and to determine the limits of accuracy of the method. These experiments have shown conclusively that:

1. Variations of temperature of solution and solvent must not exceed 0.002°.

2. Accurate regulation of the temperature of other parts of the apparatus, *i. e.*, those parts containing vapor, is unnecessary. This is because, when all air has been eliminated, equilibrium between solution and vapor is very quickly established, so that slight changes of temperature, unless they are too sudden, merely cause evaporation or condensation of slight amounts of water, without affecting pressure. If the system contains air, a change of temperature will produce change in pressure and such fluctuations are quite noticeable even with a very small amount of air.

3. If the temperature of the bath is controlled to within 0.001°, readings of pressure are constant to within 0.001 mm.

The authors believe that the measurements recorded above differ from the true values by not more than 0.001 mm. and are convinced that, with certain minor changes, the method is capable of giving results which are accurate to the third decimal place.

The experiments recorded above were made in collaboration with Mr. E. Miller who is continuing the work, and the authors expect to investigate solutions of both electrolytes and nonelectrolytes in various solvents.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.

VAPOR PRESSURES OF CERTAIN ALCOHOLIC SOLUTIONS.

BY O. F. TOWER AND A. F. O. GERMANN.

Received October 17, 1914.

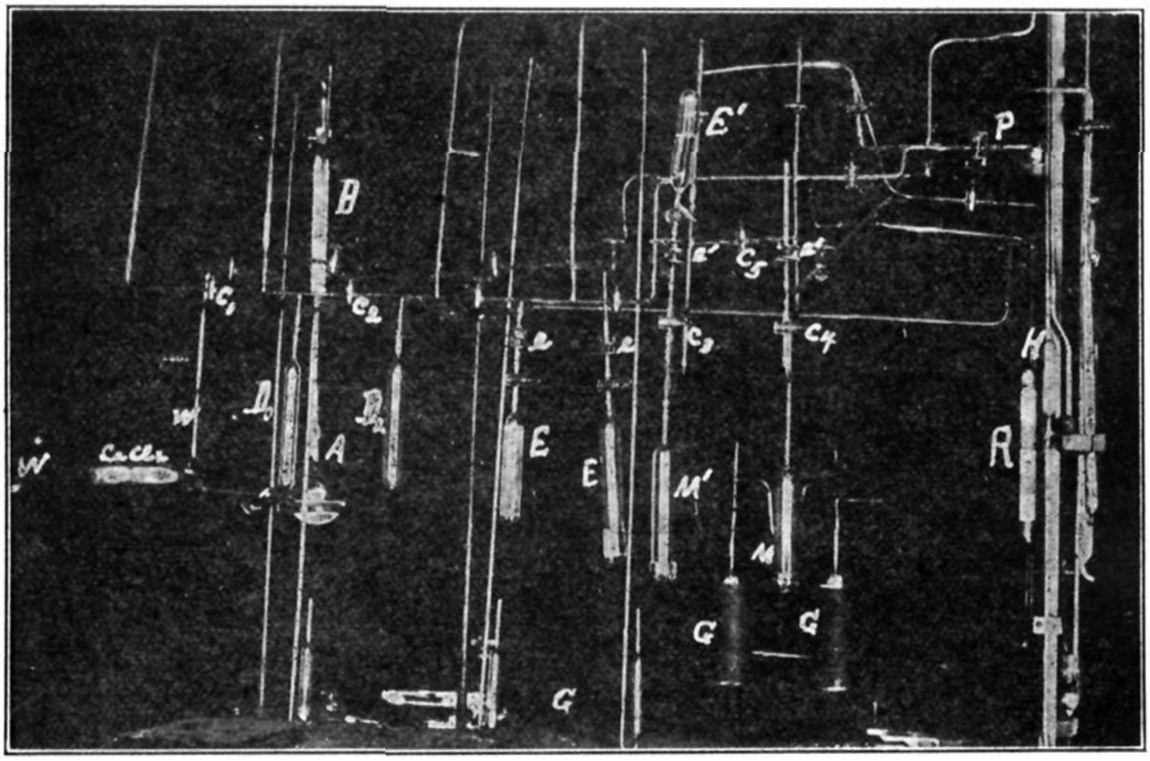
In a former paper one of us described a method for measuring vapor pressures by means of the Morley gage.[1] Satisfactory results were obtained with aqueous solutions, but with non-aqueous solutions certain difficulties were encountered which rendered the results that were reported at that time of little value. Moreover, the opinion was expressed that possibly the air-bubbling method would yield better results with this latter class of solutions. Numerous trials since then have, however, convinced us that it has no advantages over the method with the Morley gage, except at temperatures above room-temperature, and, besides, it possesses some disadvantages of its own which have caused us to return to the method with the Morley gage. The present paper, therefore, describes certain improvements in the apparatus and method of treatment of the solutions in determining the vapor pressures of non-aqueous solutions by this method.

