De = eddy diffusivity, m^2/s
d = column diameter, m
F = full-wave oscillation
H = half-wave oscillation
h_f = froth height, m
h_L = clear liquid head, m
L^* = liquid rate, $m^3/(s)$ (m of weir)
S = stable biphase
V = superficial vapor velocity, m/s
V_i = full wave oscillation velocity, m/s
W = weir height, m
$\bar{\alpha}$ = h_L/h_f = relative froth density
ϵ = eddy viscosity, m^2/s
ρ_g = gas density, kg/m^3
ρ_L = liquid density, kg/m^3
g = acceleration due to gravity, m/s^2

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Thermodynamic Consistency Using Orthogonal Collocation or Computation of Equilibrium Vapor Compositions at High Pressures

The numerical method of orthogonal collocation is used within a thermodynamically consistent framework to calculate equilibrium vapor compositions from *P-T-x* data for binary systems. The method may be used for isothermal or isobaric data in both the normal liquid and in the critical region, and it applies to any choice of standard states.

To use the method it is necessary to have experimental or estimated values of vapor phase fugacity coefficients for both components in the mixture and liquid molar volumes (isothermal case) or heats of mixing (isobaric case). If vapor composition data are available, each set of *P-T-x-y* data may be checked for thermodynamic consistency by comparing *y* (experimental) with *y* (calculated). Illustrative calculations are given. The method is shown to provide an excellent procedure for obtaining Henry's constants from *P-x* data for systems with one noncondensable component.

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SCOPE

It has been known for three generations that the Gibbs-Duhem equation can be used (1) to test complete vapor-liquid equilibrium data for consistency, or (2) to extend incomplete vapor-liquid equilibrium data.

Hundreds of papers have been written on this subject but almost all deal with low-pressure data. Many deal with the area test which Van Ness et al. (1973) have shown to be unsatisfactory. A proper test is to use only some of the data and to predict the rest using the Gibbs-Duhem

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equation. A comparison of predicted and observed data then provides a rational basis for consistency.

Essentially there are two methods for extending limited vapor-liquid data: one is purely numerical, and the other makes use of an analytical expression for the excess Gibbs free energy. A classic example of the first method is the work of Boissonas (1939); this method, in effect, numerically integrates the two-phase coexistence equation using *P*-*x* data (at constant *T*) to predict *y*. Van Ness et al. (1973) developed this technique extensively and elegantly. A classic example of the second method is that of Barker (1953) who assumes an algebraic function for the activity coefficients; this function contains unknown constants which are then found (through iteration) by fitting to isothermal *P*-*x* data.

In principle either of these methods can be applied to high pressure vapor liquid equilibrium data. Extension to high-pressure systems requires additional information, namely, the fugacity coefficients of all components along the saturation line and either the liquid molar volume (for isothermal data) or the liquid molar enthalpy (for isobaric data).

The extension of Barker's method to high-pressure systems has been described recently by Won and Prausnitz (1973). The algebraic equation used in their work expresses binary activity coefficients in the unsymmetric convention as a function of composition using three parameters. The purpose of this work is to extend the method of Van Ness et al. to high-pressure systems. A numerical method for solving differential equations, the orthogonal collocation method, is used to calculate the value of the excess Gibbs free energy at chosen values of liquid composition. From these values, the equilibrium vapor mole fractions corresponding to each experimental liquid mole fraction are calculated.

CONCLUSIONS AND SIGNIFICANCE

The method of computing equilibrium vapor compositions from *P*-*x* or *T*-*x* data involves determination of the excess Gibbs free energy by a numerical procedure. This does not in principle differ from the method used by Van Ness et al. (1973); however modification of their procedure is necessary due to the following considerations: (1) If a noncondensable component is present, a convenient standard state for that component is the infinitely dilute solution at the temperature and pressure of the system. In this case the reference fugacity is Henry's constant. The method must thus be valid for more than one type of standard states. (2) The vapor phase is nonideal. (3) The isothermal-isobaric Gibbs-Duhem equation does not apply, necessitating the evaluation of liquid mixture volumes or enthalpies. (4) The thermodynamic equations, which are solved numerically, are highly nonlinear. It is therefore necessary to use a powerful numerical technique such as the orthogonal collocation method.

A generally applicable and thermodynamically consistent method of calculating excess Gibbs free energies and hence vapor compositions from *P*-*x* or *T*-*x* data is described. The method is tested using isothermal *P*-*x* data for systems representing a wide range of behavior: low-pressure conditions, high-pressure conditions with two condensable components, and high-pressure conditions with one condensable and one noncondensable component. The case of isobaric *T*-*x* data is the subject of a subsequent paper. For data believed to be of high accuracy, the calculated vapor compositions are found to agree very well with the observed values, also in the critical region. It appears, therefore, that the extension of the procedure used by Van Ness et al. (1973) to high pressures is a useful way to predict vapor compositions for high-pressure vapor- (or gas-) liquid equilibria from isothermal *P*-*x* data. The method provides an excellent means of obtaining Henry's constants from *P*-*x* data for many systems in the case of gas-liquid equilibria.

The method is shown to be successful in the prediction of vapor compositions from *P*-*x* data at low pressures for highly nonideal systems.

Binary vapor-liquid equilibrium data are often reported as the composition of the liquid phase either at constant pressure as a function of temperature or at constant temperature as a function of pressure. According to the phase rule, this information is enough to completely characterize the system and, using the tools of classical thermodynamics, the vapor phase compositions may be calculated. At high pressures it is necessary to know vapor phase fugacity coefficients and liquid molar volumes or heats of mixing.

If the experimental data consist of pressure, temperature, and the composition of both phases, the extra experimental information may be used to test the data for thermodynamic consistency, as shown in many textbooks (Van Ness, 1964; Prausnitz, 1969). However, Van Ness et al. (1973) have shown that the commonly applied area tests are of limited value. In general, the most reliable consistency test consists of calculating *y* from *P*-*x* (or *T*-*x*) data and then comparing the calculated *y*'s with the experimentally obtained values. For thermodynamically consistent data, the difference between *y* (exp.) and *y* (calc.) will be small.

