110. *Composition, Pressure, and Temperature Relationships in Binary Azeotropic Systems.*

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Equations previously derived on thermodynamic grounds for expression of the change of composition in binary azeotropes with temperature and pressure are re-examined and developed. The exact thermodynamic relationships are of little practical utility unless supplemented with an equation of state in some form.

Using an approximate statistical thermodynamical treatment, it is shown that azeotropes formed in " strictly regular solutions " (as defined by Guggenheim and Fowler) would obey the empirical rules of azeotropic behaviour, and it is therefore suggested that many real azeotropes closely conform to these " regular or normal " azeotropes.

This leads to the development of general equations relating azeotropic composition to temperature and pressure and other determinable quantities. Comparison of calculated with experimental data shows that the equations fit the experimental results very closely in some instances.

The semi-empirical methods used by Kireev and by Carlson and Colburn for calculation of azeotropic composition are examined, and it is concluded that no better agreement between theory and experiment was obtained than is afforded by the statistical thermodynamical approximate treatment.

Although azeotropes formed in normal liquids should, and do, conform closest to the requirements of the present treatment, it also appears that the general relationships retain some validity even if the components are abnormal (*i.e.*, are associated or solvated).

In recent years a considerable extension of the use of azeotropes in fractional distillation practice has been made and it is now recognised that azeotrope formation is of common occurrence and may often be turned to advantage in devising separation processes. The variations of the azeotropic composition with boiling point and distillation pressure are of obvious practical importance. A fresh interest is thus lent to such theoretical conclusions regarding these properties of constant-boiling mixtures as thermodynamical or statistical reasoning will afford. In the present discussion, restricted to binary systems, our object has been to trace out as directly as possible the general relationship between the variables and to extract useful approximate equations which can be applied to experimental results. These equations have been tested on one or two well-studied examples where very reliable experimental data are available. That the treatment now offered is based on a critical re-examination of the diverse methods previous workers had adopted in approaching the problems will be apparent from the form in which it is developed.

The systems we consider have two components and two phases (liquid, vapour) in equilibrium, the total pressure being that of the vapour phase. Hence by the phase rule in the unrestricted case there are two degrees of freedom; *i.e.*, if the liquid composition and the temperature be fixed then the composition of the vapour and its total pressure are also determined. It will be assumed that the laws of ideal gases apply to the vapour phase and, therefore, that the partial pressures of the two components are proportional to the respective mol.-fractions. When azeotropism occurs in such systems it is defined by the condition that the liquid boils unchanged, *i.e.*, the compositions of vapour and liquid expressed in mol.-fractions are identical. Hence $p_1/P = N_1$ and $p_2/P = N_2$, and moreover, the volatility ratio α $(= p_1N_2/p_2N_1)$ equals 1 (p_1 and p_2 are the partial pressures of components 1 and 2 in equilibrium at total pressure P with a solution containing N_1 mols. of component 1 and N_2 mols. of component 2). Other related criteria are that a maximum or minimum in the curve connecting boiling point at constant pressure with liquid composition occurs at an azeotropic composition, and so also does a minimum or maximum in the curve of total pressure when, at constant temperature, pressure is plotted against liquid composition. The variation of the composition of an azeotrope with pressure and boiling point was originally taken as evidence for the view that azeotropes are not chemical compounds.

A deduction previously given by Redlich and Schutz (*J. Amer. Chem. Soc.*, 1944, **66**, 1007) of the formal thermodynamic relationships between these variations of pressure, composition, and boiling point in azeotropic systems requires modification, and the complete derivation of the necessary equations will therefore be presented. The phase rule indicates that binary two-phase systems possess two degrees of freedom. To deduce the relation between pressure and temperature, we take T (the temperature) and N_2 as variables and write $P = \mathrm{f}(N_2,T)$ and hence

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \left(\frac{\partial P}{\partial T}\right)_{N_2} + \left(\frac{\partial P}{\partial N_2}\right)_T \cdot \frac{\mathrm{d}N_2}{\mathrm{d}T} \quad \cdots\cdots\cdots \quad (1)$$

For an azeotrope $(\partial P/\partial N_2)_T = 0$, since this implies a maximum or minimum in the P–N_2 curve at constant T, and hence

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\text{az.}} = \left(\frac{\partial P}{\partial T}\right)_{N_2} \quad \cdots\cdots\cdots\cdots \quad (2)$$

The subscript az. indicates that equation (2) refers to the azeotrope. But $\partial P = \partial p_1 + \partial p_2$, hence from (2)

$$\frac{1}{P}\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\text{az.}} = \frac{1}{P}\left(\frac{\partial p_1}{\partial T}\right)_{N_2} + \frac{1}{P}\left(\frac{\partial p_1}{\partial T}\right)_{N_2}$$

or

$$T^2\left(\frac{\mathrm{d}\ln P}{\mathrm{d}T}\right) = T^2\frac{p_1}{P}\left(\frac{\partial \ln p_1}{\partial T}\right)_{N_2} + T^2\frac{p_2}{P}\left(\frac{\partial \ln p_2}{\partial T}\right)_{N_2}$$

and since for the azeotrope $p_1/P = N_1$, $p_2/P = N_2$, and $N_1 = 1 - N_2$, and since in general

