

particularly effective work in connection with the development and testing of the above apparatus.

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## THE LAWS OF "CONCENTRATED" SOLUTIONS. VI. THE GENERAL BOILING-POINT LAW.

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### 1. Purpose of the Investigation.

This investigation was undertaken: (1) for the purpose of developing an apparatus and method for measuring the boiling-point elevation of solutions, based upon the determination of the composition of the liquid phase which at a definite determinable temperature and pressure is in equilibrium with the vapor phase; and (2) to secure an experimental demonstration of the validity of the theoretical boiling-point law for ideal solutions, for much higher concentrations than have previously been investigated. Benzene was chosen as the "solvent" to be employed and the two substances diphenyl and naphthalene were selected as the "solutes," since previous studies<sup>1</sup> of the freezing-point curves for these systems had demonstrated that they behaved as ideal solutions.

### 2. Purification of Materials.

(a) **Benzene.**—Kahlbaum's "thiophen frei" benzene was allowed to stand 4 weeks in contact with pure sulfuric acid with frequent shaking. The acid always acquired a distinctly brown coloration after this treatment, due probably to presence of thiophene in the benzene. The benzene thus treated was then distilled from pure sulfuric acid and collected for preservation in a distilling flask containing metallic calcium. When benzene was desired for use this distilling flask was directly connected to the condenser of the boiling-point apparatus (Fig. 1) and the benzene distilled directly into the apparatus. The benzene obtained in this manner had a melting point of  $5.43^{\circ}$  (corr.).

(b) **Diphenyl.**—Kahlbaum's diphenyl was first recrystallized twice from absolute alcohol and dried. It was then twice distilled from metallic calcium under a pressure of about 22 millimeters, the distillate coming over at approximately  $145^{\circ}$ . The product obtained in this manner had a constant melting point of  $68.95^{\circ}$  (corr.).

<sup>1</sup> Washburn and Read, *Proc. Nat. Acad. Sci.*, 1, 191 (1915).

(c) **Naphthalene.**—500 g. of Kahlbaum's naphthalene (melting point  $79.6^{\circ}$ ) was melted and allowed to crystallize, the last 75 cc. of the liquid being discarded. The crystals were then melted and distilled under diminished pressure, the distillation temperature being between  $110$  and  $130^{\circ}$ . The middle portion of this distillate had a constant melting point of  $80.09^{\circ}$  (corr.) and was considered to be pure.

### 3. The Boiling-Point Apparatus.

Shortly after this investigation was begun Dr. F. G. Cottrell brought to our attention a new type of boiling-point apparatus of his own design which made it possible to secure a perfect equilibrium between the two phases and at the same time enabled an exact determination of the tem-

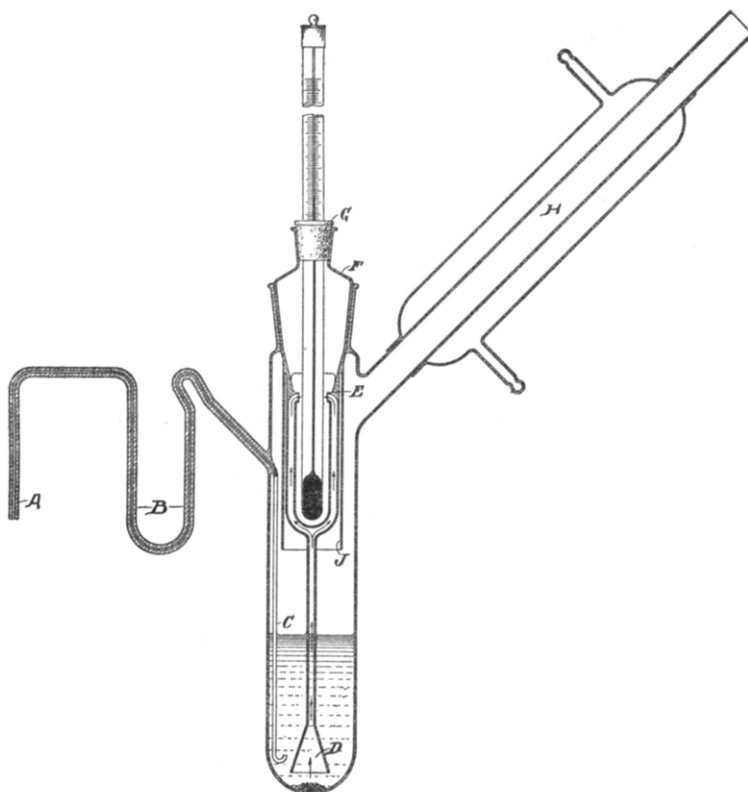


Fig. 1.

perature of this equilibrium, when *both phases* were under *exactly the same external pressure*. It was therefore decided to adapt this form of apparatus to our purposes, the principal alteration required being the addition of a withdrawal tube to enable samples of the liquid phase to be withdrawn for analysis.

