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## Predicting V-L Equilibrium Data...

**H. H. Yang**

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**Lamar State College of Technology  
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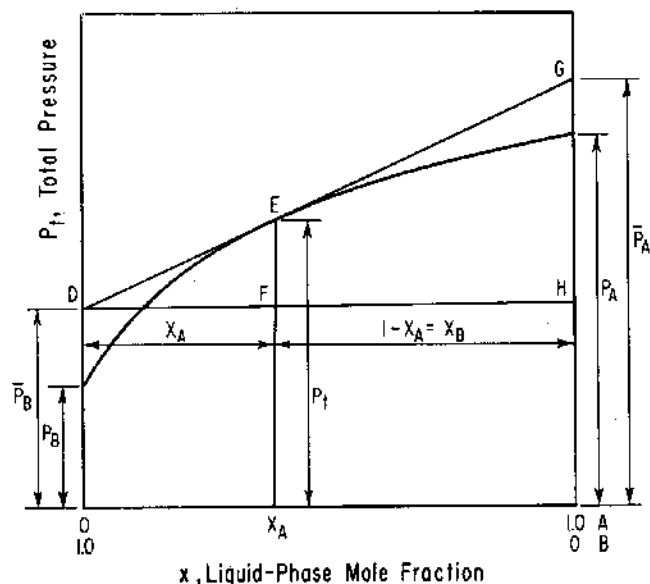


FIGURE 1—Total pressure concentration plot: It's the basis for this graphical method.

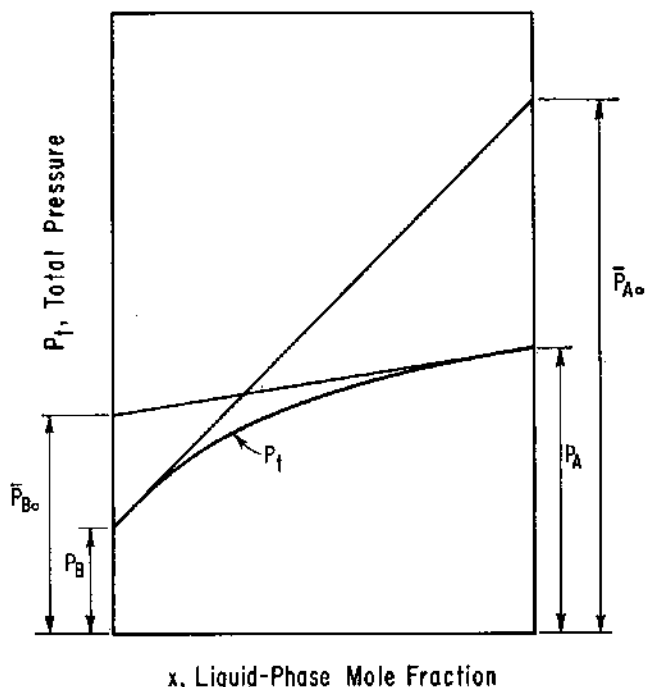


FIGURE 2—Interpretation of tangential intercepts: It shows the significance of partial molar vapor pressure.

# Predicting V-L Equilibrium Data . . .

. . . at constant temperature for binary mixtures.

This graphical method is developed from a new hypothesis.

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A NEW HYPOTHESIS permits the graphical determination of vapor-liquid equilibrium under isothermal condition. The hypothesis was derived for non-ideal binary systems. At the present time, some evidence exists that the hypothesis holds satisfactorily for binary systems with moderately non-ideal behavior. However, more experimental proof is needed for its general validity.

**The Hypothesis.** According to the hypothesis, the partial pressures of the components of a system at constant temperature may be considered as the partial molar properties. When the total pressure of a binary system at a certain temperature is plotted against the mole fraction of a component in the liquid phase, the tangential intercept of this curve would represent the "partial molar vapor pressure" of the respective component at a certain composition. The partial pressure of a component is therefore equal to the product of its partial molar vapor pressure and its mole fraction in the liquid phase.

