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CORRELATION AND PREDICTION OF ISOBARIC VAPOR-LIQUID EQUILIBRIUM

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LIST OF SYMBOLS

a = activity of a component

f = fugacity of a component

G = Gibbs' free energy

n = mols of a component in liquid

P = vapor pressure of a pure liquid

R = gas constant

t = temperature, degrees centigrade

T = temperature, degrees Kelvin

V = molal volume of a component

x = mol fraction of a component in liquid

y = mol fraction of a component in vapor

γ = activity coefficient of a component

λ = molal latent heat of vaporization

π = total pressure

INTRODUCTION

A prime factor in the design of distillation columns is a knowledge of the equilibrium existing between the liquid phase and the vapor phase usually at constant pressure. If one is lucky enough, recourse to the literature will provide him with the necessary data. However, the number of systems for which there is a lack of complete data far outweigh the number which have been subjected to a complete analysis. In any event the attainment of data experimentally is a difficult task, and it is rare indeed when two independent researchers arrive at the same results for a given system. The Gibbs-Duhem equation, of course, provides a method for checking data, but it is stressed at this point that there are three variables associated with isobaric vapor-liquid equilibrium--vapor composition, liquid composition, and the temperature of the system; therefore, since the Duhem equation is the link connecting the variables, an error in the data will be revealed should there be any. But what is incorrect? It is at this point that the researcher must decide which measurement was subject to the greatest error and smooth his data accordingly, redetermine the data, submit the results as obtained with an explanation for inconsistencies, or smooth the data by some semi-empirical relationship.

It is the purpose of this thesis to advance new methods for the correlation and prediction of isobaric vapor-liquid equilibrium data, and to demonstrate theoretically and to prove experimentally that "inconsistencies" in data at low concentrations are due only to the inadequacy of empirical integrations of the Duhem equation.

THEORY

Gibbs defined free energy by

$$dG = -SdT + Vd\pi + \sum \mu_i dn_i \tag{1}$$

where

G = Gibbs free energy
S = Entropy of system
V = Volume of system

μ_i = Chemical potential of component i

T = Absolute temperature
π = Total pressure on system
n_i = Mols of component i

At equilibrium $dG = 0$, and at constant temperature and pressure, therefore,

$$\sum \mu_i dn_i = 0 \tag{2}$$

Since for a closed system

$$\sum dn_i = 0 \tag{3}$$

$$\mu_1' = \mu_1'' = \mu_1''' = \cdots$$

$$\mu_2' = \mu_2'' = \mu_2''' = \cdots \tag{4}$$

where the primes refer to the different phases.

Lewis defined fugacity by

$$d\mu_i = RTd\ln f_i \tag{5}$$

where

R = Gas constant

f_i = Fugacity of component i

Also, at constant temperature and pressure

$$\sum n_i d\mu_i = 0 \tag{6}$$

For one mol of solution

$$\sum x_i d\ln f_i = 0 \qquad (7)$$

where

x_i = Mol fraction of component i

Activity is defined by

$$a_i = \frac{f_i}{f_i^{o}} \qquad (8)$$

where

a_i = Activity of component i

f_i^{o} = Fugacity of component i in a standard state

Therefore,

$$\sum x_i d\ln a_i = 0 \qquad (9)$$

For non-ideal liquid solutions it is best to utilize an activity coefficient defined by

$$\gamma_i = \frac{a_i}{x_i} \qquad (10)$$

where

γ_i = Activity coefficient of component i

Substituting (10) in (9) yields

$$\sum x_i d\ln \gamma_i = 0 \qquad (11)$$

Equation (11) is the most useful form of the Gibbs - Duhem equation.

Substituting (8) in (10)

$$\gamma_i = \frac{f_i}{f_i^{o} x_i} \qquad (12)$$

Assuming the fugacity in the standard state to be equal to the vapor pressure of the pure liquid, and assuming an ideal gas phase

$$\gamma_i = \frac{y_i \pi}{P_i x_i} \qquad (13)$$

where

y_i = Mol fraction of component i in the vapor

x_i = Mol fraction of component i in the liquid

π = Total pressure on the system

P_i = Vapor pressure of pure component i at the temperature of the solution

The excess free energy of a system, G^E, as designated by Scatchard and Hamer is defined by

$$G^E = RT \sum n_i \ln \gamma_i \qquad (14)$$

where

n_i = Mols of component i in the liquid

also

$$\frac{\partial G^E}{\partial n_i} = RT \ln \gamma_i \qquad (15)$$

Equations (11), (13), (14), and (15) are the basis for practically all theoretical and semi-empirical derivations for the correlation and prediction of vapor-liquid equilibrium.

Theoretical Correlation of Data for Binary Systems

If plots of $\ln\gamma_1$ and $\ln\gamma_2$ are made versus x_1, then from (11), $\frac{-x_1}{x_2} = \frac{d\ln\gamma_2/dx_1}{d\ln\gamma_1/dx_1}$. This is one means of checking binary data but is not too convenient.

If (13) is substituted in (11) there is obtained

$$\left(\frac{x_1}{y_1} - \frac{x_2}{y_2}\right)\frac{dy_1}{dx_1} = x_1\frac{d\ln P_1}{dx_1} + x_2\frac{d\ln P_2}{dx_1} \qquad (16)$$

where the subscript (1) refers to component 1.

Equation (16) is valid if the heat of mixing of the liquid phase remains essentially constant and there exists an ideal gas phase.

