

$$dp_1/dp_2 = -p_1(1-x)/p_2x$$

and

$$d \ln p_1/d \ln x = d \ln p_2/d \ln (1-x).$$

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

THE LAWS OF RAOULT AND HENRY AND THE CONSTANTS OF EBULLIOSCOPY AND CRYOSCOPY.

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1. Introductory.

The formulae for calculating ebullioscopic and cryoscopic constants are usually deduced by combining: (1) van't Hoff's equation connecting osmotic pressure with the lowering of vapor pressure; (2) the Clapeyron-Clausius equation, together with the gas laws; and (3) Raoult's law.¹ The possibility of thus calculating constants needed in determinations of molecular weights is counted among the achievements of the theory of osmotic pressure which entitle it to its central position in theoretical chemistry.

The object of the present communication is to show that the constants in question can be found on the basis of Raoult's law and the gas laws, without the use of the osmotic pressure concept; and, on the other hand, to show that Raoult's law follows, together with the law of Henry, from the Duhem-Margules equation—a purely thermodynamic relationship. While no particular originality is claimed for our considerations,² it is hoped that they may be of some value, partly because of their transparency, partly on account of their bearing on the question as to the relative scientific importance of the osmotic pressure concept. Furthermore, the ebullioscopic constants calculated by us are probably more exact than those found either on the basis of the heats of vaporization (which are seldom known accurately), or by direct ebullioscopic measurement (which involves the assumption that in the cases chosen as standard the molecular weight of the solute is normal—an assumption that is seldom free from doubt).

2. Deduction of Raoult's and Henry's Laws from the Duhem-Margules Equation.³

To a pure solvent, whose vapor pressure in the free state is P_1 , we add

¹ See Nernst, *Theoretische Chemie*, Ed. 7 (Stuttgart, 1913), pp. 148 and 283.

² See Arrhenius's first deduction of the ebullioscopic formula, in a letter quoted by Beckmann (*Z. physik. Chem.*, 4, 550-551 (1889)), and especially Beckmann and Liesche (*Ibid.*, 86, 337 (1914)). The subject matter of this present communication was in the main ready for publication in January, 1913; the ebullioscopic constants have recently been recalculated.

³ A somewhat complicated deduction of Raoult's law (but not of Henry's) was given by Story (*Phil. Mag.*, [6] 20, 97 (1910)).

an infinitesimal amount of some second substance. The molar fraction of the solvent becomes x (still very nearly 1); that of the solute, $(1 - x)$,

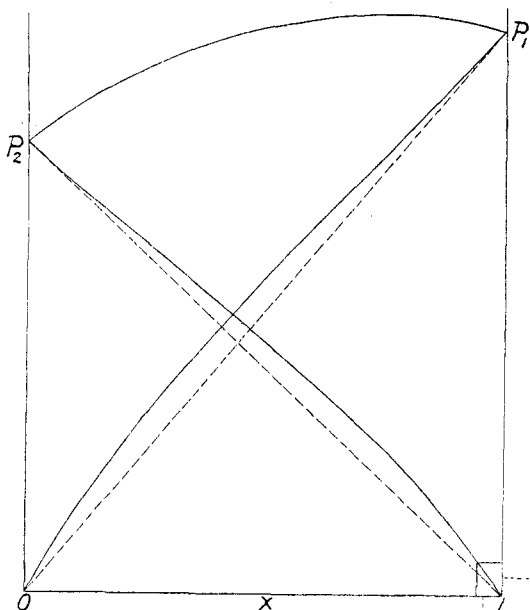


Fig. 1.

is now identically equal to $d(1 - x)$. The partial vapor pressure of the solute, p_2 , is identically equal to dp_2 . Thus $dp_2/p_2 = d \ln p_2 \equiv 1$ and $d(1 - x)/(1 - x) = d \ln (1 - x) \equiv 1$, and therefore $d \ln p_2/d \ln (1 - x) \equiv 1$. But according to the Duhem-Margules equation:

$$d \ln p_1/d \ln x = -d \ln p_2/d \ln (1 - x)$$

It follows that at the very great dilution which we are considering $d \ln p_1/d \ln x = 1$, whence $dp_1/dx = p_1/x$ and, as at our dilution $x = 1$ and $p_1 = P_1$, we find:

$$dp_1/dx = P_1,$$

which is Raoult's law.

