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of two volatile components, which cover the widest field, the vapour/liquid equilibrium method is probably the most applicable experimental approach. However, this method involves the difficulty of determination of the composition of both phases with high accuracy. Furthermore, unless such an investigation is combined with an additional volumetric study of the system, it is not possible to obtain the required thermodynamic quantities.

It will be shown below that the excess - or non-ideal - differential free energies of dilution can be obtained directly from the azeotropic data at the azeotropic conditions without any of the difficulties mentioned above. Therefore the azeotropic mixtures form a useful category for the application of statistical treatments.

On the other hand, the prediction of azeotropic properties of mixtures has a practical importance.

The aim of the present work is to examine a) the applicability of certain statistical treatments and b) the possibility of prediction of azeotropic behaviour of the systems on the basis of these theories.

The general thermodynamics of azeotropy in binary mixtures has been worked out by previous workers, [1], [2], [3], [4], [5], [6], [7], [8] almost in the same manner, paying little attention to the justification of the approximations involved.

Herzfeld et'all[2], Kireev[3], and Prigogine et'all[6] applied the expression K x_2^2 for the differential non-ideal free energy of dilution per mole of component (1) to certain azeotropes, where K is an empirical constant for a given system and x_2 is the molar fraction of component (2) in the mixture, and obtained experimental agreement with most of the azeotropic systems at constant pressure. This expression is a common result of the formulae developed by various workers using different statistical models, in a special case. In fact, if the molar volumes of the liquids concerned are identical, the formulae due to Van Laar[9], [10] and Hildebrand[11], and Guggenheim's[12] «zeroth» approximation lead to the above expression. All these treatments imply the assumption of ideal entropy of mixing, i.e. K x_2^2 also equals to the differential heat of dilution. K is calculable from the Van der Waal constants of the species in Van Laar's theory, from the heats of vaporization of the components in Hildebrand's the deviation from ideality is everywheere positive (i. e. $\Delta\mu_1^n > 0$, $\Delta\mu_2^n > 0$) then $T_a < T_1 \leqq T_2$ (i. e. azeotrope with minimum boiling point), and if the deviation is everywhere negative (i. e. $\Delta\mu_1^n < 0$, $\Delta\mu_2^n < 0$) $T_1 \leqq T_2 < T_a$ (i. e. azeotrope with maximum boiling point).

A further simplification can be introduced by assuming the approximate validity of the relationship $L_1/T_1 = L_2/T_2$ (i. e Trouton's rule) at atmospheric pressure, when from (5′) and (5″) we obtain

$$C(T_2 - T_1) = \Delta\mu_2^n - \Delta\mu_1^n \quad \cdots\cdots\cdots\cdots\cdots \quad (6)$$

where $C = L_1/T_1 = L_2/T_2$ (i. e. Trouton's constant). Since thermodynamically

$$\Delta\mu_2^n - \Delta\mu_1^n = \left(\frac{\partial \Delta G_x^n}{\partial x_2}\right)_{T,\,P} \quad \cdots\cdots\cdots\cdots \quad (6'),$$

from (6) and (6′) we have

$$C(T_2 - T_1) = \left(\frac{\partial \Delta G_x^n}{\partial x_2}\right)_{T_a,\,P} \quad \cdots\cdots\cdots\cdots \quad (7)$$

where ΔG_x^n is the non-ideal free energy of mixing per mole of mixture. Therefore the critical factor for the existence of an azeotrope is the slope of the ΔG_x^n versus x_2 curve. For the sake of brevity, let us neglect the dependence of ΔG_x^n on temperature, which corresponds to the case of regular solutions. Then, there must be a point somewhere in this curve where the slope is equal to $C(T_2 - T_1)$ for the existence of an azeotrope. If the maximum slope is smaller than $C(T_2 - T_1)$ no azeotrope is formed. Otherwise there will be azeotrope. In other words, the criterion for the existence of an azeotrope is

$$\left(\frac{d\Delta G_x^n}{dx_2}\right)_{\max} \geqq C(T_2 - T_1) \quad \cdots\cdots\cdots\cdots\cdots \quad (8).$$

If the maximum corresponds to $x_2 = 0$ or $x_2 = 1$ the sign of equality should be dropped. It follows that the smaller the difference between the boiling points of components (1) and (2) the more is the possibility of formation of an azeotrope.

b) The Shift of Azeotropic Equilibrium with Pressure:

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Statistical Thermodynamics of Binary Azeotropes

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Özet: Modern termodinamik metodlariyle ikili azeotropların termodinamiği, teşekkül şartları, basıncın azeotropik denge üzerindeki tesiri münakaşa edilmiş ve elde edilen münasebetler yardımiyle non-elektrolitik çözeltilerin yakın senelerde ileri sürülen statistik termodinamik teorilerinin reel sistemlere tatbik kabiliyeti ve bu teorilerden itibaren azeotropik vasıfların ne dereceye kadar önceden haber verilebileceği incelenmiş ve aşağıdaki sonuçlara varılmıştır:

Muhtelif müelliflerin non-ideal karışma serbest enerjilerinin mol kesrinin basit parabolik bir denklemine uyduğunu tesbit ettikleri polar azeotropların düzgün (regular) çözeltiler olmadığı gösterilmiş, bu iki müşahedenin - ancak - Guggenheim'in umumîleştirilmiş teorisinin takribî şekli ile telif edilebileceği anlaşılmış ve bu sistemlerde rastgele (random) karışma hipotezinin kabul edilebileceği sonucu elde edilmiştir.

Aynı teori etil asetat-etil alkol sistemine tatbik edilerek normal basınçtaki azeotropik denge ve karışma ısısından itibaren bu dengenin basınçla değişimi hesaplanmış ve neticelerin tecrübe ile bulunmuş değerlere daha önceki araştırıcıların non-ideal karışma entropisini ihmal eden teorilere dayanan hesap neticelerinden çok daha yakın olduğu gösterilmiştir. Bu suretle bu teorinin polar karışımlara tatbik edilebileceği ve bu sistemlerin termodinamik fonksiyonlarının ekstrapolâsyonunda faydalı olacağı ileri sürülmektedir.

