresponds to a vapor pressure lowering of less than 0.0001 mm. The concentration was always expressed in terms of mols of mannite per 1000 g. of water, the weights being reduced to the vacuum standard, and 182.12 employed as the molecular weight of mannite.

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[1] This Journal, **36**, 2440 (1914).

[2] Flügel, *Z. physik. Chem.*, **79**, 577 (1912).

RESULTS.

0.09845 *M* Mannite.

Date.	Zero.	Reading.	Zero.	Deflection (mean).
11/8/16	1.1	7.2	..	..
	1.0	7.0	..	..
	0.95	7.1	0.95	..
	..	..	1.0	6.10
11/9/16	1.0	7.1	..	..
	1.05	7.05	1.05	..
	..	7.1	1.1	6.01
11/9/16	1.9	..	..	..
	1.8	7.9	1.9	..
	1.75	7.9	1.8	..
	1.8	7.95	1.7	6.11
11/10/16	0.95	7.0	..	..
	1.0	7.0	1.0	..
	..	7.0	0.95	6.02
11/11/16	2.0	8.1	..	..
	2.0	8.15	..	..
	..	8.0	2.05	..
	..	8.1	2.05	6.08
11/11/16	2.8	8.9	..	..
	2.8	8.95	2.8	..
	2.9	8.85	2.9	6.06

Average deflection............................ 6.06 mm.

Lowering (corr. to Hg at 0°)........ = 0.0307 mm.
Maximum deviation............... = 0.0005 mm.
$k = 0.005080$

0.4938 *M* Mannite.

Date.	Zero.	Reading.	Zero.	Reading.	Deflection (mean).
12/1/16	290.05	320.1	..	..	...
	290.0	320.1	289.95	320.1	...
	290.05	320.05	289.95	320.15	30.15
12/2/16	..	320.7	290.45	320.6	...
	..	320.7	290.5	320.75	...
	..	320.7	290.5	320.75	30.22
12/2/16	290.8	321.0	..	..	...
	290.8	321.0	290.8	..	...
	..	321.0	290.85	..	30.19
12/2/16	290.4	320.55	..	..	...
	290.4	320.55	290.4	..	...
	..	320.5	290.4	..	30.13
12/3/16	290.0	320.35	..	..	...
	290.05	320.3	..	..	...
	..	320.3	290.0	..	30.31

Average deflection.................................. 30.20 mm.

Lowering (corr.)................. = 0.1542 mm.
Maximum deviation............. = 0.0007 mm.
$k = 0.005109$

0.9908 *M* Mannite.

Date.	Zero.	Reading.	Zero.	Deflection (mean)
11/17/16	2.95	63.9	..	...
	2.95	63.9	..	...
	..	63.85	2.9	60.95
11/18/16	2.1	63.05	..	...
	..	63.05	..	...
	..	63.05	2.1	60.95
11/19/16	1.15	62.1	..	...
	1.05	62.05	1.05	...
	..	62.05	1.05	60.99
11/20/16	2.95	64.0	2.9	...
	..	64.0	3.0	...
	..	64.0	3.0	61.04
11/20/16	2.65	63.7	..	...
	..	63.7	2.7	...
	..	63.6	2.65	60.99

Average deflection.................................. 60.98 mm.
Scale corrected..................................... 61.20 mm.
Lowering (corr.)............. = 0.3109 mm.
Maximum deviation......... = 0.0004 mm.
k = 0.005080

Table II.

Summary of Data.

G = g. of mannite per 1000 g. of water (*in vacuo*).
M = concentration in moles per 1000 g. of solvent.
s = scale deflection in mm.
p_0-p_1 = vapor pressure lowering in mm. mercury (mercury corr. to 0°).
$K = d/2D$
Calc. = lowering calculated according to Raoult's law.
Diff. = difference between calculated and observed lowerings.

