AN ANALYTICAL EQUATION DERIVED FROM A PERTURBATION THEORY TO CALCULATE HENRY'S CONSTANTS FOR SQUARE WELL MIXTURES

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An analytic form for Henry's constant is derived and applied to several systems. The derivation is based on the use of Leonard–Henderson–Barker perturbation theory for a square well pair potential assuming the Ponce–Renon analytical solution of the square well fluid. Computed values of Henry's constants for CH_4—Ar, CH_4—N_2, CH_4—He, CH_4—H_2, C_2H_6—N_2 and C_2H_6—CH_4 mixtures are compared with experiment. The agreement is quite satisfactory, with mean relative deviations between 2·5 and 8 per cent. Heats of solutions are also computed and compared with experiment.

In recent years there has been a growing interest in the application of liquid structure theory to the calculation of fluid phase equilibrium[1-3]. In particular, there have been many applications of perturbation theories to the calculation of excess functions of mixtures. The accuracy of such calculations is based on the assumption that the structure of liquids is primarily determined by the repulsive "hard core" part of the intermolecular potential and that the longer range attractive part of the potential provides a fairly uniform cohesive background which may be treated by perturbation theory. We adopt this point of view here.

In this paper we employ the Leonard–Barker–Henderson perturbation theory[4] to compute solubilities of gases in nonpolar fluids. Our starting point is the Neff–McQuarrie thermodynamic calculation of solubilities and related thermodynamic functions[5]. With the assumption of a square well (SW) attractive potential the terms of the perturbation series may be computed analytically up to second order and hence an analytic form for Henry's constant is derived.

The SW parameters are treated empirically and fitted to existing experimental data. The final equations are easy to use and provide reasonably accurate computed solubilities and heats of solution for the systems studied in this paper.

HENRY'S CONSTANTS FROM THE PERTURBATION THEORY

The Henry's law constant $H_{2,1}^{(\sigma)}$ of a solute (2) in a solvent (1) is defined as:

$$H_{2,1}^{(\sigma)} = \lim_{x_2 \to 0} \left(\frac{f_2}{x_2} \right), \qquad (1)$$

where f_2 is the fugacity of the solute in the solution and x_2 is its mole fraction.

By equating the fugacities of the solute in both gas and liquid phases and assuming ideality in the vapor phase, Neff and McQuarrie have shown that:

$$\ln H_{2,1}^{(\sigma)} = \ln (\varrho_1 \, kT) + \beta\mu_2^{HS} + \beta\mu_2^{CORR}, \qquad (2)$$

where

$$\varrho_1 = N_{AV}/V_1 \quad \text{and} \quad \beta = 1/kT .$$

The first term in the rhs of Eq. (2) is the ideal part, the term $\beta\mu_2^{HS}$ contains the contribution of the repulsive part of the intermolecular potential, and $\beta\mu_2^{CORR}$ contains the contribution due to molecular attractions. V_1 and N_{AV} represent respectively the molar volume of the solvent and Avogadro's number.

Neff and McQuarrie use the results of the Leonard–Henderson–Barker perturbation theory for mixtures, employing as a reference system a hard sphere fluid whose properties are given by Lebowitz's solution to the Percus–Yevick equation. They obtain the following relations:

$$\beta\mu_2^{HS} = - \ln (1 - y) + y \, \chi(y) \, R^3 + \tfrac{1}{2}[3y/(1 - y)]^2 \, R^2 + \frac{3y}{1 - y} (R^2 + R), \qquad (3)$$

where

$$y = \tfrac{1}{6}\pi\varrho_1\sigma_{11}^3 ; \quad R = \sigma_{22}/\sigma_{11}$$

and

$$\chi(y) = (1 + y + y^2)/(1 - y)^3 .$$

The last term of the rhs of Eq. (2) is given by

$$\beta\mu_2^{CORR} = 2\varrho_1\beta I_{11} - 2\varrho_1\beta I_{12} + \text{a contact term}, \qquad (4)$$

where I_{11} and I_{12} include up to second order terms in the perturbation series and represent respectively the solvent–solvent and solvent–solute interactions. They are given explicitly by[6]