In order to calculate vapor compositions from *P*-*x* or *T*-*x* data for high-pressure vapor-liquid equilibria or in order to test *P*-*T*-*x*-*y* data in this region for thermodynamic consistency, it is necessary to modify the procedure used by Van Ness et al. (1973), who only were concerned with low-pressure vapor-liquid equilibria. Modifications are necessary due to the following reasons:

1. In the critical region one component may be noncondensable, and in those cases it is convenient to use the unsymmetric convention for normalization of the activity coefficients. In this case, it is necessary to calculate Henry's constant. This convention is not used when only condensable components are present, and the consistency test must therefore be applicable to several choices of standard states.
2. Vapor-phase nonidealities must be carefully taken into account.
3. The differential Gibbs-Duhem equation includes a term containing the slope of the *P*-*x* or *T*-*x* curve. The value of this term is small at low to moderate pressures and is often neglected, but at high pressures this term cannot be neglected. In this case the liquid molar volumes

(isothermal case) or heats of mixing (isobaric case) must be known.

4. The thermodynamic equations, which are solved numerically for the activity coefficient of each component and the excess Gibbs energy, are highly nonlinear in the critical region. It is therefore necessary to use a powerful numerical technique, here orthogonal collocation.

The purpose of this work is to extend the method by Van Ness et al. to high-pressure vapor-liquid equilibria along the lines outlined above.

THERMODYNAMIC ANALYSIS

Using the tools of classical thermodynamics, it may be shown that the nonisothermal, nonisobaric Gibbs-Duhem equation leads to the following general equation: [see Van Ness (1964) or the supplement to this paper]

$$\left[VdP - \sum_i V_i^0 x_i dP_i^0\right]\frac{1}{RT} - \frac{H^E}{RT^2}dT = d\left(\frac{G^E}{RT}\right) - \sum_i \ln \gamma_i dx_i \quad (1)$$

The superscript E refers here to *excess thermodynamic properties,* the excess being with respect to the constituents in their standard states, denoted by superscript 0 $\left[\text{for example, } G^E = G - \sum_i x_i G_i^0 - G^{id}\right]$. The reader is referred to the nomenclature for further explanation of the symbols used. dP_i^0 vanishes when the standard state is at a fixed pressure. For isothermal data the standard state pressure is often equal to the system pressure in which case dP_i^0 is equal to dP and thus does not vanish.

Equation (1) is now applied to liquid systems in equilibrium with their vapors. For a binary system at saturation, (1) gives

$$\ln\gamma_1 - \ln\gamma_2 = \left(\frac{d(G^E/RT)}{dx_1}\right)_\sigma - \left[V\left(\frac{dP}{dx_1}\right)_\sigma - \sum_{i=1}^{2} x_i V_i^0\left(\frac{dP_i^0}{dx_1}\right)_\sigma\right]\frac{1}{RT} + \frac{H^E}{RT^2}\left(\frac{dT}{dx_1}\right)_\sigma \quad (2)$$

This result applies to either isothermal data, where $(dT/dx_1)_\sigma = 0$, or to isobaric data, where $(dP/dx_1)_\sigma$ and usually also $(dP_i^0/dx_1)_\sigma$ are equal to zero. The constraint of saturation is indicated by the subscript σ. For a binary mixture, the following relationship is also valid:

$$\frac{G^E}{RT} = x_1 \ln\gamma_1 + x_2 \ln\gamma_2 \quad (3)$$

which together with (2) gives

$$\ln\gamma_1 = \frac{G^E}{RT} + x_2\left(\frac{d(G^E/RT)}{dx_1}\right)_\sigma - \frac{x_2}{RT}\left[V\left(\frac{dP}{dx_1}\right)_\sigma - \sum_{i=1}^{2} x_i V_i^0\left(\frac{dP_i^0}{dx_1}\right)_\sigma\right] + \frac{x_2 H^E}{RT^2}\left(\frac{dT}{dx_1}\right)_\sigma \quad (4)$$

$$\ln\gamma_2 = \frac{G^E}{RT} - x_1\left(\frac{d(G^E/RT)}{dx_1}\right)_\sigma + \frac{x_1}{RT}\left[V\left(\frac{dP}{dx_1}\right)_\sigma - \sum_{i=1}^{2} x_i V_i^0\left(\frac{dP_i^0}{dx_1}\right)_\sigma\right] - \frac{x_1 H^E}{RT^2}\left(\frac{dT}{dx_1}\right)_\sigma \quad (5)$$

Equations (4) and (5) are completely general expressions for activity coefficients of binary systems. They express the activity coefficients in terms of the unknown G^E and a number of quantities which either are obtained from experimental information or may be calculated using an equation of state: V, V_i^0, and H^E. The derivatives $(dP/dx_1)_\sigma$ and $(dT/dx_1)_\sigma$ are the slopes of the pressure-composition and temperature-composition curves at equilibrium at constant temperature and at constant pressure respectively. Equations (4) and (5) may be used for any standard state at the temperature of the system, including the unsymmetric convention. A number of examples of standard states and the resulting simplifications of the terms

$$\frac{x_1}{RT}\left[V\left(\frac{dP}{dx_1}\right)_\sigma - \sum_{i=1}^{2} x_i V_i^0\left(\frac{dP_i^0}{dx_1}\right)_\sigma\right] \quad \text{and} \quad \frac{x_1 H^E}{RT^2}\left(\frac{dT}{dx_1}\right)_\sigma$$

are listed as special cases in Table 1. The implied choice of reference fugacities is also listed in each case. In the case of the unsymmetric convention, Case C, the reference fugacity of the noncondensable component is equal to Henry's constant at the pressure and temperature of the system (Prausnitz, 1969).