G.	*M*.	*s*.	p_0-p_1.	$k\times10^{-6}$.	Calc.	Diff.	Mol. fract. $\times10^{-4}$.	$\frac{p_0-p_1}{n/N+n}=p_0$.	$\frac{p_0-p_1}{M}$.	O. P.
17.930	0.0984	6.06	0.0307	5080	0.0311	0.0004	17.70	17.31	0.3113	2.343
36.004	0.1977	12.15	0.0614	5080	0.0622	0.0008	35.48	17.32	0.3108	4.703
53.951	0.2962	18.23	0.0922	5080	0.0931	0.0009	53.09	17.37	0.3133	7.040
71.917	0.3945	24.26	0.1227	5080	0.1239	0.0012	70.64	17.37	0.3107	9.392
89.938	0.4938	30.20	0.1536	5109	0.1547	0.0011	88.18	17.42	0.3111	11.78
108.243	0.5944	36.56	0.1860	5109	0.1858	—0.0002	105.9	17.55	0.3129	14.27
108.498	0.5958	36.63	0.1863	5109	0.1862	—0.0001	106.2	17.55	0.3128	...
126.283	0.6934	42.50	0.2162	5109	0.2164	—0.0002	123.4	17.56	0.3118	16.61
144.357	0.7927	48.71	0.2478	5109	0.2469	—0.0009	140.8	17.60	0.3126	19.07
162.332	0.8913	54.86	0.2791	5109	0.2772	—0.0019	158.0	17.66	0.3131	21.50
162.485	0.8922	55.20	0.2792	5080	0.2775	—0.0017	158.2	17.65	0.3129	...
180.451	0.9908	61.20	0.3096	5080	0.3076	—0.0020	175.4	17.65	0.3124	23.88

Above, the complete data for 0.1, 0.5 and 1.0 molar concentrations are given. A table summarizing all the results for the 12 concentrations studied is shown; the detail data for 9 solutions are omitted for the sake of brevity.

Discussion of Results.

Accuracy of the Method.—Significant errors arising from a variation in the temperature are hardly possible, as no variation could be detected by a sensitive Beckmann thermometer for days at a time. The chance errors of observation are very small as will be seen by a consideration of probabilities. Three readings at least were always made of the zero point and of each deflection. The average error of the zero-point setting was about 0.03 mm. and that of the deflection reading 0.04 mm. scale deflection. This gives an average error of each measurement of $\sqrt{(0.03)^2 + (0.04)^2} = 0.05$ mm., or for 5 observations, 0.01 mm. scale deflection. The probability that a given series of observations will be within this range is about $^4/_7$. In other words, under the conditions of the work, 4 times out of 7, the error of the observation of the lowering will be within 0.01 mm. scale deflection, corresponding to 0.00005 mm. actual lowering. However, this does not represent at all the accuracy of the method, for there may be certain constant errors whose relative values are additive in calculating the final error. 1. There may be a slight amount of air present. 2. There is a possibility that the surface concentration of the solution is not entirely overcome by stirring the solution during the reading. Altogether it is evident that the method is limited in its accuracy by these factors and not by errors of observation; *viz.*, (*a*) measuring the deflection and (*b*) analyzing the solution. The 2 separate determinations at 0.6 and at 0.9 *M* with the greater variation in the latter case of only 0.0002 mm. serve as a striking confirmation. It is believed that the values in Table II are correct within 0.0006 mm.

Raoult's Law.—Table II shows a summary of the results and gives the deviation from Raoult's law, the validity of which has been supported from theoretical considerations by van Laar, G. N. Lewis and others. In calculating the theoretical lowering the equation $\frac{p_0 - p_1}{p_0} = \frac{n}{N + n}$ was used, where p_0 is the vapor pressure of the pure solvent at the same temperature, p_1 the vapor pressure of the solution, n the number of moles of solute, and N the number of moles of solvent. p_0 has been accurately determined by Holborn and Henning and by Scheel and Heuse, who give the value 17.539 mm. The agreement of lowerings thus calculated with experimental values is much closer than when the old form of Raoult's law is used, $\frac{p_0 - p_1}{p_0} = \frac{n}{N}$. It will be seen from Col. 1, Table II that the observed values are increasingly smaller than those calculated until a maximum positive deviation is reached at about 0.4 *M*. At about 0.6 *M* the calculated and observed values are the same, and it is not until a higher concentration is reached that there is a marked negative deviation from Raoult's law. However, although the deviation in the range 0.1 to 0.8 *M* is never much greater than the 0.0006 mm. claimed as the accuracy of the method, it must be emphasized that the results are relatively accurate enough to allow us to draw some conclusions from these deviations.