Figure 1 shows a plot of the total pressure ( $P_t$ ) of a

binary system of A and B at a constant temperature vs. the mole fractions in the liquid phase ( $x_A$  and  $x_B$ ). A tangent is drawn to the curve at point E. Let  $\bar{P}_A$  be the ordinate of the tangential intercept G at  $x_A = 1.0$ . Similarly, let  $\bar{P}_B$  be that of D at  $x_B = 1.0$ . A line DH is drawn perpendicular to EF and GH. It can be seen then the following relationship holds for the similar triangles  $\triangle DEF$  and  $\triangle DGH$ .

$$EF : GH = DF : DH$$

The above equation can be expressed in terms of  $P_t$ ,  $\bar{P}_A$ ,  $\bar{P}_B$ , and mole fractions as follows:

$$(P_t - \bar{P}_B) : (\bar{P}_A - \bar{P}_B) = x_A : 1$$

Or,

$$P_t = \bar{P}_A x_A + \bar{P}_B (1 - x_A) \quad (1)$$

Since  $x_A + x_B = 1$  for a binary system, we have

$$P_t = \bar{P}_A x_A + \bar{P}_B x_B \quad (2)$$

Where  $0 \leq x_A \leq 1$  and  $0 \leq x_B \leq 1$ . Equation (2)

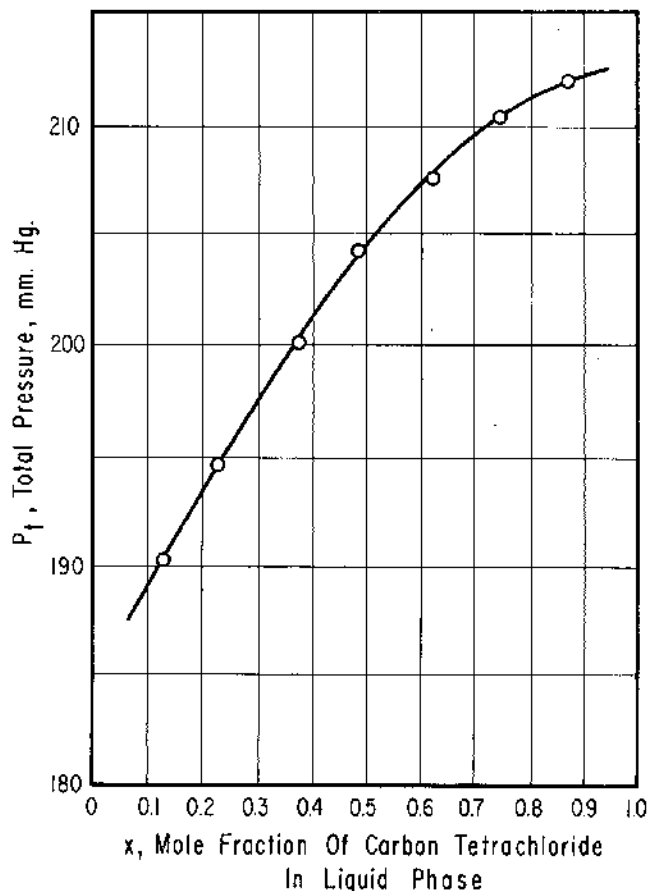


FIGURE 3—Total pressure versus liquid phase composition for the system carbon tetrachloride-benzene.

states that the total pressure  $P_t$  of a binary system is equal to the sum of products of the tangential intercept on an isothermal  $P_t - x$  plot and the respective mole fraction in the liquid phase.

According to the concept of activity coefficient, the partial pressure of a component in a non-ideal system may be expressed by the following equations.

$$p_i = \gamma_i P_i x_i$$

Therefore, for a binary system of A and B,

$$P_t = p_A + p_B$$

$$P_t = \gamma_A P_A x_A + \gamma_B P_B x_B \quad (3)$$

where  $0 \leq x_A \leq 1$  and  $0 \leq x_B \leq 1$ .

Mathematically, the necessary and sufficient conditions for Equations (2) and (3) to exist simultaneously are:

$$\gamma_A P_A = \bar{P}_A$$

$$\gamma_B P_B = \bar{P}_B$$

It follows that

$$\bar{P}_A x_A = p_A \quad (4)$$

$$\bar{P}_B x_B = p_B \quad (5)$$

Consider now the tangential intercept  $\bar{P}_A$  at  $x_A = 1.0$  as a fictitious vapor pressure of component A in the mixture. It can be seen that Equation (4) has the form

of Raoult's Law. Since the Raoult's Law regards the vapor pressure of a pure component as a molar property, the tangential intercept is consequently considered as the partial molar vapor pressure of a component. Thus, the partial pressure of component A in the mixture equals its partial molar vapor pressure times the mole fraction  $x_A$ . The same is true for component B, as is stated by Equation (5).