THE THERMODYNAMIC CONSISTENCY TEST

When both vapor and liquid phase compositions are determined experimentally, binary vapor-liquid equilibrium data are either reported as $x_i(P)$ and $y_i(P)$ at constant T or $x_i(T)$ and $y_i(T)$ at constant P. The derivatives $[dP/dx_1]_\sigma$ or $[dT/dx_1]_\sigma$ may be evaluated from the P-x_1 or T-x_1 data using a spline fitting technique as discussed in the section on orthogonal collocation. Assuming that mixture and standard state volumes and enthalpies are available from experiment, from application of an equation of state, or from any other source, Equations (4) and (5) contain three unknowns: γ_1, γ_2, and G^E. A third, independent equation is available from the definition of the activity coefficient

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i^0} = \frac{y_i \hat{\phi}_i P}{x_i f_i^0} \quad (6)$$

where $\hat{\phi}_i$ is the vapor phase fugacity coefficient of component i and is calculated using an equation of state, see Section 4. Since $\sum_i y_i P = P$,

$$P = \frac{x_1\gamma_1 f_1^0}{\hat{\phi}_1} + \frac{x_2\gamma_2 f_2^0}{\hat{\phi}_2} \quad (7)$$

Solving Equations (4), (5), and (7) for γ_1, γ_2, and G^E may be troublesome since the set of equations is highly nonlinear. A powerful numerical method for solving differential equations, orthogonal collocation, is therefore employed, see Section 5. The important point at this stage is that the activity coefficients simultaneously satisfy (4), (5), and (7). They are thus thermodynamically consistent since they automatically satisfy the nonisothermal, nonisobaric Gibbs-Duhem equation. The values of the activity coefficients obtained in this manner are used to calculate vapor phase compositions:

$$y_i(\text{calc.}) = \frac{\gamma_i x_i f_i^0}{\hat{\phi}_i P} \qquad (8)$$

and the thermodynamic consistency test consists of comparing calculated vapor mole fractions with the experimentally obtained values.

The method may be outlined as follows:

1. T, P, and x_i are known. Besides f_i^0, V_i^0, V, H^E, and the slope of the equilibrium curve are assumed known or available by calculation. The vapor phase fugacity coefficients $\hat{\phi}_i$ depend upon the vapor phase composition. Since $\hat{\phi}_i$ enter into Equation (7), they must be estimated. Choose initially $\hat{\phi}_i = 1, i = 1, 2$.
2. Solve Equations (4), (5), and (7) for γ_1, γ_2, and G^E for chosen values of x_i.
3. Calculate values of y_i for each chosen value of x_i using Equation (8).
4. Calculate new values of $\hat{\phi}_i$ using y_i from step 3 and repeat steps 2 to 4 until successive calculated values of y_i agree to within 10^{-4}.
5. Calculate the value of y_i in each data point by interpolation among the values of y_i (in the chosen points) last obtained under point 3.
6. Compare the experimentally obtained values of y_i with calculated values. If the following empirical criterion is met (see Christiansen, 1974):

$$|y_i(\text{calc.}) - y_i(\text{exp.})| \leq \Delta x_i + \Delta y_i$$

where Δx_i and Δy_i are the experimental uncertainties in the liquid and vapor mole fractions, the data point is said to be thermodynamically consistent. If

$$|y_i(\text{calc.}) - y_i(\text{exp.})| > \Delta x_i + \Delta y_i$$

two possibilities exist: (1) the data are inconsistent, or (2) the methods of calculating fugacities, molar volumes, or enthalpies are erroneous.

CALCULATION OF FUGACITY COEFFICIENTS AND LIQUID MOLAR VOLUMES

The outcome of the thermodynamic consistency test may be heavily dependent on the reliability of the determination of liquid and vapor phase thermodynamic properties. If reliable experimental values of the liquid phase molar volumes and vapor phase fugacity coefficients are available, these should be used. Unfortunately such data exist only for very few systems. To avoid loss of general applicability, it was therefore chosen to calculate these properties using an equation of state. The calculational procedure followed is generally regarded as being fairly accurate for the systems used as illustrations in the section on Results. If, however, high-pressure systems greatly different than those described in the Results are under consideration, it is recommended to check the method of calculating thermodynamic properties carefully.

The liquid phase molar volumes and vapor phase fugacity coefficients are calculated following the methods of Prausnitz and Chueh (1968). Liquid phase molar volumes at saturation are calculated using the Lyckman-Eckert-Chueh correlation. Partial molal volumes at infinite dilution $\overline{V}_i^\infty$ used in the unsymmetric normalization of activity coefficients are obtained by differentiation of the Redlich-Kwong equation of state. The molar volume of the mixture entering into the resulting equation for $\overline{V}_i^\infty$ is that calculated from the generalized correlation. Vapor phase fugacity coefficients for pure components as well as mixtures are calculated directly from the Redlich-Kwong equation of state.

The calculation of liquid phase enthalpies for liquified natural gas and related mixtures will be dealt with in a forthcoming article. Sufficiently accurate methods of calculating liquid phase enthalpies for most other systems of practical interest are not available. Only isothermal data are used as illustrations of the method in this work.

THE METHOD OF ORTHOGONAL COLLOCATION

When the expressions for the activity coefficients, Equations (4) and (5), are inserted in Equation (7), a differential equation in G^E results. Klaus and Van Ness (1967) have pointed out that G^E as a function of the composition is well represented by orthogonal functions. This indicates that the method of orthogonal collocation (Villadsen and Stewart, 1967; Villadsen, 1970) should be well suited for solving this differential equation numerically.

In orthogonal collocation the unknown function is approximated by an orthogonal polynomial, and the values of G^E are determined by successive approximations at selected points, these points being the zeroes of a Jacobi polynomial. The collocation abscissas are here chosen as the roots of Legendre polynomials. Other types of Jacobi polynomials were investigated, but only negligible variations were found.