$$I_{12} = -2\pi \int_{\sigma_{12}}^{\infty} u_{12}(r)\, g_{12}^{\mathrm{HS}}(r)\, r^2\, \mathrm{d}r + \pi \left(\frac{\partial \varrho_1}{\partial p}\right)_{\mathrm{HS}} \int_{\sigma_{12}}^{\infty} u_{12}^2(r)\, g_{12}^{\mathrm{HS}}(r)\, r^2\, \mathrm{d}r \quad (5a)$$

and

$$I_{11} = \pi N_1 \int_{\sigma_{11}}^{\infty} u_{11}(r) \left[\frac{\partial g_{11}^{\mathrm{HS}}}{\partial N_2}\right]_{\mathrm{T,V,N}} r^2\, \mathrm{d}r -$$

$$- \tfrac{1}{2}\pi N_1 \left[\frac{\partial}{\partial N_2}\left(\frac{\partial \varrho_1}{\partial p}\right)_{\mathrm{HS}}\right]_{\mathrm{T,V,N_1}} \int_{\sigma_{11}}^{\infty} u_{11}^2(r)\, g_{11}^{\mathrm{HS}}(r)\, r^2\, \mathrm{d}r -$$

$$- \tfrac{1}{2}\pi N_1 \left(\frac{\partial \varrho_1}{\partial p}\right)_{\mathrm{HS}} \int_{\sigma_{11}}^{\infty} u_{11}^2(r) \left[\frac{\partial g_{11}^{\mathrm{HS}}(r)}{\partial N_2}\right]_{\mathrm{T,V,N_1}} r^2\, \mathrm{d}r . \quad (5b)$$

In the above equations $u_{ij}(r)$ is the intermolecular potential and $g_{ij}^{\mathrm{hs}}(r)$ the hard sphere radial distribution function (RDF). Uno and coworkers[6] have used these equations to compute Henry's constant. They used a modified Kihara $(12-6)$ as the perturbation potential and found reasonably good agreement with experiment for several systems. In the next section we use the above formalism with a square well perturbation potential. This perturbation potential has the advantage of yielding analytic results.

CALCULATION OF HENRY'S CONSTANTS

We assume that the interaction potential is given by a square well potential of the following form:

$$u_{ij}(r) = \begin{cases} \infty & r < \sigma_{ij}, \\ -\varepsilon_{ij} & \sigma_{ij} < r < \lambda_{ij}\sigma_{ij}, \quad i,j = 1,2, \\ 0 & r > \lambda_{ij}\sigma_{ij}, \end{cases}$$

where $\sigma_{ij} = \tfrac{1}{2}(\sigma_{ii} + \sigma_{jj})$ and $\lambda_{ij} = \tfrac{1}{2}(\lambda_{ii} + \lambda_{jj})$. σ_{ii} is the collision diameter of molecules of species i and $\lambda_{ii}\sigma_{ii}$ is the range of the square-well potential.

The contact term that appears in Eq. (4) vanishes when substituting this potential and Eq. $(5a)$ and $(5b)$ involve integrals of the form:

$$I_{ij} = \sigma_{ij}^3 \int_1^{\lambda_{11}} g_{ij}^{\mathrm{HS}}(x)\, x^2\, \mathrm{d}x \quad i,j = 1,2, \quad (6)$$

where

$$x = r/\sigma_{ij}$$

The integral I_{11} can be expressed in a closed form by using the method of Ponce and Renon; it is given explicitly by[7,8]

$$J_{11} = \tfrac{1}{3}\lambda_{11}^3 \sigma_{11}^3 + \sigma_{11}^3 \Phi_{11}, \tag{7}$$

where $\sigma_{11}^3 \Phi_{11}$ is an analytical function defined below.

To express the integral I_{12} in terms of analytical functions we first should extend the method of Ponce and Renon to mixtures. This would involve solving expressions like

$$\int_0^\infty (g_{12}(r) - 1)\, r^2\, \mathrm{d}r$$

for a mixture of hard spheres. Instead of doing this we have employed the following mixing rule for the analytical functions

$$2\sigma_{12}(\sigma_{12}^3 \Phi_{12}) = \sigma_{22}(\sigma_{11}^3 \Phi_{11}) + \sigma_{11}(\sigma_{22}^3 \Phi_{22}) \tag{8}$$

so enabling us to calculate the integrals for the mixture in terms of pure component properties.