1. Introduction

Statistical thermodynamics of solutions of non-electrolytes has received an extensive study in recent years. The experimental verification of such theoretical treatments requires accurate and detailed thermodynamic data on binary mixtures. For mixtures

More recently a new statistical treatment developed by Longuent Higgins was applied successfully by D. Cooke to the change of azeotropic equilibrium with pressure of the system ethylene - CO_2[14]. This treatment is similar to Guggenheim's theory just mentioned in that it also leads to a non-ideal entropy and an expression for the non-ideal free energy of the form Kx_2^2, but goes further to imply that the entropy deviation from the ideal is proportional to the heat of mixing, the proportionality factor being given by the thermal data on any one of the pure components. If these data are available, on the basis of this treatment it is possible to establish the thermodynamics of mixtures from the heats of mixing observed, which is not the case with Guggenheim's generalized theory. Nevertheless, Cooke's application of the treatment is not based on the thermal data. He uses empirical parameters which make up the factor K, calculated from vapour/liquid equilibrium data. It is, therefore, reasonable to believe that an agreement to the same accuracy could be obtained also by Guggenheim's treatment since both equations are formally identical. In this application the advantage of this theory over Guggenheim's has not been made use of, and it still remains to be seen whether it really has such an advantage in practice.

It is clear from this review that the application of statistical treatments to azeotropes has been so far superficial.

In this paper it will be shown that when the heats of mixing of azeotropic mixtures of polar components are compared with the non-ideal free energies of mixing obtained from the azeotropic data large differences are observed even if some of these systems satisfy the free energy expression Kx_2^2. Secondly, the system ethyl acetate-EtOH will be subject to treatment within the frame-work of Guggenheim's generalized theory[13] which takes care of the non-ideal entropy, where we shall present a better quantitative prediction of the shift of azeotropic equilibrium than that of Coulson and Herington, from the heat of mixing and the azeotropic data at a single pressure.

First, the thermodynamics of binary azeotropes will be presented by the methods of modern thermodynamics using chemical potentials.

2. Thermodynamics of Binary Azeotropes

a) Azeotropy at Constant Pressure:

Consider a binary solution of volatile components (1) and (2) in equilibrium with the vapour phase at a constant pressure P (e. g. atmospheric pressure). Writing the chemical protentials of component (1) in both phases, we have

$$\text{(Liquid phase)} \quad \mu_1^{\alpha} = \mu_1^{o\alpha}(\mathrm{T, P}) + \mathrm{RT} \log x_1^{\alpha} + \mathrm{RT} \log \gamma_1^{\alpha} \qquad (1)$$

$$\text{(Vapour phase)} \quad \mu_1^{\beta} = \mu_1^{o\beta}(\mathrm{T, P}) + \mathrm{RT} \log x_1^{\beta} + \mathrm{RT} \log \gamma_1^{\beta} \qquad (2)$$

where μ_1 *'s*, x_1 *'s* and γ_1*'s* are the chemical potentials, molar fractions and activity coefficients of this component, respectively, in corresponding phases. Superscripts α and β refer to the liquid and vapour phases, respectively. $\mu_1^{o\alpha}(\mathrm{T, P})$ and $\mu_1^{o\beta}(\mathrm{T, P})$ are the chemical potentials of pure liquid (1) and pure vapour (1) at temperature T and pressure P. R is the gas constant. At equilibrium $\mu_1^{\alpha} = \mu_1^{\beta}$ $\therefore$ from eqns. (1) and (2) we have

$$\mu_1^{o\beta}(\mathrm{T,P}) - \mu_1^{o\alpha}(\mathrm{T,P}) = \mathrm{RT} \log x_1^{\alpha}/x_1^{\beta} + \mathrm{RT} \log \gamma_1^{\alpha}/\gamma_1^{\beta} \qquad (3).$$

In the case of azeotropes we have $x_1^{\alpha} = x_1^{\beta} \neq 1$. Hence, eqn. (3) becomes

$$\mu_1^{o\beta}(\mathrm{T,P}) - \mu_1^{o\alpha}(\mathrm{T,P}) = \mathrm{RT} \log \gamma_1^{\alpha}/\gamma_1^{\beta} \quad \cdots\cdots\cdots (4),$$

where $\mathrm{T} = \mathrm{T}_a$ i. e. the boiling point of the azeotrope at pressure P.

We shall make an assumption here by setting

$$\log \gamma_1^{\beta} \lesseqgtr \log \gamma_1^{\alpha}$$

It is a property of gaseous state that $\lim_{\mathrm{P}=0} \gamma_1^{\beta} = 1$, and the above approximation can be justified easily for low pressures of the order of 1 at. This approximation never implies, however, that the individual pure vapours behave ideally(*), but it is equivalent to neglecting the non-ideality of the mixed vapours as a

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(*) This point has not been made clear in the treatments of azeotropes by previous workers.

mixture compared to that of the liquid solution phase if the former is not highly compressed. The same approximation has been made also by other workers [15], [16] which does not introduce a serious uncertainty as long as the treatment is not extended to higher pressures. Hence, omitting the superscript α on γ_1 eqn. (4) becomes

$$\mu_1^{o\beta}(T_a, P) - \mu_1^{o\alpha}(T_a, P) = RT_a \log \gamma_1 \cdots\cdots\cdots \quad (4').$$

The left hand side of this equation is the free energy of vaporization of pure component (1) at temperature T_a and pressure P, while the right hand side is the differential non-ideal free energy of dilution of the solution with this component. Hence

$$L_1/T_1(T_1 - T_a) + \int_{T_1}^{T_a} \Delta C_{p1}\, dT - T_a \int_{T_1}^{T_a} \Delta C_{p1}\, d\log T = \Delta\mu_1^n \qquad (5)$$

where L_1 is the latent heat of vaporization of pure (1) at its boiling point T_1 at pressure P, and $\Delta C_{p1} = C_{p1}^{\beta} - C_{p1}^{\alpha}$. The sum of the two integrals in eqn. (5) is usually negligible. Then this equation reduces to

$$L_1/T_1(T_1 - T_a) = \Delta\mu_1^n \cdots\cdots\cdots\cdots\cdots \quad (5').$$