$$T^2(\partial \ln p/\partial T)_N = \bar{H}/\mathbf{R}$$

where H is the partial molal heat of vaporisation of a component from solution, we obtain after substitution and rearrangement

$$\left[\frac{\mathrm{d}\ln P}{\mathrm{d}(1/T)}\right]_{\mathrm{az.}} = -\frac{(1 - N_2)\bar{H}_1 + N_2\bar{H}_2}{\boldsymbol{R}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Equation (3) connects the variation in azeotropic pressure with the reciprocal of azeotropic boiling point and the composition and heat quantities shown on the right. When T changes, N_2 alters, and $\bar{H}_1$ and $\bar{H}_2$, besides being temperature dependent, also depend upon the composition, being defined by

$$\bar{H}_1 = (\partial H/\partial n_1)_{T,n_2} \qquad \text{and} \qquad \bar{H}_2 = (\partial H/\partial n_2)_{T,n_1}$$

where H is the latent heat of vaporisation of a solution containing n_1 and n_2 mols. of the respective components. While, therefore, (3) has the form of the Clausius–Clapeyron equation, it has no practical utility except when the numerator on the right can be treated as constant over temperature and composition ranges.

To derive the variation of azeotropic composition with temperature we choose T and N_2 as the two independent variables, in accordance with the phase-rule requirement for any binary two-phase system, and write the volatility ratio $\alpha = \mathrm{f}(T,N_2)$ and hence

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \left(\frac{\partial\alpha}{\partial T}\right)_{N_2} + \left(\frac{\partial\alpha}{\partial N_2}\right)_T \cdot \frac{\mathrm{d}N_2}{\mathrm{d}T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For an azeotropic system $\alpha = 1$, thus α = constant and $\mathrm{d}\alpha/\mathrm{d}T = 0$, hence from (4)

$$\left(\frac{\mathrm{d}N_2}{\mathrm{d}T}\right)_{\mathrm{az.}} = \left(\frac{\mathrm{d}N_2}{\mathrm{d}T}\right)_{\alpha=1} = -\frac{\left(\frac{\partial\alpha}{\partial T}\right)_{N_2}}{\left(\frac{\partial\alpha}{\partial N_2}\right)_T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Equation (5) connects the variation in azeotropic composition and boiling point with partial derivatives of α at points where $\alpha = 1$. It differs from the expression given by Redlich and Schutz (*loc. cit.*), who assumed α could be a function of *three* independent variables.

The right-hand side of (5) may be developed as follows :

$$\begin{aligned}\left(\frac{\partial\alpha}{\partial T}\right)_{N_2} &= \alpha\left(\frac{\partial\ln\alpha}{\partial T}\right)_{N_2}\\ &= \alpha\left[\frac{\partial(\ln p_1 + \ln N_2 - \ln p_2 - \ln N_1)}{\partial T}\right]_{N_2}\\ &= \alpha\left(\frac{\partial\ln p_1/p_2}{\partial T}\right)_{N_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)\\ \left(\frac{\partial\alpha}{\partial N_2}\right)_T &= \alpha\left(\frac{\partial\ln\alpha}{\partial N_2}\right)_T\\ &= \alpha\left[\frac{\partial\ln p_1/N_1}{\partial N_2} - \frac{\partial\ln p_2/N_2}{\partial N_2}\right]_T\end{aligned}$$

The Duhem–Margules equation in the form $N_1 . \partial\ln p_1/N_1 + N_2 . \partial\ln p_2/N_2 = 0$ (here $N_1 + N_2 = 1$) is combined with the foregoing to yield

$$\left(\frac{\partial\alpha}{\partial N_2}\right)_T = -\frac{\alpha}{1 - N_2} \cdot \left(\frac{\partial\ln p_2/N_2}{\partial N_2}\right)_T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and from (5), (6), and (7) we obtain

$$\left(\frac{\mathrm{d}N_2}{\mathrm{d}T}\right)_{\alpha=1} = \frac{(1 - N_2)\left(\frac{\partial\ln p_1/p_2}{\partial T}\right)_{N_2}}{\left(\frac{\partial\ln p_2/N_2}{\partial N_2}\right)_T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

in which the second term of the numerator may be replaced by $(\bar{H}_1 - \bar{H}_2)/\boldsymbol{R}T^2$ but it must be remembered that in the general case $\bar{H}_1$ and $\bar{H}_2$ are functions of N_2, *i.e.*, of T.

The combination of (8) with (3) can be made in order to derive the change of composition with pressure.

Clearly, equation (8), like (3), is of little practical utility, since the right-hand terms are more difficult to measure than those on the left and the explicit functional relationship between N_2 and T cannot be determined without integration.