Note that this mixing rule combines the integrals of the RDFs and not the functions themselves. In spirit it is similar, though strictly not a generalization, of Lebowitz's mixing rule for the RDF at contact[9]. It is important to note that this rule is basically different than mixing rules for RFDs themselves which are commonly known to be quite inaccurate. The validity of the above mixing rule has been tested by direct comparison between numerical values of I_{ij} and the values produced by Eq. (8) (ref.[8]).

The term $\sigma_{11}^3 \Phi_{11}$ arises from the solution of the compressibility equation for a binary mixture of hard spheres. This is shown in detail in reference 8. The resulting expression is

$$\sigma_{11}^3 \Phi_{11} = \frac{1}{24Y\xi_0}\left\{ Y\left(\frac{1-a_1}{a_1}\right) + \eta_2\, \sigma_{11}\left(\frac{1-a_1}{a_1} - \frac{1-a_2}{a_2}\right) \right\}, \tag{9}$$

where

$$a_1 = \frac{1}{(1-\xi)^4}\left\{ (1-\xi)^3 + (1-\xi)^2\left[3(X\sigma_{11} + Y\sigma_{11}^2) + \xi_0\sigma_{11}^3\right] + \right.$$
$$\left. + (1-\xi)\left[3X\sigma_{11}(3X\sigma_{11} + 2Y\sigma_{11}^2)\right] + 9X^3\sigma_{11}^3 \right\}$$

and

$$\xi = \sum_{i=1}^2 \eta_i\sigma_{ii}^3\,;\quad X = \sum_{i=1}^2 \eta_i\sigma_{ii}^2\,;\quad Y = \sum_{i=1}^2 \eta_i\sigma_{ii}\,;\quad \eta_i = \tfrac{1}{6}\pi\varrho_i\,;\quad \xi_0 = \eta_1 + \eta_2\,. \tag{10}$$

An entirely analogous expression for $\sigma_{22}^3 \Phi_{22}$ may be written by interchanging 2 for 1 in Eq. (9).

The macroscopic compressibility term $(\partial \varrho_1/\partial p)_{HS}$ is evaluated as the following:

$$\left(\frac{\partial \varrho_1}{\partial p}\right)_{HS} = \frac{\beta \xi_0}{\eta_1 a_1 + \eta_2 a_2}. \qquad (11)$$

Upon substitution of equations (9) to (11) into (5a) and (5b) it is possible to solve Eq. (2) for Henry's constant, obtaining a final equation in terms of the density of the mixture and of the SW parameters of the pure substances. The integrals I_{11} and I_{12} have the following forms

$$I_{11} = -\pi N_1 \varepsilon_{11} \left\{ \frac{\partial}{\partial N_2} (\sigma_{11}^3 \Phi_{11}) \right\} \left\{ 1 + \tfrac{1}{2}\varepsilon_{11}\left(\frac{\partial \varrho_1}{\partial p}\right)_{HS} \right\} - $$

$$- \tfrac{1}{2}\pi N_1 \varepsilon_{11}^2 \left\{ \frac{\partial}{\partial N_2}\left(\frac{\partial \varrho_1}{\partial p}\right)_{HS} \right\} \{ \tfrac{1}{3}\lambda_{11}^3 \sigma_{11}^3 + \sigma_{11}^3 \Phi_{11} \}, \qquad (12)$$

$$I_{12} = \pi \varepsilon_{12} \{ \tfrac{1}{3}\lambda_{12}^3 \sigma_{12}^3 + \sigma_{12}^3 \Phi_{12} \} \left\{ 1 + \tfrac{1}{2}\varepsilon_{12}\left(\frac{\partial \varrho_1}{\partial p}\right)_{HS} \right\}, \qquad (13)$$

where we use the modified Berthelot rule for ε_{12} which is given as follows

$$\varepsilon_{12} = (1 - k_{12})(\varepsilon_{11}\varepsilon_{22})^{1/2}. \qquad (14)$$

RESULTS

Calculations have been performed at various temperatures for Ar, N_2 and H_2 dissolved in CH_4, and CH_4 and N_2 dissolved in ethane. The SW parameters for the solvents are obtained by fitting PVT data along the saturation curve and are found to be temperature dependent[10]. Parameters for the solutes are obtained by fitting experimental data of pure components with the second virial equation for a SW potential fluid.

