The writer wishes to express his thanks to Prof. W. B. Schober, of Lehigh University, for the use of the laboratory and valuable apparatus in part of this work. The valuable assistance of Mr. F. B. Kingsbury and Mr. C. A. Pierle is hereby acknowledged.

PHILADELPHIA, PA.

[COMMUNICATION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

A METHOD FOR DETERMINING THE MOLECULAR WEIGHTS OF DISSOLVED SUBSTANCES BY MEASUREMENT OF LOWERING OF VAPOR PRESSURE.[1]

BY ALAN W. C. MENZIES.

Received October 26, 1910.

Among the methods available for measuring the molecular weights of substances in solution, the cryoscopic and the ebullioscopic methods are most commonly used. The method of directly measuring the lowering of vapor pressure due to the dissolved substance has not been commonly applied for molecular weight determination owing, perhaps, to the difficulty of obtaining trustworthy values of vapor pressure by the static method, even when elaborate apparatus is employed. It is proposed in the present paper to describe an apparatus and procedure by means of which, without any thermometer, molecular weights may be simply determind in the laboratory by static measurement of vapor pressure, with an accuracy at least equal to that obtained by the ebullioscopic method.

In 1858 Wüllner,[2] working with aqueous solutions, found the lowering of vapor pressure roughly proportional to the concentration of the dissolved substance. The fact that workers[3] in this field confined their observations to aqueous solution of salts, which are abnormal, prevented the recognition of the underlying regularities until as late as 1886–7. Raoult's work[4] of that epoch is the basis of the present-day cryoscopic and ebullioscopic methods.

Raoult used a barometer tube, static method for measuring vapor pressures of solvent and solution. As with all static methods, chief among the sources of error are (1) the difficulty of completely eliminating gaseous and volatil impurities, and (2) the variation of the superficial concentrations of solutions due to evaporation and condensation. Even were it sufficiently accurate, Raoult's apparatus is too cumbrous for every-day use in molecular weight determination.

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[1] Read before the American Chemical Society, Dec. 31, 1909.

[2] *Pogg. Ann.*, **103**, 529 (1858); **105**, 85 (1858); **110**, 564 (1860).

[3] For example, Pauchon, *Compt. rend.*, **89**, 752 (1879); Tammann, *Wied. Ann.*, **24**, 523 (1885); Emden, *Wied. Ann.*, **31**, 145 (1887).

[4] *Compt. rend.*, **103**, 1125 (1886); **104**, 976, 1430 (1887); **107**, 442 (1888); *Z. physik. Chem.*, **2**, 353 (1888); *Ann. chim. phys.*, [6] **15**, 375 (1888).

Air-current or air-bubbling dynamic methods for vapor pressure measurement[1] always appear promising but, perhaps on account of their inflexibility hitherto, they have not come into general use for the purpose under consideration.

After evolving his form of freezing point apparatus, Beckmann[2] turned his attention to devising a workable method of molecular weight determination by vapor pressure measurement. He discarded those methods which he tried, however, in favor of his well-known ebullioscopic method. With the benefit of the experience of these earlier workers, Biddle[3] described a vapor pressure apparatus for molecular weight determination; this, however, is somewhat complex, requires the use of a thermostat, and is applied only to the very volatil solvents, ether and carbon bisulphide.

The Apparatus.[4]—As will be seen from Fig. 1, the apparatus here proposed consists of a jacket, in which the solvent is boiled, attached to a small reflux condenser, and an inner "test-tube" furnished with a pressure gage tube and a glass stopper. The dimensions of the jacket are, length 27 cm., diameter 3.5 cm.; those of the inner "test-tube," total length 30 cm., diameter 2.3 cm. The side tube leading from the jacket to the condenser is of glass of 1 cm. bore, so that the solvent may boil under a pressure no greater than barometric. The connection may be made with an 8 cm. length of rubber tubing, furnished with a screw clip. When the glass stopper is removed and the clip closed, the vapor of the liquid boiling in the jacket is obliged to escape by blowing through the gage tube, which is open at both ends, into the test tube. The narrow (6 mm.) U-shaped side tube attached to the jacket returns the cold condensed vapor from the condenser to the lower portion of the jacket, thus avoiding chilling of the upper portion of the test tube. The latter is graduated in cubic centimeters from 15 cc. upwards, and the gage tube (diam. 5 mm.) in millimeters of length (total about 140 mm.) from above