Kireev (*Acta Physicochim., U.S.S.R.*, 1941, **14**, 371) sought to elucidate the general relationship between azeotropic compositions, pressures, and temperatures and the properties of the pure components by a somewhat different approach but one based nevertheless on thermodynamical reasoning. As his mathematical derivations are difficult to interpret and are obscured by a number of printer's errors they will be developed directly in the nomenclature used earlier in this paper. The free energy of formation from the pure components of any binary liquid mixture may be written

$$\Delta G = -\boldsymbol{R}T\,(N_1 \ln p_1^\circ/p_1 + N_2 \ln p_2^\circ/p_2)$$

where p_1° and p_2° are the vapour pressures of the two pure components. For a hypothetical ideal mixture of the same composition, $p_1 = N_1p_1^\circ$ and $p_2 = N_2p_2^\circ$, so that in this case the free energy

$$\Delta G^i = -\boldsymbol{R}T(N_1 \ln 1/N_1 + N_2 \ln 1/N_2)$$

The difference between ΔG and ΔG^i is defined as the " excess free energy " ΔG^E, and clearly

$$\Delta G^E = \boldsymbol{R}T\,(N_1 \ln p_1/N_1p_1^\circ + N_2 \ln p_2/N_2p_2^\circ) \quad . \; . \; . \; . \; . \; . \quad (9)$$

Differentiation with respect to N_2 at constant T, and remembering that $N_1 = 1 - N_2$, gives

$$\begin{aligned}\left(\frac{\partial \Delta G^E}{\partial N_2}\right)_T &= \boldsymbol{R}T\left[-\ln\frac{p_1}{N_1p_1^\circ} + (1-N_2)\,.\left(\frac{\partial \ln p_1}{\partial N_2} + \frac{1}{1-N_2}\right)\right] + \boldsymbol{R}T\left[\ln\frac{p_2}{N_2p_2^\circ} + N_2\,.\left(\frac{\partial \ln p_2}{\partial N_2} - \frac{1}{N_2}\right)\right]\\ &= \boldsymbol{R}T\left[\ln\frac{p_1^\circ}{p_2^\circ} + \ln\frac{p_2}{N_2}\frac{N_1}{p_1} + (1-N_2)\frac{\partial \ln p_1}{\partial N_2} + N_2\frac{\partial \ln p_2}{\partial N_2}\right]\\ &= \boldsymbol{R}T\left[\ln\frac{p_1^\circ}{p_2^\circ} + \ln\frac{p_2}{N_2}\frac{N_1}{p_1}\right] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10)\end{aligned}$$

The last simplification is obtained by using the Duhem–Margules relationship. Equation (10) is true for any binary liquid mixture. For an azeotrope the second term on the right is zero so that

$$(\partial\Delta G^E/\partial N_2)_T = \boldsymbol{R}T \ln p_1^\circ/p_2^\circ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

It should be noted that (11) is true only for $\alpha = 1$, and this applies only to the azeotropic condition in contrast with equations (5) and (8) which hold for any constant values of α. Clearly also (11) can only be used to obtain a relationship between azeotropic composition and temperature if a functional relationship between ΔG^E, N_2, and T can be found.

It will now be seen that the strictly thermodynamic approach has not proved very profitable, and that a less rigorous treatment may well afford a more practically useful basis for discussing quantitatively the occurrence and behaviour of azeotropes.

An Approximate Treatment based on Statistical Thermodynamical Considerations.—It has been usual to compare the properties of solutions with the assumed properties of hypothetical ideal solutions and to measure deviations from ideal behaviour. Ideal solutions cannot form azeotropes and therefore are unsuitable in many ways for introduction into the discussion of azeotropy. We suggest that " strictly regular solutions " as defined by Guggenheim and Fowler (" Statistical Thermodynamics ", p. 351) are a suitable class of solutions to be regarded as capable under certain conditions of yielding what we may call " normal or regular " azeotropes. We shall show that certain real azeotropic mixtures closely conform in behaviour with the azeotropes to which strictly regular solutions may be expected to give rise.

The conditions for the formation of a strictly regular solution are : (1) The components should pack in the same way. (2) The molar volumes should be sufficiently alike so that a mixture of the two kinds can also pack in the same way as each of the single liquids. (3) The ratio of the free volumes of the two pure liquids should not differ from unity by more than approximately 30%. (4) The molar volumes (V_1, V_2) and free volumes of both components should remain unaltered when the liquids are mixed. (5) In any given configuration of volume V given by $V = N_1V_1 + N_2V_2$ the potential energy W may be regarded as the sum of contributions from pairs of closest neighbours.

A crude statistical thermodynamical treatment of strictly regular solutions which assumes that the entropy of mixing of such a solution is the same as that of an ideal solution yields equations of the form

$$p_1 = p_1^\circ\, N_1\, \mathrm{e}^{W_{ab}N_2^2/\boldsymbol{R}T} \text{ and } p_2 = p_2^\circ\, N_2\, \mathrm{e}^{W_{ab}N_1^2/\boldsymbol{R}T} \quad . \; . \; . \; . \; . \; . \quad (12)$$

where p_1, p_2, p_1°, p_2°, N_1, and N_2 have the same significance as before and Wab is the mixing energy (Guggenheim and Fowler, *op. cit.*). For such a mixture

$$H^1 = [N_1N_2/(N_1 + N_2)]Wab \quad . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

where H^1 is the excess heat over that of an ideal solution. For an ideal solution $H^1 = 0$, $Wab = 0$, and equations (12) reduce to Raoult's equation.

