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Direct Solution of the Isothermal Gibbs-Duhem Equation by an Iterative Method for Binary Systems

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The direct technique for numerically integrating the isothermal Gibbs-Duhem equation as demonstrated by Ljunglin (1962) is advantageous because it provides a single differential equation directly relating the experimental vapor pressure data to the vapor compositions to be calculated. For a binary system with vapor and liquid phases in equilibrium at low pressure, this equation is:

$$\frac{dy}{dx} = \frac{y(1-y)}{(y-x)}\,\frac{d\ln P}{dx} \tag{1}$$

As discussed by White and Lawson (1970) and Van Ness (1970), the stepwise integration of Equation (1) must always proceed in the direction of increasing pressure, or numerical instabilities occur. This presents only minor problems for binary systems; however, possibly for this reason, the technique has never been developed for multicomponent systems.

Mixon (1965) used a numerical relaxation technique to indirectly (through the excess Gibbs free energy) solve the isothermal Gibbs-Duhem equation and successfully applied the method to a ternary system. In this note, we have applied Mixon's numerical relaxation technique to a rigorous form of Equation (1). This new direct method of solution can, in theory, be extended to multicomponent systems. The validity of the basic equations and the viability of the numerical method are demonstrated by application of the method to four systems with highly nonideal vapor pressure curves.

Using the standard thermodynamic relationships developed in texts on phase equilibrium, we can show that the rigorous counterpart to Equation (1) is

$$[1+(\alpha-1)x]\Delta Z d\ln P/dx = (\alpha-1) + x(1-x)$$
$$(\alpha-1)\,[d\ln(\phi_1/\phi_2)/dx + d\ln\alpha/dx] \tag{2}$$

where

$$\alpha \equiv y(1-x)/x(1-y) \tag{3}$$

is the relative volatility

$$\Delta Z \equiv Z^V - Z^L \tag{4}$$

is the difference between the compressibility factors for the vapor and liquid phases, and

$$\phi_i = f_i/y_iP \tag{5}$$

is the vapor phase fugacity coefficient for component i.

In Equation (2), the relative volatility (α) has been chosen to describe the vapor phase composition because it is closely related to the cost of an appropriately designed distillation column for the separation of the components and because, unlike Equation (1), Equation (2) is well defined at the points $x = 0$, $x = 1$, and $\alpha = 1$. In particular

$$\text{at}\quad x=0,\quad \alpha = 1 + \Delta Z\,d\ln P/dx \tag{6}$$

$$\text{at}\quad x=1,\quad \alpha = 1/(1-\Delta Z\,d\ln P/dx) \tag{7}$$

and

$$\text{at}\quad \alpha=1,\quad \Delta Z\,d\ln P/dx = 0 \tag{8}$$

The term $d\ln(\phi_1/\phi_2)dx$ in Equation (2) is related to a vapor phase equation of state through

$$d\ln(\phi_1/\phi_2)/dx = [\partial\ln(\phi_1/\phi_2)/\partial y]_P\,dy/dx$$
$$+\,[\partial\ln(\phi_1/\phi_2)/\partial\ln P]_y\,d\ln P/dx \tag{9}$$

in which dy/dx can be expressed in terms of α by

$$dy/dx = \frac{\alpha[x(1-x)d\ln\alpha/dx + 1]}{[1+(\alpha-1)x]^2} \tag{10}$$

An additional constraint on the $P - x$ curve at an azeotrope ($\alpha = 1$) can be developed by rearranging Equation (2) and applying l'Hospital's rule to give

$$1 - x\{\Delta Z d\ln P/dx - (1-x)$$
$$[d\ln\alpha/dx + d\ln(\phi_1/\phi_2)/dx]\}$$
$$= \frac{\Delta Z\,d\ln P/dx}{\alpha-1} = \frac{\Delta Z\,d^2\ln P/dx^2}{d\ln\alpha/dx} \tag{11}$$

Equation (11) is quadratic in $d\ln\alpha/dx$, and by requiring the discriminant in the quadratic formula to be positive,

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Table 1. Analysis of the P-x Fitting Procedure