The value of the differential operator at each collocation point x_k is determined by the following weighted sum of the function values: (Note: the subscript k refers to collocation point k, *not* component k.)

$$\left(\frac{d(G^E/RT)}{dx_1}\right)_\sigma \Bigg|_{x_k} = \sum_{l=0}^{N+1} A_{kl}(G^E/RT)_l \qquad (9)$$

where the elements of the discretization matrix A_{kl} are determined from the Legendre polynomial. N is the number of internal collocation points, and the two end points are included. The discretization matrix and the numerical properties of the Legendre polynomial, for example, the zeroes, are found by the methods of Michelsen and Villadsen (1972). The pure component properties f_i^0 and V_i^0 and the mixture properties V and $\hat{\phi}_i$ are calculated for each collocation point as explained in the previous section. If one of the reference fugacities is Henry's constant, it is evaluated as explained in the next section.

The value of the system vapor pressure at each collocation point is determined by interpolation using a spline fit to the experimental P-x curve (Klaus and Van Ness, 1967). Two adjacent data points are joined by a third-order polynomial in such a way that the first and second derivatives are continuous in the data points. Both P and $(dP/dx_1)_\sigma$ at each collocation point can now be found by interpolation.

When all of the necessary physical properties and the value of the differential operator at each internal collocation point are inserted in the differential equation for G^E, the differential equation to be solved at the N collocation

TABLE 1. SPECIAL CASES OF EQUATIONS (4) AND (5)

Case	Constant	Standard state	$\frac{x_1}{RT}\left[V\left(\frac{dP}{dx_1}\right)_\sigma - \sum_i x_iV_i^0\left(\frac{dP_i^0}{dx_1}\right)_\sigma\right]$	$\frac{x_1H^E}{RT^2}\left(\frac{dT}{dx_1}\right)_\sigma$	Reference fugacities f_i^0
A	P or T	Pure components at the temperature and pressure of the system. Low pressures only.	Approx. 0	Approx. 0	Approx. P_i^{sat}
B	T	Pure components at the temperature and pressure of the system.	$\frac{x_1}{RT}[V - x_1V_1 - x_2V_2]\left(\frac{dP}{dx_1}\right)_\sigma$	0	$P_i^{sat}\,\phi_i^{sat}\exp\int_{P_i^{sat}}^{P}\frac{V_i}{RT}dP$
C	T	Component 1: infinitely diluted in component 2 at the temperature and pressure of the system; component 2: pure 2 at the temperature and pressure of the system.	$\frac{x_1}{RT}[\overline{V} - x_1\overline{V}_1^{\infty} - x_2V_2]\left(\frac{dP}{dx_1}\right)_\sigma$	0	$f_2^0 = P_2^{sat}\,\phi_2^{sat}\exp\int_{P_2^{sat}}^{P}\frac{V_2}{RT}dP$ $f_1^0 = H_{1,2}^{(P_2^{sat})}\exp\int_{P_2^{sat}}^{P}\frac{\overline{V}_1^{\infty}}{RT}dP$
D	T	Same as B or C except that the reference pressure is an arbitrary, fixed pressure, P°.	$\frac{x_1V}{RT}\left(\frac{dP}{dx_1}\right)_\sigma$	0	$f_i^{(P^0)} = f_i^{(P_i^{sat})}\exp\int_{P_i^{sat}}^{P^0}\frac{V_i^0}{RT}dP$
E	P	Pure components at the temperature and pressure of the system.	0	$\frac{x_1}{RT^2}[H - x_1H_1 - x_2H_2]\left(\frac{dT}{dx_1}\right)_\sigma$	$P_i^{sat}\,\phi_i^{sat}\exp\int_{P_i^{sat}}^{P}\frac{V_i}{RT}dP$

points is reduced to a set of N coupled algebraic equations. These equations are now solved for G^E at each collocation point using the Newton-Raphson iteration procedure with the initial estimates of G^E given below. The iteration normally converges rapidly and is terminated when two successive values of G_k^E agree to within 10^{-6}.

As initial estimates of the excess Gibbs free energies in the symmetric convention, the following expression is used at each collocation point:

$$G_k^E = RT \cdot x_k(1 - x_k), \quad \text{all} \quad k \tag{10}$$

In the unsymmetric convention G^E in the right end point (at $x_{1,\max}$) is undetermined. This point is therefore included as a collocation point. Initial values for G_k^E are here simply taken to be

$$G_k^E = 0, \quad \text{all} \quad k \tag{11}$$

Since the zeroes of the Legendre polynomial are all between zero and one, the following variable substitution is introduced:

$$x_k' = x_k \cdot x_{1,\max} \tag{12}$$

The collocation solution is slightly dependent on the number of internal points, even for high order approximations. But as long as the number of internal points exceeds 6-7, the variation is negligible (see Christiansen, 1974).

With known values of G^E at the collocation points it is now possible to determine the activity coefficients using Equations (4) and (5), and the values of the vapor phase mole fractions are determined using Equation (8).

The determination of the vapor phase mole fractions corresponding to the experimental values of x_1 is done by interpolation between the vapor phase mole fractions obtained from the collocation solution. The interpolation is usually (but not always, see Supplement)[*] carried out using Lagrangian interpolation with the collocation points as the nodes.

CALCULATION OF HENRY'S CONSTANTS

When the method described in the previous sections is applied to binary systems containing a noncondensable component, one obtains as an added bonus an excellent procedure for evaluating Henry's constants from experimental P-x data.

Henry's constant (at the saturation pressure of the solvent) is defined as

$$H_{1,2}^{(P_2^{sat})} = \lim_{x_1\to 0}\frac{\hat{f}_1}{x_1} = \lim_{x_1\to 0}\frac{\hat{\phi}_1 y_1 P}{x_1} \tag{13}$$

As shown in Table 1, Case C, the reference fugacity for a noncondensable component is conveniently $H_{1,2}^{(P_2^{sat})}$ multiplied by a Poynting correction factor. Referring to the description of the iteration procedure in the section on the thermodynamic consistency test, this means that an initial value of $H_{1,2}^{(P_2^{sat})}$ must be estimated (compare step 1 of the iteration procedure). A convenient initial guess is

$$H_{1,2}^{(P_2^{sat})}\,(\text{INITIAL}) = 100(P - 0.99P_2^{sat})\,\hat{\phi}_1\big|_{x_1=0.01} \tag{14}$$

Using this value of $H_{1,2}^{(P_2^{sat})}$, values of y_i and $\hat{\phi}_i$ are estimated, (compare steps 3 and 4 of the iteration procedure).