Dr. Cottrell's apparatus is fully described in the preceding paper. The modified form which we employed is shown in Fig 1. The apparatus was constructed entirely of glass, the thermometer being cemented into the small ground-glass stopper G. J is a glass sheath carried on the large ground glass stopper and serves to protect the thermometer bulb from the influence of the cold liquid running down from the condenser H. In some experiments with the more concentrated solutions, which were syrupy in nature and inclined to superheat, a small inverted cone of silver foil filled with crystals of electrolytic silver was attached to the thermometer stem a short distance above the bulb so that the liquid which was squirted against the stem of the thermometer from the pumping tubes was forced to trickle down through the silver crystals before reaching the thermometer bulb. The pumping apparatus is carried on the bottom of the large ground glass stopper and is removable with it.

#### 4. Experimental Procedure.

Two pieces of apparatus (A and B) of the form shown in the figure were mounted side by side on the laboratory desk and heated by two small burners of identical form fed from the same gas cock. Each piece of apparatus was surrounded with a double sheath of asbestos paper extending from the thermometer down to the base of the gas burner so as to protect the flame from draughts. These sheaths were provided with mica windows to enable observation of the thermometer bulb and served to protect the apparatus from the influence of air currents. A small quantity of fragments of porous porcelain was placed in each apparatus to insure quiet boiling and the apparatus was then filled to a convenient depth with the pure solvent. This was accomplished by distilling the dry benzene directly into the apparatus. After the introduction of the solvent it was protected against moisture by the insertion of an inverted calcium chloride tube in the end of the condenser tube. The gas burners were then lighted and when a constant temperature was attained, the two thermometers were read. The boiling point obtained in this way was so constant that no variation whatever could be detected on a Beckman thermometer. Both thermometers were provided with electrical tappers.

The solute was introduced in the form of small pellets which were dropped into the end of the condenser tube of apparatus A. In apparatus B the pure solvent was kept boiling throughout the experiment. The difference in the readings of the two thermometers thus gave directly the value of  $\Delta t_B$ , the boiling-point elevation. This differential method of conducting the experiment is necessary because variations in the barometric pressure during a run cause very appreciable variations in the boiling point of the pure solvent and this method of eliminating the influence of the barometer is more convenient and decidedly more accurate than any

method involving the reading of the barometer and the application of a correction.

When the boiling point of the solution became constant to  $0.001^\circ$ , a sample was withdrawn for analysis. This was accomplished by bringing up a beaker of ice water around the capillary U-tube B, momentarily extinguishing the gas flames, and then applying air pressure at the end of the condenser H, the sample being collected in a small flask placed at A. Additional quantities of solvent and solute were introduced from time to time until a series of boiling-point elevations covering the desired range was eventually obtained. During the experiment the withdrawal tube C was kept free of liquid by maintaining a slight excess air pressure applied at A, which was closed with a bit of rubber tubing and a pinchcock.

### 5. Analysis of the Solutions.

The samples withdrawn from the apparatus were analyzed by determining their densities at  $25^\circ$  and then calculating the composition by means of an empirical equation connecting density with composition. The empirical equations employed together with the data upon which they were based are given in Table I below. This method of analysis did not prove to be as accurate as might be desired, but it did not seem worth while to develop a more accurate method and to repeat the experiments, since the results obtained displayed with sufficient accuracy the general behavior of these solutions with respect to the theoretical boiling-point law. It should be stated, however, that such variability as appears in the results is to be attributed to the determination of the composition of the solutions and not to the values obtained for  $\Delta t_B$ .

TABLE I.

