



01 Jan 1977

Direct Solution Of The Isothermal Gibbs-duhem Equation By An Iterative Method For Binary Systems

J. A. Martinez-Ortiz

David B. Manley

Missouri University of Science and Technology

Follow this and additional works at: https://scholarsmine.mst.edu/che_bioeng_facwork



Part of the [Biochemical and Biomolecular Engineering Commons](#)

Recommended Citation

J. A. Martinez-Ortiz and D. B. Manley, "Direct Solution Of The Isothermal Gibbs-duhem Equation By An Iterative Method For Binary Systems," *AIChE Journal*, vol. 23, no. 3, pp. 393 - 395, Wiley; American Institute of Chemical Engineers (AIChE), Jan 1977.

The definitive version is available at <https://doi.org/10.1002/aic.690230329>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Chemical and Biochemical Engineering Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

Richterich, R., *Clinical Chemistry*, S. Karger, Basel, Switzerland (1969).
 Schmid-Schönbein, H., and R. E. Wells, "Rheological Properties of Human Erythrocytes and their Influence upon the Anomalous Viscosity of Blood," *Ergebnisse der Physiol.*, **63**, 146 (1971).
 Stroeve, P., "On the Diffusion of Gases in Protein Solutions," *Ind. Eng. Chem. Fundamentals*, **14**, 140 (1975).
 ———, K. A. Smith, and C. K. Colton, "Facilitated Diffusion of Oxygen in Red Blood Cell Suspensions," Second Intern.

Symp. on Oxygen Transport to Tissue, Mainz, W. Germany, *Advances in Experimental Medicine and Biology*, G. Thews, J. Grote, and D. D. Reneau, ed., Vol. 75, p. 191, Plenum New York (1976a).
 ———, "An Analysis of Carrier-Facilitated Transport in Heterogeneous Media," *AIChE J.*, **22**, 1125 (1976b).
 Weissman, M. H., "Anomalous Oxygen Uptake by Flowing Blood," *Ann. Biomed. Eng.*, **1**, 468 (1973).
 Manuscript received September 28, 1976; revision received December 10 and accepted December 13, 1976.

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

J. A. MARTINEZ-ORTIZ

and

DAVID B. MANLEY

Chemical Engineering Department
 University of Missouri-Rolla
 Rolla, Missouri 65401

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:

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

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

$$[1 + (\alpha - 1)x] \Delta Z d \ln P/dx = (\alpha - 1) + x(1 - x) \quad (2)$$

where

$$\alpha \equiv y(1-x)/x(1-y) \quad (3)$$

is the relative volatility

$$\Delta Z \equiv Z^V - Z^L \quad (4)$$

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

$$\phi_i = f_i/y_i P \quad (5)$$

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

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

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

and

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

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

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

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

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

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

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

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

Correspondence concerning this note should be addressed to David B. Manley. J. A. Martinez-Ortiz is with Escuela de Ing. Quimica, Universidad de Costa Rica, Costa Rica, Central America.

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 $d \ln(\phi_1/\phi_2)/dx$]