SW pair parameters from fitting of second virial coefficient data are given in Table I. Solvent densities for methane and ethane are taken from literature[11,12] and the experimental and calculated values of $H_{2,1}^{(\sigma)}$ for the systems studied are shown graphically in Figs 1 to 5. The experimental Henry's constants are obtained from reduction of vapor–liquid equilibrium data.

A comparison between experimental and calculated data appears in Table II, where mean relative deviations (mrd) over the considered temperature ranges are

listed. It is seen from Figs 1, 2 and 5 that the computed Henry's constants obtained with the modified Berthelot rule for ε_{12} are within experimental uncertainties. The factor k_{12} is calculated by fitting only one experimental point. The discrepancies

TABLE I

Square Well Parameters from Fitting of Second Virial Coefficient Data

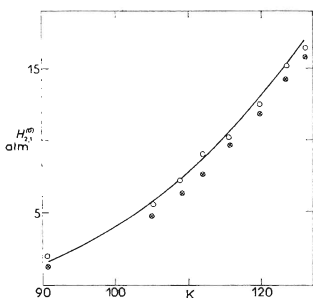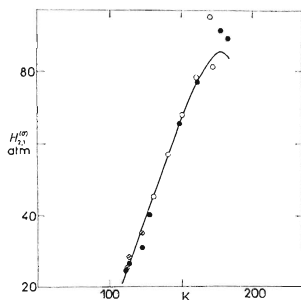| Component	Parameter		
	σ, Å	ε/K, K	λ
Ar	3·03	101·36	1·65
N_2	3·33	80·72	1·66
He	2·22	2·10	2·25
H_2	2·71	10·85	2·20
CH_4	3·50	120·22	1·66

FIG. 1

Calculated and Experimental Henry's Constants for the CH_4–Ar Mixture

The solid curve is the result of the present work with $k_{12} = 0.04580$. Calculated values with a modified Pierotti cavity model are also reported ($\otimes$ ref.[14]). Data source: $\circ$ ref.[15].

FIG. 2

Calculated and Experimental Henry's Constants for the CH_4—N_2 Mixture

The solid curve is the result of the present work with $k_{12} = 0.02415$. Calculated values with a modified Pierotti cavity model are also reported ($\otimes$ ref.[14]). Data sources: ($\bullet$ ref.[15], $\circ$ ref.[16]).

TABLE II

Mean Relative Deviations (mrd) between Experimental and Calculated Henry's Constants

$$\text{mrd} \approx \frac{1}{\text{ND}} \sum_{1}^{\text{ND}} \left| (H_{2,1\,\text{calc}}^{(\sigma)} - H_{2,1\,\text{exp}}^{(\sigma)})/H_{2,1\,\text{exp}}^{(\sigma)} \right|$$

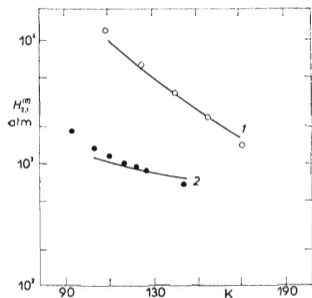| Mixture	Temperature interval, K	Number of data points ND	mrd . 100
CH_4—Ar	90·67—125·99	8	3·0
CH_4—N_2	90·67—177·59	10	4·3
C_2H_8—N_2	132·15—255·37	12	4·9
CH_4—He	109·90—169·80	5	6·7
CH_4—H_2	103·1 —144·0	6	8·3
C_2H_6—CH_4	130·39—255·39	10	3·7

FIG. 3

Calculated and Experimental Henry's Constants for the CH_4–He ($k_{12} = 0.8010$) CH_4—H_2 ($k_{12} = 0.1452$) Mixtures

