mass and cause general flow or rupture. Wherever the molecules flow over each other heat is developed as in any viscous flow. When the stress is removed the strain tends to become immediately removed, but wherever the molecules moved over one another, the removal of the strain is hindered, the last of the strain disappearing through viscous flow under a constantly diminishing stress and therefore continuing through a long interval of time. This after-effect has been found[1] in undercooled liquids as well as solids.

13. Finally the after-effect is increased as the temperature is raised in ordinary solids and this may be explained by the expansion of the substance making it easier for the particles to move over each other in viscous flow, so that the fluidity of solids increases with the temperature as is true of most liquids. Guye and his co-workers[2] have assumed that because the vibrations in lead wires die down faster than in steel, the greater loss of energy in the former signifies that lead is more viscous than steel. Exactly the opposite conclusion seems preferable. Steel then is to be regarded as much more viscous than lead and for that very reason strains in steel are produced without nearly so much viscous flow as in lead or pitch.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

IS THE DUHEM-MARGULES EQUATION DEPENDENT ON THE IDEAL GAS LAWS?

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In view of the importance of the Duhem-Margules equation in the theory of physical mixtures, no apology is necessary for raising the question as to whether it is a purely thermodynamic relationship, and therefore reliable under all circumstances, or requires modification in form as soon as vapors begin to deviate from the simple gas laws. That the latter is the case, would seem to be indicated by the fact that the gas laws are employed, at one stage or another, in every deduction of the equation that has been brought forward.[3] But closer study leads to the opposite conclusion: that the Duhem-Margules equation is absolutely general, that it must hold as true for all actual vapors, up to the critical points, as it would if the vapors behaved like ideal gases.

It is, of course, indifferent which form of thermodynamic procedure is

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[1] Barus, *Am. J. Sci.*, [3] **45**, 87 (1893).

[2] *Arch. sci. phys. nat.*, **26**, 136, 263 (1906); **29**, 49 (1909); **30**, 133 (1910).

[3] Duhem, *Ann. de l'École normale sup.*, [3] **4**, 9 (1887); Margules, *Sitzungsbericht der Wiener Akademie*, **104**, II, 1243 (1895); Ostwald, *Lehrbuch der allgemeinen Chemie*, II, **2**, pp. 636–640 (Ed. 2, Leipzig, 1902); Nernst, *Theoretische Chemie*, p. 115 (Ed. 7, Stuttgart, 1913).

selected for the present scrutiny. For the sake of shortness and simplicity, we choose the method of reversible distillation and will follow Luther's form of demonstration.[1]

Let a given binary mixture contain g_1 grams of the first component and g_2 grams of the second component, and let the corresponding partial vapor pressures be p_1 and p_2.[2] We imagine this mixture divided into two halves. Then, with the aid of a semi-permeable membrane, we transfer, by isothermal and reversible distillation, the slight quantity Δg_1 grams of the first component from the first to the second half. And next, with the aid of another semi-permeable membrane, we similarly transfer Δg_2 grams of the second component from the first to the second half of the mixture. We make $\Delta g_1/\Delta g_2 = g_1/g_2$; *i. e.*, the small quantities transferred are in the same ratio as the total quantities of the components in the original mixture. Then the system is after the two distillations in the same state thermodynamically as before. And as the distillations were isothermal and reversible, the algebraic sum of the work involved in them must be zero: $W_1 + W_2 = 0$.

We proceed to calculate W_1 and W_2. Let, during the first distillation, the pressure p_1 of the first component in the first half of the mixture change to $p_1 - {}^1/_2\, dp_1$, and let the pressure in the second half of the mixture change from p_1 to $p_1 + {}^1/_2\, dp_1$, making a total difference of dp_1 after the first distillation. The distillation consisted, to begin with, in the reversible evaporation of Δg_1 grams; and in view of the narrow limits involved, the evaporation may be regarded as having taken place under constant pressure, namely the average pressure $p_1 - {}^1/_4\, dp_1$. If we denote by v'_1 the volume of one gram of the vapor under this average pressure, then the work gained by the evaporation is $+\Delta g_1(p_1 - {}^1/_4\, dp_1)v'_1$. During the reversible condensation of the vapor in the second half of the mixture, the average pressure, likewise assumed constant, must be $p_1 + {}^1/_4\, dp_1$, and if v''_1 denotes the volume of one gram of the vapor under this pressure, then the work involved in the condensation is $-\Delta g_1(p_1 + {}^1/_4\, dp_1)v''_1$.