The gage and the method of carrying out the readings were described

---

[1] O. F. Tower, THIS JOURNAL, 30, 1219 (1908).

in detail in the former paper and need not be repeated here. The accompanying photograph will give an idea of the general appearance of the new apparatus. The gage *GG* is in the background, while the tubes containing the solvent and the solutions *MM'* are shown in the foreground.



The principal improvement in the apparatus is the arrangenemt for purifying the solvent and introducing it into the tubes *M* and *M'* entirely out of contact with air. This portion of the apparatus was modeled after that used in Ph. A. Guye's laboratory (Geneva) for the purification of gases by liquefaction and fractional distillation in a vacuum. The removable flask *A*, in which the preliminary purification and desiccation were carried out, was connected by means of a carefully ground-in glass joint to the reflux condenser *B*, filled with glass beads. This communicated with the fractional distillation tubes D_1 and D_2 through stopcocks C_1 and C_2. Each tube was provided with a mercury manometer and vacuum connections to both water suction and mercury pumps. The former was connected at *W* through fused calcium chloride; the latter, of the type described by Cardoso and one of us,[1] at *P* through phosphorus pentoxide. All stopcocks were lubricated with viscous rubber grease, soluble in ether but not in alcohol.

After the solvent had been purified, as well as possible, in contact with the air, the containing flask *A* was placed in position and the air and any dissolved gases pumped out with the water suction pump. Then the bulk of the liquid was distilled at room-temperature into D_1, rejecting the

---

[1] Germann and Cardoso, *J. chim. phys.*, **10**, 306 (1912).

higher boiling fractions. Just previously D_1 had been rinsed out with the vapor of the liquid to be introduced,[1] and during the distillation it was surrounded by a mixture of ice and salt. Then followed a series of fractional distillations between D_1 and D_2, always discarding the first and last fractions as the least pure.

The next step was to secure a sample of the purified solvent from which weighed portions could be introduced into the vapor pressure tubes, out of contact with the air. This was accomplished by means of the weighing tubes *EE*, each provided with a stopcock and a flat ground joint *ee*.[2] These weighing tubes were secured to the apparatus by means of brass screw clamps.[3] The solvent was distilled into one of these tubes. One of the two following methods was then used to introduce the liquid into the vapor tension tubes: *M* was first filled to a suitable height with the pure solvent, after having been completely evacuated, dried in contact with phosphorus pentoxide, and rinsed several times with the vapor of the solvent. By the first method the filling was accomplished by simple distillation from the weighing tube. From a theoretical standpoint this method of procedure must result in giving two fractions in *M* and *M'*, with a very small difference of vapor tension, without the presence of the dissolved salt in *M'*. This would therefore influence, to a slight extent, the magnitude of $p - p'$. Practically the error thus caused would be vanishingly small, owing to the care taken in purifying the solvent. However, to be on the safe side this method was abondoned, and the following method was employed in our later work:

M and *M'* were provided with special exit tubes, extending vertically upward, bearing the stopcocks C_3 and C_4, and terminating in flat ground joints. This enabled fixing the weighing tube containing the solvent in an inverted position over the vapor tension tubes, as shown at E'. The capillary tubes between C_3, or C_4, and the stopcock of the weighing tube were provided with vacuum connections, so that they could be evacuated independently of other portions of the apparatus.[4] Then by opening the two stopcocks concerned, the solvent flowed through the capillary connecting tubes into *M* or *M'*; the stopcock of the weighing tube was closed when the nesessary volume of solvent had flowed out, *M* was cooled with cold water or ice for a few minutes, and finally the weighing tube was removed.[5]

---

[1] In a general way the precautions exercised throughout the preliminary operations were the same as those described in detail by Germann (*J. chim. phys.*, **12**, 66 (1914))..

[2] The advantage of these joints over those ordinarily used is that any two make a pair, so that they are interchangeable. For detailed drawing and description, see Guye, *Arch. Sci. phys. nat.*, Geneva, [4] **27**, 586 (1909).

[3] For drawings and details see Boubnoff and Guye, *J. chim. phys.*, **9**, 295 (1911).

[4] This was also true of every portion of the apparatus capable of isolation.

[5] It may be objected that in both methods the weight of solvent introduced into

A simplified Macleod pressure gage, *H*, was used to evaluate the degree of vacuum in the apparatus. The phosphorus pentoxide tube *R* was used to evacuate the apparatus when alcohol vapors alone were present, this by virtue of its affinity for the alcohols.

The readings were made at a temperature of 15°, instead of at 0° as in the former series, for the reason that the vapor pressures being higher at this temperature, $p - p'$ would have a greater magnitude, and could thus be read off with less relative error. The temperature was maintained by surrounding the tubes MM' with a water-bath, through which water at 15° was constantly circulating.

The solvents employed were methyl and ethyl alcohol. It was therefore necessary to determine their vapor pressures at 15°, which was done in exactly the same manner as described in the former paper for determining these pressures at 0°;[1] *i. e.*, by means of a manometer connecting with the tube *M*. Behind the manometer was a millimeter scale, on which the mercury heights were read off by means of a cathetometer. These readings were made at frequent intervals during the course of the year and varied but little. The average values of a large number of such observations are:

	Vapor pressure at 15°.
Methyl alcohol	73.61[2] mm.
Ethyl alcohol	32.18[3] mm.

Potassium iodide, lithium chloride and benzil[4] were the substances used as solutes. Each of these represented to a certain extent a different type. Potassium iodide is an electrolyte which has little tendency to combine with solvents; lithium chloride is an electrolyte which is very hygroscopic, *i. e.*, it has a tendency to combine with the solvent; benzil

---

M', found by taking the difference between the weights of the weighing tube before and after filling *M'*, would be too great by the amount of vapor remaining in the tubes between the weighing tube and *M'*, when the stopcocks were closed. However, the volume of these tubes was made as small as possible by using very short lengths and by selecting tubes of small bore—capillary tubes in the second method. In the first method the pressure was quite small—a few millimeters only—since the distillation was carried out at about —20°; in the second method the pressure was somewhat higher, but the volume was very much smaller, so that the amount of solvent lost under the most exaggerated conditions was always less than the accuracy of the weighings. Assuming, for example, in the first method, one meter of glass tubing 5 mm. in diam., filled with vapor at 20° over the liquid solvent at —10°, the loss would be 0.05 mg. with methyl alcohol, and 0.03 mg. with ethyl alcohol.

[1] Tower, *Loc. cit.*, p. 1228.

[2] 34 measurements; probable error of average 0.016 mm.

[3] 15 measurements; probable error of average 0.028 mm.