Assuming the volume of the liquid phase to be negligible and employing the Clausius-Clapeyron equation

$$\frac{d\ln P_i}{dT} = \frac{\lambda_i}{TV_iP_i} \qquad (17)$$

where

λ_i = Molal latent heat of vaporization of pure component i

V_i = Molal volume of component i in the vapor

equation (16) becomes

$$\left(\frac{x_1}{y_1} - \frac{x_2}{y_2}\right)\frac{dy_1}{dx_1} = \frac{1}{T}\left(\frac{\lambda_1 x_1}{P_1V_1} + \frac{\lambda_2 x_2}{P_2V_2}\right)\frac{dT}{dx_1} \qquad (18)$$

Redlich and Kister have designated the quantity $\frac{1}{T}\left(\frac{\lambda_1}{P_1V_1} + \frac{\lambda_2}{P_2V_2}\right)$ by $\frac{1}{s}$ and by solving (18) for x_1 obtained

$$x_1 = y_1\left(1 + \frac{y_2}{s}\frac{dT}{dy_1}\right) \qquad (19)$$

The limiting values of the variables* may be obtained in a slightly more elegant manner than that of Redlich and Kister. By employing l'Hospital's Rule as x_1 approaches zero in (18)

$$\left(\frac{dx_1}{dy_1} - 1\right)\frac{dy_1}{dx_1} = \frac{1}{s}\ \frac{dT}{dx_1}$$

Therefore,

$$\frac{dy_1}{dx_1} = 1 - \frac{1}{s}\ \frac{dT}{dx_1} \tag{20}$$

at $x_1 = 0$

and

$$\frac{dy_2}{dx_2} = 1 - \frac{1}{s}\ \frac{dT}{dx_2} \tag{21}$$

at $x_2 = 0$

The relative volatility, α, is defined by

$$\alpha = \frac{y_1 x_2}{y_2 x_1} \tag{22}$$

Therefore

$$\alpha = \frac{dy_1}{dx_1} = 1 - \frac{1}{s}\ \frac{dT}{dx_1} \tag{23}$$

at $x_1 = 0$

and

$$\alpha = \frac{dx_2}{dy_2} = \frac{1}{1 - \frac{1}{s}\ \frac{dT}{dx_2}} \tag{24}$$

at $x_2 = 0$

also,

$$\gamma_1 = \frac{\pi}{P_1}\ \frac{dy_1}{dx_1} = \frac{\pi}{P_1}\left(1 - \frac{1}{s}\ \frac{dT}{dx_1}\right) \tag{25}$$

at $x_1 = 0$

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*They are used in the smoothing procedure.

and

$$s = \frac{\pi}{P_2}\frac{dy_2}{dx_2} = \frac{\pi}{P_2}\left(1 - \frac{1}{s}\frac{dT}{dx_2}\right) \qquad (26)$$

at $x_2 = 0$

Redlich and Kister outline in detail the smoothing procedure which utilizes (19). As has been pointed out in the introduction, however, (19) involves essentially three variables and which of the data are to be smoothed is a moot point. It would be highly desirable to have two of the variables determined with a high degree of precision.

Other equations which the author considers to be of fundamental importance are obtained by differentiating (18) and in turn letting x_1 approach zero and x_2 approach zero, thus*

$$\frac{d^2y_1}{(dx_1)^2} = \frac{\frac{1}{s}\left[\frac{1}{T}\frac{d^2T}{dx_1{}^2} - \frac{1}{T^2}\left(\frac{dT}{dx_1}\right)^2\right] - \frac{dy_1}{dx_1}\left(1 - \frac{dy_1}{dx_1}\right)}{\frac{dx_1}{dy_1} - 1 - 1/2\,\frac{dy_1}{dx_1}} \qquad (27)$$

as $x_1 \rightarrow 0$

and

$$\frac{d^2y_2}{dx_2{}^2} = \frac{\frac{1}{s}\left[\frac{1}{T}\frac{d^2T}{dx_2{}^2} - \frac{1}{T^2}\left(\frac{dT}{dx_2}\right)^2\right] - \frac{dy_2}{dx_2}\left(1 - \frac{dy_2}{dx_2}\right)}{\frac{dx_2}{dy_2} - 1 - 1/2\,\frac{dy_2}{dx_2}} \qquad (28)$$

as $x_2 \longrightarrow 0$

For illustration purposes let it be supposed that component (1) has the lower boiling point, and that the system either produces a minimum azeotrope or that no azeotrope is formed. It is then clear that $\frac{dy_1}{dx_1}$ is

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*Since the derived equations are to be used only for qualitative deductions, s has been held constant.

greater than one as x_1 approaches zero. Therefore, the denominator of (27) must be less than zero, and the quantity $(dy_1/dx_1 - 1)dy_1/dx_1$ must be greater than zero. In the usual case d^2T/dx_1^2 is equal to or greater than zero so that the absolute value of $-(dT/dx_1)^2/s$ is less than the other quantities in the numerator and d^2y_1/dx_1^2 will be negative. However, it may happen that d^2T/dx_1^2 will be less than zero. In that event it is most probable that the numerator will be negative producing a positive value for d^2y_1/dx_1^2. When this occurs, the relative volatility and activity coefficient of component (1) will go through a maximum, possibly at an extremely small value of x_1. The rise to the maximum may be quite sharp and the algebraic solutions to the Duhem equation (presented later) cannot cope with the situation unless, of course, a prohibitive number of constants are employed. The same line of reasoning may be applied to maximum boiling mixtures.

Theoretical Correlation of Data for Multicomponent Systems

The work of Redlich and Kister may be extended to ternary systems by noting that

$$x_1\left(\frac{\partial \ln \gamma_1}{\partial y_1}\right)_{y_2} + x_2\left(\frac{\partial \ln \gamma_2}{\partial y_1}\right)_{y_2} + x_3\left(\frac{\partial \ln \gamma_3}{\partial y_1}\right)_{y_2} = 0 \tag{29}$$

and

$$x_1\left(\frac{\partial \ln \gamma_1}{\partial y_1}\right)_{y_3} + x_2\left(\frac{\partial \ln \gamma_2}{\partial y_1}\right)_{y_3} + x_3\left(\frac{\partial \ln \gamma_3}{\partial y_1}\right)_{y_3} = 0 \tag{30}$$