Soln. No.	G. benzene.	G. soln.	% solute.	Sp. gr. $25^\circ/25^\circ$ . $D_S$ .	Mole fraction of solute $x_1$ .		% deviation. Obs.-calc.
					(Obs.)	(Calc.)	
0.....	...	...	0.0000	0.874212	0	0	0
	Diphenyl; $x_1 = 3.6981 (D_S - D_B) + 12.164 (D_S - D_B)^2$ .						
1.....	43.4150	47.1627	7.94	0.884995	0.041890	0.041290	+0.24
2.....	43.1700	50.8944	15.177	0.895170	0.083096	0.082847	+0.3
3.....	43.7341	60.9270	23.130	0.914051	0.166051	0.16663	-0.37
4.....	43.6130	57.7053	29.795	0.908424	0.140642	0.14076	-0.08
5.....	44.4117	73.2226	39.347	0.930565	0.247313	0.24702	+0.12
	Naphthalene; $x_2 = 4.4717 (D_S - D_B) + 11.50 (D_S - D_B)^2$ .						
1.....	43.9872	47.3681	7.137	0.883902	0.044742	0.044411	+0.74
2.....	43.7507	52.1503	16.107	0.896385	0.104739	0.104805	-0.06
3.....	43.5910	54.4274	19.910	0.901699	0.131557	0.131603	-0.05
4.....	43.6737	59.9486	27.148	0.911965	0.185058	0.18521	-0.08
5.....	43.7507	67.1145	34.812	0.922979	0.245522	0.24542	+0.04

### 6. Calculation of the Results.

In order to obtain the correct value of  $\Delta t_B$  for a solution, it is necessary to apply certain corrections to the thermometer readings. The nature

and magnitude of these corrections for some of the solutions investigated here are displayed in Table II. The expression "Reference Thermometer" in the table signifies the thermometer in the apparatus containing the pure solvent. Its mercury column was adjusted at such a height and so protected that its stem exposure correction was negligible. The stem temperature of the other thermometer was determined each time. The "stem exposure correction," the "calibration correction" and the "setting factor" correction were applied in the usual manner as described on the Bureau of Standards certificate which accompanied each of our thermometers.

The "barometric correction" expresses the variation in the boiling point of the pure solvent as shown by the data in Col. 3, this variation being due to a falling barometer.<sup>1</sup>

TABLE II.

Illustrating the Method of Applying the Necessary Corrections to the Observed Boiling-Point Data. Solutions of Diphenyl in Benzene.

1. Soln. No.	2. Barometer reading.	3. 4. 5. Thermometer readings.			6. Calibration correction.
		Refer- ence ther- mometer.	Solution ther- mometer.	Stem correction thermometer.	
0.....	744.5	3.605°	1.085°	28.1°	+0.005°
4.....	744.3	3.593	2.730	28.5	+0.019
10.....	744.0	3.577	4.100	28.5	+0.030
13.....	742.9	3.538	5.453	28.9	+0.042

Soln. No.	7. Δ <i>B</i> . Preliminary value.	8. Setting factor correction.	9. Stem exposure correction.	10. Barometric correction.	11. Solute v. p. Δ <i>t</i> ' correction	12. Δ <i>B</i> . Corrected value.
	0.....	0.000°	0.000°	0.000°	0.000°	0.000°
4.....	1.638	+0.023	+0.013	+0.012	+0.003	1.709
10.....	3.040	+0.043	+0.025	+0.028	+0.006	3.142
13.....	4.405	+0.062	+0.036	+0.067	+0.009	4.579

The "solute vapor pressure correction" Col. 11, required some further explanation as it is, we believe, a correction which has hitherto been entirely neglected. In using the theoretical boiling-point law it is always assumed that the solute is "non volatile," since this is the assumption upon which the law is derived. If, in a given case, this assumption is not fulfilled, it is necessary to apply a correction for the partial vapor pressure of the solute above the solution. Provided this vapor pressure is small, no appreciable error will be introduced in applying the correction which can be accomplished in the following manner:

<sup>1</sup> All of these corrections could of course have been avoided by substituting a differential set of thermocouples in place of the two thermometers, since the e. m. f. of such an arrangement would correspond directly to the actual boiling-point elevation. It seemed best, however, to employ in this investigation only such apparatus as is commonly found in chemical laboratories, as it was thought that one result of the investigation might be a boiling-point method which could be employed by the organic chemist for the accurate determination of molecular weights.