For each iteration, $\hat{\phi}_1 y_1 P/x_1$ is calculated at each internal collocation point, and a new value of $H_{1,2}^{(P_2^{sat})}$ is determined according to (13) for the subsequent iteration. The extrapolation to $x_1 = 0$ is carried out using Lagrangian extrapolation with the N internal points as the interpolation nodes. At the end of the iteration procedure, an internally consistent Henry's constant is obtained.

The values of $\hat{\phi}_1 y_1 P/x_1$ at the four collocation points closest to $x_1 = 0$ for the last iteration are shown in Table 2 for a few typical systems. It is easy to see that the extrapolation to $x_1 = 0$ can be performed with a high degree of certainty. This is due to the following two reasons:

1. For systems where the critical temperatures of the solute and solvent are not far apart, for example the CO—CH_4 system (see Figure 5), the gas phase mole fraction of the solute y_1 is not close to one. Furthermore, y_1 changes rapidly with the pressure at low values of x_1, and x_1 does not. Under these circumstances it is usually difficult to obtain a true equilibrium gas sample because the sampling itself disturbs the system equilibrium. So even though the analytical procedure itself may introduce a smaller relative error in y_1 than in x_1 at low values of x_1 (such is for example the case for gas chromatography), the overall experimental procedure will often result in a relative error in y_1 which is comparable to or larger than the relative error in x_1. Using experimental values of y_1

The Supplement, which contains a complete listing of the computer program and sample outputs, may be obtained from Aa. Fredenslund for $10.00.

TABLE 2. CALCULATION OF HENRY'S CONSTANTS

System	Mole fraction solute, x_1*	$\frac{\hat{f}_1}{x_1}$, atm	Henry's constant, atm $H_{1,2} = \lim_{x_1 \to 0} \frac{\hat{f}_1}{x_1}$
$CH_4(1)$-$C_3H_8(2)$ at −75°F	0.0074	69.9	71.5
	0.0390	67.7	(Prausnitz and Won,
	0.0939	67.8	1973: 69.1)
	0.1693	67.4	
$CO(1)$-$CH_4(2)$ at 137.1°K	0.0047	32.4	32.8
	0.0244	31.0	(Christiansen et al.,
	0.0579	30.2	1973: 33.8)
	0.1023	30.5	
$CO(1)$-$CH_4(2)$ at 164.0°K	0.0146	55.5	55.6
	0.0721	55.7	(Christiansen et al.,
	0.1579	55.9	1973: 62.4)
	0.2466	54.8	
$CO(1)$-$CH_4(2)$ at 178.0°K	0.0035	67.7	67.8
	0.0179	67.5	(Christiansen et al.,
	0.0412	67.4	1973: 72.3)
	0.0695	66.3	

* These mole fractions are not experimental values, but rather internal collocation points.

in the calculation of $\hat{f}_1$ may thus introduce an unnecessary extra scatter in the $\hat{f}_1$ vs. x_1 plot. This problem is avoided in this work and that of Won and Prausnitz (1973) by using thermodynamically consistent values of y_1 in the calculation of $\hat{f}_1$.

2. The G^E vs. x_1 curve is fitted very well over the whole composition range using the numerical method of this work. This means that also activity coefficients at infinite dilution γ_i^∞, and hence Henry's constants, are determined with a relatively high degree of certainty.

It should be pointed out that in order to successfully use the method of orthogonal collocation for the calculation of Henry's constant it is necessary to have good *P*-*x* data including data in the dilute region. The reliability of the obtained Henry's constant is of course no better than that of the *P*-*x* data. Also, if the critical temperatures of the solute and solvent are far apart as in for example the N_2—H_2O system, the gas phase solute mole fraction is very close to one. The use of $y_1(\text{exp})$ rather than $y_1(\text{calc})$ in the calculation of $\hat{f}_1$ for these systems does not introduce any significant error.

The values of the Henry's constants obtained for the CH_4—C_3H_8 and CO—CH_4 systems are shown in Table 2.

For the CH_4—C_3H_8 system at −75°F there is relatively good agreement between the Henry's constant obtained by Won and Prausnitz (1973) and that obtained in this work.

For the CO—CH_4 system, deviations up to 10% are found between the Henry's constants reported by Christiansen et al. (1973) and those obtained in this work. The Henry's constants reported by Christiansen et al. were calculated by extrapolating values of $\hat{\phi}_1 y_1(\text{exp}) P / x_1(\text{exp})$ to $x_1 = 0$. The method of calculating $\hat{\phi}_1$ was virtually the same as the method used here. In spite of the fact that that the CO—CH_4 data appear to be thermodynamically consistent (see Figure 5), the extrapolation by Christiansen et al. was quite difficult to carry out due to some scatter in the *P*-y_1 data in the dilute region. The result was what is now believed by the authors to be erroneous values of the Henry's constants. As is evident from Table 2, these difficulties do not exist when the present method is used.

The authors wish to point out that Henry's constants have been calculated for a large number of systems using the method described above (Christiansen, 1974). The results shown in Table 2 are representative of these calculations. The method is found to be a highly reliable procedure for calculating Henry's constants from good *P*-*x* data.

RESULTS

Illustrations covering Cases A, B, and C of Table 1 are considered below.