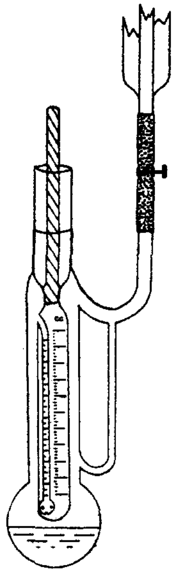

Fig. 1.

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[1] Cf. Regnault, *Ann. chim. phys.*, [3] 15, 129. Tammann, *Wied. Ann.*, **35**, 322. Walker, *Z. physik. Chem.*, 2, 602. Will and Bredig, *Ber.*, 22, 1084. Carveth and Fowler, *J. Physic. Chem.*, **8**, 313. Kahlenberg, *Science*, 22, 74. Earl of Berkeley and Hartley, *Proc. Roy. Soc. London*, **77**, 156. Perman, *Proc. Roy. Soc., London*, 72, 72. Lincoln and Klein, *J. Physic. Chem.*, 11, 318. Krauskopf, *Ibid.*, 14, 489.

[2] *Z. physik. Chem.*, 4, 532.

[3] *Am. Chem. J.*, 29, 341.

[4] This may be had from the Central Scientific Co., 349 W. Michigan Street, Chicago, Ill.

downwards. The two sets of graduations are readable from aspects at right angles to each other, so as to avoid confusion. At its foot, the gage tube is blown into a small bulb in which are pierced a number of holes to distribute the vapor as it issues. A glass stopper, with a glass-rod handle (length 12 cm.), fits the constricted neck (diam. 12 mm.) of the test tube, while the test tube itself fits into its jacket by a ground joint. The purpose of the jacket is to maintain the test tube and its contents at a constant temperature—the boiling point of the solvent—while the purpose of the test tube is to contain the solution whose vapor pressure is being measured. The pressure measurment is made in terms of the difference of level of the solution in the gage tube and the test tube, that is, in terms of millimeters of a liquid of low density compared to mercury. Differences of pressure that are small in terms of millimeters of mercury may therefore be measured with accuracy, and this permits of the use of very dilute solutions.

The Procedure.—The procedure followed in making a molecular weight determination may properly be described in some detail. The bulb of the jacket is charged two-thirds full with the pure solvent, the empty "test tube" replaced in position, and the liquid boiled with a small naked flame for ten minutes under its reflux condenser, in order to expel dissolved gases. The flame is then removed, the test tube taken out and charged two-thirds full with the boiled-out liquid from the jacket and replaced in position with its stopper left out. The liquid in the jacket is again boiled for a minute to expel air, after which the screw-clip is closed sufficiently to cause a vigorous bubbling of vapor through the liquid in the test tube. After this "blowing-through" process has continued two or three minutes, the stopper is warmed up by inserting it obliquely in position. Vapor can still escape, but the condensed liquid collects to form several drops above the stopper. When this has taken place, the stopper is pushed home, the liquid above it serving to make the joint gas-tight, and at the same moment the screw clip is fully opened. At this stage, the temperature of the liquid in the test tube is slighly higher than the boiling point, because the liquid in the jacket has been boiling under a slightly increased pressure in order to cause the "blowing-through." The apparatus must therefore be allowed to stand for a few minutes until the temperature of the vapor chamber adjusts itself to the true boiling point of the solvent. As the jacket is clamped loosely only at its neck, the apparatus may be shaken occasionally with a jerking motion, by way of stirring.