From the vapor pressure  $p_0$  of the pure liquid solute at the temperature of the boiling solution  $T_B$ , calculate the partial vapor pressure  $p_1$  of the solute above the solution by means of the relation<sup>1</sup>

$$p_1 = p_0 x_1. \quad (1)$$

Now, the partial vapor pressure of the solvent above the solution will be lower than the external pressure by the amount  $p_1$ . In order to make the partial vapor pressure of the solvent equal the external pressure it would be necessary to further raise the temperature of the solution by a slight amount,  $\Delta t'$ , which can be calculated from Crafts equation<sup>2</sup>

$$\Delta t' = c T_B p_1. \quad (2)$$

In this manner this correction was calculated for the two solutes, diphenyl and naphthalene. For naphthalene the maximum value of the correction for the range of temperature covered by this investigation was  $0.073^\circ$ , and for diphenyl  $0.026^\circ$ . In the case of naphthalene the necessary vapor-pressure data for the fused material were available in the literature, so that the required values of  $p_0$  for this substance could be interpolated from the graph of these data. In the case of diphenyl the

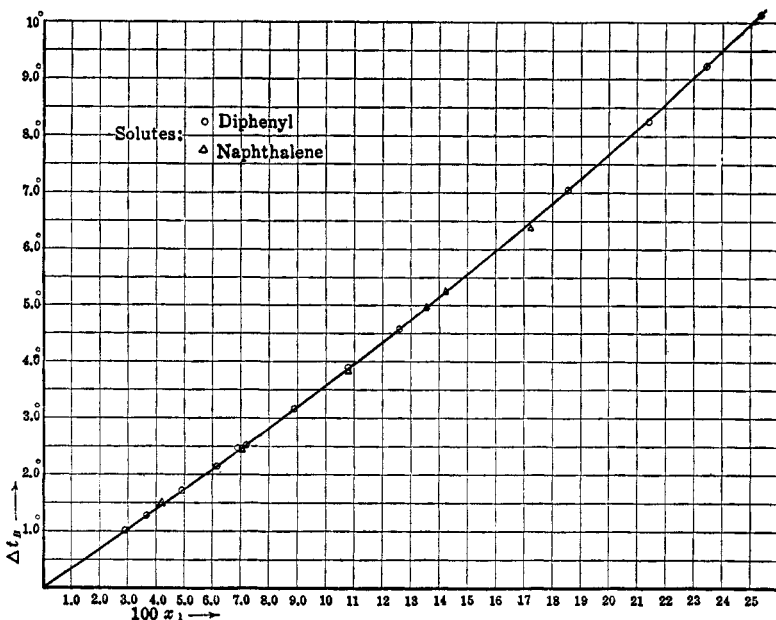


Fig. 2.—The boiling-point law for ideal solutions. The curve is the graph of the integral of the theoretical Equation 9. The points represent observed values of  $\Delta t_B$  for solutions of naphthalene and of diphenyl in benzene.

<sup>1</sup> Washburn, "Principles of Physical Chemistry," p. 144, McGraw-Hill Book Co., New York, 1915.

<sup>2</sup> Cf. Washburn, *Loc. cit.*, p. 57.

necessary vapor-pressure data were not available. In order therefore, to obtain the required  $p_0$  values for liquid diphenyl, use was made of the rule of Ramsay and Young, employing benzene and naphthalene, respectively, as reference substances and using the value  $254.9^\circ$  as the normal boiling point of diphenyl. Both reference substances yielded practically identical  $p_0$  values for diphenyl at the various temperatures.

### 7. The Results.

In Table III the final results obtained in this investigation are tabulated. Col. 1 shows the values of the measured boiling-point elevations and Col. 2 the corresponding compositions of the solutions (expressed as mole fraction of the solute) as obtained by analysis. Col. 3 shows the compositions of these solutions as calculated from the observed values of  $\Delta t_B$  by means of the theoretical boiling-point law for ideal solutions in the manner explained below. Col. 4 shows the percentage difference between the calculated and observed compositions. It will be noted that these

TABLE III.

Comparison between the observed composition of the boiling solution and the composition calculated from the boiling-point elevation ( $\Delta t_B$ ) by means of the theoretical boiling-point law for ideal solutions (Equation 9).

$x_1$  = mole fraction of the solute.

1 —  $x_1$  = mole fraction of the benzene.