Similarly, for component (2) we have

$$L_2/T_2(T_2 - T_a) = \Delta\mu_2^n \cdots\cdots\cdots\cdots\cdots \quad (5'').$$

Here $\Delta\mu_1^n$ and $\Delta\mu_2^n$ are the differential non-ideal free energies of dilution of components (1) and (2), respectively. Eqns. (5′) and (5″), which are identical with those derived by earlier workers [6], [7], [8], determine the azeotropic conditions if the functions $\Delta\mu_1^n(x, T)$ and $\Delta\mu_2^n(x, T)$ are experimentally or theoretically established. It appears from these equations that the azeotropy is a manifestation of the non-ideal behaviour of solutions.

It is interesting to note that eqn. (5) (or (5′) and (5″)) permits the calculation of the non-ideal free energies of dilution at the azeotropic conditions without any knowledge of the actual composition and the volumetric behaviour of the phases.

Let $T_1 \leq T_2$. It can be seen from eqns. (5′) and (5″) that if theory, but only from the heat of mixing in Guggenheim's treatment. None of the above authors considered, however, whether the empirical parameter K (i.e. α in Prigogine's eqn. 40.35), obtainable from the azeotropic data, were consistent with the thermal behaviour of these mixtures The systems chosen by Prigogine et'al can hardly conform to the assumption of ideal entropy of mixing, as admitted by the authors, since they contain highly polar molecules which very likely cause orientations or disorientations on mixing. Such a comparison would, therefore, fail to indicate the above mentioned consistency. Recently, Kuhn and Massini[8] reported similar results on five azeotropic hydrocarbon mixtures. They calculate K for these systems a) from the azeotropic data, b) from the heat of mixing, and c) from the London theory of dispersion forces. On the whole, all these calculations give different results. Their argument lies, however, within the assumption of the expression K x_2^2 for which it would be desirable to have some experimental confirmation.

Hence, the applicability of these theories in the prediction of azeotropic properties is not warranted by these formal agreements. However, these agreements are significant in view of a recent conception[13] of the constant K. This point will be discussed in Section 3.

These theories have been less successful in application to the shift of azeotropic equilibrium with pressure. Carlson and Colburn[4] applied the general Van Laar[9], [10] equation to the shift of azeotropic equilibrium of the system ethyl acetate - EtOH using empirical parameters. However, the agreement was poor. Later, the theory of strictly regular solutions due to Guggenheim[12] was applied, in its «zeroth» approximation, to the same problem with the systems ethyl acetate - EtOH and HCl - H_2O by Coulson and Herington[7]. Although the former system satisfies the expression K x_2^2 well, they could not obtain any better agreement either. Here again a comparison between the parameters (A and B calculated by Carlson and Colburn, and W_{ab} in Coulson and Herington's paper) and the thermal data is lacking. This comparison would show that these systems exhibited large non-ideal entropies of mixing. Apparently, this is the reason for the discrepancy between the calculations of these authors and the azeotropic data observed.

Going back to eqn. (4′), we have

and similarly,
$$\left.\begin{aligned}\Delta\mu_1^o(\mathrm{T},\mathrm{P}) &= \Delta\mu_1^n(x_2,\mathrm{T},\mathrm{P})\\ \Delta\mu_2^o(\mathrm{T},\mathrm{P}) &= \Delta\mu_2^n(x_2,\mathrm{T},\mathrm{P})\end{aligned}\right\} \cdots\cdots\cdots\cdots \quad (9),$$

where $\Delta\mu_1^o$ and $\Delta\mu_2^o$ are the free energies of vaporization of pure (1) and (2), respectively. $\Delta\mu^n$ *'s* have been already defined. Eqns. (9) determine the azeotropic conditions. By eliminating one of the three variables (x, T, P) in eqns. (9), in principle, we obtain

$$\begin{aligned}x_2 &= x_2(\mathrm{T})\\ x_2 &= x_2(\mathrm{P})\\ \mathrm{P} &= \mathrm{P}(\mathrm{T})\end{aligned}$$

We shall, however, first work out the derivatives of these functions. Differentiating eqns. (9) we obtain

$$\left.\begin{aligned}\frac{\partial\Delta\mu_1^o}{\partial \mathrm{T}}d\mathrm{T}+\frac{\partial\Delta\mu_1^o}{\partial \mathrm{P}}d\mathrm{P} &= \frac{\partial\Delta\mu_1^n}{\partial x_2}dx_2+\frac{\partial\Delta\mu_1^n}{\partial \mathrm{T}}d\mathrm{T}+\frac{\partial\Delta\mu_1^n}{\partial \mathrm{P}}d\mathrm{P}\\ \frac{\partial\Delta\mu_2^o}{\partial \mathrm{T}}d\mathrm{T}+\frac{\partial\Delta\mu_2^o}{\partial \mathrm{P}}d\mathrm{P} &= \frac{\partial\Delta\mu_2^n}{\partial x_2}dx_2+\frac{\partial\Delta\mu_2^n}{\partial \mathrm{T}}d\mathrm{T}+\frac{\partial\Delta\mu_2^n}{\partial \mathrm{P}}d\mathrm{P}\end{aligned}\right\} \quad (10).$$