Equations (29) and (30) completely define any ternary system. Substituting (13) gives

$$\frac{x_1}{y_1} - \frac{x_3}{y_3} = \frac{1}{s}\left(\frac{\partial T}{\partial y_1}\right)_{y_2} \tag{31}$$

and

$$\frac{x_1}{y_1} - \frac{x_2}{y_2} = \frac{1}{s}\left(\frac{\partial T}{\partial y}\right)_{y_3} \tag{32}$$

where

$$\frac{1}{s} = \frac{1}{T}\left(\frac{\lambda_1}{P_1V_1} + \frac{\lambda_2}{P_2V_2} + \frac{\lambda_3}{P_3V_3}\right)$$

Solving (31) and (32)

$$x_1 = y_1\left[1 + \frac{y_3}{s}\left(\frac{\partial T}{\partial y_1}\right)_{y_2} + \frac{y_2}{s}\left(\frac{\partial T}{\partial y_1}\right)_{y_3}\right] \tag{33}$$

$$x_2 = y_2\left[1 + \frac{y_3}{s}\left(\frac{\partial T}{\partial y_1}\right)_{y_2} - \frac{1 - y_2}{s}\left(\frac{\partial T}{\partial y_1}\right)_{y_3}\right] \tag{34}$$

Thus, by plotting T against y_1, at constant values of y_2 and y_3 and evaluating the slopes of the curves at given vapor compositions the values of liquid composition should be satisfied by (33) and (34). The extension to higher order multicomponent systems would lead to an increasing number of equations. Thus, for a quaternary system three equations are necessary y_3 and y_4, y_3 and y_2, and y_2 and y_4 being held constant each time.

Semi-Empirical Equations for Binary Systems

There are many ways in which semi-empirical equations are derived in the literature. The author here presents a slightly different approach mainly because of its generality and ease of extension to multicomponent systems.

The excess free energy per mol must be zero when $x_1 = 0$ and when $x_2 = 0$. Therefore

$$T(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) = x_1 x_2 f_{1-2}(x_1) \qquad (35)$$

where $f_{1-2}(x_1)$ is some function of liquid composition.

Differentiating (35) and substituting (11)

$$T(\ln \gamma_1 - \ln \gamma_2) + x_1 x_2 f_{1-2}(x_1) \frac{d \ln T}{dx_1} = x_1 x_2 f'_{1-2}(x_1) + (x_2 - x_1) f_{1-2}(x_1) \qquad (36)$$

All other methods are based on (15) which assumes constant temperature and the term $x_1 x_2 f_{1-2}(x_1) \frac{d \ln T}{dx_1}$ does not appear in the final result. Although (11) was derived for conditions of constant temperature and pressure it is obvious that setting the left hand side of (16) equal to zero would be quite meaningless, and that if (35) is taken as the starting point for the subsequent derivations then (36) must remain as is. However, whether a system be isothermal or isobaric the quantity $x_1 \ln \gamma_1 + x_2 \ln \gamma_2$ is for the most part a smooth curve and the author feels justified in writing

$$x_1\ln\gamma_1 + x_2\ln\gamma_2 = x_1x_2f_{1-2}(x_1) \qquad (37)$$

Equation (36) now becomes

$$\ln\frac{\gamma_1}{\gamma_2} = x_1x_2f'_{1-2}(x_1) + (x_2-x_1)f_{1-2}(x_1) \qquad (38)$$

Solving (37) and (38) yields

$$\ln\gamma_1 = x_2^2\left[f_{1-2}(x_1) + x_1f'_{1-2}(x_1)\right] \qquad (39)$$

$$\ln\gamma_2 = x_1^2\left[f_{1-2}(x_1) - x_2f'_{1-2}(x_1)\right] \qquad (40)$$

Any two of the equations (38) through (40) completely define any binary system.

Although van Laar (20) used an entirely different approach in effect he chose

$$f_{1-2}(x_1) = \frac{1}{a_0 + a_1x_1} \qquad (41)$$

Margules' (8) equations appear when

$$f_{1-2}(x_1) = b_0 + b_1x_1 \qquad (42)$$

Scatchard and Hamer (16) in effect chose

$$f_{1-2}(x_1) = \frac{c_0 + c_1x_1}{\left(x_1 + \frac{V_2}{V_1}x_2\right)^2} \qquad (43)$$

In deriving their equations Scatchard and Hamer assumed the molal volume of the liquid phase to be equal to $V_1x_1 + V_2x_2$. It seems to the author, however, that the deviations from ideality are caused by the volume changes due to mixing. In studies by Tucker (19) and Mason (9) they found that Scatchard's equations were not too much of an improvement on van Laar's on Margules' equations and in some cases were worse than one or the other. The author presents here two new functions which he thinks warrant some study,

$$f_{1-2}(x_1) = g_0 e^{g_1 x_1} \qquad (44)$$

and

$$f_{1-2}(x_1) = \frac{h_0 + h_1 x_1}{x_1 + \frac{V_2}{V_1} x_2} \qquad (45)$$

Equation (44) should give results quite similar to van Laar's equations and like the latter cannot produce a maximum in the activity coefficient curves. Equation (45) differs from Scatchard's only in that the denominator is not squared thereby minimizing the effect of that quantity.

Wohl's (22) equations could be derived by setting $\frac{V_2}{V_1}$ in (43) equal to $\frac{q_2}{q_1}$ where q is designated by him as the "effective molal volume." Since such a quantity is not directly measurable his equations are only a slight improvement on Scatchard's equations. It would probably be more desirable to write

$$f_{1-2}(x_1) = \frac{k_0 + k_1 x_1}{1 + k_2 x_1} \qquad (46)$$

as again squaring the denominator appears to be entirely fortuitous.

Carlson and Colburn have pointed out that

Margules' equations give better results when the components have comparable molal volumes, whereas the van Laar equations work better when molal volumes are unequal.

Clark (3) has shown that some systems are governed by the relations

$$\frac{y_1}{y_2} = a \frac{x_1}{x_2} + b \qquad (47)$$

$$\frac{y_2}{y_1} = a' \frac{x_2}{x_1} + b' \qquad (48)$$

where (47) is used for large concentrations of x_1 and (48) for large concentrations of x_2.