**Theoretical Consideration.** The physical significance of the partial molar vapor pressure may be stated as follows. The partial pressure of a component in a homogeneous binary system, ideal or non-ideal, follows a general equation in the following:

$$p_i = \bar{P}_i x_i \quad (6)$$

For ideal systems at a constant temperature, the total pressure ( $P_t$ ) is linear with the concentration in the liquid phase ( $x$ ). Equation (6) reduces to Raoult's Law as shown below:

$$p_i = P_i x_i \quad (7)$$

Hence

$$\bar{P}_i = P_i \quad (8)$$

For non-ideal systems at constant temperature, the tangential intercepts of an isothermal  $P_t - x$  plot bear resemblance to the activity coefficients of non-ideal components in that they change with concentrations. Referring to Figure 2, the intercept at  $x_A = 1.0$  may be seen to range from  $\bar{P}_{A0}$  to  $P_A$ . For a system containing only component A, the tangential intercept of  $x_A = 1.0$  equals exactly the vapor pressure of pure component A. For a system containing only component B, the tangential intercept at  $x_A = 1.0$  is  $\bar{P}_{A0}$ , which represents the maximum value of  $\bar{P}_A$ . Since  $x_A = 0$  for such a system,

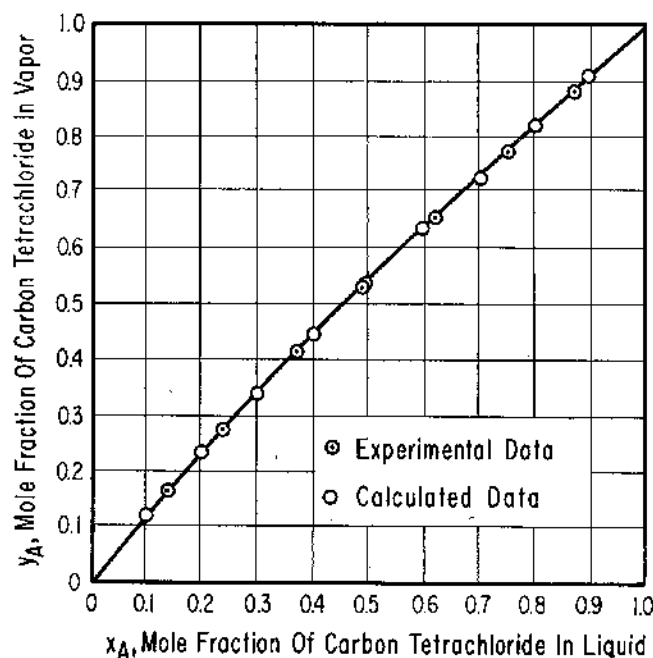


FIGURE 4—Equilibrium diagram of system carbon tetrachloride-benzene: Calculated and experimental values are in excellent agreement.