Now, eliminating dP, dT and dx_2 in (10) successively

$$\frac{dx_2}{d\mathrm{T}}=\frac{\left(\frac{\partial\Delta\mu_1^o}{\partial \mathrm{P}}-\frac{\partial\Delta\mu_1^n}{\partial \mathrm{P}}\right)\left(\frac{\partial\Delta\mu_2^o}{\partial \mathrm{T}}-\frac{\partial\Delta\mu_2^n}{\partial \mathrm{T}}\right)-\left(\frac{\partial\Delta\mu_2^o}{\partial \mathrm{P}}-\frac{\partial\Delta\mu_2^n}{\partial \mathrm{P}}\right)\left(\frac{\partial\Delta\mu_1^o}{\partial \mathrm{T}}-\frac{\partial\Delta\mu_1^n}{\partial \mathrm{T}}\right)}{\left(\frac{\partial\Delta\mu_1^o}{\partial \mathrm{P}}-\frac{\partial\Delta\mu_1^n}{\partial \mathrm{P}}\right)\frac{\partial\Delta\mu_2^n}{\partial x_2}-\left(\frac{\partial\Delta\mu_2^o}{\partial \mathrm{P}}-\frac{\partial\Delta\mu_2^n}{\partial \mathrm{P}}\right)\frac{\partial\Delta\mu_1^n}{\partial x_2}} \quad (11,a)$$

$$\frac{dx_2}{d\mathrm{P}}=\frac{\text{Numerator of (11, a)}}{\left(\frac{\partial\Delta\mu_2^o}{\partial \mathrm{T}}-\frac{\partial\Delta\mu_2^n}{\partial \mathrm{T}}\right)\frac{\partial\Delta\mu_1^n}{\partial x_2}-\left(\frac{\partial\Delta\mu_1^o}{\partial \mathrm{T}}-\frac{\partial\Delta\mu_1^n}{\partial \mathrm{T}}\right)\frac{\partial\Delta\mu_2^n}{\partial x_2}} \quad (11,b)$$

$$\frac{d\mathrm{P}}{d\mathrm{T}}=\frac{\text{Denominator of (11,b)}}{\text{Denominator of (11,a)}} \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (11,c).$$

It will be noticed that $\partial\Delta\mu_1^o/\partial\mathrm{P}$ and $\partial\Delta\mu_2^o/\partial\mathrm{P}$ are the volume changes on vaporization of pure liquids (1) and (2); $\partial\Delta\mu_1^n/\partial\mathrm{P}$ and $\partial\Delta\mu_2^n/\partial\mathrm{P}$ are the differential volume changes on dilution in the liquid phase; $-\partial\Delta\mu_1^o/\partial T = \Delta S_1^o$ and $-\partial\Delta\mu_2^o/\partial T = \Delta S_2^o$ i. e. the entropies of vaporization of pure (1) and(2); $-\partial\Delta\mu_1^n/\partial T = \Delta\bar{S}_1^n$ and $-\partial\Delta\mu_2^n/\partial T = \Delta\bar{S}_2^n$ i.e. the differential non-ideal entropies of dilution at the azeotropic conditions of the components (1) and (2), respectively. Here, we shall make two easily justifiable approximations, viz.

(i) The volume of the liquid phase is negligible compared to that of the vapour phase.

(ii) The molar volumes of pure vapours, at the same temperature and pressure, are identical. In other words, both vapours have a common gas imperfection coefficient β defined by

$$V_1 = V_2 = RT/P + \beta \,.$$

This assumption cannot be far from reality and it is certainly much safer than neglecting β's all together.

Hence, eqns. (11, a), (11, b) and (11, c) reduce to

$$\frac{dx_2}{dT} = \frac{\left(\Delta S_2^o - \Delta S_1^o\right) - \left(\Delta\bar{S}_2^n - \Delta\bar{S}_1^n\right)}{1/x_2\,\partial\Delta\mu_1^n/\partial x_2} \quad \dots\dots\dots\dots\dots\dots \quad (12),$$

$$\frac{dx_2}{dP} = (RT/P + \beta)\,\frac{\left(\Delta S_2^o - \Delta S_1^o\right) - \left(\Delta\bar{S}_2^n - \Delta\bar{S}_1^n\right)}{1/x_2\,\partial\Delta\mu_1^n/\partial x_2\left[\left(\Delta S_1^o - \Delta\bar{S}_1^n\right)x_1 + \left(\Delta S_2^o - \Delta\bar{S}_2^n\right)x_2\right]} \quad (13)$$

$$\text{and } \frac{dP}{dT} = \frac{\left(\Delta S_1^o - \Delta\bar{S}_1^n\right)x_1 + \left(\Delta S_2^o - \Delta\bar{S}_2^n\right)x_2}{RT/P + \beta} \quad \dots\dots\dots\dots\dots \quad (14),$$

respectively. Noting that

$$T\left[\left(\Delta S_1^o - \Delta\bar{S}_1^n\right)x_1 + \left(\Delta S_2^o - \Delta\bar{S}_2^n\right)x_2\right] = x_1 L_1^a + x_2 L_2^a - \Delta H_x$$

where L_1^a and L_2^a are the latent heats of vaporization of component (1) and (2) and ΔH_x is the heat of mixing per mole of mixture at the azeotropic conditions, eqns. (13) and (14) become

$$\frac{dx_2}{dP} = (RT^2/P + \beta T)\,\frac{\left(\Delta S_2^o - \Delta S_1^o\right) - \left(\Delta\bar{S}_2^n - \Delta\bar{S}_1^n\right)}{1/x_2\,\partial\Delta\mu_1^n/\partial x_2\left(x_1 L_1^a + x_2 L_2^o - \Delta H_x\right)} \quad (13')$$

and

$$\frac{d\log P}{d\,1/T} = -\frac{x_1 L_1^a + x_2 L_2^a - \Delta H_x}{R + \beta P/T} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (14'),$$

respectively. It will be seen from eqn. (13′) that for a regular solution $\left(\text{i. e. } \Delta\bar{S}_1^n = \Delta\bar{S}_2^n = 0\right)$, if $\Delta S_1^o = \Delta S_2^o$, the composition of the azeotrope is not affected by the change of pressure. The quantity $x_1 L_1^a + x_2 L_2^a - \Delta H_x$ in eqn. (14′) is the heat of vaporization of one mole of azeotrope. Thence, this is formally a Clausius-Clapeyron equation and can be used to calculate the heat of mixing ΔH_x from P-T-x data if L_1^a, L_2^a and β are known.