Case A

The ethanol-toluene system at 35°C was chosen to illustrate Case A. This system is a member of the alcohol-hydrocarbon family of systems, which generally is considered difficult to represent using the ordinary models for the excess Gibbs free energy (Abbott and Van Ness, 1974). As indicated in Table 1, there is no need for

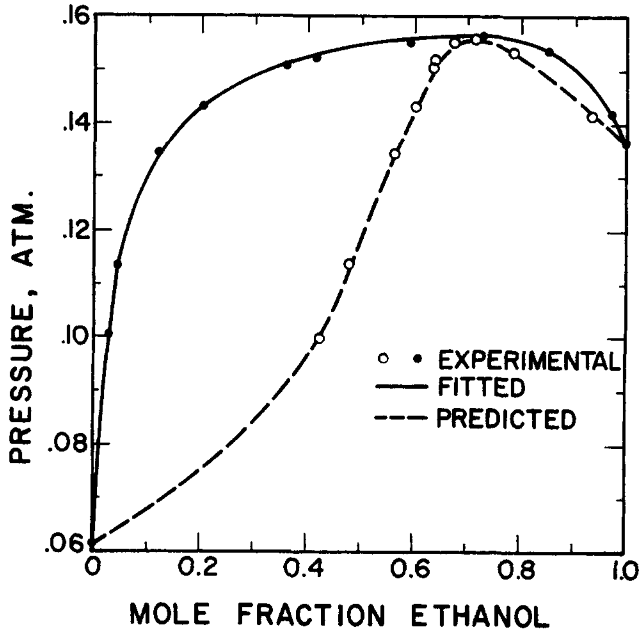

Fig. 1. *P*-*x*-*y* diagram for ethanol-toluene at 35°C (data from Kretschmer and Wiebe, 1949).

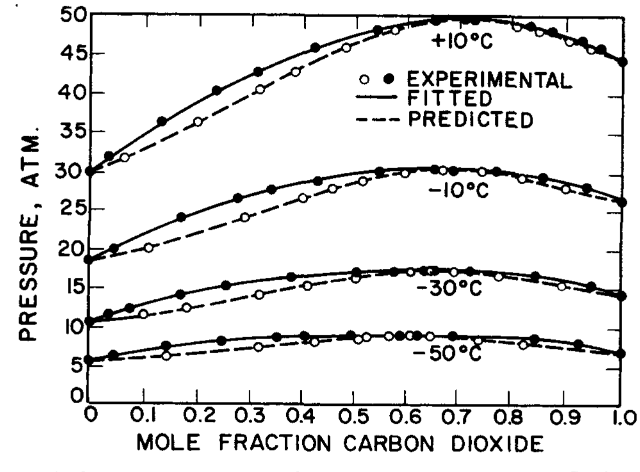

Fig. 2. *P*-*x*-*y* diagram for the CO_2-C_2H_6 system (data from Fredenslund and Mollerup, 1974).

TABLE 3. THE RESULTS OF THE CONSISTENCY TEST

System	Temperature, °K	$\overline{\Delta y_a}$[(1)]	Number of data points with $\lvert y_i\,(\text{calc.}) - y_i\,(\text{exp.})\rvert \leq 0.008$[(2)]	Number of data points with $\lvert y_i\,(\text{calc.}) - y_i\,(\text{exp.})\rvert > 0.008$[(2)]
Ethanol-toluene	308.15	0.0060	8	2
CO_2-C_2H_6	223.15	0.0067	7	4
	243.15	0.0033	12	0
	263.15	0.0026	11	0
	283.15	0.0024	13	0
CO-CH_4	137.1	0.0072	6	2
	164.0	0.0092	4	2
	178.0	0.0036	4	0
CH_4-C_3H_8	213.71	0.0068	10	3
CH_4-C_3H_8(3)	213.71	0.0033	10	1

(1) $\overline{\Delta y_a} = \frac{1}{m} \sum_{i=1}^{m} \lvert y_i\,(\text{calc.}) - y_i\,(\text{exp.})\rvert$

m = number of data points (excluding pure components).

(2) Estimated value of $\Delta x_i + \Delta y_i$.

(3) Excluding the critical point and the one closest to it.

evaluating fugacity coefficients or liquid molar volumes here.

The results are shown in Figure 1. It is seen that the predicted P-y curve is very close to the experimental points. The mean deviations between the experimental and calculated vapor mole fractions are given in Table 3.

Case B

For binary systems at high pressures and both components condensable the standard states may be chosen to be the pure components at the temperature and pressure of the system. In this case, vapor phase nonidealities are taken into account via fugacity coefficients, and the correction term $(x_1 V^E/RT)\,[dP/dx_1]_\sigma$ must be included. $\hat{\phi}_1$ and V^E are calculated as already explained.

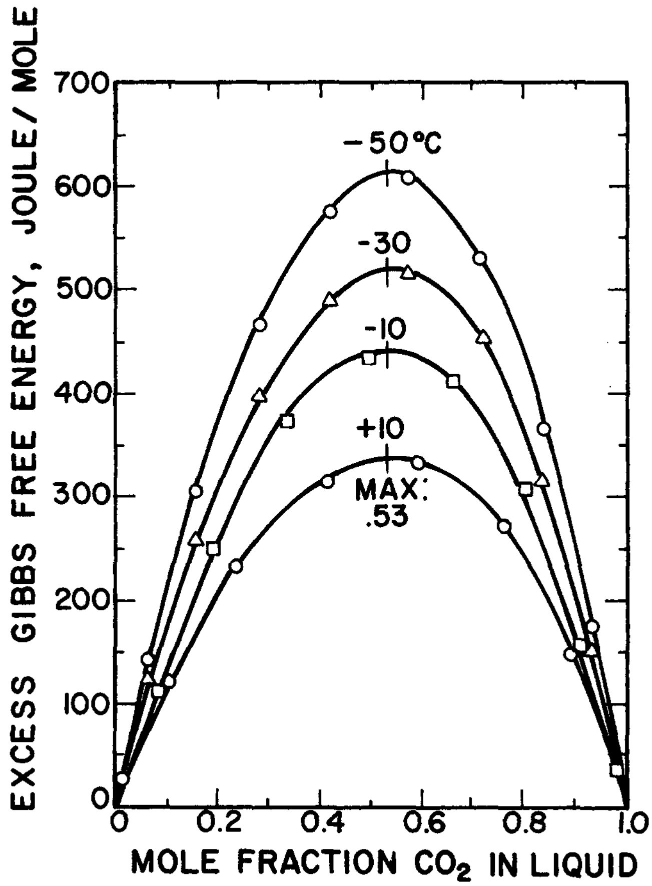

Fig. 3. Excess Gibbs free energy for the ethane-carbon dioxide system.