Binary system	Type of fit for the P-x data	Root mean square ΔP, mm Hg
Chloroform-ethanol at 55°C	Spline fit— 10 intervals 39 points	0.25
Acetone-chloroform at 50°C	Polynomial fit— 6th degree 69 points	0.60
Chloroform-methanol at 50°C	Spline fit— 10 intervals 38 points	0.27
Chloroform-*n*-heptane at 50°C	Polynomial fit— 3rd degree 39 points	0.26

we get [Equations (8), (9), and (10) have been used to evaluate $d\ln(\phi_1/\phi_2)/dx$]

$$-\left(\frac{d^2P}{dx^2}\right)_{az} \leq \frac{P}{4x(1-x)}\left\{\frac{1+x(1-x)[\partial\ln(\phi_1/\phi_2)/\partial y]_P}{\Delta Z}\right\} \quad (12)$$

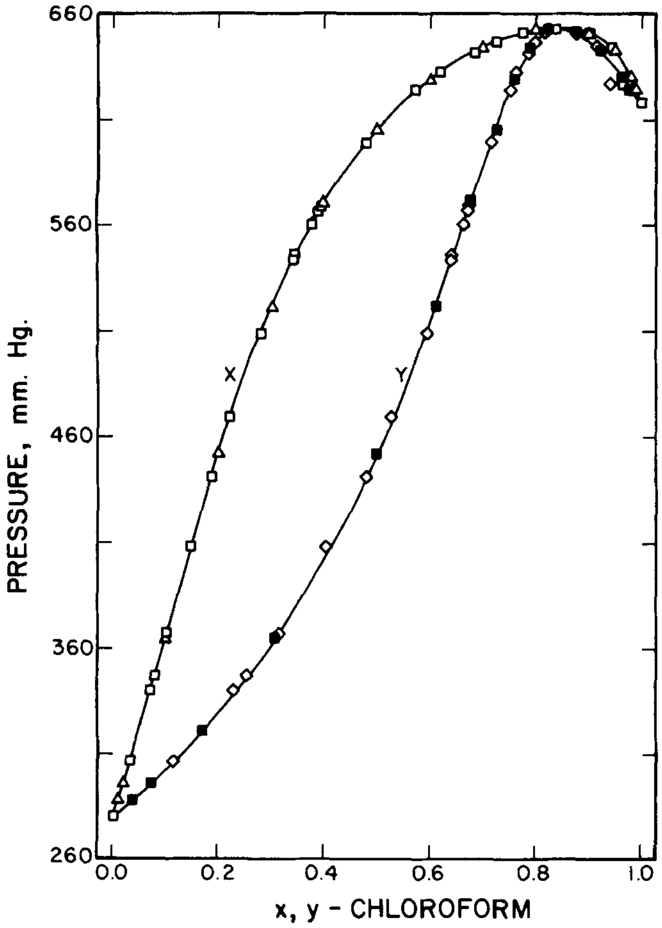

Fig. 1. Vapor pressure at 55°C binary: chloroform-ethanol. Experimental data points by Scatchard and Raymond (1938).

□ Raw P-x data △ Smoothed P-x data

◇ Raw P-y data ■ Smoothed P-y data

Solid line through the P-x points from a spline fit. Solid line through the P-y points is the solution to Equation (2).

Equations (2), (9), and (10) plus a vapor phase equation of state and liquid phase specific volumes are all that are needed to calculate thermodynamically consistent vapor compositions from experimental total pressure data.

The numerical solution of Equation (2) combines Newton's method with block relaxation. A function F is defined at each $x = x_i$ on a grid by

$$F_i \equiv [1+(\alpha-1)x]\Delta Z\, d\ln P/dx - (\alpha-1)$$
$$- x(1-x)(\alpha-1)\,[d\ln(\phi_1/\phi_2)/dx + d\ln\alpha/dx] \quad (13)$$

$d\ln\alpha/dx$ [which also occurs implicitly in $d\ln(\phi_1/\phi_2)/dx$] is evaluated by using finite differences, so that

$$(d\ln\alpha/dx)_i = \frac{(\ln\alpha)_{i+1} - (\ln\alpha)_{i-1}}{2\Delta x} \quad (14)$$

where Δx is the grid step size.

The unknown in Equation (13) is the relative volatility α. We then define the $(n+1)$st approximation to $\ln(\alpha)$ as

$$(\ln\alpha)_i^{n+1} = (\ln\alpha)_i^n + a_i^n \cdot pk \quad (15)$$

and bring the $(n+1)$st approximation to $\ln\alpha$ closer to the real value.