[4] We also attempted to use tetramethylammonium iodide, but found it so slightly soluble in the alcohols that no very trustworthy results could be obtained. Two of our best determinations with this substance dissolved in methyl alcohol are given in the table and are also shown in the curves for the sake of comparison.

is a nonelectrolyte and a nonhygroscopic substance. These were all purified preparations of C. A. F. Kahlbaum. The first was further purified by repeated crystallization from methyl alcohol. The lithium chloride was precipitated from aqueous solution by saturation with hydrogen chloride gas. The benzil was not further purified.

No fundamental changes were made in the gage portion of the apparatus, and therefore the readings were made precisely as described in the former paper.[1] It may however, be noted that M and M' were made of soft glass instead of Jena glass, and that the mercury valve between M and M' was replaced by a stopcock, C_5, as was also the valve between the vapor pressures tube and the mercury pump. A new lot of specially well-ground Geissler stopcocks were employed throughout the apparatus and gave excellent satisfaction. We were, therefore, not troubled by leaks about the stopcocks, which was sometimes the case in the former work. While making a reading, M and M' were constantly shaken, as otherwise there was a great variation in the values obtained. Even under the best conditions and with the great care exercised, considerable fluctuations in the reading would sometimes occur which were entirely inexplainable. This was especially true when using dilute solutions. In such cases readings were repeated under different conditions until a set which remained fairly constant was obtained. All of this consumed a great deal of time. Besides, with a complicated apparatus of this kind, leaks would frequently occur which were difficult to locate, so that the progress of the work was very slow. This can easily be understood when it is stated that the gathering of the results given in this paper occupied our available time for about twelve months.

The results are given in the accompanying tables. The headings of the first two columns are easily intelligible. The third column gives the lowering of the vapor pressure produced by the dissolved substance as obtained from the gage readings (p = the vapor pressure of the solvent, p' = the vapor pressure of the solution). The fourth column contains the molecular weight of the solute, calculated from the formula, $m = \frac{gM}{p - p'/p'}$.[2] The fifth column, n, gives mols of solute dissolved in one mol of solvent. The sixth column contains an expression, the value of which ought to be constant, if there is no change of molecular state.

The results have also been plotted in curves, using the observed lowering of the vapor pressure as ordinates and the concentrations of Column 2 as abscissas. The most probable trend of the curve in each case is seen to be a straight line. This is to be expected from a consideration of the

---

[1] Tower, *Loc. cit.*, p. 1223.

[2] *Loc. cit.*, Formula 1, p. 1224. Formula 2 might have been employed, but the values differ very little from those obtained from Formula 1.

SOLVENT, METHYL ALCOHOL. (VAPOR TENSION AT 15°, 73.61 MM.).

Solute, Potassium Iodide (M. W., 166.02).

Gram solute in 1 g. solvent.	Grams solute in 1 mol solvent.	$p - p'$.	m.	n.	$\frac{p - p'}{n}$.
0.13673	4.379	3.230	95.4	0.02636	119.7
0.12686	4.063	2.918	98.4	0.02444	119.4
0.10664	3.416	2.484	97.8	0.02057	120.8
0.09469	3.033	2.1855	99.1	0.01825	119.8
0.09167	2.936	2.1265	98.7	0.01767	120.6
0.077245	2.474	1.780	99.8	0.01489	119.5
0.06566	2.103	1.514	100.2	0.01267	119.5
0.05744	1.840	1.324	100.4	0.01107	119.6
0.04883	1.564	1.123	100.9	0.00942	119.2
0.04350	1.393	0.974	103.8	0.00839	116.1
0.03266	1.046	0.798	95.5	0.00630	126.7
0.01726	0.5528	0.423	95.7	0.00333	127.0
0.009503	0.3044	0.238	93.9	0.00183	130.1
0.006181	0.1980	0.154	94.5	0.00119	129.4
0.003709	0.1188	0.0743	117.6	0.000716	103.8
0.002192	0.0702	0.0577	89.4	0.000423	108.4

Solute, Lithium Chloride (M. W., 42.40).