3. Heat of Mixing and Azeotropy in Polar Systems and the Significance of Agreement with the Quadratic Free Energy Expression

In this section we shall evaluate the non-ideal free energies of formation of certain azeotropes of polar liquids at atmospheric pressure from the azeotropic data and compare them with the heats of formation determined calorimetrically.

From eqns. (5′) and (5″) we obtain the non-ideal free energy of formation of one mole of azeotrope

$$\Delta G_a^n = x_1 L_1/T_1 (T_1 - T_a) + x_2 L_2/T_2 (T_2 - T_a) \qquad (15)$$

where x_1 and x_2 refer to the azeotropic composition. ΔG_a^n was calculated from eqn. (15) for seven azeotropic polar systems on which heat of mixing data were available in "International Critical Tables„. The results of these calculations are given in Table I, together with the data used.

Table I.

Heats, Non-ideal Free Energies and Entropies of Formation of Azeotropes Containing Polar Liquids at Normal Pressure

					Cal/Mol/Deg.				Cal/Mol.		
No.	Comp. (1)	Comp. (2)	T_1 C°	T_2 °C	L_1/T_1	L_2/T_2	T_a °C	x_2	ΔG_a^n	ΔH_a	$T_a \Delta S_a^n$
1	MeOH	Benzene	64.7	80.2	24.95	20.86	58.34	0.386	273	113	—160
2	CS_2	Acetone	46.25	56.25	20.04	21.98	39.25	0.39	231	319	88
3	Acetone	$CHCl_3$	56.25	61.2	21.98	21.03	64.5	0.655	—108	—450	—342
4	$CHCl_3$	MeOH	61.2	64.7	21.03	24.95	53.5	0.35	203	10	—193
5	$CHCl_3$	EtOH	61.2	78.3	21.03	26.79	59.3	0.16	115	110	—5
6	Acetone	MeOH	56.4	64.7	21.98	24.95	55.7	0.20	57	110	53
7	Ethyl acetate	EtOH	77.15	78.30	21.69	26.32	71.81	0.461	141	324	183

The data on *x's*, L*'s* and T*'s* were taken also from I. C. T. except for the system No. 7. For this system the boiling points of components and the azeotropic data were taken from Horsley's [17] Tables of Azeotropes and Non-azeotropes, L_2 (9250 Cal/Mol.) from the work of Fiock et'al [18], and L_1 (7600 Cal/Mol.) from Young's data given in "Landolt-Börnstein Tabellen„(1935). The heats of formation ΔH_a which are tabulated in Table I were obtained by interpolating the data on heats of mixing in I.C.T. to azeotropic compositions. It will be seen from this table that there are significant differences between the heats and non-ideal free energies of formation (or mixing) leading to very appreciable non-ideal entropies of mixing ΔS_a^n which are also given in Table I, except in the case of system No 5. The apparent agreement between ΔG_a^n and ΔH_a for this system is quite coincidental, since Scatchard et'al [15] have shown that the system is by no means regular and that ΔS_x^n takes positive and negative values depending upon the composition. At a particular composition ΔS_x^n becomes zero. Now, the azeotropic composition happens to be in the neighbourhood of this point.

Since, according to eqns. (5′) and (5″), the non-ideal free energy determines the azeotropic properties of mixtures, it is, therefore, clear that these properties cannot be predicted from the heat of mixing alone, indeed by any theory which neglects the non-ideal entropy.

However, as previous workers point out (see Sec. 1), some of these azeotropes do satisfy the non-ideal free energy expressions of the form

$$\left.\begin{aligned} \Delta\mu_1^n &= Kx_2^2 \\ \Delta\mu_2^n &= Kx_1^2 \end{aligned}\right\} \quad \dots\dots\dots\dots\dots\dots \quad (16)$$

which, as mentioned earlier, are common results of various such theories. This agreement is also shown here in Fig. 1. At the azeotropic conditions, from eqns. (5′), (5″) and (16) we obtain the relationship

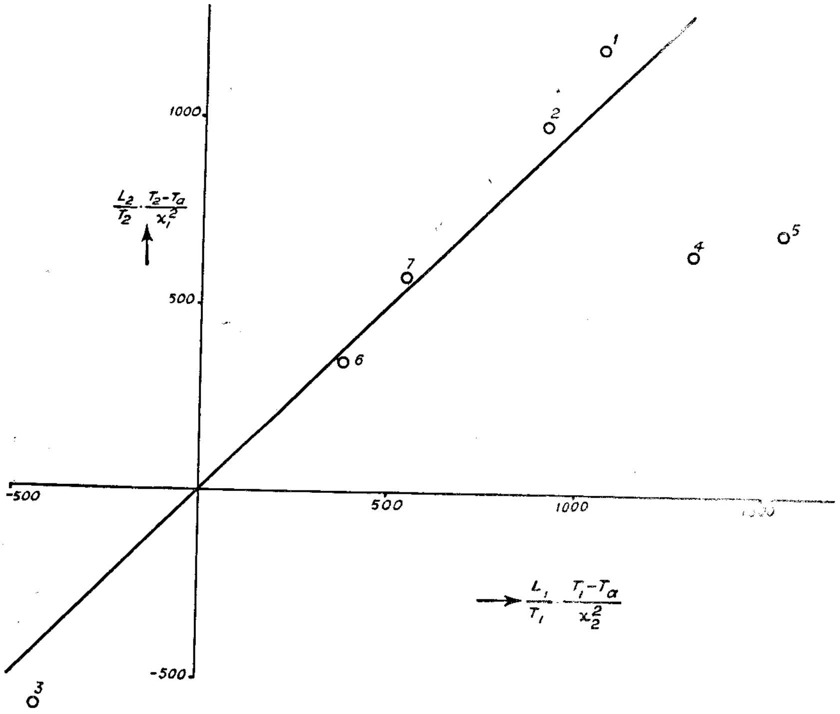

Fig. 1

$$\frac{L_1}{T_1}\,\frac{T_1-T_a}{x_2^2} = \frac{L_2}{T_2}\,\frac{T_2-T_a}{x_1^2} = K \quad \dots\dots\dots\dots \quad (16').$$

In Fig. 1, where the straight line drawn in represents the eqn. (16′), the left hand side of this equation is plotted egainst the right hand side for the azeotropes listed in Table I (*). It will be seen that the systems No. 1, 2, 3, 6 and 7 agree well with eqns. (16), while Nos. 4 and 5 do not.