## V-L Equilibrium Data . . .

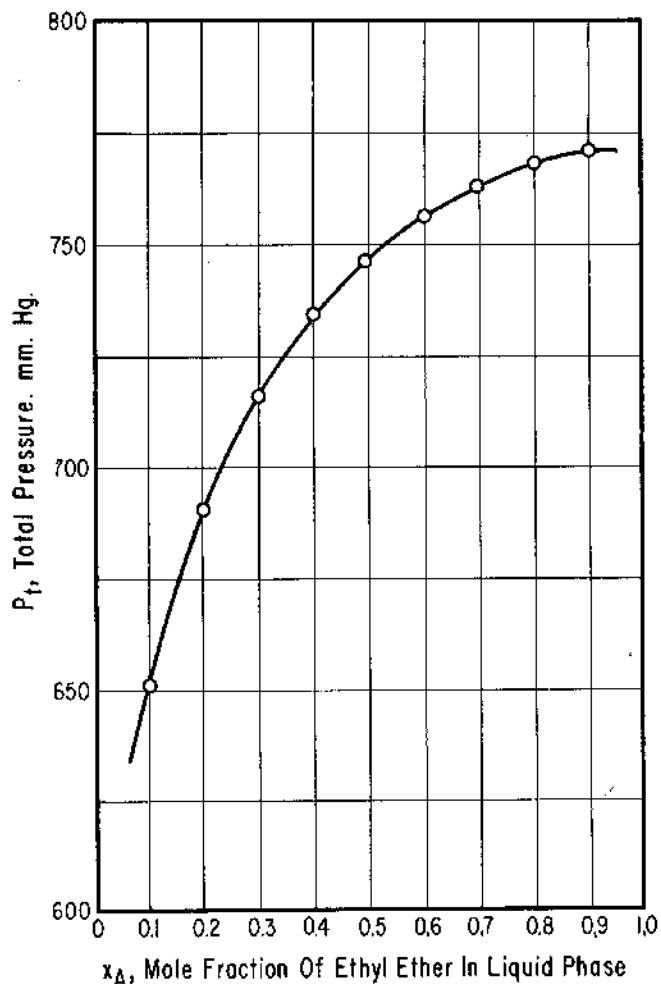


FIGURE 5—Total pressure versus liquid-phase composition for system ethyl ether-methyl iodide.

it is true that  $p_A = (\bar{P}_{A0})(0) = 0$  according to Equation (6).  $\bar{P}_{A0}$  may nevertheless be regarded as the partial molar vapor pressure of component A corresponding to an infinitely dilute solution of A in B.

For a small concentration range in the neighborhood of  $x_A = 0$ , the  $P_t = x$  curve may be assumed linear and consequently  $\bar{P}_{A0}$  is constant. We have, therefore

$$p_A = \bar{P}_{A0} x_A \text{ where } x_A \cong 0 \quad (9)$$

Equation (9) is identical to Henry's Law which is expressed in the following conventional form:

$$p_A = H^* x_A \text{ when } x_A \cong 0 \quad (10)$$

It follows that

$$\bar{P}_{A0} = H \quad (11)$$

for a very dilute solution.

It may perhaps be stated at this point that both Raoult's Law and Henry's Law are only two special cases of Equation (6). This, on the other hand, reflects the generality of the hypothesis.

Referring again to Figure 1, the tangent line to a  $P_t - x$  curve can be represented by the following equation.

$$\bar{P}_A = \bar{P}_B + \frac{\partial P_t}{\partial x_A} \quad (12)$$

Since

$$P_t = \bar{P}_A x_A + \bar{P}_B x_B \quad (2)$$

Differentiate Equation (2).

$$\frac{\partial P_t}{\partial x_A} = \bar{P}_A + x_A \frac{\partial \bar{P}_A}{\partial x_A} + \bar{P}_B \frac{\partial x_B}{\partial x_A} + x_B \frac{\partial \bar{P}_B}{\partial x_A}$$

For a binary system,  $x_A + x_B = 1$  and hence  $\frac{\partial x_B}{\partial x_A} = -1$ .

$$\frac{\partial P_t}{\partial x_A} = \bar{P}_A + x_A \frac{\partial \bar{P}_A}{\partial x_A} - \bar{P}_B + x_B \frac{\partial \bar{P}_B}{\partial x_A}$$

Substituting Equation (12) into the above equation, we have

$$x_A \frac{\partial \bar{P}_A}{\partial x_A} + x_B \frac{\partial \bar{P}_B}{\partial x_A} = 0 \quad (13)$$

Or,

$$x_A \partial \bar{P}_A + x_B \partial \bar{P}_B = 0 \quad (14)$$

Equation (14) expresses the relationship between the partial molar vapor pressures and concentrations of a binary system at a constant temperature.

**Isothermal Vapor-Liquid Equilibria.** On the basis of the hypothesis derived above the isothermal vapor-liquid equilibria may be discussed in the following.

**(1) Binary Systems.** For a binary system at constant temperature and moderate pressure, assume that the Dalton's Law holds for the vapor phase. The partial pressure of one of the components is then equal to