If the dissolved gases have been removed, and if the solvent is perfectly pure and dry, the relative levels of the liquid in the test tube and gage tube will now be precisely the same as they were before the stopper was inserted; unless the solvent has been very carefully purified, however, such theoretical perfection will not be quite attained. It is obvious that the liquid in the gage tube stands somewhat the higher of the two, on account of capillarity, as shown in Fig. 2 (*a*). This reading of difference of level is taken as the zero reading, and affords an excellent test of the adequate purity of the solvent. Should the zero reading be unsatisfactory, the process of blowing-through may be repeated until at least constant results are obtained. All readings are conveniently made with the help of a small lens.

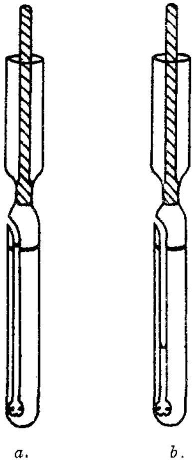

Fig. 2.

On removing the stopper, the substance may now be introduced in the form of weighed pastils, or otherwise. Solution is assisted by a gentle "blowing-through," which is necessary also to remove air. When the liquid is judged to be homogeneous and air-free, the stopper is again inserted, exactly as before, and the apparatus allowed to stand with shaking every half minute or so. At this stage the shaking, which should jerk the solution so as to wash the upper portion of the vapor-chamber walls, is very essential if surface films of abnormal concentration are to be avoided. By the circulation it causes, shaking also hastens the cooling of the central portions of the solution to the boiling point of the pure solvent. At no time, of course, must the boiling of the pure solvent in the jacket be interrupted. In about ten minutes, when the difference of level (see Fig. 2 (*b*)) after successive shakings has become constant, the reading is made and corrected by the zero reading.[1] The stopper is now removed and the volume of the solution read off, the liquid above the stopper being first removed by filter paper.

Further measurements may be made at different concentrations, either by adding more solute or else by blowing through for some time and so adding more pure solvent. Such further measurements are, however, usually unnecessary, since, with the very dilute solutions employed, the values first obtained are hardly improved by the method of extrapolation to infinit dilution.

In the case of solvents as volatil as carbon disulphide, a common test-tube filled with cold water may be inserted in the projecting upper portion of the "test tube" during the blowing-through process, if necessary to assist condensation. If, for any solvent, the rubber connection is considered objectionable, a glass stopcock[2] of large bore may take the place of the screw clip, and the use of rubber be entirely avoided.

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[1] If the apparatus be allowed to stand over a couple of minutes without shaking a slow change of level appears, caused by distillation within the vapor chamber towards the stopper.

[2] To regulate more easily the passage of small quantities of vapor, notches should be filed at the sides of the holes piercing the stopper of the cock.

Calculation of Results.—From the well-known relationship

$$p - p' = P\sigma/(\rho - \sigma)$$

where, at any temperature, p is the vapor pressure of the pure solvent, p' that of the solution, P the osmotic pressure of the solution, ρ its density and σ the density of the vapor under the pressure[1] p, one may, in the case of very dilute solutions, by assuming van't Hoff's law and making the appropriate substitutions for P and σ, deduce for a barometric height of 760 mm.:

$$p - p'(\text{in mm. mercury}) = n \cdot m \cdot 760/1000\ (\rho - \sigma)$$

where n is the number of dissolved moles per liter of solution, and m is the molecular weight of the solvent in the gaseous state. In millimeters of solution partially counterpoised by vapor of density σ, this would become, if $n = 1$,

$$p - p'\ (\text{in mm. solution}) = m \cdot 760 \cdot 13.59/1000 \cdot (\rho - \sigma)^2$$

where 13.59 is the density of mercury at 0°. By assuming that $\rho - \sigma$ is equal to the density of the pure solvent[2] at its boiling point, one may thus calculate for a series of solvents the values of $K_{760} = p - p' =$ the lowering of vapor pressure in mm. of boiling solvent that would be caused by the presence of one mole of non-volatil solute in one liter of solution, the barometer being normal. The values of K_{760} for some of the common solvents are as follows:

Solvent.	Density at boiling point.	K_{760}.
Benzene	0.8149	1214
Alcohol	0.7389	871.5
Water	0.9587	202.5
Chloroform	1.4101	620.4
Acetone	0.7518	1061
Ether	0.6968	1577
Carbon disulphide	1.2223	526.6
Ethyl acetate	0.8302	1320
Ethylene dibromide	1.9423	514.6

If desired, the actual value for ρ for any solution may be found directly by making a weighing of the test tube and its contents, in addition to reading off the volume of the solution, and σ may be calculated. This, however, is unnecessary for the ordinary purposes of molecular weight determination, and was not done in the examples given below.