In order to facilitate comparison and to magnify the deviations the value of the lowering may be divided by the concentration. Hence it is often the custom to examine vapor pressure results in the light of the molecular lowering value, $(p_o - p_1)/M$, and for that reason this value has been plotted against concentration in Fig. 4 (upper curve). However, this function has no theoretical significance, as will be seen; since

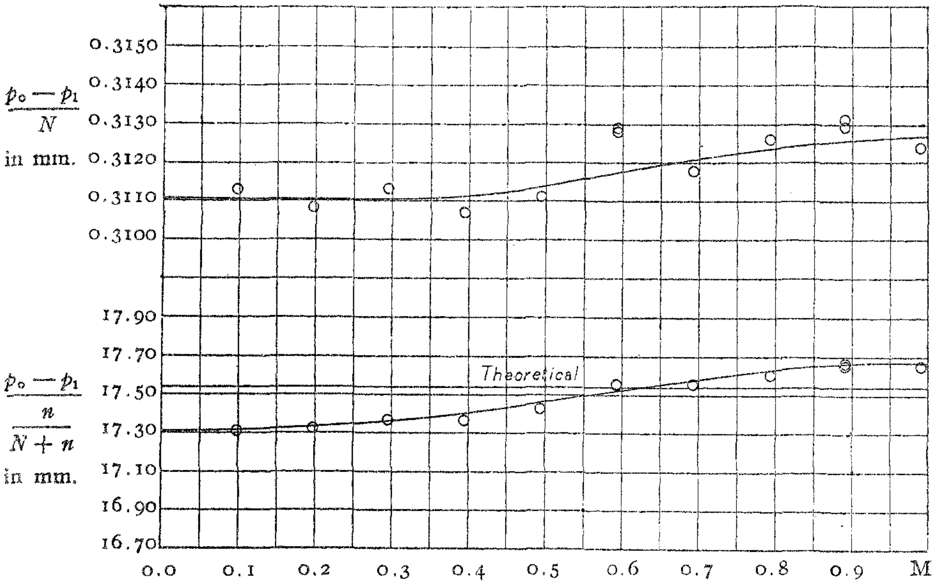

Fig. 4.—Upper Curve—Molecular lowering of Mannite solutions at 20° C. Lower Curve—The ratio of the vapor pressure lowering to the Molar Fraction.

$$p_o - p_1 = p_o \frac{n}{N + n}$$

the molecular lowering,

$$\frac{p_o - p_1}{n} = \frac{p_o}{n + N}.$$

The function, $p_o/N + n$, is a decreasing one, with respect to *n*. It seems that it is often thought that molecular lowerings should be constant, but for an ideal solution the molecular lowering curve is concave downward, only slightly, however, in dilute solutions. Thus it is evident that conclusions drawn from the molecular lowering curve may be misleading.

It is more logical to calculate the value of the lowering divided by the mol fraction, which, according to Raoult's law, is a constant, *viz.*, the vapor pressure of water at the temperature in question.

$$\frac{p_0 - p_1}{\dfrac{n}{N + n}} = p_0.$$

This function has a real meaning. The value of this function is plotted against concentration in Fig. 4 (lower curve). An examination of the curve gives one a clear and accurate idea of the behavior of mannite solutions. The smoothness of the curve in the dilute region, where a difference of 0.001 mm. would bring a value quite out of line, indicates the normal character of aqueous mannite solutions up to 0.5 *M*, above which slight irregularities begin. The rise in the curve in the higher concentrations may be attributed to hydration. It is unfortunate that we are limited in further investigation by the solubility of this substance.