The solid curves are the results of the present work. Data sources: ○ ref.[17], CH_4—He; ● ref.[18] CH_4—H_2.
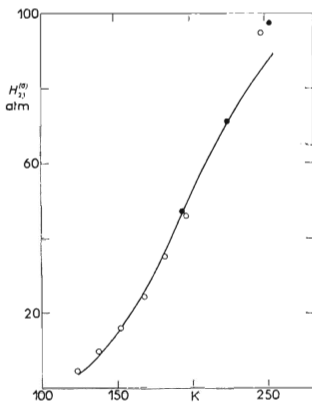
FIG. 4

Calculated and Experimental Henry's Constants for the C_2H_6-CH_4 Mixture

The solid curve is the result of the present work with $k_{12} = -0.001369$. Data sources: ○ ref.[19], ● ref.[20], ⊙ ref.[21] (sixth point from the top).

between experimental and calculated points are generally greater for the CH_4—H_2 and CH_4—He mixtures (see below).

A further and perhaps more sensitive test of the theory involves the computed temperature dependence of Henry's constant which is given by the following expression

$$\frac{1}{T}\left(\frac{\partial \ln H_{2,1}^{(\sigma)}}{\partial (1/T)}\right)_p = \beta \Delta H^\sigma , \qquad (15)$$

where from Eq. (2)

TABLE III
Calculated and Experimental Heats of Solution (J/mol)

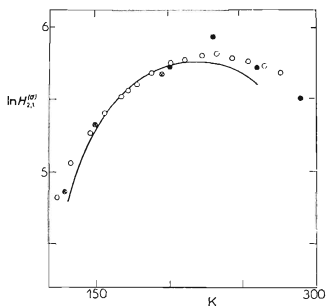| Mixture	T, K	ΔH^σ experimental	ΔH^σ calculated
CH_4—Ar	105·00	—5 889	—6 105
CH_4—N_2	138·44	—3 603	—3 497
CH_4—He	139·83	5 397	4 071
CH_4—H_2	116·50	1 882	1 130
C_2H_6—CH_4	158·15	—7 362	—7 954

FIG. 5
Calculated and Experimental Henry's Constants for the C_2H_6—N_2 Mixture
The solid curve is the result of the present work with $k_{12} = 0.04815$. Data sources: ○ ref.[22], ● ref.[23] ⊗ ref.[24].

Square well parameters from fitting of liquid densities for methane and ethane, σ and ε/k are expressed in terms of polynomials in T and Tr respectively:

$$\sigma = \sigma_0 + \sigma_1 T + \sigma_2 T^2 \quad (\lambda = 1{\cdot}75)\,.$$

$$\varepsilon/k = (\varepsilon/k)_0 + (\varepsilon/k)_1\, T + (\varepsilon/k)_2\, T^2\,,$$

and

$$\sigma/\alpha = \sigma_0' + \sigma_1' Tr + \sigma_2' Tr^2 + \sigma_3' Tr^3 + \sigma_4' Tr^4 + \sigma_5' Tr^5 \quad (\lambda = 1{\cdot}652)\,,$$

$$\left(\alpha = 7{\cdot}77755\right) \frac{\varepsilon/k}{T_c} = (\varepsilon/k)_0' + (\varepsilon/k)_1' Tr + (\varepsilon/k)_2' Tr^2 + (\varepsilon/k)_3' Tr^3 +$$

$$+ (\varepsilon/k)_4' Tr^4 + (\varepsilon/k)_5' Tr^5\,.$$

$\sigma_0' = 0{\cdot}591949;\ \sigma_1' = -0{\cdot}181240;\ \sigma_2' = 0{\cdot}667677;\ \sigma_3' = -1{\cdot}46187;\ \sigma_4' = 1{\cdot}47819;$
$\sigma_5' = -0{\cdot}568292; (\varepsilon/k)_0' = 0{\cdot}59401; (\varepsilon/k)_1' = 3{\cdot}002510; (\varepsilon/k)_2' = -10{\cdot}74220; (\varepsilon/k)_3' =$
$= 16{\cdot}64250;\ (\varepsilon/k)_4' = -12{\cdot}29150;\ (\varepsilon/k)_5' = 3{\cdot}48962;\ \sigma_0 = 0{\cdot}398393\,.\,10^1;\ \sigma_1 =$
$= -0{\cdot}298948\,.\,10^{-2};\ \sigma_2 = 0{\cdot}338333\,.\,10^{-5};\ (\varepsilon/k)_0 = 0{\cdot}964062\,.\,10^2;\ (\varepsilon/k)_1 =$
$= 0{\cdot}976976\,.\,10^{-1}; (\varepsilon/k)_2 = -0{\cdot}288810\,.\,10^{-3};$