Experimentally, Raoult's law holds true generally not only at infinite dilution (*i. e.*, at $x = 1$), but up to concentrations of at least 5 molar per cent. (*i. e.*, between $x = 1$ and $x = 0.95$). Within these limits the slope of the curve representing the partial pressures of the solvent remains constant and equal to P_1 ; in other words, within these fairly wide limits the partial pressure curve is coincident with the straight line connecting the points $x = 0$ and $p_1 = P_1$. Since, thus, $d \ln p_1/d \ln x$ remains equal to unity, the Duhem-Margules equation teaches that also

$$d \ln p_2/d \ln (1 - x) = 1.$$

Integrating this within the permissible limits, we get:

$$p_2 = k(1 - x),$$

where k is an integration constant.¹ But this last equation expresses nothing else than Henry's law: that the solubility of a gas or vapor is proportional to the pressure. Only, as the equation shows, the "solubility" must be measured in terms of the molar fraction of the solute.

Raoult's and Henry's laws are thus intimately connected through the

¹ In certain cases, though not frequently, $k = P_2$, which is the vapor pressure of the solute in the isolated state.

Duhem-Margules equation, and each law is seen to hold to the same limits of concentration as the other.

3. Ebullioscopic Constants.

To 100 g. of a solvent, the molecular weight of whose vapor at the boiling point T is M_o , and whose vapor pressure at the same temperature is P_1 , we add Δ grams of a substance of molecular weight M . The result is a depression of P_1 , to the smaller value p_1 . On the other hand, we cool a quantity of the pure solvent to a temperature, say, t degrees below its boiling point, so that its vapor pressure P_1 is lowered again to the value p_1 . We now *assume* that, if we should raise both the temperature T of our solution and the temperature $T - t$ of the solvent t degrees, their lowered vapor pressures p_1 would rise back to one and the same value P_1 . By making this assumption we commit an error. For the rise of the partial pressure of the solvent *in the solution* between T and $T + t$ will *not* generally be the same as the rise of the vapor pressure of the pure solvent between the temperatures $T - t$ and T . If, however, the amount Δ grams of solute in our solution is infinitely small, then the properties of solution and solvent approach identity, and the error involved in our assumption becomes infinitely small.

Under these conditions, then, no error is really committed by equating the rise of vapor pressure per degree in the solution and the rise of vapor pressure per degree in the pure solvent: $(P_1 - p_1)/t = dP_1/dT$. From this we have:

$$t = (P_1 - p_1)dT/dP_1 \quad (1)$$

We now introduce Raoult's law, in the form $p_1 = P_1x$, or rather in the form $P_1 - p_1 = P_1(1 - x)$. The symbol x represents the molar fraction of the solvent in the solution:

$$x = \frac{100/M_o}{100/M_o + \Delta/M}$$

Equation (1) now becomes:

$$t = P_1(1 - x)dT/dP_1 = P_1 \left(1 - \frac{100/M_o}{100/M_o + \Delta/M} \right) \frac{dT}{dP_1} = P_1 \left(\frac{\Delta/M}{100/M_o + \Delta/M} \right) \frac{dT}{dP_1}$$

Since Δ is infinitely small, we may write:

$$t = \frac{P_1 \Delta/M}{(100/M_o)(dP_1/dT)};$$

and as t is the elevation of the boiling point caused by the addition of Δ/M mols of the solute, E , the elevation per *one* mol of solute, is

$$E = \frac{P_1}{(100/M_o)(dP_1/dT)}.$$

The molecular weight M_o of the vapor of the solvent is found by determining the specific volume of the vapor and applying the gas laws (which

are perfectly reliable for the pressures of an ordinary boiling point determination): $M_o = RT/P_1v$. Therefore, finally:

$$E = \frac{RT}{100 v dP_1/dT} \quad (2)$$

That both the specific volume of the vapor at the boiling point and the variation of vapor pressure with the temperature, needed in Formula 2, can be measured with considerable accuracy, is indicated by many data in the literature; not only do the measurements of one and the same observer usually appear consistent among themselves, but the measurements of different investigators, carried out at different periods, are often in excellent agreement. For instance, according to Wüllner and Grotrian, the specific volume of chloroform vapor is 0.226 liters; according to Young it is 0.229 liters. Again, according to Young (1889) the vapor pressure of benzene between 70° and 80° increases by 20.62 millimeters for each degree, while according to Smith and Menzies (1910) the increase is 20.65 mm.; between 80° and 90°: 25.25 (Young) and 25.05 (Smith and Menzies); between 90° and 100°: 32.8 (Young) and 33.0 (Smith and Menzies); between 100° and 110°: 40.4 (Young) and 40.3 (Smith and Menzies); between 110° and 120°: 49.0 (Young) and 48.9 (Smith and Menzies). Similarly, values of E for acetic acid calculated by Equation 2 from the pressure measurements of Landolt (1868), Ramsay and Young (1886), Kahlbaum (1894), and the data given by Young in his paper of 1910, vary only between 32.4 and 33.4. On the other hand, the figures found by direct ebullioscopic measurement vary between 25.4 and 30.7, and the figures calculated from the heat of vaporization vary between 29.8 and 35.7.