$$p_i = P_t y_i = \bar{P}_i x_i \quad (15)$$

Hence,

$$y_i = \frac{\bar{P}_i x_i}{P_t} \quad (16)$$

Equation (16) indicates that the vapor phase com-

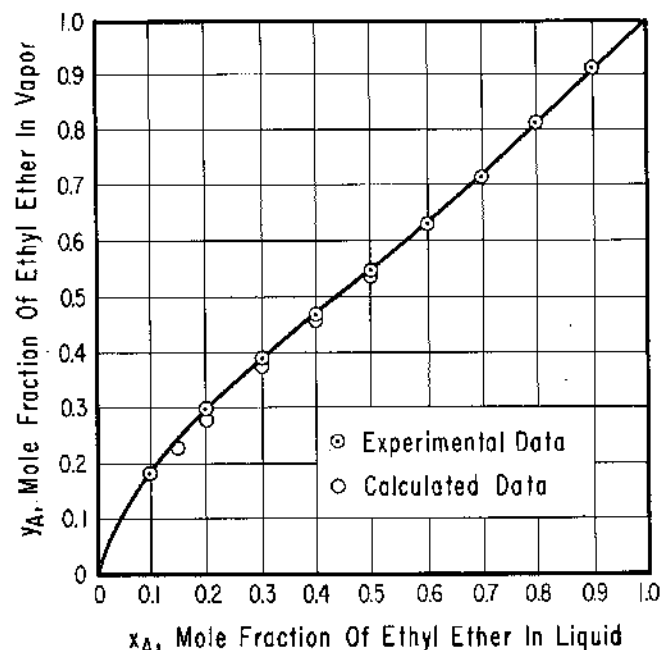


FIGURE 6—Equilibrium diagram of system ethyl ether-methyl iodide: Again, calculated and experimental values are very close.

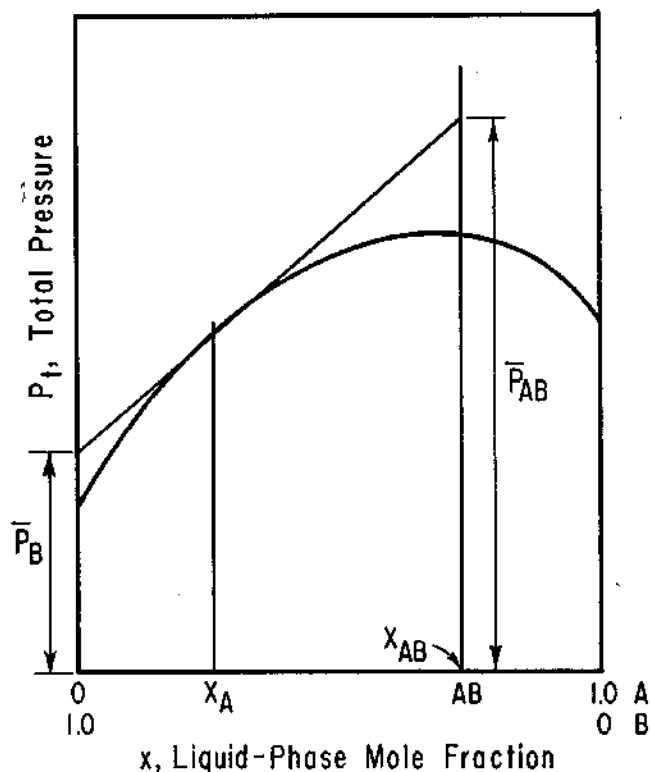


FIGURE 7—Azeotropic binary system: These systems must be treated in a special way.

position of a component can be calculated from the knowledge of  $P_t$ ,  $\bar{P}_i$  and  $x_i$ .

In other words, the analysis of vapor-phase composition of a binary system may be avoided in the study of phase equilibria. Actually, the total pressure ( $P_t$ ) of a binary system may readily be determined as a function of its liquid-phase composition ( $x$ ) by experimental methods. The partial molar vapor pressure ( $\bar{P}$ ) can then be determined graphically from the  $P_t-x$  plot. Such procedure is of considerable value in estimating the phase equilibria of those systems which offers extreme difficulties in the analysis of vapor-phase composition. The system butadiene-styrene may be mentioned as a good example.

The systems, carbon tetrachloride-benzene, and ether-methyl iodide, were examined in a manner described above. Graphs and calculations are shown in Figures 3-6 and Tables 1-2. The experimental data of total pressure of the binary system<sup>1</sup> were first plotted against the liquid-phase composition of one component as illustrated in Figure 3. The tangential intercepts of this component on  $P_t-x$  plot were obtained graphically and entered in Tables 1 and 2. The vapor-phase composition of the system was then calculated by means of Equation (16). The calculated and experimental values of vapor-phase composition plotted in Figures 4 and 6 showed excellent agreement.