The more refined treatment of strictly regular solutions (Guggenheim and Fowler, *op. cit.*, p. 358) indicates that equations (12) are a good first approximation to the fuller treatment (see also Kirkwood, *J. Physical Chem.*, 1939, **43**, 97, who arrives at a similar conclusion) and they will be taken therefore as the basis for our discussion of azeotropism. We note first that these equations are of the same form as the Margules equation as derived by Porter (*Trans. Faraday Soc.*, 1920, **16**, 336), where $Wab/\boldsymbol{R}T = \beta$, a constant, since the Porter equation applies at constant temperature. The Porter equation is known to correlate fairly accurately the partial pressure of a component and the liquid composition (at constant temperature) except when one or other component is highly associated (see, *e.g.*, Glasstone, " Textbook of Physical Chemistry ", 1940, p. 699).

The application of a set of equations such as (12) to describe the behaviour of an azeotropic system is simply made. The equations are written in the form $p_1 = p_1^\circ N_1\gamma_1$ and $p_2 = p_2^\circ N_2\gamma_2$, where γ_1 and γ_2 are the activity coefficients of the components. For an azeotrope, $p_1N_2/p_2N_1 = 1$, and hence

$$\ln p_1^\circ/p_2^\circ + \ln \gamma_1/\gamma_2 = 0$$

For the particular case under consideration $\gamma_1 = e^{WabN_2^2/\boldsymbol{R}T}$ and $\gamma_2 = e^{WabN_1^2/\boldsymbol{R}T}$, so after substitution and rearrangement we obtain, remembering that $N_1 + N_2 = 1$,

$$N_2(\text{az.}) = \tfrac{1}{2}\,(1 - \boldsymbol{R}T/Wab\,.\,\ln p_1^\circ/p_2^\circ) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (14)$$

A number of conclusions can be drawn from equation (14).

Conditions for the existence of an azeotrope. For an azeotrope to have existence, N_2(az.) in equation (14) must lie between 0 and 1, *i.e.*

$$\ln p_1^\circ/p_2^\circ < Wab/\boldsymbol{R}T \quad \text{and} \quad \ln p_2^\circ/p_1^\circ < Wab/\boldsymbol{R}T$$

Since Wab is in general not large, $|p_1^\circ - p_2^\circ|$ must be small for an azeotrope to be formed. This is the physical basis of the empirical rule given by Timmermans (" Les Solutions Concentrées ", 1936, p. 161), *viz.*, that azeotropy is greatly favoured when the pure components are a close-boiling pair.

Maximum and minimum azeotropes. The sign of Wab, in equation (12), determines whether deviations from ideality are positive or negative. If Wab is positive in sign we have positive deviations, and if an azeotrope is formed we have maxima in curves of pressure–composition (at constant temperature) and minima in curves of b. p.–composition (at constant pressure). On the other hand, if Wab is negative the above maxima and minima are interchanged. The only factor which tends to make Wab negative is compound formation between the components, *e.g.*, solvation of hydrogen chloride by water; thus in a maximum b. p. azeotrope this effect must outweigh those factors which operate in the reverse sense, namely, differences between the internal pressure, polarity, molecular size, or degree of association of the components in the liquid state. Thus maximum b. p. azeotropes occur far less commonly than the opposite type.

Direction of change of azeotropic composition with temperature. In the statistical thermodynamical derivation of equation (12) it is assumed that Wab is invariant with temperature, an assumption considered by Guggenheim and Fowler (*op. cit.*) to be a close approximation to reality. We will therefore take Wab as independent of temperature, and hence by differentiating equation (14) with respect to T,

$$\frac{dN_2}{dT} = -\tfrac{1}{2}\,\boldsymbol{R}/Wab\left[\ln p_1^\circ/p_2^\circ + T\,.\,\frac{d \ln p_1^\circ/p_2^\circ}{dT}\right] \quad . \; . \; . \; . \; . \; . \quad (15)$$

Clearly the sign of dN_2/dT depends upon the sign of Wab, so that *ceteris paribus* the variation of concentration with temperature for maximum b. p. azeotropes will be in the reverse sense to that of the minimum b. p. type.

We next consider the terms in the bracket in equation (15). It has already been shown that for most azeotropes $|p_1^\circ - p_2^\circ|$ must be small and hence $\ln p_1^\circ/p_2^\circ \sim 0$, so that the sign of the bracketed quantity is determined by the second term, which is usually numerically the larger. This second term can be expanded in two alternative forms, which will be considered separately.

(1) By using the Clausius–Clapeyron equation we may write

$$T\frac{\mathrm{d}\ln p_1^\circ/p_2^\circ}{\mathrm{d}T} = \frac{H_1 - H_2}{\boldsymbol{R}T}$$

where H_1 and H_2 are the latent heats of vaporisation of the pure components 1 and 2. For a minimum b. p. azeotrope Wab is positive, so that $-\frac{1}{2}\boldsymbol{R}/Wab$ is negative. Hence if $H_2 > H_1$ then the right-hand side of equation (15) is positive, and a rise in temperature will cause an increase in the concentration of the component with the higher latent heat of vaporisation in the pure state.

Since Wab is negative for a maximum b. p. azeotrope, the converse conclusions result for this type by similar reasoning.

These rules are identical with the form of Wrewsky's empirical rule as usually quoted (see, *e.g.*, Young, " Distillation Principles and Processes," p. 61).