0.05434	1.741	5.76	20.5	0.04103	140.4
0.04170	1.336	4.34	21.3	0.03150	137.8
0.03352	1.074	3.344	22.6	0.02533	132.0
0.03073	0.9843	2.868	24.3	0.02320	123.6
0.02689	0.8612	2.660	23.0	0.02032	130.9
0.02144	0.6869	2.057	23.9	0.01620	127.0
0.01718	0.5504	1.740	22.7	0.01298	134.1
0.01682	0.5388	1.542	25.2	0.01270	121.4
0.01195	0.3828	1.125	24.7	0.00903	124.6
0.009587	0.3071	1.0065	22.1	0.00724	139.0
0.009218	0.2953	0.7768	27.7	0.00697	111.5
0.007165	0.2295	0.7627	21.9	0.00541	141.0
0.006195	0.1984	0.5871	24.7	0.00468	125.4
0.005123	0.1641	0.3923	30.6	0.00387	101.4
0.002451	0.0785	0.1448	39.8	0.00185	78.3

Solute, Tetramethylammonium Iodide (M. W., 201.03).

0.003865	0.1238	0.0397	229.3	0.000616	64.4
0.002890	0.09256	0.0218	312.4	0.000461	47.3

Solute, Benzil (M. W., 210.08).

0.03662	1.173	0.332	259.0	0.00558	59.5
0.03144	1.007	0.320	230.7	0.00479	66.8
0.020665	0.6619	0.192	253.2	0.00315	60.9
0.01055	0.3380	0.100	248.4	0.00161	62.1

SOLVENT, ETHYL ALCOHOL (VAPOR TENSION AT 15°, 32.18 MM.).

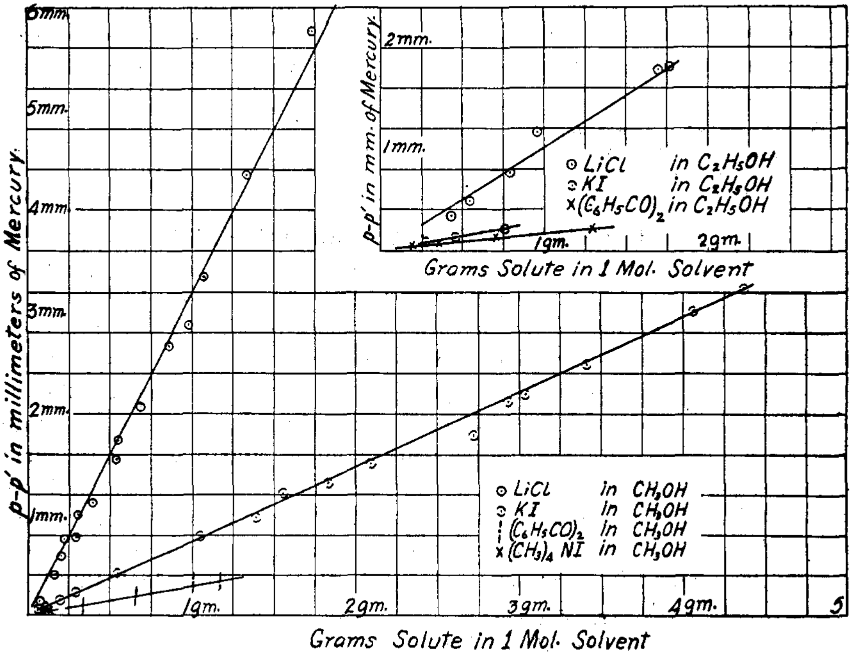
Solute, Potassium Iodide (M. W., 166.02).

0.01671	0.7694	0.1897	129.7	0.00463	41.0
0.009916	0.4566	0.1127	129.8	0.00275	41.0
0.006134	0.2825	0.0628	144.0	0.00170	36.9

SOLVENT, ETHYL ALCOHOL (VAPOR TENSION AT 15°, 32.18 MM.) (*Continued*).