It can be concluded, therefore, that although the majority of azeotropes satisfy the eqns. (16), the actual theories behind these expressions, which assume the ideal entropy of mixing, cannot describe the thermodynamic and azeotropic behaviour of such systems, and that Prigogine et'al' [6] and Coulson et'al' [7] results with particular reference to Guggenheim's [12] approximate theory of strictly regular solutions are unjustifiable (see Sec. 1). Nevertheless, the agreement in most cases with (16) bears an interesting significance as regards to Guggenheim's [13] generalized theory in its «zeroth» approximation. This treatment leads to eqns. (16) with the consideration that the constant K is not an energy but a free energy term, and given by

$$K = zN(w - T\varepsilon) \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (17)$$

where z is the co-cordination number of packing in the quasi — solid lattice, N is the Avogadro number, T is the absolute temperature, w is the energy of formation of a single contact between two unlike molecules on destroying the contacts between the molecules of the same species, and ε is the corresponding entropy of formation of such a contact; and implies the assumption of random mixing. The parameters w and ε are independent of the composition of the mixture. Now, the above mentioned observations on azeotropes can be reconciled by this treatment since it takes care of the non-ideal entropy. Namely, from eqns. (16) and (17) we obtain

$$\left.\begin{aligned} \Delta\mu_1^n &= zN(w - T\varepsilon)\,x_2^2 \\ \Delta\mu_2^n &= zN(w - T\varepsilon)\,x_1^2 \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots\cdots \quad (18),$$

$$\left.\begin{aligned} \Delta\overline{H}_1 &= zNw\,x_2^2 \\ \Delta\overline{H}_2 &= zNw\,x_1^2 \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (19),$$

and

(*) This type of a plot is more advantageous than that used by Prigogine [6], since the co-ordinates give directly the constant K, and hence it gives the opportunity of comparing the deviations from ideality of the systems concerned. The farther the points from the origin the greater is the deviation.

$$\left.\begin{array}{l}\Delta\bar{S}_1^n = zN\varepsilon x_2^2 \\ \Delta\bar{S}_2^n = zN\varepsilon x_1^2\end{array}\right\} \quad \cdots\cdots\cdots\cdots \quad (20).$$

$\Delta\bar{H}_1, \Delta\bar{H}_2$ and $\Delta\bar{S}_1^n$, $\Delta\bar{S}_2^n$ are the differential heats and non-ideal entropies of dilution of the corresponding components.

In Guggenheim's [13] more exact treatment, which takes into account also the effect of non-random mixing ("first„ approximation), however, the quadratic form of these equations with respect to the molar fractions does not exist. The greater the absolute value of $|w - T\varepsilon|$ the greater is the deviation from the quadratic form. Yet the expressions are still symmetrical with respect to the molar fractions. Therefore the observed experimental agreement with eqns. (18) simply means that the effect of non-random mixing is negligible and that the non-ideal entropies of mixing are arising mainly from ε in such polar systems. The existence of a ε would mean that the changes are taking place in the rotational and vibrational partition functions of the molecules due to orientations or in their free volumes, on mixing. Such factors, especially orientation, is very likely to be effective in mixtures containing polar molecules as those listed in Table I.

The deviations from eqns. (18) observed in the case of systems No. 4 and 5 cannot be explained, however, by the effect of non-random mixing on the basis of this theory. As the points representing Nos. 1, 2 and 4, 5 in Fig. 1 are about the same distances from the origin (see foot note on p: 13), according to eqn. (17), they correspond approximately to the same magnitudes of $|w - T\varepsilon|$. Since we found that the effect of non—random mixing is negligible in Nos. 1 and 2, then it would also be so in Nos. 4 and 5 It is not surprising to find that the latter systems totally reject the theory since it has been shown by other detailed experimental investigations [15], [19] that these systems (i. e. $CHCl_3 - EtOH$ and $CHCl_3 - MeOH$) exhibit rather asymmetrical excess thermodynamic functions with respect to the molar fractions to such an extent that the heat and the non—ideal entropy of mixing even change signs as the composition varies [15]. The interpretation of such behaviour would require the parameters w and ε to be dependent of the composition which, as quoted elsewhere [20], appears to be a serious deficiency of the up-to-date theories.

6. Prediction of the Shift of Azeotropic Equilibrium

In this section Guggenheim's [13] generalized theory, in its «zeroth» approximation, which has been outlined in Section 3, will be applied to the shift of azeotropic equilibrium formulated in Section 2, b. The treatment will be confined to the relationship between the azeotropic composition and the temperature, i. e. eqn. (12).