(2) Alternatively we may write

$$T\frac{\mathrm{d}\ln p_1^\circ/p_2^\circ}{\mathrm{d}T} = T\left[\frac{1}{p_1^\circ}\frac{\mathrm{d}p_1^\circ}{\mathrm{d}T} - \frac{1}{p_2^\circ}\frac{\mathrm{d}p_2^\circ}{\mathrm{d}T}\right]$$

$$\sim \frac{T}{p_1^\circ}\left[\frac{\mathrm{d}p_1^\circ}{\mathrm{d}T} - \frac{\mathrm{d}p_2^\circ}{\mathrm{d}T}\right]$$

The approximation is justified because in general $|p_1^\circ - p_2^\circ|$ is small. If $\mathrm{d}p_1^\circ/\mathrm{d}T > \mathrm{d}p_2^\circ/\mathrm{d}T$ then the sign of the bracketed quantity in equation (15) is positive, and $\mathrm{d}N_2/\mathrm{d}T$ will be negative, *i.e.*, the azeotropic composition moves towards that component which has the lower $\mathrm{d}p^\circ/\mathrm{d}T$ (in the pure state) as temperature decreases. This is equivalent to the statement that the percentage of that component in a binary azeotropic mixture which has the lower value of $\mathrm{d}p^\circ/\mathrm{d}T$ increases as the pressure decreases, which is the rule arrived at empirically by Merriman (quoted by Young, *op. cit.*, p. 61).

We thus see that Merriman's and Wrewsky's rules may be given an identical basis. Our consideration of strictly regular solutions has shown that the properties derived for the azeotropes which they form accord closely with the behaviour of real azeotropes as expressed in empirical generalisations. This lends support to the suggestion that normal or regular azeotropes should be considered as a class of strictly regular solutions.

Approximate relation between azeotropic composition and boiling point. We now examine equation (14) with the aim of seeing how far simple approximate quantitative expressions derivable from it fit actual data recorded for real azeotropes.

The simple integrated form of the Clausius–Clapeyron equation yields for the pure components

$$\ln p_1^\circ = -H_1/\boldsymbol{R}T + C_1 \quad \text{and} \quad \ln p_2^\circ = -H_2/\boldsymbol{R}T + C_2$$

where C_1 and C_2 are constants. Insertion of these relationships in (14) and rearrangement yields

$$N_2 = \tfrac{1}{2}\left[1 + \frac{H_1 - H_2}{Wab} + \frac{C\boldsymbol{R}}{Wab}T\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

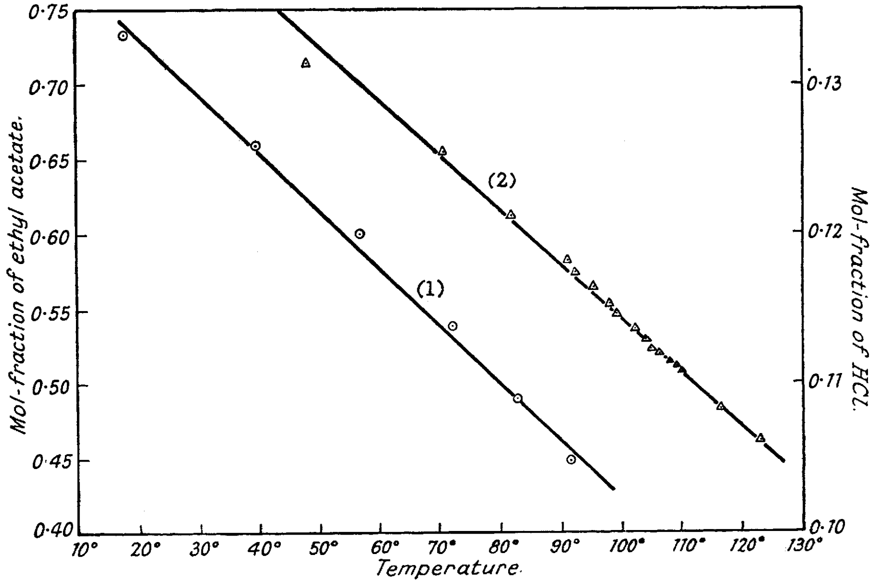
where $C = C_1 - C_2$.

Equation (16) clearly indicates a direct linear relation between the mol.-fraction N_2 and the azeotropic b. p., T. Naturally, a similar relation exists for N_1 and T, since the components are not distinguished in any way.

Reference to plots of experimental data for the azeotropic systems benzene–*cyclo*hexane and ethyl acetate–carbon tetrachloride shows that in these cases where the solutions approach strict regularity a straight-line relation is obeyed (Redlich and Schutz, *loc. cit.*). However, several other examples show the same behaviour although it is improbable that these can be classified as strictly regular (ethyl alcohol–chloroform, methyl alcohol–methyl acetate, heptane–ethyl alcohol, toluene–ethyl alcohol; see Redlich and Schutz, *loc. cit.*). Such plots may clearly be useful even for systems in which one of the components is associated, *e.g.*, ethyl alcohol–ethyl acetate; but they will not serve to correlate the data on the system water–ethyl alcohol, which is known to be very irregular—here the heat of mixing depends markedly on the temperature. Similar experimental data for the well-studied systems ethyl alcohol–ethyl acetate and hydrogen chloride–water (Merriman, *J.*, 1913, **103**, 1801; Bonner and Wallace, *J. Amer. Chem. Soc.*, 1930, **52**, 1747) are plotted in Fig. 1.