Von Babo's Law and the Heat of Dilution.—The temperature coefficient of the vapor pressure of solutions is of interest, and for this purpose comparison of the results at 20° with those at other temperatures will be made. There are no data of sufficient accuracy on the vapor pressures of mannite solutions at other temperatures, and we resorted to indirect comparison by means of boiling-point and freezing-point data. Loomis[1] found that the molecular freezing-point lowerings of mannite solutions are perfectly constant. The accurate freezing-point work of Adams,[2] using very dilute solutions, has shown Loomis to be slightly in error, but this is negligible for the present comparison. The most concentrated solution measured by Hall and Harkins,[3] using Adams' method, was 0.1197 and they confirmed closely the lowering found by Loomis. Recently Braham[4] has determined the lowering of 2 concentrations of mannite solutions, obtaining value slightly higher than those of Loomis.

The relation between the freezing-point lowering and the vapor pressure of a solution is[5]

$$ln\ \frac{p_0}{p} = -\frac{M}{R}\int_{T_F}^{T_0} \frac{L_F dT}{T^2},$$

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[1] Loomis, *Z. physik. Chem.*, **32**, 599 (1897).

[2] Adams, This Journal, **37**, 481 (1915).

[3] Hall and Harkins, *ibid.*, **38**, 2658 (1916).

[4] Braham, *ibid.*, **41**, 1707 (1919).

[5] This expression is often deduced simply from the equation of Clausius-Clapeyron for the variation of the vapor pressure of water with the temperature and a similar one for ice, since at the freezing-point of a solution its vapor pressure is equal to that of ice.

where L_F is the latent heat of the solvent and T_0 and T_F are, respectively, the freezing-points (absolute) of solvent and solution. Assuming that L_F is independent of temperature the right-hand member becomes $\frac{ML_Ft}{RT_0T_F}$, where t is the lowering. However, it is known that the heat of fusion decreases with lowering temperature and it is necessary to introduce a slightly different expression to take care of this. This variation is fundamentally the variation of the specific heat of ice, and Jüttner[1] puts, $L_F = L_0 + a(T_F + T_0)$, where L_F and L_0 are the heats of fusion at T_F and T_0 and $a = S - S'$, the difference between the specific heats of water and ice at T_F. This gives the expression

$$ln \frac{p_0}{p_1} = \frac{M}{R}\left[\frac{L_0}{T_0}\frac{t}{T_F} + a\, ln\left(1 + \frac{t}{T_F}\right)\right]. \qquad \text{(I)}$$

He calculated the values of $ln\, p_0/p$ for mannite solutions using $L_0 = 80.7$ and $a = 0.504$ cal. The heat of fusion and the specific heat of ice have since been accurately determined by Dickinson and Osborne,[2] who obtained $L_0 = 79.67$ $\text{cal}_{15°}$ and $S' = 0.5052$ $\text{cal}_{15°}$. Recalculating, using these figures, $R = 1.985$ and $S = 1.007$, values about 1.5% lower are obtained and are given in Column 4 of Table III.

Callendar[3] has treated this question similarly but has included also the variation of the specific heats with temperature. The expression is

$$ln \frac{p_0}{p} = \frac{ML_0t}{RT_FT_0} + \frac{1}{T}\int_{T_0}^{T_F}(S - S')dT - \int_{T_0}^{T_F}(S - S')\frac{dT}{T}.$$

The specific heat of water is not known accurately below 0° but the integrals are solved by making different assumptions as to the variation of $S - S'$ with temperature. Nernst[4] states that this varies inversely with the temperature just below 0°. Callendar's final expression on this basis is

$$ln \frac{p_0}{p'} = \frac{ML_0t}{RT_FT_0} + \frac{aM}{R}\left(\frac{t}{T_F} + \frac{T_0}{T_F} + ln\frac{T_F}{T_0}\right). \qquad \text{(II)}$$

Values calculated by this equation differ only slightly from those from Equation I, and are given in Column 5 of Table III. It was also found that the simplified expression, proposed by Callendar

$$ln \frac{p_0}{p'} = \frac{ML_0t}{RT_0^2} = 0.9695t$$

gives values practically identical with those of his rigid expression, since t is never greater than 1°.