The P-x-y diagram for the carbon dioxide-ethane system is shown on Figure 2. It is seen that there is almost no deviation between the calculated and observed P-y curves. The mean deviations between the observed and calculated vapor mole fractions are given in Table 3. The excess Gibbs free energy based on the standard states of Case B is shown as a function of the mole fraction carbon dioxide in the liquid phase on Figure 3. The effect of the number of internal collocation points on the deviation between the observed and calculated vapor phase mole fractions for the data at −30°C is shown on Figure 4. Although small variations in the deviations are seen to exist, the general trend in the deviations is seen to be the same for all three numbers of internal collocation points.

The carbon dioxide-ethane data are seen to be very consistent.

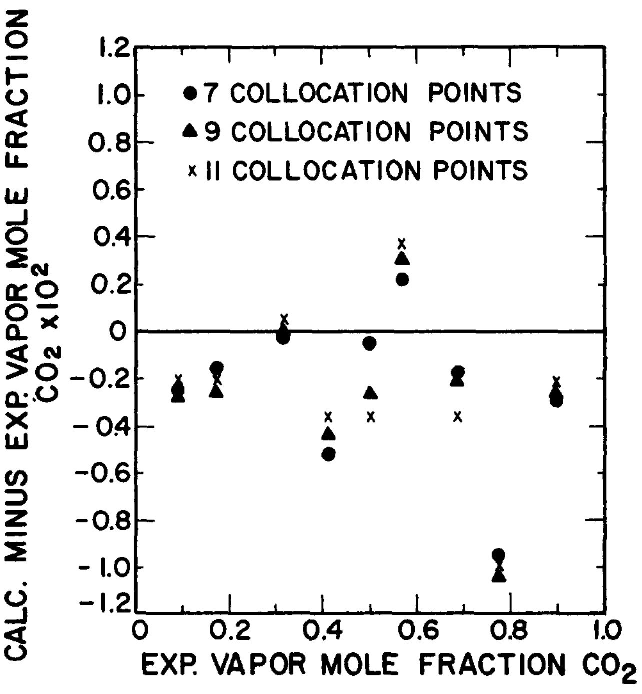

Fig. 4. The effect of the number of internal collocation points. The CO_2-C_2H_6 system at −30°C.

Case C

When one component is noncondensable the unsymmetric convention for normalization of the activity coefficients is used. For the condensable component (2) the standard state is the same as under Case B, and for the noncondensable component (1) the standard state is the infinitely dilute solution of component 1 in the solvent (2) at the temperature and pressure of the system. It is now necessary to calculate Henry's constants (see previous section) and the partial molal volume of component 1 in 2 at infinite dilution in addition to the thermodynamic properties calculated in Case B.

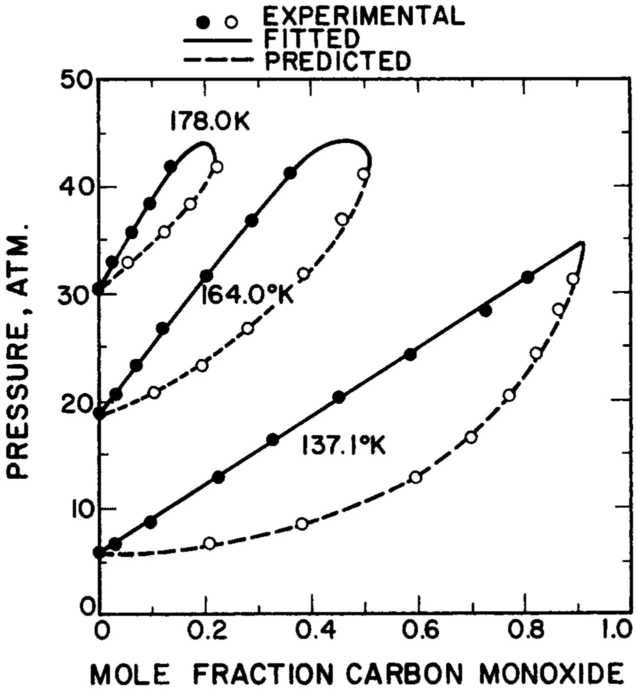

Fig. 5. P-x-y diagram for the CO-CH_4 system (data of Christiansen et al., 1973).

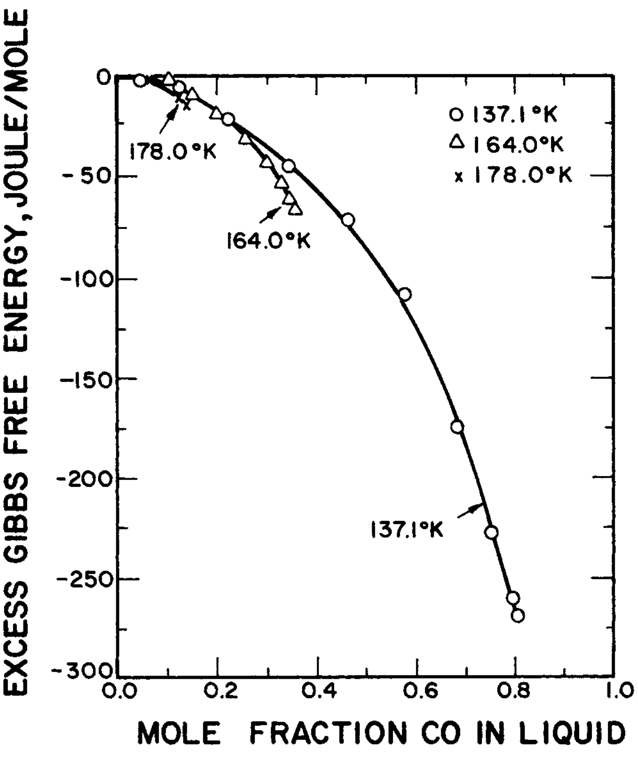

Fig. 6. Excess Gibbs free energy for the CO-CH_4 system (unsymmetric convention).