The figures given in Table I were obtained by plotting the latest available measurements on a sufficiently large scale and "smoothing" the curves, —which yielded somewhat more precise results than would have been found by linear interpolation. In all cases, to attain greater reliability, the E 's were calculated for the atmospheric pressures 730, 760 and 780 mm., and plotted with respect to these pressures; then a straight line was drawn as nearly as possible to the three points, and the E 's read off from the line. The table gives in each case the value of E thus obtained for 760 mm. and, in the last column, the correction to be added for every 10 mm. between 760 and 780 mm., or subtracted for every 10 mm. between 760 and 730 mm. We are inclined to believe that most of these ebullioscopic constants are within, say, 2% of the true values.

TABLE I.—EBULLIOSCOPIC CONSTANTS.

No.	Solvent.	Boiling point under 760 mm.	dP_1/dT (atm).	v (liters).	E (760 mm.).	Correction per 10 mm.
1	Acetic acid.....	118.51°	0.0308	0.318	32.8	0.08
2	Benzene.....	80.15	0.0309	0.364	25.8	0.24
3	Bromobenzene.....	155.83	0.0251	0.211	66.5	0.60
4	Carbon disulfide.....	46.00	0.0325	0.335	24.9	0.20

TABLE I (continued).

No.	Solvent.	Boiling point under 760 mm.	dP_1/dT (atm.).	v (liters).	E (760 mm.).	Correction per 100 mm.
5	Chlorobenzene.....	131.98	0.0271	0.282	43.5	0.24
6	Chloroform.....	60.19	0.0329	0.229	36.4	0.10
7	Cyclohexane.....	80.88	0.0301	0.337	28.7	0.11
8	Di-isobutyl.....	109.26	0.0282	0.162	68.9	0.38
9	Di-isopropyl.....	58.10	0.0320	0.304	28.0	0.14
10	Ethyl alcohol.....	78.26	0.0379	0.613	12.4	0.10
11	Ethyl ether.....	34.42	0.0358	0.320	22.1	0.07
12	Ethyl formate.....	54.48	0.0347	0.353	21.9	0.06
13	Ethyl acetate.....	77.13	0.0317	0.313	29.0	0.12
14	Ethyl propionate.....	99.01	0.0312	0.287	34.1	0.20
15	Fluorobenzene.....	85.41	0.0301	0.295	33.1	0.22
16	Heptane (normal).....	98.42	0.0292	0.292	35.8	0.22
17	Hexane (normal).....	68.59	0.0313	0.310	28.9	0.07
18	Iodobenzene.....	188.47	0.0239	0.175	90.7	0.42
19	Methyl alcohol.....	64.67	0.0399	0.829	8.4	0.09
20	Methyl formate.....	31.92	0.0377	0.408	16.3	0.10
21	Methyl acetate.....	57.11	0.0345	0.357	22.0	0.09
22	Methyl propionate....	79.59	0.0330	0.316	27.7	0.16
23	Methyl butyrate.....	102.62	0.0309	0.282	35.4	0.18
24	Methyl isobutyrate...	92.48	0.0297	0.277	36.4	0.16
25	Octane (normal).....	125.80	0.0284	0.264	43.7	0.05
26	Pentane (normal).....	35.98	0.0354	0.336	21.3	0.12
27	Pentane (iso).....	28.02	0.0365	0.326	20.8(?)	..
28	Propyl alcohol.....	97.14	0.0365	0.489	17.1	0.12
29	Propyl formate.....	81.20	0.0325	0.317	28.3	0.08
30	Propyl acetate.....	101.68	0.0299	0.286	36.1	0.10
31	Stannic chloride.....	114.20	0.0263	0.117	103.2	1.0
32	Water.....	100	0.0358	1.651	5.18	0.07
33	Carbon tetrachloride*	76.50	0.0314	0.181	50.5	0.36

The pressure and temperature values used in calculating this table are based on the following measurements:

- For (1) Ramsay and Young, *J. Chem. Soc.*, **59**, 903 (1891).
 For (2) Smith and Menzies, *J. Am. Chem. Soc.*, **32**, 1453 (1910).
 For (3), (5), (15) and (18), Young, *J. Chem. Soc.*, **55**, 486 (1889).
 For (4) Battelli, *Mém. Accad. Torino*, **41**, I (1890); **42**, I (1891).
 For (6) Regnault, *Mem. de l'Acad.*, **26**, 339 (1862).
 For (7), (12), (20), (27) and (33) Young, *Sc. Proc. R. Dublin Soc.*, [N. S.] **12**, 374 (1910).
 For (8) and (9) Young and Fortey, *J. Chem. Soc.*, **77**, 1126 (1900).
 For (10) Ramsay and Young, *Phil. Trans.*, **177**, I, 123 (1886).
 For (11) and (19) Ramsay and Young, *Phil. Trans.*, **178A**, 57 (1887).
 For (13), (14), (21), (22), (23), (24), (29) and (30) Young and Thomas, *J. Chem. Soc.*, **63**, 1191 (1893).
 For (16) Young, *Ibid.*, **73**, 675 (1898).
 For (17) Young and Thomas, *Ibid.*, **67**, 1075 (1895).
 For (25) Young, *Ibid.*, **77**, 1145 (1900).
 For (26) Young, *Ibid.*, **71**, 446 (1897).

* Added in proof.

For (28) Ramsay and Young, *Phil. Trans.*, **180**, 137 (1889).

For (31) Young, *Phil. Mag.*, [5] **34**, 512 (1892).

For (32) Regnault (recalculated by Broch), Landolt-Börnstein, *Tabellen* (Ed. 4, Berlin, 1912, pp. 366-367).

The specific volumes used in the table are based on the following data:

For (1), (2), (3), (5), (7), (8), (9), etc., to (31), and (33) Young, *Sc. Proc. R. Dublin Soc.*, [N. S.] **12**, 374 (1910).

For (4) and (6) Wüllner and Grotian, *Wied. Ann.*, **11**, 556 (1880).

For (32) Zeuner, see Landolt-Börnstein, *Tabellen* (Ed. 4, Berlin, 1912, p. 369).

4. On Measurement of the Lowering of Vapor Pressure with the Aid of a Beckmann Ebullioscope.

It may be of interest to record here that a Beckmann ebullioscope, connected with an empty tank by *sufficiently wide tubing*, can be used for determining the lowering of vapor pressures at constant temperature. In making the measurements tabulated below, we used tubing of 1 cm. internal diameter and a tank of 100 liters capacity. No other "manostat" was necessary.¹ The pressures, which were considerably below that of the atmosphere, were measured with the aid of a baromanometer with a mirror scale. Kahlbaum's thiophene-free benzene was used as a solvent. Our naphthalene had been twice sublimed, twice recrystallized from alcohol, washed with water, and dried over phosphorus pentoxide. The anthracene had been similarly purified by repeated sublimations and repeated recrystallizations from alcohol. The molecular weights were calculated by the formula:

$$M = M_o(g/G)[p_1/(P_1 - p_1)],$$

where the symbols M , M_o , P_1 , and p_1 have the same meaning as in the preceding section; G and g are the weights of solvent and solute, respectively. Here the variation of the vapor pressure of the solvent with the temperature is not needed, and thus one source of error is eliminated.

In the practice of the organic laboratory, M_o may in the case of all "unassociated" solvents be assumed equal to the normal molecular weight. That the results are as good as those usually obtained from elevations of the boiling point under constant atmospheric pressure, is indicated by the following measurements:

1. *Determination of the Molecular Weight of Naphthalene in Benzene.*—Weight G of benzene taken = 26.53 g. The observed pressure P_1 of the pure solvent was 639.85 mm. The molecular weight of benzene vapor, M_o , assumed = 78.1. Found:

g .	p_1 mm.	M .
0.7913	628.7	131.3
1.3141	621.6	131.7
1.8411	614.5	131.3
2.3446	607.4	129.2
3.3453	594.3	128.5

The normal molecular weight of naphthalene is 128.06.

¹ See Beckmann, *Z. physik. Chem.*, **79**, 565 (1912).