The extrapolation of such plots of N_2 against T to $N_2 = 0$ and $N_1 = 1$ permits the temperatures to be found at which azeotropes cease to exist, but is of course subject to the condition that the latent heats H_1 and H_2 and Wab remain constant and independent of temperature. The upper temperature may be above the critical temperature, or in its vicinity, and the lower temperature below the freezing point of one of the components. In addition, minimum b. p. azeotropes may separate into a two-phase liquid system as the temperature is lowered; this occurs when $Wab/\mathbf{R}T > 2$ (for detailed discussion see Guggenheim and Fowler, *loc. cit.*, and Kirkwood, *loc. cit.*). Hence in practice there may not be an upper or lower temperature limit for the azeotropy, although in some cases both or either may exist.

FIG. 1.



(1) *Ethyl acetate–ethyl alcohol : Data of Merriman as quoted by Carlson and Colburn* (Ind. Eng. Chem., 1942, **34**, 581).
(2) *Hydrogen chloride–water : Data of Bonner and Wallace* (J. Amer. Chem. Soc., 1930, **52**, 1747).

Approximate relations between total pressure of an azeotropic mixture and temperature, and between the pressure and composition. From the second equation of (12), inserting $p_2 = N_2P$ (since the gases are perfect) and eliminating N_2 by means of equation (14), we have

$$\ln P = \ln p_2^\circ + \frac{Wab}{\mathbf{R}T}\left[\tfrac{1}{2} + \frac{\mathbf{R}T}{2Wab}\ln\frac{p_1^\circ}{p_2^\circ}\right]^2$$

As shown above $|p_1^\circ - p_2^\circ|$ is in general small; hence the term containing $(\ln p_1^\circ/p_2^\circ)^2$ on the right-hand side of the above equation can be neglected. Hence

$$\ln P \sim \ln p_2^\circ + \frac{Wab}{4\mathbf{R}T}\left[1 + \frac{2\mathbf{R}T}{Wab}\ln\frac{p_1^\circ}{p_2^\circ}\right]$$

$$\sim \frac{Wab - 2(H_1^\circ + H_2^\circ)}{4\mathbf{R}T} + D$$

$$\sim A/\mathbf{R}T + D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

which is of the simple Clausius–Clapeyron form and shows that $-(1 - N_2)\bar{H}_1 + N_2\bar{H}_2$ in equation (3) is approximately constant for a strictly regular solution.

Elimination of T between (17) and (16) gives an equation relating azeotropic composition and pressure of the form

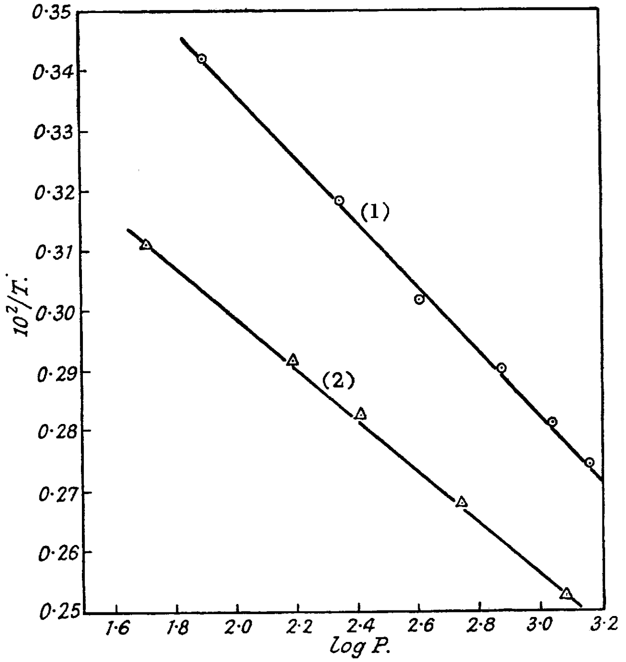
$$N_2 \sim A_1/(\ln P - D) + C_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

From (17), $D \longrightarrow \ln P$ as $T \longrightarrow \infty$ and hence $D > \ln P$ and we may write

$$N_2 \sim -\frac{A_1}{D\left(1 - \frac{\ln P}{D}\right)} + C \qquad \sim -\frac{A_1}{D}\left(1 + \frac{\ln P}{D}\right) + C \qquad \sim A'' \ln P + C'' \quad . \quad . \quad (19)$$

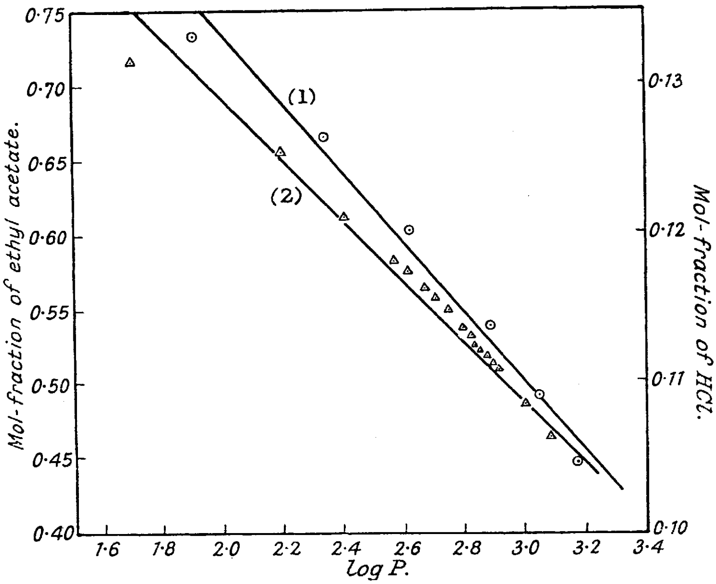
where A'' and C'' are constants.