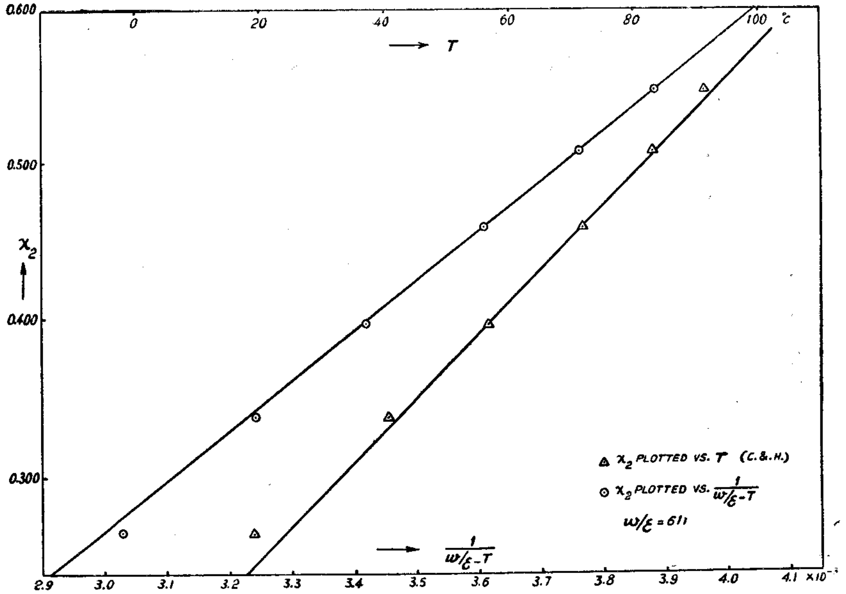

Fig. 2

Thus applying eqns. (18) and (20) to (12) we have

$$dx_2/dT = \frac{\Delta S^o_2 - \Delta S^o_1 + zN\varepsilon\,(2x_2 - 1)}{2zN\,(w - T\varepsilon)} \cdots\cdots\cdots (21).$$

If $\varepsilon = 0$, which corresponds to regular solutions, eqn. (21) becomes identical with that derived by Coulson et'al (loc. cit.). It appears from(21)that in that case x_2 would be a linear function of T. Expecting to obtain this linearity, Coulson et'al plotted the azeotropic composition in molar fraction against the azeotropic temperature for the system ethyl acetate-EtOH using Merriman's [21] data observed at various pressures. This plot is reproduced in Fig. 2. It is clear from the trend of the points that there is a significant deviation from linearity. They have also integrated (21) with $\varepsilon = 0$ and arrived at an expression of the form

$$x_2 = x_2^o + \frac{\Delta S_2^o - \Delta S_1^o}{2 W_{ab}} (T - T^o) \quad \cdots\cdots\cdots\cdots \quad (22)$$

where x_2^o is the composition at the temperature T^o at atmospheric pressure, W_{ab} is zNw (or K in (16′)) in our notation. Then obtaining W_{ab} by (16′) at atmospheric pressure, they calculated x_2 at other temperatures from (22). They have obtained ΔS_2^o and ΔS_1^o from the vapour pressures of pure components. Their results are given in Table II together with Merriman's experimental data. It will be seen that the agreement is poor. Besides, the parameter W_{ab} (590 Cal.) calculable by (22) from the average slope of the claimed straight line in their plot (Fig. 2) is inconsistent with that (1307 Cal.) obtained from heat of mixing (Table I).

Table II.

Variation of Azeotropic Composition with Temperature of the System Ethyl acetate — EtOH

	x_2 = Molar fraction of EtOH				
T °C	Exptl.	Calc. by C. &. H.	Dev. from exptl.	Calc. from eqn. (47)	Dev. from Exptl.
18.7	0.266	0.294	.028	0.276	.010
40.5	0.340	0.361	.021	0.344	.004
56.3	0.399	0.404	.005	0.400	.001
71.8	0.461	(0.461)	.000	(0.461)	.000
83.1	0.510	0.500	−.010	0.510	.000
91.4	0.549	0.520	−.029	0.550	.001
			Mean ±.015		Mean .003

These disagreements are not at all surprising since we find that this system is by no means regular (see Table I). On the other hand, it will be seen from Fig. 1 that the system obeys the relationship (16′). Thence, the eqns. (18) should be applicable with a reasonable accuracy provided that ε is not neglected.

It can be shown from the assumptions introduced in Section 2, b that the difference $\Delta S^o_2 - \Delta S^o_1$ is independent of pressure. Then we have

$$\Delta S^o_2 - \Delta S^o_1 = L_2/T_2 - L_1/T_1 + \int_{T_2}^{T} \Delta C_{p2}\, d\log T - \int_{T_1}^{T} \Delta C_{p1}\, d\log T$$

or neglecting the temperature dependence of ΔC_p's

$$\Delta S^o_2 - \Delta S^o_1 = L_2/T_2 - L_1/T_1 - \Delta C_{p1} \log T_2/T_1 + (\Delta C_{p2} - \Delta C_{p1}) \log T/T_2 \quad \ldots\ldots (23).$$

In order to solve the differential equation (21) we shall neglect the last term in (23) to make $\Delta S^o_2 - \Delta S^o_1$ independent of T. In other words we shall assume $\Delta C_{p2} = \Delta C_{p1}$. Since

$$\frac{d\left(\Delta S^o_2 - \Delta S^o_1\right)}{dT} = \frac{\Delta C_{p2} - \Delta C_{p1}}{T}$$

the higher the temperature and the smaller the difference $\Delta C_{p2} - \Delta C_{p1}$ the more correct is the following treatment. Thus integrating (21) we have

$$x_2 = \frac{A}{w/\varepsilon - T} + B \quad \ldots\ldots\ldots\ldots\ldots\ldots (24)$$

where A is an integration constant which must be determined empirically from the azeotropic data at a single pressure, and B is given by

$$B = -\frac{L_2/T_2 - L_1/T_1 - \Delta C_p \log T_2/T_1}{zN\varepsilon} + 1/2 \quad \cdots\cdots (25).$$

It must be noted that eqn. (24) predicts the curvature exhibited by the points in Coulson et'al' plot (Fig. 2). Since eqns. (19) and (20) lead to

$$\Delta H_x = zNw\, x_1 x_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (26),$$

$$\Delta S^n_x = zN\varepsilon\, x_1 x_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (27),$$

at any composition we have

$$w/\varepsilon = \Delta H_x / \Delta S^n_x \quad \ldots\ldots\ldots\ldots\ldots\ldots (28).$$

Using the values of ΔH_x and ΔS^n_x at the azeotropic composition at atmospheric pressure given in Table I we found from (28)

$w/\varepsilon = 611$ °K for the system ethyl acetate-EtOH. Then the experimental values of x_2 (i. e. molar fraction of EtOH in the azeotrope) were plotted against $\frac{1}{w/\varepsilon - T}$ also in Fig. 2, which according to (24) should fall in a straight line. It will be seen from this figure that the agreement is perfect at four points at higher temperatures and on the whole is better than that obtained by Coulson and Herington. As the temperature decreases the points tend to divert slightly from the straight line. It can be argued that this departure at lower temperatures is possibly due to the neglected term in (23). From the straight line so defined we find empirically that $A = 295$ °K and $B = -0.648$. In other words, the expression

$$x_2 = 295/(611 - T) - 0.648 \quad \cdots\cdots\cdots\cdots \quad (29)$$

describes the azeotropic behaviour of the present system perfectly well at temperatures higher than ca. 50°C.