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[1] Jüttner, *Z. physik. Chem.*, 38, 110 (1901).

[2] Osborne, *Bur. Standards Sci. Paper*, 248 (1918).

[3] Callendar, *Proc. Roy. Soc. A.*, 80, 446 (1908).

[4] Nernst, *Trans. Faraday Soc.*, 6, 117 (1910).

Vapor pressure ratios may be obtained from boiling-point elevation values by application of the same fundamental equation, but a surer method is to find the atmospheric pressure from the boiling temperature of the pure solvent. This becomes p_1 the vapor pressure of the solution, when the boiling temperature is raised slightly above that of the solvent. Then the vapor pressure of the pure solvent for that final temperature is found by the use of tables. This gives p_o and p_1 at the same temperature. Jüttner has calculated the values of $ln\ p_o/p_1$ from Beckmann's[1] data which are given in Column 7 of Table III, while the observed values of the present authors are given in Column 6.

TABLE III.

Comparison of Vapor Pressure Ratios at 20° with those Obtained from Freezing-and from Boiling-Points.

			$ln\ p_o/p_1$			
	F. pt. lowering, t.		0° — t.			
M.	Obs.	Calc.	I.	II.	20°.	100° + t'.
0.1013	0.1874	0.1857	0.00181	0.00182	0.00180	...
0.131	..	..	...	...	0.00233	0.00235
0.2061	0.3807	0.3776	0.00368	0.00369	0.00366	...
0.268	..	..	...	...	0.00479	0.00451
0.2709	0.505	0.4962	0.00488	0.00490	0.00481	...
0.5323	0.9835	0.9737	0.00950	0.00953	0.00945	...
0.537	..	..	...	...	0.00957	0.00951
0.546	1.019	1.005	0.00985	0.00988	0.00974	...
0.801	..	..	...	...	0.01438	0.01448
1.018	..	..	...	...	0.01902	0.01915

The calculated values of t, given in Column 3, are obtained, using Callendar's equation, from the values of $ln\ p_o/p_1$ determined experimentally at 20° by the authors, assuming that this function is the same at the freezing-point or is independent of temperature. Von Babo's law states that the relative lowering of vapor pressure is independent of the temperature. And Kirchhoff's equation for the heat of dilution is a quantitative statement of the deviations from Von Babo's law.

$$H = RT^2\, \partial/\partial T\ (ln\ p_o/p_1).$$

H is the heat of dilution and is here defined as the heat which must be added to keep the temperature constant when one gram of solvent is added to an infinite amount of solution. Von Babo's law is thus a special case of Kirchhoff's equation and merely states that

$$\partial/\partial T\ (ln\ p_o/p_1) = 0.$$

Hence the function $ln\ p_o/p_1$ is a very convenient one to use in dealing with the variation of vapor pressure with temperature.

It is seen that the calculated freezing-point lowerings are slightly smaller than the observed, which deviation is roughly proportional to the concen-

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[1] Jüttner, *Z. physik. Chem.*, **6**, 459 (1890).

tration. Von Babo's law does not hold exactly, therefore, and the $ln\ p_0/p_1$ curve for 0° lies slightly over that for 20° and the heat of dilution is negative. The $ln\ p_0/p_1$ values at 100° lack smoothness as the lowest concentration is somewhat out of line, but the smoothed curve lies under the 20° curve for the lower concentrations (below 0.8 M), showing a decrease in $ln\ p_0/p_1$ from 0° to 20° to 100°. For the lowest concentration the values of this function agree quite closely for 0°, 20°, and 100°, which means a very small (negative) heat of dilution. Pratt[1] has measured the heat evolved when solutions of mannite are diluted, but the data are empirically expressed and do not admit of quantitative comparison. However, his observations are in qualitative agreement with the deduction as regards sign and order of magnitude of the heat by dilution. The mean heat of dilution between 0° and 20° for a 0.5 M solution is roughly —0.5 cal, using the data in Table III and Kirchhoff's equation. For the concentrations 0.8 and 1.0 M, the $ln\ p_0/p_1$ at 100° are greater than those at 20°, indicating that the heat of dilution changes sign with increasing concentration, a not unusual phenomenon. It is significant that this takes place in the same concentration as that in which the deviation from Raoult's law is marked.