By a simple transformation these equations may be written

$$\frac{x_2}{y_2} = a + (1-a+b)\, x_2 \qquad (49)$$

and

$$\frac{x_1}{y_1} = a' + (1 - a' + b')\, x_1 \qquad (50)$$

Equations (49) and (50) make a better plot than (47) and (48), and the author has further found that it may be necessary to add another term to what is now a power series in x. The equations are not adaptable for the prediction of data but may be used for correlations. They also break down if the relative volatility goes through a maximum.

Semi-Empirical Equations for Ternary Systems

The algebraic solution to the Duhem equation is derived by noting that

$$x_1\ln\gamma_1+x_2\ln\gamma_2+x_3\ln\gamma_3 = x_1x_2f_{1-2}(x_1)+x_1x_3f_{1-3}(x_1)$$
$$+x_2x_3f_{2-3}(x_2)+x_1x_2x_3(l_0+l_1x_2+l_2x_3) \qquad (51)$$

Differentiating with respect to x_1 first holding x_2 constant and then x_3 constant and substituting (11) gives

$$\ln\frac{\gamma_1}{\gamma_3} = x_1x_3f'_{1-3}(x_1)+(x_3-x_1)f_{1-3}(x_1)+x_1f'_{1-2}(x_1)$$
$$+f_{1-2}(x_1)-f_{2-3}(x_2)+(x_3-x_1)l_0+l_1+x_2+l_2x_3-l_2x_3-l_2x_1x_3) \qquad (52)$$

and

$$\ln\frac{\gamma_1}{\gamma_2} = x_1x_2f'_{1-2}(x_1)+(x_2-x_1)f_{1-2}(x_1)+x_3x_1f'_{1-3}(x_1)$$
$$+f_{1-3}(x_1)-x_2f'_{2-3}(x_2)-f_{2-3}(x_2)-l_1x_1x_2+(x_2-x_1)(l_0+l_1x_1+l_2x_2) \qquad (53)$$

Equations (52) and (53) completely define algebraically any ternary system. The equations are completely general in that any of the equations (41) through (46) may be used to evaluate the binary constants. If only binary data are known then l_0, l_1, and l_2 are set equal to zero. The binary functions are chosen, of course, according to which best fit the binary data.

Correlation of Binary Data Employing Algebraic Equations

Substituting (42) in (38) yields

$$\ln \frac{\gamma_1}{\gamma_2} = b_o(x_2-x_1) + b_1x_1(2x_2-x_1) \qquad (54)$$

Gilmont (5) has rearranged this equation slightly and outlines in detail a procedure for calculating the values of the constants and also the number needed as (42) is actually a power series in x_1. The procedure is rather time consuming.

Another method which is sensitive to temperature measurement and usually produces a scattering of points is arrived at by substituting (42) in (39) and (40) obtaining Margules' equations,

$$\frac{\ln\gamma_1}{x_2^2} = b_o + 2b_1x_1 \qquad (55)$$

$$\frac{\ln\gamma_2}{x_1^2} = b_o - b_1 + 2b_1x_1 \qquad (56)$$

Thus, plots of $\frac{\ln\gamma_1}{x_2^2}$ and $\frac{\ln\gamma_2}{x_1^2}$ against x_1 should produce a pair of parallel lines and the constants thereby evaluated.

Similarly, for the van Laar equations obtained by substituting (41) in (39) and (40),

$$\frac{\ln\gamma_1}{x_2^2} = \frac{a_o}{(a_o+a_1x_1)^2} \qquad (57)$$

$$\frac{\ln\gamma_2}{x_1^2} = \frac{a_o + a_1}{(a_o+a_1x_1)^2} \qquad (58)$$

White (21) suggests plotting $(\ln\gamma_1)^{-\frac{1}{2}}$ against x_1/x_2 and $(\ln\gamma_2)^{-\frac{1}{2}}$ against x_2/x_1. This tends to bunch points at one end of the plot and spread them out at the other end. An improvement would be to plot $x_2/(\ln\gamma_1)^{\frac{1}{2}}$ and $x_1/(\ln\gamma_2)^{\frac{1}{2}}$ against x_1 thereby giving a more equal weight to the points as is the case for the Margules type plot.

The above methods could be improved upon if it were possible to rectify data easily by employing a three constant equation. The author has been able to accomplish this in the following manner:

Adding one more constant to the power series (42) and substituting in (39) and (40) produces

$$\ln\gamma_1/x_2^2 = b_0 + 2b_1x_1 + 3b_2x_1^2 \tag{59}$$

$$\ln\gamma_2/x_1^2 = b_0 - b_1 + 2(b_1 - b_2)x_1 + 3b_2x_1^2 \tag{60}$$

Subtracting (60) from (59)

$$\ln\gamma_1/x_2^2 - \ln\gamma_2/x_1^2 = b_1 + 2b_2x_1 \tag{61}$$

Therefore, if a three constant Margules' equation is representative of the data, then b_1 and b_2 may be readily evaluated from a plot of $\ln\gamma_1/x_2^2 - \ln\gamma_2/x_1^2$ versus x_1. Next, b_0 is found by calculating $\ln\gamma_1/x_2^2 - 2b_1x_1 - 3b_2x_1^2$, $\ln\gamma_2/x_1^2 + b_1 + 2(b_2 - b_1)x_1 - 3b_2x_1^2$, or $\ln(\gamma_1/\gamma_2) - b_1x_1(2 - 3x_1) - b_2x_1^2(3 - 4x_1)/(x_2-x_1)$ for the experimental points and averaging the values obtained. If the values of b_0 do not remain essentially constant, then some other means of correlation must be resorted to. The author has developed a procedure which utilizes (46). (This function may be designated as the "Margules-van Laar" function). The equations involved are

$$\left[\ln\gamma_1/x_2^2 - \ln\ {}_2/x_1^2\right]^{-\frac{1}{2}} = (k_1-k_0k_2)^{-\frac{1}{2}} + k_2(k_1-k_0k_2)^{-\frac{1}{2}}x_1$$

$$k_2 = \text{slope/intercept}$$

$$k_0 = \frac{(1 + k_2x_1)^2\ln\gamma_1/x_2^2 - x_1(2 + k_2x_1)/\text{intercept}^2}{1 + k_2x_1(2 + k_2x_1)}$$

$$k_1 = k_0k_2 + \text{intercept}^{-2}$$

$$\ln\gamma_1/\gamma_2 = \frac{k_0(1-2x_1-k_2x_1^2) + k_1x_1\left[2-3x_1+k_2x_1(1-2x_1)\right]}{(1+k_2x_1)(1+k_2x_1)}$$

If neither of the above two methods gives a good correlation, then it is suggested that the Clark equations as modified by the author be used.