$\Delta t_B$ obs.	$x_1$ obs.	$x_1$ calc.	% dev. Calc.-obs.
Diphenyl.			
1.024	0.02886	0.03001	+0.030
1.281	0.036654	0.03733	+0.022
1.333	0.037992	0.038733	+0.023
1.709	0.048984	0.04939	+0.014
2.152	0.061290	0.061790	+0.017
2.456	0.070135	0.070063	-0.002
2.466	0.069387	0.070205	+0.026
2.521	0.071786	0.071710	-0.002
2.716	0.07523	0.076700	+0.048
3.142	0.088950	0.088480	-0.016
3.285	0.093725	0.092171	-0.052
3.911	0.107550	0.108650	+0.036
4.579	0.125410	0.125710	+0.010
7.044	0.185255	0.184238	-0.039
8.250	0.214225	0.213155	-0.045
9.237	0.234256	0.234132	-0.005
10.146	0.253204	0.253330	+0.005
Naphthalene.			
1.478	0.041687	0.04293	+0.043
2.430	0.070121	0.069376	-0.024
3.890	0.107793	0.108200	+0.014
4.967	0.135288	0.135530	+0.006
5.238	0.142206	0.142360	+0.003
6.368	0.172038	0.169470	-0.088

differences are not greater than the experimental errors of the determination of the observed compositions. (Cf. Table I.)

### 8. The Boiling-Point Law for Ideal Solutions.

For solutions within which the thermodynamic environment<sup>1</sup> does not vary with the composition the fundamental law of boiling-point elevation, when the solute is "non-volatile" is

$$d \Delta t_B = \frac{-R(T_{B_0} + \Delta t_B)^2}{L_v} d \log x. \quad (3)$$

In order to integrate this it first is necessary to express  $L_v$  as a function of  $\Delta t_B$ . Since  $L_v$  is necessarily independent of  $x$  for the class of solutions under consideration, it is necessary only to know the manner in which the heat of vaporization of the pure solvent varies with the temperature. If the integral of Equation 3 is to be used only over moderate temperature ranges it will usually suffice to treat  $L_v$  as a linear function of  $\Delta t_B$ , that is, the problem reduces itself to the evaluation of the constant  $a$  in the equation

$$L_v = L_B - a \Delta t_B \quad (4)$$

where  $L_B$  is the molal heat of vaporization of the pure solvent at its boiling point.

In the case of benzene, values of  $L_v$  at a series of temperatures have been determined by Griffiths and Marshall,<sup>2</sup> who found that their results could be adequately expressed by an equation equivalent to the following:

$$L_v = L_0 - a(T_{B_0} + \Delta t_B) \quad (5)$$

where  $a = 12.34$  and  $L_0 = 11,725.3$  cal. For  $80.35^\circ$  this equation gives  $L_v/M = 94.37$  cal. At this temperature Tyrer<sup>3</sup> found by direct measurement the value 94.35 cal. thus confirming the equation of Griffiths and Marshall.

In case direct determinations of  $L_v$  at a series of different temperatures are not available, the value of the constant  $a$  in Equation 4 may be approximately calculated with aid of the purely thermodynamic relationship

$$-a = \frac{dL_v}{d\Delta t_B} = \frac{dL_v}{dT} = c_p - C_p + \frac{L_v}{T} - \frac{L_v}{v_o} \left( \frac{\partial V_o}{\partial T} \right)_p \quad (6)$$

which combined with the Berthelot equation of state

$$pv_o = RT \left( 1 + \frac{9 p T_c}{128 p_c T} \left( 1 - 6 \frac{T_c^2}{T^2} \right) \right) \quad (7)$$

gives

$$-a = c_p - C_p + \frac{L_v 9 p T_c}{128 p_c T^2} \left( 1 - 18 \frac{T_c^2}{T^2} \right). \quad (8)$$

<sup>1</sup> Washburn, *Loc. cit.*, pp. 135, 164 and 33.

<sup>2</sup> Griffiths and Marshall, *Phil. Mag.*, 41, 38 (1896).

<sup>3</sup> Tyrer, *J. Chem. Soc.*, 99, 1641 (1911).



Thus, in this manner we find for benzene, at its normal boiling point,  $C_p = 23.4$  cal.,<sup>1</sup>  $C_p = 34.17$  cal.,<sup>2</sup>  $L_v/T_B = 20.86$  cal./deg.,  $p/p_c = 1/47.89$ ,  $T_c/T_B = 561.6/353.5$ , and hence  $a = 12.9$ , which checks, within the accuracy of the data employed, the value 12.34 found by Griffiths and Marshall by direct experiment.