The carbon monoxide-methane system is chosen to illustrate Case C, and the result is shown in Figure 5 and Table 3. It was necessary to exclude the two upper experimental points from each isotherm due to failure of the calculation of fugacity coefficients in the immediate vicinity of the critical point. Similar calculations for the argon-methane system (Christiansen, 1974) show convergence all the way to the critical point.

The excess Gibbs free energy (excess with respect to the standard states, here the unsymmetric convention) for the carbon monoxide-methane isotherms is shown as a function of composition in Figure 6.

Data for the CH_4—C_3H_8 at −75°F (213.71°K) (Wichterle and Kobayashi, 1972) are shown in Figure 7. It is seen that except very near the critical point the agreement between observed and calculated vapor mole fractions is excellent. The mean deviation is given in Table 3. This result is as good as the result of Won and Prausnitz (1973), who calculated vapor mole fractions for the same isotherm. If the critical point and the point nearest to it are excluded from the calculations the mean deviation is lowered by a factor of two.

DISCUSSION

All of the P-x-y data used as illustrations above are found to be thermodynamically consistent, since

$$|y_i(\text{calc.}) - y_i(\text{exp.})| \leq \Delta x_i + \Delta y_i$$

for most of the data points.

If this were not the case, two possibilities exist: (1) The data are thermodynamically inconsistent. (2) The methods used to calculate fugacity coefficients and molar volumes produce erroneous results. There is apparently no

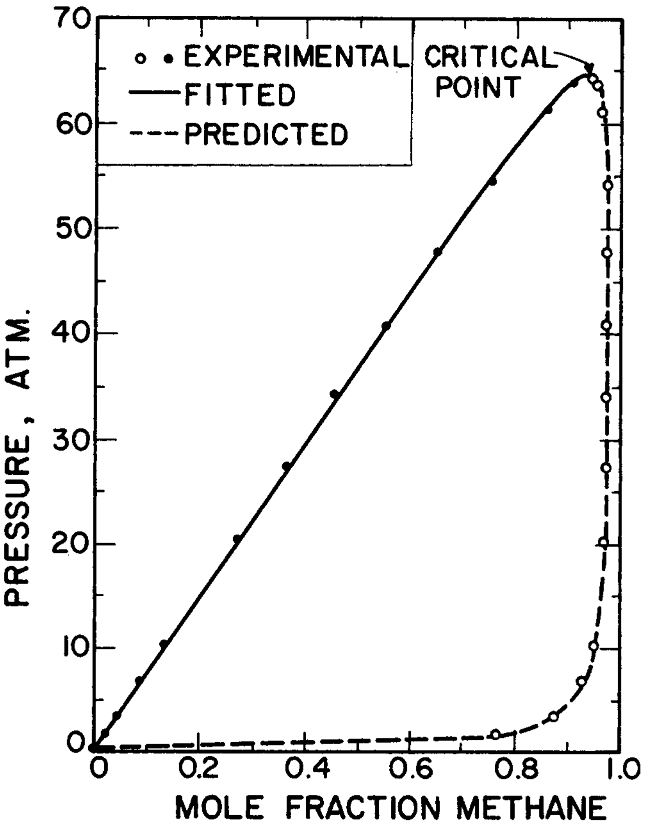

Fig. 7. P-x-y diagram for the CH_4-C_3H_8 system at −75°F (data from Wichterle and Kobayashi, 1972).

statistical method available for distinguishing between these possibilities, and it is therefore not possible to reject experimental data a priori if the above criterion is not met.

The methods of this work are shown to provide an excellent means of extending the work of Van Ness et al. (1973) to high pressures, provided vapor phase fugacity coefficients and liquid phase molar volumes may be estimated or are available from experimental information. This is basically an alternate method to that of Won and Prausnitz (1973), who extended the work of Barker (1953) to high pressures.

The method of Won and Prausnitz does not require interpolation among the P-x data points, which is advantageous when only a few data points are available. When sufficient data points are available, the method of orthogonal collocation provides a better estimate of the activity coefficients. Since the approach to solving the differential equation mainly consists of solving a set of algebraic equations, it is relatively easy to use high-order approximations and to check the correctness of the solution by varying the order of the approximation.

Algebraic expressions for the excess Gibbs free energy as a function of composition, which are used in Barker's method, tend to deviate most from experimental data in the dilute regions. Thus, provided a sufficient number of P-x data points are available, the method of orthogonal collocation should give a more correct estimate of Henry's constant. Both methods can in principle be extended to multicomponent high-pressure systems. Little is known about algebraic equations for multicomponent activity coefficients in the critical region, and the use of the numerical method appears therefore in this case to be more straightforward.

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NOTATION

b = constant in Redlich-Kwong equation of state
f = fugacity
G = Gibbs free energy
H = enthalpy of a mixture
H_i = enthalpy of pure component i
$H_{1,2}$ = the Henry's law constant for component 1 in component 2
N = number of internal collocation points excluding the end points
n = number of moles
P = pressure, atm
R = gas constant
S = entropy
T = temperature
V = molar volume of mixture
V_i = pure component molar volume
x = liquid phase mole fraction
y = vapor phase mole fraction

Greek Letters

γ = activity coefficient
Δ = mixing property
ϕ = fugacity coefficient
Ω = constant in Redlich-Kwong equation of state

Subscripts

1, 2, i = components
k, l = collocation abscissas for component no. 1
σ = along the saturation line
c = critical property
r = reduced property
exp. = experimental value
calc. = calculated value
max = maximum value of mole fraction

Superscripts

E = excess property
L = liquid phase property
G = gas phase property
id = ideal gas
sat = saturated condition
$\wedge$ = mixture component fugacity
— = partial molal property
∞ = infinite dilution
0 = standard state

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