FIG. 2.



(1) *Ethyl acetate–ethyl alcohol : Data of Merriman* (J., 1913, **103**, 1801) *as quoted by Carlson and Colburn* (Ind. Eng. Chem., 1942, **34**, 581).
(2) *Hydrogen chloride–water : Data of Bonner and Wallace* (J. Amer. Chem. Soc., 1930, **52**, 1747).

FIG. 3.



(1) *Ethyl acetate–ethyl alcohol.*
(2) *Hydrogen chloride–water.*

In Fig. 2, ln P is plotted against $1/T$ for the azeotropic systems ethyl acetate–ethyl alcohol and hydrogen chloride–water (the experimental values for P and T being taken from the data of Merriman, and of Bonner and Wallace, *locc. cit.*). A good straight line results in each case. In Fig. 3, N_2 is plotted against ln P for the same systems. Here the curves show definite departures from linearity and it appears that equation (18) is not accurately approximated by equation (19). An alternative and more exact expression for the relationship between N_2 and $\ln P$ is discussed later [see equation (22)].

An Examination of Other Methods for the Calculation of Azeotropic Relationships.—Kireev (*loc. cit.*) has discussed the calculation of variations in azeotropic composition with temperature and pressure on the basis of equation (11). He suggests that for many solutions experimental values of ΔG^E satisfy an empirical relationship of the form $\Delta G^E = N_1N_2K^1$ where K^1 is a constant and independent of N_2 but possibly a function of T. It can readily be shown that this is equivalent to assuming that the properties of such solutions are described by the Margules–Porter equation at constant temperature. Thus, insertion of equations (12) in (9), which is true without restriction for any liquid solution, gives

$$\begin{aligned}\Delta G^E &= \boldsymbol{R}T[N_1 \ln e^{WabN_2^2/\boldsymbol{R}T} + N_2 \ln e^{WabN_1^2/\boldsymbol{R}T}] \\ &= N_1N_2\, Wab \\ &= N_1N_2K^1 \text{ where } K^1 = Wab \quad \dots\dots\dots\dots \quad (20)\end{aligned}$$

Differentiation of (20) with respect to N_2 at constant T and combination with equation (11) yields

$$(1 - 2N_2)K^1 = \boldsymbol{R}T \ln p_1^\circ/p_2^\circ \quad \dots\dots\dots \quad (21)$$

which is necessarily identical with equation (14) already derived. Insertion of the azeotropic limitation in equation (9) by writing $p_1 = N_1P$ and $p_2 = N_2P$, combination with (20), and elimination of K^1 between the resulting equation and (21) gives

$$(1 - 2N_2)(\ln P - \ln p_1^\circ) = N_2^2\,(\ln p_1^\circ - \ln p_2^\circ)$$

which can be solved for N_2 by adding $N_2^2(\ln P - \ln p_1^\circ)$ to both sides whence

$$(1 - N_2)^2\,(\ln P - \ln p_1^\circ) = N_2^2(\ln P - \ln p_2^\circ)$$

$$\frac{(1 - N_2)^2}{N_2^2} = \frac{\ln P/p_2^\circ}{\ln P/p_1^\circ} = y$$

$$N_2^2\,(1 - y) - 2N_2 + 1 = 0$$

and

$$N_2(\text{az.}) = \frac{1}{1 + \sqrt{y}} = \frac{1}{1 + \sqrt{\dfrac{\ln p_2^\circ - \ln P}{\ln p_1^\circ - \ln P}}} \quad \dots\dots\dots \quad (22)$$

(The negative root of $\pm\, y$ is chosen in order to make $N_2 < 1$.)

Equation (22), which was first derived by Kireev, relates the composition of the azeotrope to its pressure and the vapour pressures of the pure components at the boiling point of the azeotrope. In the derivation no assumption regarding the temperature-dependence of K^1 (in equation 20) need be made, although, as we have seen, for strictly regular solutions K^1 should vary only slightly with temperature as it equals *Wab*. Kireev found that the equation satisfactorily correlated experimental data for a number of systems, which, as this discussion reveals, should be the case provided they satisfy the Margules–Porter equation at constant temperature.

The variation of composition with temperature was considered by Kireev on the basis of a suggestion that K^1T = constant = C_4 for certain solutions. Insertion of this condition in (21) and replacement of the $\ln p_1^\circ/p_2^\circ$ term by equivalent latent heat terms from the Clausius–Clapeyron equation yields

$$N_2\,(\text{az.}) = \tfrac{1}{2}\left[1 + \frac{H1 - H2}{C_4}\,T + C_5T^2\right] \quad \dots\dots\dots \quad (23)$$

where $C_5 = (C_2 - C_1)\boldsymbol{R}/C_4$ and C_1, C_2, and C_4 have been defined already.