**(2) Azeotropic Systems.** There was some evidence that a straight-forward application of this hypothesis fails to predict the isothermal phase equilibria of azeo-

TABLE 1  
Graphical Calculation of Phase Equilibrium

System: Carbon tetrachloride—Benzene at 40° C

A—Carbon Tetrachloride

B—Benzene

$x_A$	$\bar{P}_A$ , mm Hg	$P_t$ , mm Hg	$y_A$ calc.
0	.....	.....	0
0.1	231.5	188.4	0.1228
0.2	228	193.0	0.2362
0.3	224.8	197.3	0.3418
0.4	221.7	201.0	0.4412
0.5	219.2	204.3	0.5364
0.6	216.8	207.0	0.6284
0.7	214.9	209.2	0.7191
0.8	213.6	210.9	0.8102
0.9	212.7	211.9	0.9033
1.0	212.4	212.4	1.0

TABLE 2  
Graphical Calculation of Phase Equilibrium

System: Ether—Methyl iodide at 35° C

A—Ether

B—Methyl iodide

$x_A$	$\bar{P}_A$ , mm Hg	$P_t$ , mm Hg	$y_A$ calc.	$y_A$ expt.
0	.....	.....	0	.....
0.15	997	872.5	0.222	.....
0.2	947	690.3	0.274	0.2952
0.3	868.5	716.1	0.363	0.3843
0.4	825	734.1	0.443	0.4653
0.5	800.5	746.8	0.536	0.5440
0.6	787.8	756.8	0.625	0.6252
0.7	781.3	762.8	0.717	0.7140
0.8	776.8	768.1	0.809	0.8096
0.9	774	771.5	0.903	0.9050
1.0	.....	.....	1.0	.....

tropic systems satisfactorily. Consequently, an azeotropic system may be treated in an alternate way. Referring to Figure 7, an azeotropic system of A and B with a maximum total pressure is shown. It is assumed that a fictitious compound AB exists at the azeotropic composition. There would be then two homogeneous systems in the entire range of composition, B—AB and AB—A. For a tangent drawn to the  $P_t-x$  curve of mixture B—AB, the following geometric relationship may be derived.

$$P_t = \bar{P}_{AB} \frac{x_A}{x_{AB}} + \bar{P}_B \left( 1 - \frac{x_A}{x_{AB}} \right) \quad (17)$$

The first term at the right-hand side of Equation (17) may be assumed to be the partial pressure of the fictitious compound AB. The second term would then represent the partial pressure of compound B. At moderate pressure, the vapor-phase composition may be estimated by Equation (18) in the following

Since  $y_B = \frac{P_B}{P_t}$

Hence  $y_B = \frac{\bar{P}_B}{P_t} \left( 1 - \frac{x_A}{x_{AB}} \right) \quad (18)$

**(3) Ternary Systems.** A possible generalization of the hypothesis is related to the prediction of phase equilibria of a homogeneous ternary system. This would include the experimental work of preparing a series of

