A Method for Multicomponent Equilibrium Calculations by Using Dew Point Pressure-Vapor Composition Data

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Numerical integration of total vapor pressure-liquid composition curves with the Gibbs-Duhem equation is an established tool for calculating vapor-liquid equilibria of binary systems (*1* to *9*). The procedure is usually employed with isothermal data, since isobaric data may require accurate values of the heat of mixing. In contrast, it has only rarely been used for multicomponent systems. This is largely explained by the increasing complexity of the calculational procedures and the greater quantity of data required as the number of components is increased beyond 2.

Mixon et al. (*10*) have given a general procedure for isothermal multicomponent total pressure-liquid composition data. It is essentially a generalization of the method of Tao (*9*) for binary mixtures. Though the method is fairly complex, it is well within the capability of any high speed computer.

A second procedure has recently been proposed which, though much simpler, lacks generality (*11*). It starts with the equation originally proposed by Ljunglin and Van Ness (*8*) for binary systems:

$$\frac{dy_1}{dP} = \frac{\psi y_1(1-y_1)}{y_1 - x_1} \tag{1}$$

Separating the variables, the equation was written for multicomponent systems as

$$\left(\frac{\partial y_1}{\partial x_1}\right)_{\substack{n_j\\ j=2,3,4,\ldots}} = \frac{\psi y_1(1-y_1)}{y_1 - x_1}\left(\frac{\partial P}{\partial x_1}\right)_{\substack{n_j\\ j=2,3,4,\ldots}} \tag{2}$$

in which n_j refers to constant mole numbers for all components except component 1, and ψ is a correction for gas phase nonideality. The derivatives are taken such that all mole fractions except x_1 remain in a fixed ratio as x_1 is varied. It can be shown that this is exact for an ideal liquid phase. Unfortunately, it is not correct for nonideal liquid phases in multicomponent systems, as will be explained later.

DEW POINT PRESSURE METHOD

All the above methods, both binary and multicomponent, employ bubble point pressures and composition with the Gibbs-Duhem equation for the calculation of the vapor-phase composition. There is no reason, however, why dew point pressures and vapor-phase compositions cannot be used. While the equipment for dew point measurements is more complex, such apparatus have been constructed, and variations could easily be designed.

Generally, the sample would be vaporized and the isothermal pressure-volume relations recorded until condensation occurred, as noted by a break in the pressure-volume curve; if the pressure rise is rapid as compared with heat transfer, the process will be nearly adiabatic. Then $\Delta T/\Delta P \cong v/C_p$. Since the apparent heat capacity will include the latent heat, it will show a large change at the dew point. An obvious bonus from this procedure would be the byproduct pressure-volume data from which fugacity coefficients could be calculated. The unavailability of the latter is frequently the weakness in the total pressure method. Fortunately, there is also an enormous simplification in the resulting equations as compared with the corresponding liquid-phase calculations.

At constant temperature, the Gibbs-Duhem equation may be written as

$$\sum_{i=1}^{N} x_i\, d\mu_i = v_l\, dP \tag{3}$$

At equilibrium, the chemical potentials are equal in each phase, and the gas-phase chemical potentials can be substituted for those of the liquid. For the gas phase

$$\mu_i = \mu_i^0 + RT\ \ln f_i$$

or

$$\mu_i = \mu_i^0 + RT\ \ln \phi_i p_i$$

and, since $p_i = Py_i$

$$\mu_i = \mu_i^0 + RT\ \ln \phi_i y_i P \tag{4}$$

in which ϕ_i is the fugacity coefficient of component i in the gas phase given by

$$\ln\frac{f_i}{p_i} = \ln\phi_i = \int_0^P \left(\frac{\overline{V}_i}{RT} - \frac{1}{P}\right) dP \tag{5}$$

and y_i is the vapor phase mole fraction. Substituting Equation (4) in (3), we get

$$\sum_{i=1}^{N} x_i\, d\ln\phi_i + \sum_{i=1}^{N} \frac{x_i}{y_i}\, dy_i = \left(\frac{v_l}{RT} - \frac{1}{P}\right) dP \tag{6}$$

Now we will restrict ourselves to a change in vapor composition in which the ratios of all mole fractions remain the same except one component which we will designate as component one. (This is the same result that would be obtained if the number of moles of component one changed but all other mole numbers remained constant.) Then, Equation (6) becomes

$$\sum_{i=1}^{N} x_i\left(\frac{\partial \ln\phi_i}{\partial n_1}\right)_{n_j,T} + \frac{x_i}{y_i}\left(\frac{\partial y_i}{\partial n_1}\right)_{n_j,T} = \left(\frac{v_l}{RT} - \frac{1}{P}\right)\left(\frac{\partial P}{\partial n_1}\right)_{n_j,T} \tag{7}$$

where n_j represents n_2, n_3, --- n_N. Now

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$$y_i = \frac{n_i}{n_1 + \sum_{j=2}^{N} n_j}$$

$$\left(\frac{\partial y_i}{\partial n_1}\right)_{n_j} = -\frac{n_i}{\left[n_1 + \sum_{j=2}^{N} n_j\right]^2} = -\frac{y_i}{n_T}$$

$$\left(\frac{\partial y_1}{\partial n_1}\right)_{n_j} = \left[\partial\left(\frac{n_1}{n_1 + \Sigma\, n_j}\right) \Big/ \partial n_1\right]_{n_j} = \frac{\Sigma n_j}{{n_T}^2} = \frac{1-y_1}{n_T}$$