Vapor Pressure and Osmotic Pressure.—The relation between osmotic pressure and vapor pressure has been discussed by a number of authors, using different methods and resulting in a number of equations which differ only slightly according to the conditions and definitions chosen. The integral equation of A. W. Porter[2] covers all of these and is an expression for solutions of any compressibility and under any hydrostatic pressure. Introducing the limits corresponding to the conditions, neglecting compressibility and using the gas law for the vapor pressure he obtains.

$$\text{O. P.} = \frac{RT}{V_s}\, ln\, \frac{p_0}{p_1}.$$

V_s is the increase in volume when one gram of solvent is added to a large amount of solution, and is a function of the density.[3] This was found to be a correction of about 0.1%. The calculated values of the osmotic pressure are given in Column 10, Table II. Final direct measurements of the osmotic pressure have not been made, but will be the object of a future investigation.

Summary.

1. The vapor pressure lowerings of aqueous mannite solutions have been determined over the range of its solubility.

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[1] *J. Franklin Inst.*, **185**, 663 (1918).

[2] Porter, *Proc. Roy. Soc. A.*, **79**, 519 (1907).

[3] Gouy and Chaperon, *Ann. chim. phys.*, [6] **12**, 384 (1887).

2. The presence of dissolved air as a source of error has been eliminated by a new method of preparing the solutions.

3. A mean deviation from Raoult's law of only 0.0006 mm. is observed up to 0.8 *M* concentration.

4. By comparison with freezing-point lowerings it is found that $ln\ p_0/p_1$ decreases with the temperature or, the heat of dilution is a small negative value for concentrations up to 0.5 *M*. Comparisons with boiling-point determinations show that this changes to a positive quantity in the higher concentrations.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA.]

THE THERMODYNAMIC PROPERTIES OF THE IONS OF SOME STRONG ELECTROLYTES AND OF THE HYDROGEN ION IN SOLUTIONS OF TENTH MOLAL HYDROCHLORIC ACID CONTAINING UNI-UNIVALENT SALTS.

BY HERBERT S. HARNED.

Received July 8, 1920.

Introduction.

In two earlier communications[1] from measurements of the electromotive forces of cells of the types

H_2 | MeCl(*c*) in HCl (0.1) | saturated KCl | calomel electrode and
Hg | HgCl | KCl (*c* + 0.1) | KCl (0.1) | HgCl | Hg
H_2 | KCl (*c*) in HCl (0.1) | HgCl | Hg,

the author has shown that the hydrogen ion activity of 0.1 *M* hydrochloric acid as measured by this method is increased by the addition of salts to the acid. On account of the difficulties attending the calculation of the electromotive forces of the cells

H_2 | MeCl (*c*) in HCl (0.1) ||[2] HCl (0.1) | H_2

from the above data, due largely to the present incomplete knowledge of liquid junction potentials, and a distrust of some of the earlier interpretations of the results, this investigation has been extended with the object of obtaining the complete thermodynamic data at 25° for the last mentioned series of cells containing potassium, sodium, and lithium chlorides. In this manner, the so-called "neutral salt effect" has been studied in a more searching manner from the thermodynamic point of view.

From the point of view of the theory of solutions a number of important contributions have been made comparatively recently. The first in importance of these is the hypothesis of complete dissociation of strong

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[1] THIS JOURNAL, 37, 2460 (1915); 38, 1986 (1916).

[2] Double bar indicates that liquid potential has been eliminated.