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[1] Should $p - \dfrac{p - p'}{2}$ be preferred, since with this apparatus $p - p'$ has values from about 3 to 7 mm. of mercury, the constants K would become from one-quarter to one-half per cent. smaller.

[2] At their boiling points under 760 mm., σ for carbon bisulphide, benzene, chloroform and alcohol has a value about 0.24, 0.33, 0.31 and 0.32 per cent., respectively, of ρ. If the densities of the solutions used in this apparatus exceeded the density of the pure solvent by precisely these amounts, no error would be committed by the assumption made.

The change of ρ due to a change of boiling point of the solvent caused by a barometric divergence of 10 mm. from the normal is of the order of 1 part in 1000, and is therefore negligible.

Knowing the value of K_{760} as given above, the molecular weight may be calculated from the formula

$$M = 1000\, W \cdot K \cdot B / L \cdot V \cdot 760$$

where W is the weight of solute added, L is the measured lowering of pressure in mm., V is the volume of the solution in cc., and B is the barometric height.

Examples of Results.—The table below gives examples of the results obtained with six solvents. The benzene was the crystallizable, thiophene-free product of Kahlbaum and was dried and distilled over sodium The carbon disulphide was distilled once. The alcohol, also Kahlbaum's, was dried and distilled over barium oxide. The chloroform was freed from alcohol by washing with chromic acid mixture and dried over calcium chloride. A quantity of acetone, from the disulphite compound, was distilled once with a Hempel's fractionating tube, and the first portion of the distillate taken. The solutes were also the preparation of Kahlbaum, and were used without further purification other than drying. In the table, the results of Beckmann[1] and of Walker and Lumsden[2] are added for comparison. The figures refer to the lowest and the highest concentrations which they used:

Weight of solute.	Volume of solution.	Lowering observed.	Molecular weight found.	Beckmann found.	W & L found.
		Solvent, Water.			
		Potassium Nitrate, 101.			
0.611	36.7	57.1	56.9		53
0.611	37.7	56.9	57.0		
0.611	38.2	56.4	56.6		
		Sodium Chloride, 58.5.			
0.351	38.0	56.2	32.5		32
0.579	40.4	84.4	33.3		
0.488	33.8	84.4	33.4		
		Solvent, Benzene.			
		Naphthalene, 128.			
0.3115	48.1	60.1	128.6	141–144	139–141
0.5118	49.1	105.2	127.5		
0.3237	46.1	65.2	128.0		
0.5092	46.8	101.6	127.3		
		Anthracene, 178.			
0.336	45.0	48.5	186.2	192	184–187

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[1] *Z. physik. Chem.*, 6, 437.

[2] *J. Chem. Soc.*, **73**, 502.

Weight of solute.	Volume of solution.	Lowering observed.	Molecular weight found.	Beckmann found.	W & L. found.
Solvent, Carbon Disulphide.					
Naphthalene, 128.					
0.4166	43.2	32.2	126.3	131–141	
0.7632	43.8	69.6	128.6		
1.0386	44.3	95.7	125.9		
Anthracene, 178.					
0.8504	44.7	55.0	178.2	175–185	
1.4255	46.5	90.8	173.9		
1.8503	51.0	109.0	171.4		
Solvent, Alcohol.					
Naphthalene, 128.					
0.425	37.0	64.1	153.7	148–155	147–157
Mercuric Chloride, 271.					
1.058	42.0	83.0	260.2	263–271	261–263
Solvent, Chloroform.					
Naphthalene, 128.					
0.447	43.1	47.5	133.4	128–133	125–126
0.865	43.5	93.6	129.9		
0.804	44.7	81.5	136.0		
Solvent, Acetone.					
Naphthalene, 128.					
0.3264	41.9	60.4	133.2	128–155	
0.3424	39.6	68.6	131.8		
0.3424	39.7	68.6	131.9		
0.4874	40.8	92.2	133.5		

