Multicomponent, Multiphase Vapor-Liquid Equilibrium Data from the Method of Intersecting Isochores

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Recently, we proposed the method of intersecting isochores as a technique for collecting vapor-liquid equilibrium data for binary systems without measuring composition (Hall, Eubank, Myerson, and Nixon, 1975). In this note, we shall demonstrate how the technique also applies to multicomponent, multiphase systems still without requiring composition measurements.

The method of intersecting isochores exploits the observation that for different overall compositions in a given system, isochores intersect in the two-phase region. Figure 1 presents a visual illustration of this statement. For a binary system, the phase rule dictates that at the point of intersection no degrees of freedom exist; therefore, the phase densities and phase compositions are identical for the two overall compositions. Measurement of the phase densities, for example, with a magnetic densimeter, allows calculation of the phase compositions from simple material balances:

$$(\rho_F Z)_1 = Y\phi_1\rho_V + X(1-\phi_1)\rho_L \quad (1)$$

$$(\rho_F Z)_2 = Y\phi_2\rho_V + X(1-\phi_2)\rho_L \quad (2)$$

$$\phi_i = \frac{\rho_{F_i} - \rho_L}{\rho_V - \rho_L} \quad (3)$$

where ρ is the density, Z is the overall composition, Y is the vapor phase composition, X is the liquid phase composition, and the subscripts F, V, and L denote properties of overall mixture, saturated vapor, and saturated liquid, respectively. Clearly, simultaneous solution of Equations (1) and (2) will produce Y and X.

While the binary, two-phase solution demonstrated the power of intersecting isochores, the usefulness of this technique is not restricted to this simple situation. For future reference denote this solution S(2,2) for Solution (2 components, 2 degrees of freedom). Now let us examine the binary, three-phase problem. The phase rule reveals

$$f = c + 2 - p = 2 + 2 - 3 = 1 \quad (4)$$

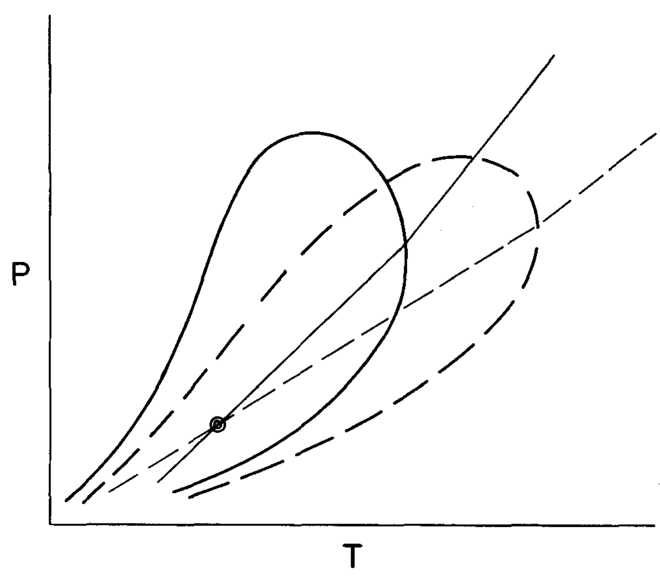

Fig. 1. Illustration of method of intersecting isochores. Solid lines represent one overall composition; dashed lines represent another overall composition.

where f denotes degrees of freedom, c is the number of components, and p is the number of phases. This is actually a simpler situation than that of S(2,2), for here the isochores need not intersect; they only need to be at the same T or P. Isochores usually result from changing the temperature of a constant volume system so the data can easily be collected at the same temperature. Under these conditions, simultaneous solution of Equations (1) and (2) produces S(2,1). The point solution S(2,0) is of little interest.

A shift to ternary systems S(3,1) is identical with S(2,1), and S(3,2) is identical with S(2,2). Thus ternary, three-phase and ternary, four-phase systems represent the same difficulty as binary systems. The ternary, two-phase system is equally simple but of greater dimensionality. Normally, when ternary data are collected, the mole ratio of two components is fixed, and the third component is

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introduced to this mixture in varying proportions. The fixed mole ratio is a phase rule restriction, so the degrees of freedom become

$$f = c + 2 - p - r = 3 + 2 - 2 - 1 = 2 \qquad (5)$$

Therefore, $S(3,3)$ reduces to $S(2,2)$, and ternary systems are also amenable to study by the method of intersecting isochores without composition measurements.