Now, Equation (7) becomes

$$\sum_{i=1}^{N} x_i \left(\frac{\partial \ln\phi_i}{\partial n_1}\right)_{nj,T} + \frac{(1-y_1)x_1}{y_1 n_T} - \sum_{i=2}^{N} \frac{x_i}{y_i}\,\frac{y_i}{n_T} = \left(\frac{v_l}{RT} - \frac{1}{P}\right)\left(\frac{\partial P}{\partial n_1}\right)_{nj,T} \quad (8)$$

but

$$\left(\frac{\partial P}{\partial n_1}\right)_{nj,T} = \left(\frac{\partial P}{\partial y_1}\,\frac{\partial y_1}{\partial n_1}\right)_{nj,T} = \left(\frac{\partial P}{\partial y_1}\right)_{nj,T} \frac{1-y_1}{n_T}$$

$$\left(\frac{\partial \ln\phi_i}{\partial n_1}\right)_{n,jT} = \left(\frac{\partial \ln\phi_i}{\partial y_1}\,\frac{\partial y_1}{\partial n_1}\right)_{nj,T} = \left(\frac{\partial \ln\phi_i}{\partial y_i}\right)_{nj,T} \frac{1-y_1}{n_T}$$

Substituting in (8) and canceling, we obtain

$$\sum_{i=1}^{N} x_i \left(\frac{\partial \ln\phi_i}{\partial y_1}\right)_{nj,T} (1-y_1) + \frac{(1-y_1)x_1}{y_1} - \sum_{i=2}^{N} x_i = \left(\frac{v_l}{RT} - \frac{1}{P}\right)\left(\frac{\partial P}{\partial y_1}\right)_{nj,T} (1-y_1)$$

But

$$\sum_{i=2}^{N} x_i = 1 - x_1$$

Substituting and dividing by $1 - y_1$ and rearranging, we get

$$\frac{y_1 - x_1}{y_1(1-y_1)} = \left(\frac{1}{P} - \frac{v_l}{RT}\right)\left(\frac{\partial P}{\partial y_1}\right)_{nj,T} + \sum_{i=1}^{N} x_i \left(\frac{\partial \ln\phi_i}{\partial y_1}\right)_{nj,T} \quad (9)$$

This can be solved for x_1 to give

$$x_1 = y_1 - y_1(1-y_1)\left(\frac{1}{P} - \frac{v_l}{RT}\right)\left(\frac{\partial P}{\partial y_1}\right)_{nj,T} - y_1(1-y_1)\sum_{i=1}^{N} x_i \left(\frac{\partial \ln\phi_i}{\partial y_1}\right)_{nj,T} \quad (10)$$

Inspection of Equation (9) shows why Equation (2) was invalid, in general, for multicomponent mixtures. By assuming an ideal gas phase and by ignoring the liquid phase volume, Equation (2) becomes

$$\left(\frac{\partial y}{\partial x_1}\right)_{n_j\left(\substack{\text{liquid}\\\text{phase}}\right),T} = \frac{y_1(1-x_1)}{y_1 - x_1}\left(\frac{\partial P}{\partial x_1}\right)_{n_j\left(\substack{\text{liquid}\\\text{phase}}\right),T} \frac{1}{P}$$

and Equation (9) becomes

$$\left(\frac{\partial y_1}{\partial P}\right)_{n_j\left(\substack{\text{gas}\\\text{phase}}\right),T} = \frac{y_1(1-y_1)}{y_1 - x_1}\,\frac{1}{P}$$

To make these equations identical, the partial in the second equation must be separated and written in terms of liquid-phase composition. This is not valid and will hold only if mole ratios in the liquid phase remain constant when those in the gas phase are constant. This is only generally true for ideal solutions.

Equation (10) may be used to solve directly for liquid compositions when pressure-vapor compositions are measured at constant mole ratios. Excellent results were obtained in an example in which the $p - y$ data were computer generated, and $\left(\frac{\partial P}{\partial y_1}\right)_{nj,T}$ and $\left(\frac{\partial \ln\phi_i}{\partial y_1}\right)_{nj,T}$ were calculated from spline fits of $p - y$ and $\ln\phi_i - y$ curves. Other expressions may be derived as follows:

$$d\ln\phi_i = \left(\frac{\partial \ln\phi_i}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial \ln\phi_i}{\partial P}\right)_{T,n_i} dP + \sum_{k=1}^{n}\left(\frac{\partial \ln\phi_i}{\partial n_k}\right)_{T,P,n_j} dn_k \quad (11)$$

from which

$$\left(\frac{\partial \ln\phi_i}{\partial y_1}\right)_{T,n_j} = \left(\frac{\partial \ln\phi_i}{\partial P}\right)_{T,n_i}\left(\frac{\partial P}{\partial y_1}\right)_{T,n_j} + \left(\frac{\partial \ln\phi_i}{\partial y_1}\right)_{T,P,n_j} \quad (12)$$