Combining Equation 3 with Equation 5 and integrating, we have finally

$$R \log_{10} x = a \log_{10} \frac{T_{B_0} + \Delta t_B}{T_{B_0}} - \frac{L_0 \Delta t_B}{T_{B_0}(T_{B_0} + \Delta t_B) 2.303} \quad (9)$$

Thus, if benzene is our solvent, the quantities in this equation have the following values:  $\Delta t_B$  = the boiling-point elevation produced by dissolving in the benzene such a quantity of a nonvolatile solute that the mole fraction of the benzene in the resulting solution is  $x$ ;  $R = 1.986$  cal./deg.;  $a = 12.34$ ;  $T_{B_0}$  = the absolute boiling point of the pure benzene when the boiling point of the solution under the same external pressure is  $T_{B_0} + \Delta t_B$ ; and  $L_0 = 11,725.3$  cal.

Substituting  $\Delta t_{B_0} = 1^\circ, 2^\circ, 3^\circ$ , etc.,  $T_{B_0} = 352.8^\circ$  (the value for 743 mm.) and solving the equation for  $x$ , a set of values are obtained which locate the curve shown in Fig. 2, that is, this curve is the graph of the theoretical Equation 9 for the solvent benzene, the points shown being those obtained experimentally in this investigation.

### 9. Boiling-Point Elevation and Barometric Pressure.

Since  $\Delta t_B$  is a function of  $T_{B_0}$  and this in turn depends upon the external pressure, it is obvious that the boiling-point elevation for a given solution will depend upon the barometric pressure at the time of the experiment. By differentiating Equation 9 with respect to  $T_{B_0}$  we obtain

$$\frac{1}{\Delta t_B} \frac{d(\Delta t_B)}{dT_{B_0}} = \left[ \frac{L_0(2T_{B_0} + \Delta t_B)}{T_{B_0}^2(T_{B_0} + \Delta t_B)} - \frac{a}{T_{B_0}} \right] \left[ \frac{T_{B_0} + \Delta t_B}{L_0 - a(T_{B_0} + \Delta t_B)} \right]. \quad (10)$$

Now the differential coefficient  $dT_{B_0}/dP$  can be obtained either thermodynamically<sup>3</sup> or, with sufficient accuracy for our present purpose, by the use of Craft's Rule according to which

$$dT_{B_0}/dP = cT_{B_0}. \quad (11)$$

where  $c$  is a constant characteristic of the class of substances to which the solvent belongs.

By combining Equations 10 and 11 we obtain the following expression for the pressure coefficient of the boiling-point elevation:

$$\frac{1}{\Delta t_B} \left( \frac{d\Delta t_B}{dP} \right) = c \left[ \frac{L_0(2T_{B_0} + \Delta t_B)}{T_{B_0}^2(T_{B_0} + \Delta t_B)} - a \right] \left[ \frac{T_{B_0} + \Delta t_B}{L_0 - a(T_{B_0} + \Delta t_B)} \right] \quad (12)$$

<sup>1</sup> Wiedemann, *Wied. Ann.*, 2, 195 (1877).

<sup>2</sup> Mills and MacRae, *J. Phys. Chem.*, 14, 797 (1910).

<sup>3</sup> Washburn, *Loc. cit.*, p. 123.

By integrating this expression between the limits  $P = 760$  and  $760 + \Delta P$  and  $\Delta t_B = \Delta t_{B_1}$  and  $\Delta t_{B_1} + \Delta t_B$ , a general expression for the correction  $\Delta t_B''$  in terms of  $\Delta P$  can be obtained. It will usually suffice, however, to employ the differential equation directly. Thus if we substitute in Equation 12 the data for benzene, for which  $c = -0.0122\%$  per mm., we find, for  $T_{B^*} = 353.5^\circ$ ,

$$\frac{1}{\Delta t_B} \frac{d(\Delta t_B)}{dP} = \begin{cases} 0.027\% \\ 0.030\% \\ 0.032\% \end{cases} \text{ per mm., for } \Delta t_B = \begin{cases} 1^\circ \\ 5^\circ \\ 10^\circ \end{cases}$$

or in round numbers, the value of  $\Delta t_B$  increases  $0.03\%$  for each mm. increase in barometric pressure.