Example:

Robinson and Gilliland (14) give examples of Mason's use of the van Laar and Margules' equations for the system acetone-chloroform, the equilibrium data having been determined by Rosanoff and Easley (15).

In the case of the Margules' equations $\ln\gamma_1/x_2^2$ is plotted against x_2, and $\ln\gamma_2/x_1^2$ is plotted against $x_2+\frac{1}{2}$ so that a single line should go through all the points. There is a considerable amount of scattering for both the van Laar and Margules' plots.

The values of $\ln\gamma_1/x_2^2$ and $\ln\gamma_2/x_1^2$ are taken directly from the text in the following table (the subscript (1) refers to the acetone):

x_1	$\frac{\ln \gamma_1}{x_2^2}$	$\frac{\ln \gamma_2}{x_1^2}$	$\frac{\ln \gamma_1}{x_2^2} - \frac{\ln \gamma_2}{x_1^2}$	$\frac{\ln \gamma_1}{x_2^2} + 0.342(x_2 - x_1)$
0.9145	+2.04	-0.591	2.63	-0.874
0.8590	+0.350	-0.599	0.949	-0.844
0.7955	-0.217	-0.621	0.404	-0.823
0.7388	-0.296	-0.680	0.384	-0.843
0.6633	-0.396	-0.737	0.341	-0.848
0.5750	-0.486	-0.744	0.258	-0.795
0.4771	-0.600	-0.760	0.160	-0.744
0.3350	-0.613	-1.094	0.481	-0.981
0.2660	-0.706	-1.101	0.395	-0.941
0.2108	-0.675	-0.986	0.311	-0.789
0.1375	-0.726	-1.937	1.211	-1.689
0.1108	-0.936	-1.239	0.303	-0.973

It is apparent there is no definite trend in the values of $\frac{\ln \gamma_1}{x_2^2} - \frac{\ln \gamma_2}{x_1^2}$. A rough plot of the points further substantiated this observation. It was decided, therefore, that b_2 could be dropped from equations (59) and (60) for this system and b_1 determined by averaging the values of $\frac{\ln \gamma_1}{x_2^2} - \frac{\ln \gamma_2}{x_1^2}$ between $x_1=0.2108$ and $x_1=.7955$. The average value is 0.342. The values of b_0 are calculated in the last column, the average being

-0.860 (the value at $x_1 = 0.1375$ was neglected). Since $\frac{P_1}{P_2}$ is approximately 1.16 for all values of x_1 substitution in (54) gives

$$\ln\alpha = -.710 + 2.40x_1 - 1.03x_1^2$$

Mason obtained

$$\ln\gamma_1 = -(0.11 + 0.74\, x_2)\, x_2^2$$

$$\ln\gamma_2 = -(0.48 + 0.74\, x_2)\, x_1^2$$

which on simplification becomes

$$\ln\alpha = -0.70 + 2.44\, x_1 - 1.11\, x_1^2$$

Mason obtained his constants by drawing an "optimum line." No graph at all was required in this paper to obtain practically the same result. His results as tabulated in the text show a good correlation is obtained.

Prediction of Binary Data From Azeotropic Data

The procedure in the texts involves more trial and error than is actually required for the prediction of data from azeotropic data. It is fairly obvious that equation (39) is the key to the problem because of the usually slight variation of $\frac{P_1}{P_2}$ with temperature. One of the functions (41) through (45) must be decided upon* and the constants evaluated from equations (39) and (40). Equation (38) is then written in the form

$$\ln\alpha = \ln\frac{P_1}{P_2} + x_1x_2f'_{1-2}(x_1) + (x_2-x_1)f_{1-2}(x_1) \tag{62}$$

and the constants substituted in (62).

The temperature of the system is evaluated from (39) or (40) by solving for P_1 or P_2 thus

$$\ln P_1 = \ln\frac{y_1\pi}{x_1} - x_2^2\left[f_{1-2}(x_1) + x_1f'_{1-2}(x_1)\right] \tag{63}$$

$$\ln P_2 = \ln\frac{y_2\pi}{x_2} - x_1^2\left[f_{1-2}(x_1) - x_2f_{1-2}(x_1)\right] \tag{64}$$

If at the calculated temperature $\frac{P_1}{P_2}$ is very different from the first assumption then recalculation is necessary. Equation (62) is used by the author throughout the thesis for calculating

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*From the studies of Tucker and Mason the Margules' equations seem to be the most preferable, but no more than a rough estimation of data should be expected.

values of alpha.

Binary Systems Having Two Liquid Phases

It is permissible to correlate or predict data for two phase systems by utilizing any of the functions (41) through (46) but only in the one phase regions. This fact has been overlooked by most investigators, or, when it is admitted, correlations and predictions are still attempted over the entire range of liquid composition with, perhaps, a two constant van Laar equation. For instance, Carlson and Colburn (2) have developed equations for the prediction of data from limiting solubility data. They employed the van Laar function (41) and noted that for the two phase region

$$\gamma_1 x_1 = K_1 \qquad (65)$$

$$\gamma_2 x_2 = K_2 \qquad (66)$$

Therefore,

$$\gamma_1' x_1' = \gamma_1'' x_1'' \qquad (67)$$

$$\gamma_2' x_2' = \gamma_2'' x_2'' \qquad (68)$$

where the superscripts refer to the boundaries of the two phase region.