From Equation (5)

$$\left(\frac{\partial \ln\phi_i}{\partial P}\right)_{T,n_i} = \left(\frac{\overline{V}_i}{RT} - \frac{1}{P}\right)$$

Substituting this and Equation (12) into Equation (10), we get

$$x_1 = y_1 - y_1(1-y_1)\left[\left[\frac{\sum_i x_i \overline{V}_i - v_l}{RT}\right]\left(\frac{\partial P}{\partial y_1}\right)_{T,n_j} + \sum x_i \left(\frac{\partial \ln\phi_i}{\partial y_1}\right)_{T,P,n_j}\right] \quad (13)$$

If the gas phase may be considered an ideal solution

$$\phi_i = f_i/p_i = \frac{f_i^0 y_i}{P y_i} = \frac{f_i^0}{P}$$

in which f_i^0 is the fugacity of pure i at the temperature and pressure of the mixture, so

$$\left(\frac{\partial \ln\phi_i}{\partial y_1}\right)_{T,P,n_j} = 0$$

and

$$\overline{V}_i = v_i$$

Then, Equation (13) may be reduced to

$$x_1 = y_1 - y_1(1-y_1)\left[\frac{\sum_{i=1}^{N} x_i v_i - v_l}{RT}\right]\left(\frac{\partial P}{\partial y_1}\right)_{T,n_j} \quad (14)$$

or

$$x_1 = y_1 - y_1(1 - y_1)\left[\frac{\sum_{i=1}^{N} x_i z_i}{P} - \frac{v_l}{RT}\right]\left(\frac{\partial P}{\partial y_1}\right)_{T,n_j} \tag{15}$$

This can be iterated by assuming the vapor phase to be a perfect gas on the first trial. In this event, $\frac{\sum_i x_i z_i}{P} = \frac{1}{P}$, which is identical to Equation (10) with the last term neglected.

NOTATION

f = fugacity
n = number of moles
N = number of components in a solution
P = total pressure
p = partial pressure
$\overline{V}$ = partial molar volume
v = molar volume
x = liquid-phase mole fraction
y = gas-phase mole fraction
z = compressibility factor
ϕ = fugacity coefficient, f/p

Subscripts

i = any component or all components
j = all components but one
k = any component
l = liquid phase
T = total
1 = component 1

Superscripts

0 = pure component

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Friction Factors and Pressure Drops for Sinusoidal Laminar Flow in an Annulus

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Hershey and Song (*1*) examined the friction factors and pressure drops for sinusoidal flow of water and blood in rigid tubes. As pointed out in their paper, the pulsatile flow phenomenon is of great importance in many engineering applications, such as in pumping systems and heat and mass transfer operations. This analysis is concerned with the same problem in an annulus. The problem is first solved for the generalized case, where the initial velocity distribution is an arbitrary function of radial coordinate and the pressure gradient an arbitrary time-dependent quantity. The governing momentum equation is solved by double transformation technique. The solution agrees with that of special case (*2*).

The Navier-Stokes equation reduces, under the present assumptions, to

$$\frac{\partial u}{\partial t} = -\frac{g_c}{\rho}\frac{dp}{dz}(t) + \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial u}{\partial r}\right) \tag{1}$$

and the appropriate boundary conditions are

$$u(r, 0) = U(r) \tag{2}$$

$$u(R_1, t) = 0 \tag{3}$$

$$u(R_2, t) = 0 \tag{4}$$

To solve Equation (1) subject to conditions (2) to (4), we first use the finite Hankel transformation (3) with respect to r, defined by

$$\bar{u}(\xi_i, t) = \int_{R_1}^{R_2} ru(r, t)Z_0(\xi_i r)\,dr \tag{5}$$

where

$$Z_0(\xi_i r) = J_0(\xi_i r)Y_0(\xi_i R_2) - J_0(\xi_i R_2)Y_0(\xi_i r) \tag{6}$$

and the eigenvalues ξ_i are the positive roots of

$$J_0(\xi R_1)Y_0(\xi R_2) - J_0(\xi R_2)Y_0(\xi R_1) = 0 \tag{7}$$

Then, the Laplace transformation with respect to t is defined by

$$\bar{\bar{u}}(\xi_i, s) = \int_0^\infty \bar{u}(\xi_i, t)e^{-st}dt \tag{8}$$

Equation (1) with the conditions (2) to (4) is transformed, with certain arrangement, to

$$\bar{\bar{u}}(\xi_i, s) = \frac{\bar{U}(\xi_i)}{s + \nu\xi_i^2} - \frac{1}{s + \nu\xi_i^2}\frac{dp}{dz}(s)$$