This particular value of the pressure coefficient of course applies strictly only to benzene at its normal boiling point. As a matter of fact, however, the pressure coefficient of  $\Delta t_B$  will be of approximately the same order of magnitude for all liquids at their normal boiling points, since this coefficient can be shown to be approximately equal to twice the value of the Craft's constant for the liquid, provided  $\Delta t_B$  is not too large (say not greater than  $5^\circ$ ) and provided the boiling point is not too close to the critical point of the liquid.

For the boiling-point elevations determined in the present investigations the extreme variation of the barometer was not great enough to necessitate correcting the observed values to a common barometric pressure since the values obtained are compared only with one another and with the theoretical equation computed for the average barometric pressure which prevailed during the experiments. This correction is one which should always be considered, however, especially in any comparison involving the use of data obtained by different observers at different times and places and therefore under possibly very different barometric conditions. For example, it is quite possible that two observers working with identical solutions might obtain values for the boiling-point elevation which differed by 5 to 10%, owing to the differences in the barometric pressures at which their measurements were made. Some of the apparent discrepancies in the "ebullioscopic constants" reported in the literature may possibly be traced to this cause.

#### 10. The Determination of Molecular Weights by the Boiling-Point Method.

By substituting  $1 - x_1$ , where  $x_1$  is the mole fraction of the solute, in place of  $x$  in Equation 3, and then integrating with the aid of Maclaurin's theorem, an expression for  $\Delta t_B$  as a power series in  $x_1$  is obtained. For sufficiently dilute solutions the terms containing the higher powers of  $x_1$  will be negligible in comparison with the term containing the first power, and the expression will under these conditions reduce to

$$\Delta t_B = \frac{RT_{B_0}^2}{L_v} x_1 = \frac{RT_{B_0}^2}{L_v} \frac{N_1}{N + N_1}. \quad (13)$$

Again, if the solution is so dilute that  $N_1$ , the number of moles of solute, is negligible in comparison with  $N$ , the number of moles of solvent, this equation may be written

$$\Delta t_B = \frac{RT_{B_0}^2}{L_v} \frac{N_1}{N} \quad (14)$$

and if we let  $\underline{N}_1$  be the number of moles of solute in 1000 g. of solvent this becomes

$$\Delta t_B = \left( \frac{MRT_{B_0}^2}{1000 L_v} \right) \underline{N}_1 = k_B \underline{N}_1, \quad (15)$$

where  $k_B$  is the so-called "ebullioscopic constant" or molal boiling-point raising for the solvent in question. In determining molecular weights by the boiling-point method it has heretofore been customary to employ Equation 15 and if it is desired to ascertain only the approximate value of the molecular weight, this procedure is, of course, in most cases sufficiently accurate. It should be pointed out, however, that the use of Equation 15 for calculating molecular weights introduces unnecessary errors which can be avoided by using the general integral of Equation 3. For example, suppose that in order to determine the molecular weight of a substance in aqueous solution at  $100^\circ$ , the boiling-point raising for the solution is determined; and suppose that a solution containing 200 g. of the substance in 1000 g. of water gives  $\Delta t_B = 1.000^\circ$ , accurate to  $0.001^\circ$ . If we calculate the molecular weight of the substance, we find 97.2 from Equation 9, 98.6 from Equation 13, and 102.2 from Equation 15. If an accuracy of 1% is desired, it is evidently necessary to use Equation 9 in calculating the value of  $M_1$  in this instance. The use of Equation 15 would give a result in error by 5%.

If benzene were the solvent instead of water and if 38.73 g. of the substance dissolved in 1000 g. of benzene gave  $\Delta t_B = 1.000^\circ$ , accurate to  $0.001^\circ$ , then the calculated values of  $M_1$  would be 97.2 from Equation 9, 98.5 from Equation 13, and 101.6 from Equation 15, very nearly the same values as in the case of water.

The experimental method employed in the present investigation, as well as the nature of the results obtained, indicate that the boiling-point method can be employed for determining molecular weights with a high degree of accuracy, provided that proper precautions and methods of calculation are employed and provided a suitable solvent is available. The comparisons given above show that for accurate results it is necessary to use the general integral of Equation 3 in calculating the molecular weight  $M_1$  of the solute. This molecular weight, of course, appears in Equation 3 in the quantity  $x$ , which is equal to

$$x = \frac{m/M}{m/M + m_1/M_1},$$

$M$  being the molecular weight of the solvent, and  $m$  and  $m_1$  the masses of solvent and solute, respectively.