The obvious effect of fixing a mole ratio in the ternary system is to convert it into an effective binary system. One component is a lumped binary, and the remaining component is a natural one. Obviously, this technique can be extended to a lumped component with any number of natural components in it, thereby converting any multicomponent mixture into an effective binary for which $S(2,2)$ would apply. In summary, we may write

$$\left.\begin{array}{l} S(2,0) = S(3,0) = S(4,0) = \ldots \\ S(2,1) = S(3,1) = S(4,1) = \ldots \\ S(2,2) = S(3,2) = S(4,2) = \ldots \\ S(2,2) = S(3,3)^* = S(4,3)^* = \ldots \\ S(2,2) = S(3,3)^* = S(4,4)^* = \ldots \end{array}\right\} \qquad (6)$$

where the superscript* denotes utilizing the effective binary concept.

In our earlier paper (Hall, Eubank, Myerson, and Nixon, 1975) we utilized a Burnett apparatus as the basic instrument for collecting binary data by the method of intersecting isochores. This apparatus is also advantageous for multicomponent systems. Hall and Eubank (1974) described a technique for making mixtures very precisely in a Burnett apparatus. Their procedure consisted of filling one Burnett cell with pure a and measuring the pressure P_a, then filling the other Burnett cell with pure b and measuring the pressure P_b. By allowing the two cells to communicate at this point, they produce a mixture whose composition is

$$x_b = \frac{B}{A+B} \qquad x_a = 1 - x_b \qquad (7)$$

where A and B are

$$A = \frac{P_a}{z_a} \qquad B = (N-1)\frac{P_b}{z_b} \qquad (8)$$

z_i is the compressibility factor of pure i at P_i and N is the Burnett cell constant. To study a ternary with a fixed mole ratio of the first two components, we first make a binary mixture of these components in this manner then isolate and evacuate the second Burnett cell. Now, pure component c can be introduced into the second cell at P_{c1}. When the cells are connected, a mixture results with composition

$$x_c = \frac{C}{A+B+C} \qquad x_b = \frac{B}{A+B+C} \qquad x_a = 1 - x_b - x_c \qquad (9)$$

where A and B remain as in Equation (8), and C is

$$C = N(N-1)\frac{P_{c1}}{z_{c1}} \qquad (10)$$

To change the composition of component c, again isolate, evacuate, and then fill the second Burnett cell with pure c at P_{c2}; then connect the Burnett cells. Equation (9) again provides the composition, but Equation (10) becomes

$$C = N(N-1)\frac{P_{c1}}{z_{c1}} + N^2(N-1)\frac{P_{c2}}{z_{c2}} \qquad (11)$$

In general, C will be

$$C = (N-1)\sum_{k=1}^{KC} N^k (P_{ck}/z_{ck}) \qquad (12)$$

where KC is the number of additions of component c. Note that the ratio of x_a/x_b remains constant as required. Repetition of the experiment for various ratios of x_a/x_b will map the surface. Similar manipulations would produce quaternary mixtures or any other multicomponent mixtures.

We believe that this note completes the basic description of the method of intersecting isochores for collecting precise VLE data at varying conditions without measuring composition. This method should be especially useful in systems such as widely varying molecular weights or polarities, multiphase, multicomponent. These systems are very difficult to sample, and yet the magnetic densimeter will routinely measure the phase densities.

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NOTATION

A = dummy variable for Equation (9)
B = dummy variable for Equation (9)
C = dummy variable for Equation (9)
c = number of components in phase rule
f = degrees of freedom from phase rule
KC = number of additions of component c
N = Burnett cell constant
p = number of phases in phase rule
P = pressure
r = number of restrictions in phase rule
$S(c,f)$ = dummy variable indicating various solutions
T = temperature
X = mass fraction liquid
x = mole fraction liquid
Y = mass fraction vapor
Z = mass fraction feed
z = compressibility factor

Subscripts

a, b, c, i = various components
F = feed
L = liquid
V = vapor

LITERATURE CITED

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