From (57) and (58)

$$\ln \frac{\gamma_1'}{\gamma_1''} = a_0 \left[\frac{x_2'^2}{(a_0+a_1x_1')^2} - \frac{x_2''^2}{(a_0+a_1x_1'')^2} \right] \qquad (69)$$

$$\ln \frac{\gamma_2'}{\gamma_2''} = (a_0+a_1)\left[\frac{x_1'^{2}}{(a_0+a_1x_1')^2} - \frac{x_1''^{2}}{(a_0+a_1x_1'')^2}\right] \quad (70)$$

By substituting (67) and (68) in (69) and (70) it is then possible to calculate a_0 and a_1.

The fallacy in the above argument stems from the fact that γx is set up as a constant at two points rather than throughout the two phase region. The author has developed a procedure which would enable one to calculate the constants for Margules' equations from solubility data only. The result is a different set of equations for each of the one phase regions. However, in some trial calculations poor results have been found; trying the same thing for the van Laar equations led to equations which were far too cumbersome to be useful. The author has concluded that it is necessary to have both solubility data and azeotropic data.

From the azeotropic data the constants in (65) and (66) may be calculated and, therefore, the activity coefficients at the points of limiting solubility can be evaluated. The constants for the Margules' equations may now, of course, be obtained. There is, however, one serious drawback as there is usually a one phase region which is of only small extent. The component present in the larger amount will in this case have an activity coefficient very near unity, and when this occurs the empirical equations are never adaptable. To overcome this difficulty advantage is taken of the fact that plot of gamma versus liquid composition is differentiable at all points.

Supposing component (1) to be present in a small amount at the point of limiting solubility by differentiating (55) and (65) and equating at x_1'

$$2x_1'x_2'\left[b_o + b_1(2x_1' - x_2')\right] = 1 \tag{71}$$

From (55)

$$\ln \gamma_1' = x_2'^2\left(b_o + 2b_1x_1'\right) \tag{72}$$

The constants b_o and b_1 are then evaluated from (71) and (72).

Example:

From the measurements of Stockhardt and Hull (17) the points of limiting solubility for the system n-butanol - water are $x_1' = 0.025$ and $x_1'' = 0.45$. At the azeotrope $x_1 = 0.25$, $t = 92.7°C$, $P_1 = 287$ mm., $P_2 = 582$ mm. The subscript (1) refers to the butanol.

At the azeotrope

$$\gamma_1 = \frac{760}{287} = 2.65$$

$$\therefore \gamma_1' = \frac{2.65(0.25)}{0.025} = 26.5$$

Solving (71) and (72)

$$b_0 = 4.16$$

$$b_1 = -17.6$$

From (50)

$$\ln\alpha = \ln\frac{P_1}{P_2} + 4.16(x_2 - x_1) - 17.6x_1(2x_2 - x_1) \qquad (73)$$

Equation (73) is valid, therefore, for values of x_1 less than or equal to 0.025.

At the azeotrope $\gamma_2 = \frac{760}{582} = 1.305$

$$\gamma_2'' = \frac{1.305(0.75)}{0.55} = 1.78$$

$$\gamma_1'' = \frac{2.65(0.25)}{0.45} = 1.47$$

For the sake of variety the van Laar equations will be used. Solving (57) and (58) for the constants and then subtracting (58) from (57)

$$\ln\alpha = \ln\frac{P_1}{P_2} + \frac{0.324x_2^2 - 0.724\,x_1^2}{(0.324 + 0.400x_1)^2} \qquad (74)$$

Equation (74) is valid for values of x_1 greater than or equal to 0.45.

If only azeotropic data is used then

$$\ln \alpha = \ln \frac{P_1}{P_2} + \frac{x_2^2 - 2.49\, x_1^2}{0.306(1+1.49x_1)^2} \qquad (75)$$

Carlson and Colburn utilizing the solubility data at 100°C arrived at

$$\log \alpha = \log \frac{P_2}{P_1} + \frac{1.34\, x_1^2 - 2.20\, x_2^2}{(x_1+2.20\, x_2)^2} \qquad (76)$$

where the subscript (2) now refers to the butanol.

The results are compared with the measured values of Stockhardt and Hull in the following table:

x_1	Exp.	(73)(74)	(75)	(76)
0.002	25.7	29.6	13.0	10.9
0.006	21.8	24.7	12.1	10.1
0.012	19.6	18.7	11.1	9.22
0.020	15.8	13.6	9.52	8.25
0.025	13.0	13.0	9.02	7.85
0.450	0.407	0.407	0.389	0.411
0.695	0.224	0.206	0.208	0.208
0.743	0.204	0.190	0.193	0.189
0.930	0.139	0.146	0.153	0.143

Although the agreement is not perfect (73) and (74) certainly are a great improvement on either (75) or (76).

Determination of Binary Data From Boiling Point Data

Were it possible to obtain two fairly precise measurements such as the liquid phase composition and boiling temperature then it would be theoretically possible to calculate the vapor composition data from the Duhem equation. The ebulliometric methods of Swietoslawski (18) provide such a means of doing so.

Once having obtained the boiling points as a function of liquid composition one could then proceed in one of three ways:

(1) Determine the limiting values, of $\frac{dT}{dx}$ at $x_1 = 0$ and $x_2 = 0$, substitute (25) and (26) to obtain γ_1 and γ_2, and interpolate for the remaining data by means of (38) employing some choice of (45).

(2) Graphically integrate the Duhem equation over the entire range of x.

(3) Graphically integrate the Duhem equation a part of the way (at least to the maximum value of relative volatility) and interpolate for the remaining data by one of the empirical equations.

Procedure (2) would require many experimental points and entail a good deal of calculation although it would be the most accurate. Procedure (1) is the simplest but most inaccurate since if a point of inflection did exist in the t-X diagram it would be "overlooked" by the empirical equations. For these reasons procedure (3) would seem to be the most logical of the three.