In order to have: $\Delta g_1(p_1 - {}^1/_4\, dp_1)v'_1 = \Delta g_1(p_1 + {}^1/_4\, dp_1)v''_1$, we must make the assumption that the product of pressure and volume is constant, but only within limits differing by ${}^1/_2\, dp_1$; further, that product need not at all equal RT/M_1 (where M_1 is the molecular weight of the component in question). All we thus assume is that, no matter what the shape of

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[1] See Ostwald, *Loc. cit.*, pp. 639–640.

[2] The partial pressure of each component is the pressure that would be established in a closed space separated from the vessel containing the mixture by a membrane permeable to all sorts of molecules of that component only. If the components of a binary mixture form no mixed molecular complexes, then the total pressure π is equal to the sum of the two partial pressures as just defined: $\pi = p_1 + p_2$. But the Duhem-Margules equation, generalized, applies to mixtures of any number of components, and whether association of different molecules is possible or not.

the pv curve plotted with respect to p, whether it is — in conformity with the gas laws—a straight line parallel to the p-axis, or not, *two of its ordinates separated by an indefinitely small interval are equal.*

The work W_1, then, involved in our first distillation is only that required to compress the Δg_1 grams of vapor from $p_1 - {}^1/_4\, dp_1$ to $p_1 + {}^1/_4\, dp_1$. And here again we do not use the ideal gas laws when we write: $-W_1 = -{}^1/_2 \Delta g_1 v_1 dp_1$, where v_1 denotes the average volume of one gram within the narrow interval of pressures. Analogously, without employing the gas laws, we get for the work involved in the distillation of the second component: $+W_2 = +{}^1/_2 \Delta g_2 v_2 dp_2$. And therefore: ${}^1/_2 \Delta g_1 v_1 dp_1 + {}^1/_2 \Delta g_2 v_2 dp_2 = W_1 + W_2 = 0$, or $g_1 v_1 dp_1 + g_2 v_2 dp_2 = 0$; whence: $dp_1/dp_2 = -g_2 v_2/g_1 v_1$. Substituting for v_1 and v_2 (the volumes of 1 gram) their reciprocals g'_1 and g'_2, the weights of 1 cc., we get:

$$dp_1/dp_2 = -g'_1 g_2/g_1 g'_2 \qquad \text{(A)}$$

If our original mixture is confined within a closed vessel, and an indefinitely small amount of it is allowed to evaporate, then, while g_1/g_2 represents the ratio of the weights of the two components in the liquid, g'_1/g'_2 will equal the ratio of the weights in the vapor (the two vapors being enclosed within the same space).

This expression (A) is the Duhem-Margules equation in the simplest form. The above mode of deduction frees the equation from its supposed dependence on the ideal gas laws and shows it to possess the rank of a purely thermodynamic law, from which there can be no deviation. If this were not true, then, since the behavior of vapors generally differs from that of ideal gases, dp_1/dp_2 would generally *not* be equal to $-g'_1 g_2/g_1 g'_2$. When, now, the total vapor pressure π ($= p_1 + p_2$) is a maximum or a minimum, $\delta\pi = 0$ and dp_1 must equal $-dp_2$, so that $dp_1/dp_2 = -1$. Then, (A) not being strictly true, $g'_1 g_2/g_1 g'_2$ would *not* equal 1; in other words, vapor and liquid would *not* have the same composition, and evaporation would yield fractions respectively more and less volatile than the original mixture—which is impossible, since π is a maximum or a minimum. We conclude that expression (A), the Duhem-Margules equation, must be strictly true.

If we choose to speak in terms of molar fractions, then, in order that (A) should remain true, g_1 and g'_1 must be divided by the same molecular weight M_1, and g_2 and g'_2 by the same molecular weight M_2. The molar fractions x and $1 - x$ of the liquid phase will thus be based on the same molecular weights as the molar fractions of the vapor. And if the partial pressures are taken to be proportional to the molar fractions in the vapor, which must necessarily be the case if the "molecular weights" themselves are defined on the basis of the gas laws, then expression (A) turns into the more familiar forms of the Duhem-Margules equation:

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

and

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

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

BY M. A. ROSANOFF AND R. A. DUNPHY.

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)).