This expression contains a term involving the square of the temperature, but if C_5 is small, or if the temperature ranges over which measurements are made is restricted, it may be difficult to detect a deviation from linearity due to the T^2 term in a plot of N_2 against T. In fact, experimental data for numerous systems are fitted by a linear relation, as has been shown already, and (23) will not be discussed further.

A method used by Carlson and Colburn (*Ind. Eng. Chem.*, 1942, **34**, 581) for calculating the change in the composition with temperature of the azeotrope ethyl acetate–ethyl alcohol involved several successive operations. First, the activity coefficients, γ_1 and γ_2, of the two components were evaluated from $\gamma_1 = P_{\text{az.}}/p_1^\circ$ and $\gamma_2 = P_{\text{az.}}/p_2^\circ$. Here, $P_{\text{az.}}$ is the total pressure at the boiling point of the azeotrope and p_1° and p_2° are the vapour pressures of the pure components at this temperature. Data at atmospheric pressure were used for this calculation of γ_1 and γ_2, and the values so obtained were used to calculate the van Laar constants. From these constants the ratio γ_1/γ_2 was calculated at, and plotted against, different compositions at constant temperature and then, on the assumption that the van Laar constants are not dependent on temperature, the composition at other temperatures was found from the relationship $\gamma_1/\gamma_2 = p_2^\circ/p_1^\circ$, which is true for the azeotrope, in conjunction with the plot of γ_1/γ_2 against N_2. To facilitate the calculation, experimental values of p_1°/p_2° were plotted against temperature.

It is of interest to compare the calculations made in this way with those made more directly from equation (14). By rearrangement the latter equation yields

$$(2N_2 - 1) = \frac{(2N_2^* - 1)}{T^* (\ln p_1^\circ/p_2^\circ)^*} \times T \ln p_1^\circ/p_2^\circ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where the starred values refer to a known composition of the azeotrope (N_2^*) at one temperature (T^*). If for the pure components p_1°/p_2° is known as a function of T, then N_2, the azeotropic composition at any boiling point T, can be secured from equation (24).

In the table the observed values of N_2 and T (Merriman, *loc. cit.*) are compared with the calculated. The composition at 760 mm. pressure and at a temperature of 71·8° was taken as the known value in both calculations.

Ethyl acetate–ethyl alcohol azeotrope.

Composition, N_2 = mol.-fraction of ethyl acetate.

		Calculated.	
Temp.	Exptl.	by Carlson and Colburn.	by eqn. (24).
18·7°	0·734	0·787	0·706
40·5	0·660	0·677	0·639
56·3	0·601	0·602	0·596
71·8	0·539	(0·539)	(0·539)
83·1	0·490	0·498	0·500
91·4	0·451	0·480	0·480
Standard deviation of an individual calculated value :		0·022	0·019

Clearly, the experimental data are fitted as well by equation (24) as by the Carlson and Colburn procedure.

Validity of the Approximate Treatment.—It has been shown that all the methods of calculation we have discussed rest upon an assumption that either the Margules–Porter or the van Laar equation adequately describes the behaviour of the liquid–vapour systems at constant temperature. The methods of relating variation of azeotropic composition with temperature used by Kireev and by Carlson and Colburn have each an empirical element; Kireev takes K^1T as constant, and Carlson and Colburn assume that the A and B constants of the van Laar equations are temperature-independent—an assumption with no real theoretical justification.

Statistical thermodynamical reasoning suggests that the equations (12) which serve as basis for the present approximate treatment should describe to a good approximation the behaviour of strictly regular solutions.*

It follows from the definition of strictly regular solutions (p. 600), and from the conclusion that in general the boiling points of the components must be close together if an azeotrope is to exist, that an azeotrope formed between normal liquids will usually conform to the behaviour of a regular azeotrope and be described by the equations we have used. It is rather surprising,

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* Since this manuscript was prepared, a memoir by Prigogine (*J. Phys. Radium*, 1944, **5**, 185) has become available. This author also considers azeotropes formed from strictly regular solutions and derives an equation equivalent to (14). He demonstrates that this equation is compatible with the empirical rule of Roozeboom connecting the direction of change of composition with temperature. The relationship between log P and $1/T$ is also studied. An equation of the type

$$\frac{N_2^2}{(1 - N_2)^2} = \left(\frac{H_1/T_1}{H_2/T_2}\right)\left(\frac{T_1 - T}{T_2 - T}\right)$$

is deduced where T_1 and T_2 are the boiling points of the pure components and T the boiling point of the azeotrope. The validity of the equation in the simple form where $H_1/T_1 = H_2/T_2$ was tested by using experimental data for azeotropes formed between halides and ethyl alcohol.

nevertheless, that some at least of the azeotropic mixtures containing associated components also appear to conform fairly closely to equations (16), (17), and (19) (*e.g.*, ethyl acetate–ethyl alcohol) and so also do some azeotropes in which one component is heavily solvated by the other (*e.g.*, hydrogen chloride–water).

A preliminary report on the relationships which we have derived has appeared in *Nature* (1946, **158**, 198).

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