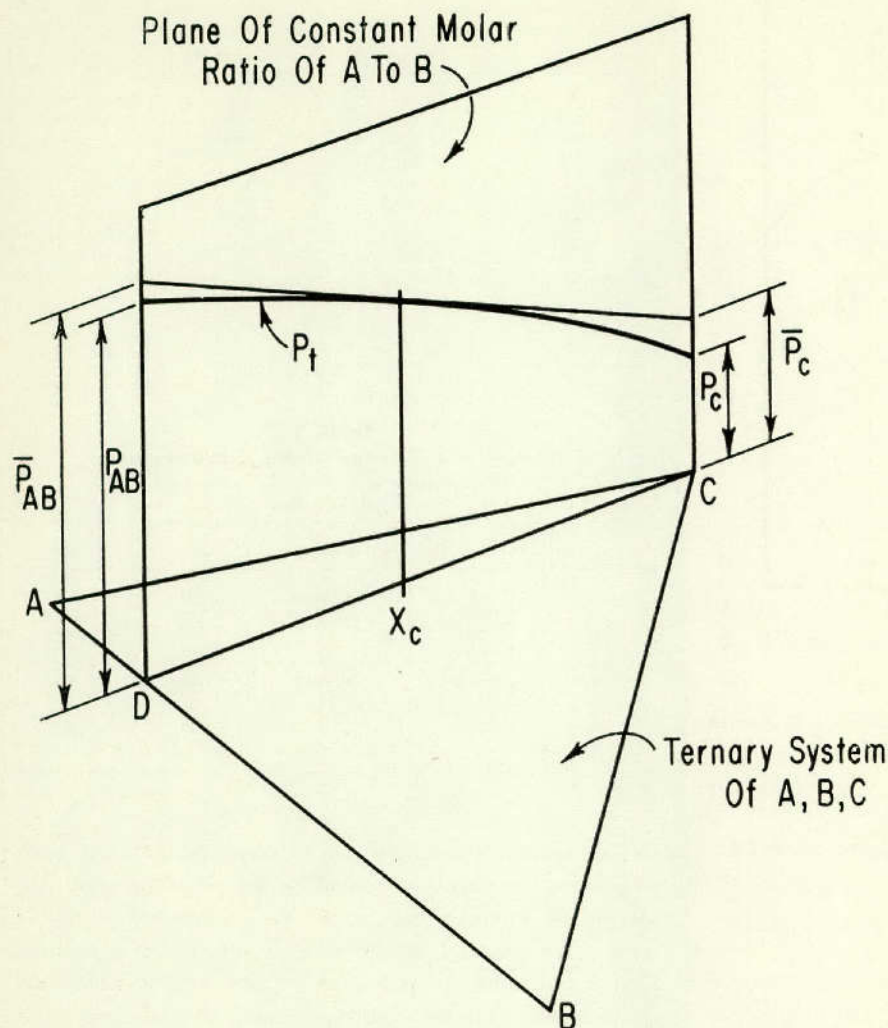


FIGURE 8—Pressure-concentration plot for a ternary system: The hypothesis may be used for this case, too.

ternary mixtures which contain approximately constant amounts of two components in the liquid phase.

Figure 8 shows the triangular diagram of such a ternary system A-B-C. The composition of this series is represented by line CD since it contains a constant amount of A and B for a concentration range from  $x_C = 0$  to  $x_C = 1.0$ . The total pressure of the system is plotted against  $x_C$  on a vertical plane CDEF. This curve intercepts  $x_C = 1.0$  at the vapor pressure of pure C. It intercepts  $x_C = 0$  at  $P_{AB}$ , the total pressure of a binary system A-B alone. A tangent is drawn to the  $P_t - x_C$  curve. The tangential intercepts are designated as  $\bar{P}_{AB}$  at  $x_C = 0$  and  $P_C$  at  $x_C = 1.0$ . It may be shown that

$$P_t = \bar{P}_{AB}(1 - x_C) + \bar{P}_C x_C \quad (19)$$

In accordance with the hypothesis of tangential intercept, the term  $\bar{P}_C x_C$  in Equation (19) is to represent the partial pressure of C in the ternary system. The vapor-phase concentration  $y_C$  would therefore be estimated by the following equation.

$$y_C = \frac{\bar{P}_C x_C}{P_t} \quad (20)$$

About  
the  
Author



H. H. YANG is an assistant professor of chemical engineering at Lamar State College of Technology, Beaumont, Texas. Before coming to the U. S. in 1952 to take graduate studies in chemical engineering, Dr. Yang was assistant process engineer for Chinese Petroleum Corp.'s Kaohsiung refinery on Formosa. He is a graduate of China's National Chung Chen University, holds an M.S. degree from the University of Notre Dame, and a Ph.D. degree from the University of Michigan.

Comment

The phase equilibria of a few binary systems of hydrocarbons were also examined according to Equation (16) and showed satisfactory agreement with experimental data in the literature. Experimental work pertaining to the extensive evaluation of the hypothesis, however, is not available at this time. The author welcomes any criticism, suggestion and assistance for the development of this proposed hypothesis.

NOMENCLATURE

- A, B, C, i = components in a homogeneous mixture
- p = partial pressure of component
- P = vapor pressure of a pure component
- P = tangential intercept on a  $P_t - x$  plot, or partial molal vapor pressure of a component in a mixture
- $P_t$  = total pressure of a homogeneous mixture
- x = mole fraction of a component in the liquid phase
- y = mole fraction of a component in the vapor phase
- $\gamma$  = activity coefficient

LITERATURE CITED

Chu, J. C., "Distillation Equilibrium Data," Reinhold, New York, 1950.