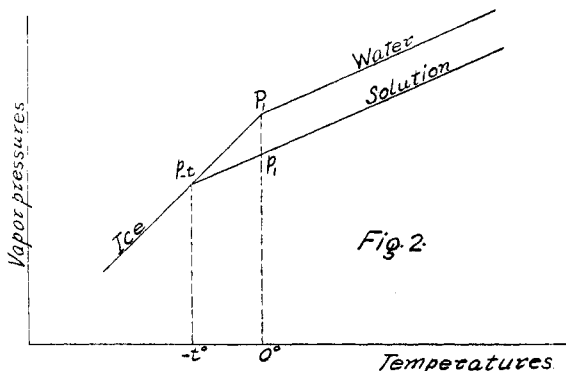
2. *Determination of the Molecular Weight of Anthracene in Benzene.*—Weight G of anthracene taken = 29.740 g. The observed pressure P_1 of the pure solvent was 639.7 mm. The molecular weight of benzene vapor, M_o , assumed = 78.1. Found:

g.	p_1 mm.	M .
0.5676	634.6	185.4
0.8696	631.9	184.8

The normal molecular weight of anthracene is 178.08.

5. Cryoscopic Constants.

Let the straight lines in Fig. 2, marked "Ice," "Water," and "Solution," represent the tangents to the corresponding vapor-pressure curves at the points P_1 , again P_1 , and p_1 , respectively. If the solution under consideration is infinitely dilute, then the points P_1 , p_1 , and p_i are infinitely near together, and the tangents may be considered in place of the vapor-pressure curves themselves, without any finite error being committed.



What is sought is the depression t of the freezing point, caused by the addition to 100 g. of the solvent, the molecular weight of whose vapor may be M_o , of an infinitely small quantity Δ grams, or Δ/M mols, of solute. Geometrically, what is sought is the t corresponding to the point of intersection of the ice and solution lines. The ice line passes through P_1 , which represents the vapor pressure of the solvent at the freezing point; and its slope may be denoted by $\partial p_i / \partial t$ (the subscript i referring to ice). The equation of the ice line is therefore:

$$p_i = P_1 + (\partial p_i / \partial t) \cdot t \quad (3)$$

The solution line passes through the point p_1 , which represents the vapor pressure of the solution at the freezing temperature of the solvent. The slope of this line is the same as that of the water line, since the solution is infinitely dilute (see section 3 above). It may be denoted by $\partial p_w / \partial t$ (the subscript w referring to water, the pure solvent). Then the equation of the solution line is:

$$p_s = p_1 + (\partial p_w / \partial t) \cdot t \quad (4)$$

At the freezing point of the solution $p_i = p_s = p_1$. Hence, from (3) and (4):

$$P_1 + (\partial p_i / \partial t) \cdot t = p_1 + (\partial p_w / \partial t) \cdot t$$

and

$$t = - \frac{P_1 - p_1}{\partial p_i / \partial t - \partial p_w / \partial t} \quad (5)$$

Now we apply Raoult's law and, accordingly, substitute for $P_1 - p_1$ its equal $P_1(1 - x)$, as in section 3. Remembering further, that x , the molar fraction of the solvent, is

$$x = \frac{100/M_o}{100/M_o + \Delta/M},$$

and that the solution is infinitely dilute, equation (5) becomes:

$$t = - \frac{P_1 \Delta / M}{(100/M_o)(\partial p_i / \partial t - \partial p_w / \partial t)}$$

Finally, since $M_o = RT/P_1 v$, where v is the specific volume of the vapor of the solvent, the depression E per *one* mol of solute becomes:

$$E = - \frac{RT}{100 v (\partial p_i / \partial t - \partial p_w / \partial t)} \quad (6)$$

Unlike the corresponding expression for the molecular elevation of the boiling point, this expression (6) for the constant of cryoscopy has scarcely more than theoretical interest; for the *difference* of the two slopes involved is usually small and difficult to determine with precision. Here van't Hoff's formula, based on the heat of fusion of the solvent, will usually be of greater practical advantage. Both expressions (2) and (6) turn into the commonly used Van't Hoff formulae if combined with the Clapeyron-Clausius equation; for ebullioscopic purposes, as we have seen, this transformation is not desirable.

In conclusion we would point out that, since Raoult's law follows from the Duhem-Margules equation, and since the molar fractions in the latter are based on the molecular weights, not in the *liquid* mixture, but in the *vapors* emitted by it—the curious idea suggests itself that all ebullioscopic and cryoscopic measurements indicate molecular weights, not really of the substances in solution, but of their *vapors* emitted by the solution. That the molecular weight of the "solvent" in Raoult's law is that of the solvent's vapor, is generally recognized.

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THE SEPARATION OF YTTRIUM FROM THE YTTRIUM EARTHS. PART II.

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In a previous paper, the authors have shown several methods of separating yttrium from the yttrium earths, the most efficient of which were, the fractional precipitation of the chromates and the fractional precipi-