Equation (18) is repeated here so that the reader may have it before him.

$$\frac{dy_1}{dx_1} = \frac{y_1 y_2}{s(x_1 - y_1)} \frac{dT}{dx_1} \tag{18}$$

One method would be to assume that

$$\frac{\Delta y_1}{\Delta x_1} = \text{constant} \tag{77}$$

for small increments in x, calculate y_1'' at x_1'', determine $\frac{dy_1}{dx_1}''$ at x_1'', average $\frac{dy_1}{dx_1}'$ and $\frac{dy_1}{dx_1}''$, use the new $\frac{dy_1}{dx_1}$ to redetermine y_1'', and repeat until there was no further change in y_1''. However, if the absolute value of $\frac{dT}{dx_1}$ is continuously increasing and such a procedure is carried out, it will be found that the successive values of $\frac{dy_1}{dx_1}$ increase without limit. It is possible to take very small increments and disregard the averaging process, but the values of y_1 thus obtained will still lag the true values to some extent. Therefore, the author suggests expanding $\frac{1}{s} \frac{dT}{dx_1}$ in a power series in x_1 as follows:

$$\frac{1}{s}\,\frac{dT}{dx_1} = \sum B_n x_1^n \tag{78}$$

Also, let

$$y_1 = \sum A_n x_1^{n+1}. \tag{79}$$

Therefore,

$$\frac{dy_1}{dx_1} = \sum (n+1)A_n x_1^n \tag{80}$$

Substituting in (18)

$$\frac{\sum (n+1)A_n x_1^n}{\sum A_n x_1^n \left[1 - \sum A_n x_1^{n+1}\right]} = \frac{\sum Anx_1^n \sum B_n x_1^n}{1 - \sum A_n x_1^n} \tag{81}$$

Equation (81) was solved by equating the coefficients of like powers of x_1 to zero. The results are

$$A_0 = 1 - B_0$$

$$A_1 = \frac{A_0(A_0B_0 - B_1)}{2A_0 - 1}$$

$$A_2 = \frac{A_0(2A_1B_0 + A_0B_1 - B_2) - A_1(2A_1 + B_1)}{3A_0 - 1}$$

$$A_3 = \frac{A_0(2A_2B_0 + A_0B_2 - B_3) + A_1(A_1B_0 + 2A_0B_1 - B_2) - A_2(B_1 + 5A_1)}{4A_0 - 3} \tag{82}$$

Experimental Work

Altsheler (1), et al, made some very precise measurements of the equilibria for the system ethanol-water with a new type of still and found the relative volatility to go through a maximum at a mol fraction of ethanol of approximately 0.002. They were unable to explain the "anomaly" and thought the results to be thermodynamically inconsistent, but on the basis of what has gone before it can be expected that the temperature-composition diagram has a point of inflection at some value of x less than or equal to 0.002. The author attempted to check this premise by measuring the boiling points for this system at low alcohol concentrations and solving for the constants in (79). The boiling points at the alcohol rich end were also determined so that the remaining data could be obtained by interpolation.

Price did the glass blowing and constructed a differential type ebulliometer, a simple type ebulliometer, and an ebulliometer of the type for measuring boiling points when one component is more volatile than the other; these instruments are discussed in detail by Swietoslawski (18). The boilers were all wired for electric heating and the simple ebulliometer was also fitted with a stopcock in the line leading back to the boiler. The stopcock arrangement is required for the third type of ebulliometer.

The alcohol used for the water rich end was the azeotrope which was distilled at about 740 mm. and, therefore, contained approximately 95.6 % by weight of ethanol. (An error of 0.2 % would in no way affect the results). It had a temperature difference of 0.000° C between the boiling temperature and the condensation temperature thus attesting of its purity as an azeotrope.

Absolute alcohol was prepared by purifying 99.9 % ethanol with sodium and ethyl formate as suggested by Delcamp. The runs in this case were made as soon as a large enough sample had distilled over. The entire distillation apparatus was closed except for a drying tube containing calcium chloride. A boiling temperature difference of 0.000° C was found for the alcohol, and it was also found to boil 0.136° C higher than the azeotrope. Noyes and Warfel (10) obtained 0.126° C, Dietrich and Grossman (4) 0.14° C, and Young and Fortey (23) 0.15° C.

The hydrostatic head in the ebulliometer was 0.026° C and this value could be duplicated repeatedly.

The change in barometric pressure was determined by means of the condensation temperature in the differential ebulliometer in which was distilled water.

The mixtures were boiled until equilibrium was reached (approximately ten minutes). After recording the temperature in both ebulliometers the powerstat was turned off, the hold up retained by means of the stopcock, and the boiler drained and completely dried. If the latter were not done it was found that the glass particles adhering to the walls of the boiler to prevent superheating lost their effectiveness. More of the original sample was then added and the boiling point again determined. It was, of course, somewhat lower the second time. The process was repeated until no further change in boiling point was noted. No more than two refills were ever actually needed and for the extremely low concentrations only one refill was required. In the case of the alcohol rich end the simple type ebulliometer was used in the same manner, and since the relative volatility is approximately one it was found that there was no detectable difference in boiling temperature when refilled.