Gram solute in 1 g. solvent.	Grams solute in 1 mol solvent.	$p-p'$.	m.	n.	$\frac{p-p'}{n}$.
Solute, Lithium Chloride (M. W., 42.40).					
0.03824	1.761	1.795	29.8	0.04156	43.2
0.03685	1.697	1.770	29.1	0.04002	44.2
0.02088	0.9614	1.1585	25.8	0.02268	51.1
0.01726	0.7947	0.7538	33.1	0.01875	40.2
0.01186	0.5463	0.4870	35.6	0.01289	37.8
0.009425	0.4340	0.3397	40.7	0.01024	33.2
Solute, Benzil (M. W., 210.08).					
0.02823	1.300	0.198	210	0.00619	32.0
0.01543	0.7105	0.119	191	0.00338	35.2
0.007968	0.3669	0.0590	200	0.00175	33.7
0.004260	0.1962	0.0295	214	0.000934	31.6

calculated molecular weights of Column 4. In the case of potassium iodide and lithium chloride these quantities are less than the formula weights, as might be predicted. The strange thing is that the values are so constant throughout the different dilutions. In other words, the calculated molecular weights do not show that these salts are any more dissociated in dilute solution than in concentrated. This is also confirmed by the ebullioscopic measurements of Jones[1] with potassium iodide in



---

[1] *Z. physik. Chem.*, 31, 129, *et seq.* (1899).

methyl and ethyl alcohols. He found the degree of dissociation to be very nearly constant in both cases, and to have a value of about 50% in methyl alcohol and 25% in ethyl alcohol. This is exactly in accord with our values for the lowering of the vapor tension. The conductivity determinations of Zelinsky and Krapiwin[1] showed substantially the same thing, although other observers[2] have found that the molecular conductivity increases with the dilution in very dilute solutions.

Why the calculated molecular weight should remain constant over such a range of concentrations is difficult to explain. It may have something to do with the combination of the salts with the solvents and to the progressive combination of the ions with the solvents. However, in such a case, one would not expect potassium iodide to be so subject to these effects as lithium chloride.[3] If, in plotting the curves, the values of n, in the fifth column, had been used as abscissas instead of the concentrations of the second column, all of the curves would be thrown closer together, and those of potassium iodide and lithium chloride in methyl alcohol would be almost superimposed, indicating almost identical molecular states.

As to benzil, its molecular weight in ethyl alcohol seems to be normal, while in methyl alcohol it seems to be associated with one or two molecules of the solvent.

MORLEY CHEMICAL LABORATORY,
WESTERN RESERVE UNIVERSITY,
CLEVELAND, OHIO.

A MODIFIED PRECISION BAROMETER.

BY ALBERT F. O. GERMANN.

Received October 17, 1914.

In the determination of the densities of gases by the various precision methods involving the measurement of volume, pressure, temperature, and mass,[4] the evaluation of the pressure is perhaps the most difficult, and the values obtained for this factor are always much less accurate than those obtained for the temperature, volume, and mass, particularly when the first two are taken at the temperature of melting ice, and the mass is taken as the average of the mass of several samples of gas simultaneously taken. A great many special barometers and manometers have been designed in an effort to eliminate the errors to which this type

---

[1] *Z. physik. Chem.*, **21**, 38 (1896).

[2] See Carrara, *Gazz. chim. ital.*, [1] **26**, 119 (1896); also Turner, *Am. Chem. J.*, **40**, 558 (1908).

[3] According to Turner and Bissett, *J. Chem. Soc.*, **103**, 1904 (1913), lithium chloride forms no compounds with methyl alcohol above 10°, but with ethyl alcohol $LiCl.4C_2H_5OH$ exists up to a temperature of 17.4°.

[4] See, for example, article by the author, *J. chim. phys.*, **12**, 66 (1914).