In order to obtain the value of a_i^n in Equation (15), we apply Newton's method to Equation (13):

$$F_i^{n+1} = F_i^n + \sum_i \left(\frac{\partial F}{\partial\ln\alpha}\right)_i^n a_i^n \quad (16)$$

in which the partial derivatives are calculated from Equation (13). We would like to determine a value of a_i^n so that $F_i^{n+1} = 0$, which is the solution to Equation (13). Incorporating this condition into Equation (16), substituting F_i' for $(\partial F/\partial\ln\alpha)_i^n$, and expanding the summation term, we get

$$F'_{i-1}a^n_{i-1} + F_i'a_i^n + F'_{i+1}a^n_{i+1} = -F_i^n \quad (17)$$

Applying Equation (17) to all mesh points on the x axis, we obtain M equations by assuming M mesh points and M unknowns a_1 through a_M. This results in a tridiagonal matrix, which can be solved very efficiently by using the method of Bruce et al. (1953).

To start the iterative procedure for the solution of Equation (13), initial estimates for α were calculated from Equation (2) by assuming $d\ln\alpha/dx = 0$. Also, a convergence factor, pk in Equation (15), was introduced in order to speed convergence. A value of 0.5 for pk worked best.

RESULTS

To test the method, several sets of data were used. The classical P-x-y data of Scatchard and Raymond (1938) for the chloroform-ethanol binary system at 55°C were used because they are known to be of the highest quality, they contain an azeotrope, and they are nonideal. Several studies using different approaches have been made with this data (Mixon et al., 1965; Nagata and Ohta, 1974; Abbott and Van Ness, 1975). The three systems reported by Abbott and Van Ness (1975) were used because of their variety in nonideal behavior and because the P-x data appear to be of the highest quality. These systems are acetone-chloroform (negative deviations from Raoult's law and a maximum boiling-point azeotrope), chloroform-methanol (positive deviations from Raoult's law and a minimum boiling-point azeotrope), and chloroform-*n*-heptane (positive deviations from Raoult's law and no axeotrope).

In these calculations, we assumed the virial equation of state

$$Z^V = 1 + BP, \quad \text{where} \quad B = y_1B_{11} + y_2B_{22} + y_1y_2\delta_{12} \tag{18}$$

for the vapor phase, and

$$v^L = x_1v_1{}^L + x_2v_2{}^L \tag{19}$$

for the liquid phase. The P-x data were correlated with polynomials or spline fits as shown in Table 1.

In each of the four cases, convergence was sensitive to the value of pk (the convergence parameter) and to the nature of the P-x equation chosen to fit the data. However, after several trials, each case was satisfactorily solved. The results for the chloroform-ethanol system are shown in Figure 1.

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NOTATION

a = increment for α
B = second virial coefficient
f = fugacity
F = function of α and x
P = pressure
pk = convergence parameter
v = specific volume
x = liquid mole fraction of component 1
y = vapor mole fraction of component 1
Z = compressibility factor
α = relative volatility
δ = binary interaction parameter
ϕ = fugacity coefficient

Subscripts

i, j = component, grid point

Superscripts

L = liquid phase
n = iteration
V = vapor phase

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Light Transmission Through Bubble Swarms

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Light transmission is a well-developed technique for determining particle size in dispersions (Rose and Lloyd, 1946; Boll and Sliepcevich, 1956; Dobbins and Jizmagian, 1966), and it has often been adopted for measurement of interfacial area in liquid-liquid and gas-liquid dispersions (Calderbank, 1958; Lee and Ssali, 1971; Trice and Rodger, 1956). The theory for the attenuation of the light beam has been given by a number of workers (Rose and Lloyd, 1946; Calderbank, 1958). Mclaughlin and Rushton (1973) have recently published a numerical confirmation of the theory for polydisperse systems, and the same result has been obtained more simply by Curl (1974).

The equation which applies is

$$\log_{10}\left(\frac{I_o}{I}\right) = \frac{Kal}{9.21} \tag{1}$$

Equation (1) holds when scattered light is not received by the detector, and K is approximately unity for particles having $d > 100\ \mu\text{m}$.

Experimental verification of the equation for gas-liquid systems has apparently been confined to low values of gas holdup, and reported holdups are less than 7% (Calderbank, 1958). This is probably because it is difficult to generate bubble swarms of well-defined properties at gas holdups much above 7%. Even for solid-liquid and liquid-liquid dispersions, however, Equation (1) has

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