In order to determine the molecular weight of a given solute, the solvent selected should be one which resembles the solute chemically as nearly as possible. Thus if the solute is an aliphatic hydrocarbon, the solvent should, if possible, also be an aliphatic hydrocarbon. It should be remembered, of course, that the molecular weight obtained will be the molecular weight in the solution and if association or dissociation occurs these factors will naturally influence the value of the molecular weight obtained, and if the molecular weight of the substance in the gaseous state is desired it would, of course, be necessary to employ a solvent which does not dissociate or associate the solute. It might, of course, be true that in a given instance no such solvent could be found. A mere solvation of the solute by the solvent, when not accompanied by dissociation or association, need not, however, necessarily affect the accuracy of the result, since the influence of this factor may be eliminated as explained further below. Of two solvents equally suitable as far as chemical resemblance to the solute is concerned, the one for which the quantity  $T_{B_0}^2/L_v$  has the higher value will obviously give the more accurate results, or since  $T_{B_0}/L_v$  will be approximately a constant (Trouton's rule) this means that the higher the boiling point of the solvent the larger will be its molal boiling-point raising.

Having chosen a suitable solvent the following situations may exist: (1) The latent heat of vaporization of the solvent is known, but its temperature coefficient is not known. In such case the quantity  $a$  can be calculated with the aid of Berthelot's equation of state, as explained in Section 8 above, provided the necessary specific heats and critical data are available. If these data are not available the quantity  $a$  can be calculated by determining the boiling point of a solution, employing a solute of known molecular weight, and substituting the result in Equation 9. (2) Neither the latent heat of vaporization nor its variation with the temperature are known. In this case both of these quantities can be determined with the aid of Equation 9 by making two determinations of the boiling-point raising, one giving  $\Delta t_B$  equal to approximately  $3^\circ$  and another giving  $\Delta t_B$  equal to approximately  $6^\circ$ , employing a solute of known molecular weight.

If it is desired to avoid the necessity of withdrawing a sample of the boiling solution and analyzing it each time the determination of a boiling point is made, this can be done by standardizing a given piece of apparatus, using a solute of known molecular weight. This standardization can be accomplished by introducing known weights of solvent and solute

into the apparatus, determining the boiling point of the solution, and then calculating the amount of solvent present in the vapor phase and in the condenser, with the aid of Equation 9, the values of  $L_v$  and of  $a$  being known. With a given sized flame and uniform conditions of experimentation it is probable that the amount of solvent which exists outside of the solution at its boiling point will be practically a constant for a given piece of apparatus. Having determined the boiling-point raising for a given solution and having applied the necessary corrections as explained in Section 6, the molecular weight of a solute can then be accurately calculated with the aid of Equation 9, provided of course, that the solute and solvent are sufficiently alike chemically to make the laws of ideal solutions applicable. This assumption can, of course, be tested by making a series of boiling-point determinations and noting whether they all give the same value for the molecular weight.

If there is reason to believe that solvation occurs, the true molecular weight of the unsolvated solute can still be calculated from Equation 9, provided the solution is an ideal solution, that is, provided Equation 9 is really applicable when the influence of solvation is taken account of. In order to do this it is only necessary to substitute the following expression for  $x$  in Equation 9:

$$x = \left( \frac{1000}{M} - sN_1 \right) \div \left( \frac{1000}{M} - sN_1 + \underline{N}_1 \right)$$

and to make two boiling-point determinations, one giving  $\Delta t_B$  equal to, say,  $3^\circ$ , and another giving  $\Delta t_B$  equal to  $6^\circ$ , and from the two expressions thus obtained the quantity  $s$ , which represents the number of solvent molecules combined with each solute molecule, can be eliminated. This procedure will then give an accurate value of the molecular weight of the solute provided of course, that  $s$  is constant over the temperature range in question, and provided that the solution is sufficiently near an ideal solution to make Equation 9 applicable.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY,  
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## A UNIQUE CASE OF A LIQUID THAT EXHIBITS A MINIMUM SOLUBILITY IN AN UNSTABLE REGION.

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### Introductory.

When the hydrate of 3,5-dimethoxy-acetophenetide described in another article<sup>1</sup> was first prepared and its approximate solubilities in

<sup>1</sup>"The Synthesis of Certain Substituted Pyrogallol Ethers, Including a New Acetophenetide Derived from the Ethyl Ether of Syringic Acid," Bogert and Ehrlich, *THIS JOURNAL*, **41**, 798 (1919).