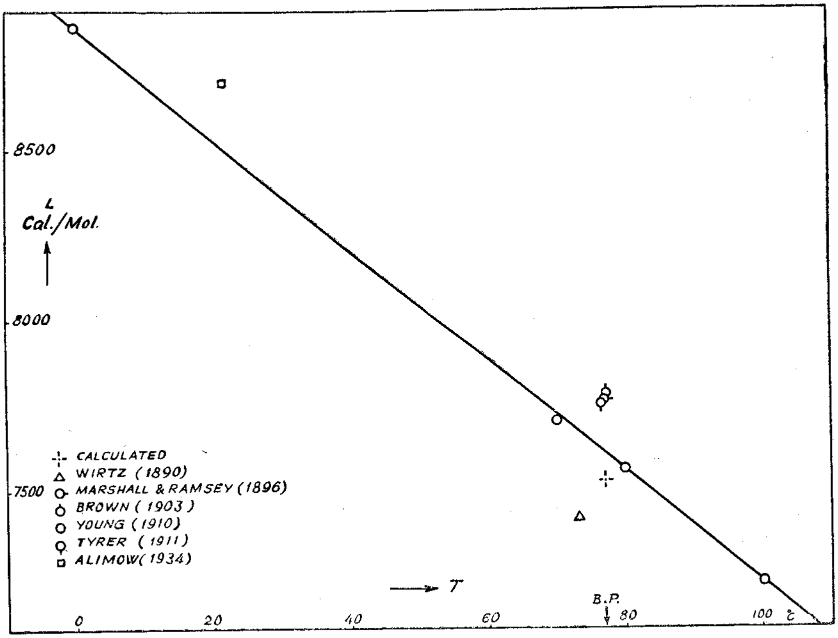

Fig. 3

Latent Heat of Vaporization of Ethyl Acetate at Various Temperatures

Now we must see how far this empirical B agrees with its theoretical value given by (25). $zN\varepsilon$ can be obtained from (27) and Table I, and found to be 2.14 Cal./Mol./deg. As can be seen from (25), B depends rather critically on the accuracy of L_2 and L_1. Although the data on the latent heat of vaporization of EtOH given by Fiock et'al [18] are very reliable, unfortunately the data in literature on that of ethyl acetate are somewhat discordant. This is shown in Fig. 3. We, therefore, worked out L_1 from the empirical B using Fiock et'al' data on L_2 (9250 Cal./Mol.) and ΔC_p (20.5 Cal /Mol./deg.) for EtOH to see whether it agrees with the direct calorimetric data within the uncertainty just mentioned. Thus we obtained $L_1 = 7520$ Cal./Mol. It will be seen from Fig. 3 that this figure does not disagree significantly with the data in literature. Now, assuming that this figure is correct, we could calculate B back, and evaluate the constant A from the azeotropic data at a single-say atmospheric - pressure. In this way we should, of course, obtain - now theoretically - the very same equation (29) from which we can calculate x_2 's at other azeotropic temperatures. The results of these calculations are given in Table II. Comparing these and Coulson et'al' results with the experimental data it appears that the present treatment provides a better prediction.

We can conclude, therefore, that the present system satisfies the non-ideal free energy expression (18) well with the parameters w and ε independent of x, T and P. The numerical values of these parameters are given by $zNw = 1307$ Cal./Mol. and $zN\varepsilon = 2.14$ Cal./Mol./deg.

5. Summary and Conclusion

The use of the chemical potentials facilitates the establishment of a rigorous thermodynamic treatment of azeotropes. Combining with various statistical mechanical formulae, the thermodynamic relationships so obtained were applied to actual azeotropes and the following conclusions were reached.

The azeotropic behaviour of mixtures containing polar liquids reveals that such systems are invariably irregular, yet the majority of them satisfy a quadratic expression for the non-ideal free energy of mixing. Therefore, the particular reference made by the previous workers to the theories which neglect the entropy deviation from the ideal for the explanation of the latter observation is spurious. This behaviour can be explained by the "zeroth„ approximation of Guggenheim's generalized theory. The most probable source of the negative and positive non-ideal entropies observed is orientation or disorientation of the particles on mixing. The entropy deviation from the ideal due to non-random mixing is neglible compared to that arising from this effect. It appears, therefore, that the "zeroth„ approximation of the generalized theory should be applicable to such systems even more satisfactorily than the «first» approximation of Guggenheim's earlier theory.

The system ethyl acetate - EtOH satisfies the quadratic expression for the non-ideal free energy. But it is irregular. The «zeroth» approximation of Guggenheim's generalized theory is found applicable to this system in confirmation of the statement made above. On the basis of this treatment the shift of azeotropic equilibrium can be predicted satisfactorily from the azeotropic data at a single pressure and the heat of mixing determined at one composition. Therefore the above mentioned theory appears to be promising in the field of prediction of the shift of azeotropic equilibrium and in extrapolation of the thermodynamic functions of non-ideal mixtures observed at a single point provided that they obey the quadratic expression for the non-ideal free energy of mixing. The origin of the unsatisfactory result of Coulson and Herington's approach to the same problem lies in neglecting the temperature dependence of their parameter W_{ab}. The deficiency of the formulae of regular solutions may not emerge in problems such as those dealt with by Herzfeld et'al, Kireev and Prigogine et'al as long as they do not necessitate a derivation of this parameter with respect to temperature as in the case of the shift of azeotropic equilibrium tackled by Coulson et'al and Carlson et'al.

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