The following are the data obtained (the subscript (1) refers to the ethanol):

Run	Grams Azeotrope	Grams Water	Barometric Beckmann	Boiling Pt. Beckmann	t (°C)	x_1
1	0.000	[illegible]	2.161	3.020	100.000	0.00000
2	0.778	432	2.159	2.850	99.832	0.00067
3	1.55	439	2.130	2.618	99.629	0.00131
4	2.27	441	2.147	2.445	99.439	0.00192
5	2.93	435	2.160	2.293	99.274	0.00250
6	4.81	442	2.167	1.880	98.854	$0.004\underset{7}{\overline{0}}6$
7	8.18	450	2.160	1.137	98.118	0.00679
8	0.356	425	2.160	2.940	99.121	0.00031
9	1.02	434	2.123	2.751	99.769	0.00089
10	1.99	492	2.135	2.560	99.566	0.00151
11	1.40	449	2.190	2.730	99.681	0.00116

Run	Grams Ethanol	Grams Water	Barometric Beckmann	Boiling Pt. Beckmann	t (°C)	x_2
1	---	0.000	2.313	2.217	78.35	0.00000
2	140	1.66	2.305	2.137	78.278	0.0295
3	110	2.34	2.306	2.100	78.240	0.0516
4	141	2.01	2.313	2.132	78.265	0.0352
5	---	0.000	2.318	2.222	78.35	0.00000
6	110	0.416	2.320	2.198	78.324	0.00961
7	109	0.527	2.310	2.181	78.317	0.0122
8	88.6	0.463	2.310	2.178	78.314	0.0132
9	196.9	0.267	2.300	2.186	78.332	0.00700
10	75.2	0.139	2.289	2.180	78.337	0.00495
11	103	3.80	2.280	2.050	78.216	0.0860

The data are plotted on the accompanying graphs. As was predicted there is a point of inflection at a mol fraction of ethanol of about 0.0012. The data at this end of the diagram were represented by the equation

$$t = 100 - 248x_1 - 8000x_1^2 - (10)^7 x_1^3 \qquad (83)$$

Therefore,

$$\frac{dT}{dx_1} = -248 - 1.6(10)^4 x_1 - 3(10)^7 x_1^2 \tag{84}$$

Since $\frac{1}{s} = 0.03565$

$$\frac{1}{s}\frac{dT}{dx_1} = -8.85 - 571 x_1 - 1.07(10)^6 x_1^2 \tag{85}$$

Solving for the constants in (82)

$A_0 = 9.85$

$A_1 = 255$

$A_2 = 3.8(10)^5$

$A_3 = -4.6(10)^6$

Therefore,

$$y_1 = x_1 \quad 9.85 + 255x_1 + 3.8(10)^5 x_1^2 - 4.6(10)^6 x_1^3 \tag{86}$$

The values of y_1 in equilibrium with x_1 greater than 0.0012 were calculated by means of the procedure outlined under equation (77). The calculated results are tabulated here:

x_1	y_1	α	γ_1
0.0000	0.00000	9.85	4.42
0.0002	0.00198	9.92	4.46
0.0004	0.00400	10.05	4.51
0.0006	0.00608	10.20	4.58
0.0008	0.00824	10.40	4.67
0.0010	0.01048	10.60	4.76
0.0012	0.01280	10.80	4.84
0.0015	0.0164	11.12	4.98
0.0020	0.0222	11.32	5.10
0.0025	0.0275	11.30	5.07
0.0030	0.0326	11.20	5.04
0.0050	0.0529	11.10	5.00

γ_2 is unity for all values of x_1.

The value of γ_2 when x_2 = D was found to be 2.53. The Margules equations give for interpolation between $x_1 = 0.00500$ and $x_1 = 1.000$

$$\ln\alpha = \ln\frac{P_1}{P_2} + 1.634 - 4.678\, x_1 + 2.115\, x_1^2 \qquad (87)$$

The calculated results are compared with the results of Altsheler on the accompanying plot. Agreement is good and in the low alcohol concentration range the values of y_1 agree within 1 %.

Summary and Conclusions

It was demonstrated qualitatively that if a T-X diagram contained a point of inflection in a region of low concentration, then an α-X plot would go through a maximum. Altsheler's equilibrium data for the system ethanol-water was thought by him to be thermodynamically inconsistent since at a mol fraction of ethanol of about 0.002 alpha reached a maximum. Boiling points experimentally determined by the author did indeed show a point of inflection, and the vapor-liquid equilibrium data calculated by a method developed by the author gave excellent agreement with Altsheler's data. As a result, support was lent to the following: (1)The Gibbs-Duhem equation is consistent over the entire range of liquid composition (2)The determination of boiling points by means of Swietoslawski's apparatus gives accurate results (4)Vapor-liquid equilibrium may be accurately determined by means of boiling points alone.

It was shown on a theoretical basis that it is impossible to correlate or predict data for partially miscible systems by means of a single two constant semi-empirical equation. A method for the prediction of the entire range of data employing solubility data and azeotropic data was developed. In an example of its use on the system n-butanol-water, results were fairly good. Since partially miscible systems show extremely non-ideal behavior, and the prediction of data necessitates extrapolation, only a rough estimation of data should be expected. For instance, the system furfural-water deviates from ideality to such an extent that no semi-empirical equation is capable of representing the data for the furfural rich one phase region. (There is a point of inflection in the T-X diagram).

Two new methods for the algebraic correlation of data were presented. They are superior to previous methods of correlation since they afford rectification of data directly even though three constants are employed. It was suggested that if a good correlation could not be obtained due to inapplicability of the equations that as a last recourse the Clark equations, as modified by the author, be used. The latter have been shown by Clark and Mason to give good correlations in all cases tested. The author has found that in two cases (acetone-chloroform, methanol-water) better results were obtained by adding another term to the modified equations. However, they are not as yet capable of being extended to the correlation or prediction of data for multicomponent systems thereby limiting their utility.

New empirical functions for the integration of the Duhem equation were advanced which may be used either for the prediction or correlation of data; however, no hard and fast rule could be layed down as to which function should be employed. It would probably be desirable to predict data by both tho van Laar and Margules' equations and average the results.

A procedure for the prediction of binary vapor-liquid equilibrium data from azeotropic data which eliminates much of the trial and error was suggested as was a method for the correlation of multicomponent data by means of the Duhem equation.

Apparently, algebraic solutions to the Duhem equation may not be valid in the dilute regions because of "abnormal" behavior of molecular interactions in those regions. For the system ethanol-water the anomalous behavior of the partial molal volumes is indeed a fact(13). The author strongly suspects that a great many systems exhibit this behavior and further research is suggested along these lines.

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