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

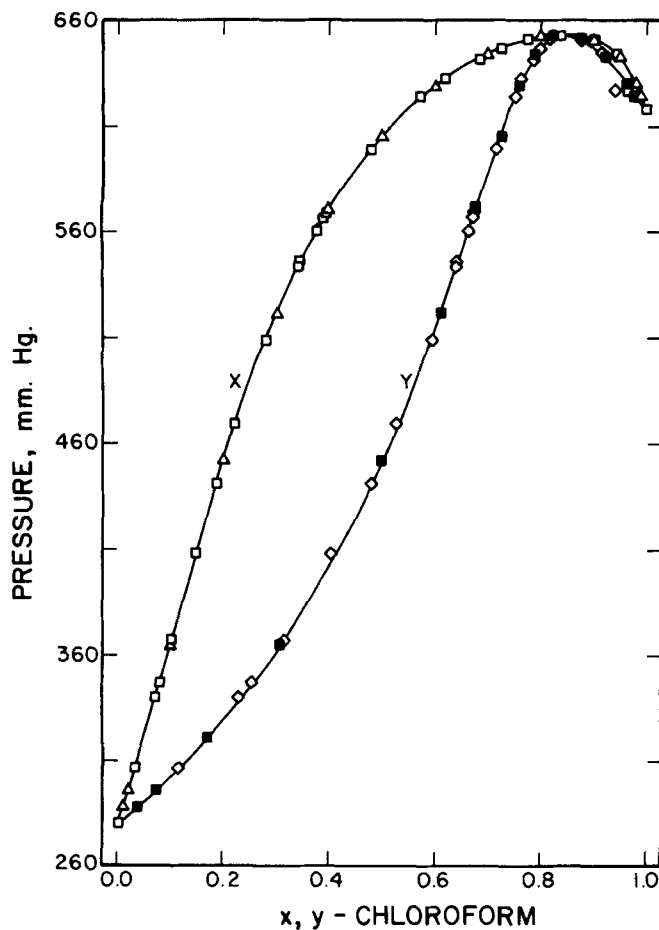


Fig. 1. Vapor pressure at 55°C binary: chloroform-ethanol. Experimental data points by Scatchard and Raymond (1938).

- 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):

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

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 $(\partial F/\partial \ln \alpha)_i$, and expanding the summation term, we get

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

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 azeotrope).

In these calculations, we assumed the virial equation of state

$$Z^V = 1 + BP, \quad \text{where} \quad B = y_1 B_{11} + y_2 B_{22} + y_1 y_2 \delta_{12} \quad (18)$$

for the vapor phase, and

$$v^L = x_1 v_1^L + x_2 v_2^L \quad (19)$$

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.

ACKNOWLEDGMENT

Computational services were provided by the Department of Chemical Engineering at the University of Missouri-Rolla. Financial support for the research was provided by the Petroleum Research fund, administered by the American Chemical Society and by the Department of Chemical Engineering at the University of Missouri-Rolla.

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

LITERATURE CITED

- Abbott, M. M., J. K. Floess, G. E. Walsh, and H. C. Van Ness, "Vapor-Liquid Equilibrium: Part IV, Reduction of P - X Data for Ternary Systems," *AIChE J.*, **21**, 72 (1975).
- Abbott, M. M., and H. C. Van Ness, "Vapor-Liquid Equilibrium: Part III, Data Reduction with Precise Expression for GE ," *ibid.*, 62 (1975).
- Bruce, G. H., D. W. Peaceman, H. H. Rachford, and J. D. Rice, "Calculations of Unsteady-State Gas Flow Through Porous Media," *Trans. Am. Inst. Min. Met. Petrol. Engrs.*, **198**, 79 (1953).
- Ljunglin, J. J., and H. C. Van Ness, "Calculation of Vapor-Liquid Equilibria from Vapor Pressure Data," *Chem. Eng. Sci.*, **17**, 531 (1962).
- Mixon, F. O., B. Gumowshi, and B. H. Carpenter, "Computation of Vapor-Liquid Equilibrium Data from Solution Vapor Pressure Measurements," *Ind. Eng. Chem. Fundamentals*, **4**, 455 (1965).
- Nagata, I. and T. Ohta, "Computation of Vapor-Liquid Equilibrium Data from Binary and Ternary Vapor Pressure and Boiling Point Measurements," *Ind. Eng. Chem. Process. Design Develop.*, **13**, 304 (1974).
- Scatchard, G., and C. L. Raymond, "Vapor Liquid Equilibrium, II, Chloroform-Ethanol Mixtures at 35, 45, and 55°," *J. Am. Chem. Soc.*, **60**, 1278 (1938).
- Van Ness, H. C., "On Integration of the Coexistence Equation for Binary Vapor-Liquid Equilibrium," *AIChE J.*, **16**, 18 (1970).
- White, N., and F. Lawson, "The Integration of the Gibbs-Duhem Equation for a Binary Two Phase System at Constant Temperature," *Chem. Eng. Sci.*, **25**, 225 (1970).
- Manuscript received November 23, 1976, and accepted January 14, 1977.*

Light Transmission Through Bubble Swarms

M. J. LOCKETT

and

A. A. SAFEKOURDI

Department of Chemical Engineering
 University of Manchester Institute
 of Science and Technology
 Manchester 1, England

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

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

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

A. A. Safekourdi is at Arya-Mehr University, P.O. Box 3406, Tehran, Iran.