For the following determinations I am indebted to Mr. Severin Gertken, who was without previous experience of molecular weight determination by any method:

Weight of solute.	Volume of solution.	Lowering observed.	Molecular weight found.	Beckmann found.	W. & L. found.
Solvent, Carbon Disulphide.					
Benzil, 210.					
1.851	47.4	98.9	206.5	217	
Benzophenone, 182.					
1.069	47.2	59.6	195.9	182–187	
1.069	47.3	59.7	196.3		
Naphthalene, 128.					
0.988	51.6	77.4	127.6	131–141	
Solvent, Benzene.					
Benzil, 210.					
0.650	50.3	26.1	203.0	216–256	
Ethyl Benzoate, 150.					
0.662	53.2	90.5	164.5	163–172	

Weight of solute.	Volume of solution.	Lowering observed.	Molecular weight found.	Beckmann found.	W. & L. found.
Solvent, Water.					
Boric Acid, 62.					
1.201	43.0	90.7	61.6	64.6–66.9	
1.147	46.7	79.2	62.1		
1.147	46.3	81.2	61.4		
Potassium Chloride, 74.6.					
1.001	44.8	102.2	44.2		
1.001	45.0	103.1	43.2		
1.001	45.2	102.4	43.3		

In the values found for the molecular weight, the first decimal place has been retained for purposes of comparison, but it is of little value.

Comparison with Ebullioscopic Methods.—That this method possesses greater potentialities for accuracy than the ebullioscopic method will be admitted when it is considered that an elevation of boiling point of 0.1° corresponds to a measured lowering of vapor pressure of, for example, 37, 55 and 37 mm., respectively, for water, alcohol and benzene. It should therefore be possible, with like accuracy, to employ. with this method, much more dilute solutions. This leads to the consideration of a chief source of error of the ebullioscopic methods when the more dilute solutions are employed, namely, change of boiling point due to change of barometric pressure during the experiment. To cause an error of temperature of 0.05°—fifty per cent. of the quantity measured in the case above considered—the barometer need change only 1.36 mm., 1.5 mm. and 1.2 mm., respectively, for water, alcohol and benzene. Such barometric changes affect the results of the method here described scarcely at all, since the temperature of the jacket varies proportionally, and thus automatically corrects this error. Change of barometer influences the result only by slightly affecting the constant K, which depends on absolute barometric height, as indicated above. It may be pointed out that, in the case of the ebullioscopic methods, the constant used is customarily obtained experimentally and not by calculation from theory as in the case of the method here outlined.

The time occupied in a first determination by this method may be thirty to forty minutes, including the necessary weighing. In discussing the Beckmann boiling point method, H. Biltz[1] states that 'it usually requires one hour, but often two, and sometimes, indeed, several hours, to obtain a constant temperature in the boiling vessel.' How much of this trouble is due to slow change of zero of the thermometer is difficult to say. Presumably very little, as the Landsberger type of apparatus is much more expeditious, in the form, for example, devised by McCoy.[2]

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[1] "Pract. Methods for Determining Molecular Weights," Transl. by Jones and King, p. 155.

[2] See *Am. Chem. J.*, 23, 357 (1900).

Apropos of the thermometer, it will be recalled that a Beckmann thermometer whose degree is correct at zero is 3.6 per cent. in error[1] at 100°. Accordingly, whenever a Beckmann thermometer is employed at temperatures far from that at which its degree is correct, a correction for this error becomes necessary, although it is frequently omitted. The absence of any thermometer in the present apparatus simplifies slightly the reading of the volume of the solution; when a thermometer is present, it must first be removed.

In this apparatus, the 1 cc. graduations have a distance apart of about 2.8 mm., which makes the estimation of tenths satisfactory.

A considerable error is incident to both Berkmann and Landsberger methods when the correction for varying head of liquid above the thermometer bulb is neglected. Such an error does not here appear, for it is on the measurement of precisely such heads of liquid that the present method is based.

The use of a reflux condenser avoids the errors caused by change of temperature due to fractionation of the jacketing liquid inherent in the Landsberger method and its modifications.

The Identity of Vapor Pressure as Determined by the Static and by the Dynamic Methods.—It was tacitly assumed above that the statically determind vapor pressure of a pure liquid at its boiling point, determind dynamically, should be precisely the pressure under which the liquid boiled. In other words, it was taken for granted that if p is measured statically for any particular t, the same t will be arrived at dynamically by a boiling point measurement if p be the same. As is well known, however, it was by no means always agreed that this is the case.[2]

The apparatus here described is well adapted for testing the facts. The vapor pressure of the pure solvent in the test tube is a "static" vapor pressure, and is measured at the dynamically attained temperature of the vapor from the pure solvent boiling in the jacket. The pressure comparison is made by a differential gage of a liquid of low specific gravity, instead of, for example, by the difference of level of two mercury columns, one of which has a small depth of another liquid lying on its surface. With benzene, for instance, a pressure difference of 0.5 mm. of mercury, obtained in other methods by subtraction of much larger numbers of mm. and the application of not a few corrections, is, by this method, seen directly on a single small apparatus as a difference of level of 8.3 mm. of benzene at its boiling point (which is the manometer liquid). More important than simplicity of the pressure reading, however, is the possibility of boiling out dissolved gases until constant results are ob-

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[1] *Z. Instrum.*, 1896, 202.

[2] References to the extensive literature of the controversy on this subject may be found in Ostwald's *Lehrbuch,* Vol. I, 308.

tained; because failure to realize this possibility has been a chief cause of inconsistences in all measurements by the static method.

As, therefore, it seemed of interest to determin whether any small difference could be detected between static and dynamic results, the experiment was made with pure water, alcohol and benzene. The following figures refer to benzene, which had recently been distilled over sodium, but was not boiled out in the jacket. The differences of pressure, Δp, are in mm. of benzene at its boiling point, while the times, T, refer to the number of minutes of the "blowing-through" process:

Δp	6.3	2.5	0.9	0.1	0.1
T	5.0	6.0	8.0	10.0	12.0

The zero reading was that found when the stopper was removed. It will be seen that the difference of pressure finally observed was not larger than the limits of the error of observation.

It was shown in a similar way that, if any difference exists between the vapor pressure at the boiling point as measured dynamically and statically of the liquids water and alcohol, then such difference does not exceed 0.01 mm. of mercury.

Purpose and Scope.—In the present paper, the purpose has been to describe a molecular weight apparatus and its every-day application in cases where the greatest refinement is not aimed at. When opportunity offers, it is proposed to carry the measurements to their highest accuracy, and to make such applications of the method as promise to be most productive.

[COMMUNICATIONS FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

A CONVENIENT FORM OF APPARATUS FOR THE MEASUREMENT OF THE VAPOR DENSITIES OF EASILY VOLATIL SUBSTANCES.[1]

BY ALAN W. C. MENZIES.

Received October 26, 1910.

By the very slight modification here explained, the apparatus described in the preceding paper may be simply adapted for the rapid and accurate measurement of vapor densities of easily volatil substances.

The principle employed is that of the measurement of the increase of pressure that occurs when a known weight of substance is introduced into a closed vessel at constant temperature, high enough to completely volatilize the substance.[2]

The Modification Required.—The closed chamber is provided by

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[1] Read before the American Chemical Society, July 15, 1910.

[2] For other work in this field cf. Gibson Dyson, *Chem. News*, **55**, 88 (1887); Bleier and Kohn, *Monatsh.*, 20, 909; **21**, 575; Lumsden, *J. Chem. Soc.*, **83**, 342; Blackman, *Chem. News*, 100, 13; etc.