$$\beta\, \Delta H^\sigma = \frac{1}{T}\left[\frac{\partial(\beta\mu_2^{\text{HS}})}{\partial(1/T)}\right]_p + \frac{1}{T}\left[\frac{\partial(\beta\mu^{\text{CORR}})}{\partial(1/T)}\right]_p + \alpha T - 1 \tag{16}$$

and

$$\alpha = \frac{1}{V_1}\left(\frac{\partial V_1}{\partial T_1}\right)_p \tag{17}$$

Calculated values of the heats of solution, ΔH^σ, are listed in Table III. It is readily noted that predictions for ΔH^σ are quite good for Ar and N_2 in CH_4 and for CH_4 in C_2H_6 while disagreement with experimental data is observed for CH_4—He and CH_4—H_2 mixtures.

This may be due to a number of factors, not necessarily due to errors in the theory but rather to inaccuracies in the pair potential parameters used for He and H_2. Another factor may be some thermodynamic inconsistencies in the experimental Henry's constants reported.

CONCLUSION

We have put forward an analytical formulation for dilute solution properties based on the application of Leonard–Barker–Henderson perturbation theory. Accurate

values of Henry's constants are obtained over fairly wide temperature ranges for several systems. One empirical parameter appears in the formulation and it is computed by fitting one experimental point for the solute–solvent system. All other parameters are determined from pure fluid properties. The satisfactory agreement between our calculations and experimental data has suggested a way of generating the parameter k_{12} from experimental Henry's constants. Well established procedures usually obtain this parameter from second virial coefficient or from excess properties[13]. However it is often difficult to obtain precise values of k_{12} since the uncertainty of experimental data contributes to a large dispersion in the value of this parameter. That was not found to be the case in this work; values of k_{12} obtained here had little scatter when determined by fitting Henry's constant at different temperatures. The constancy of this parameter is quite encouraging and will be the subject of a forthcoming paper.

The accuracy of this method for the C_2H_6—CH_4 is particularly significant given the importance of hydrocarbon systems and the usual difficulties involved in the calculation of their solubility properties.

REFERENCES

1. Gubbins K. E.: AIChE J. *19*, 684 (1973).
2. McQuarrie D. A.: *Statistical Mechanics*. Harper & Row, New York 1976.
3. Barker J. A., Henderson D.: Rev. Mod. Phys. *48*, 587 (1976).
4. Leonard P. J., Henderson D., Barker J. A.: Trans. Faraday Soc. *66*, 2439 (1970).
5. Neff R. O., McQuarrie D. A.: J. Phys. Chem. *77*, 413 (1973).
6. Uno K., Sarashina E., Arai Y., Saito S.: J. Chem. Eng. Jap. *8*, 201 (1975).
7. Ponce L., Renon H.: J. Chem. Phys. *64*, 638 (1976).
8. Ponce L.: *Thesis*. University of Paris, Paris 1977.
9. Lebowitz J. L.: Phys. Rev. *133*, A895 (1964).
10. Thiebault O., Pouly F., Fabries J. F., Ponce L.: Report 6RP 77—02, Centre Réactéurs et Processus, ENSMP Paris, (1977).
11. Goodwin R. D.: NBS Technical Note 653, National Bureau of Standards, 1974.
12. Straty G. C., Tsumura R.: J. Res. Nat. Bur. Stand., *80A*, B—1 (1976).
13. Kohler F.: Ber. Bunsenges. Phys. Chem. *81*, 1038 (1977).
14. Monfort J. P., Pérez J. L.: Chem. Eng. J. *16*, 205 (1978).
15. Pérez J. L.: *Thesis*. Universidad Nacional de México; México City 1977.
16. Kidnay A. J., Miller R. C., Parrish W. R., Hiza M. J.; Cryogenics *15*, 531 (1975).
17. Devaney W. E., Rhodes H. C., Tully P. C.: J. Chem. Eng. Data *16*, 158 (1971).
18. Orentlicher M., Prausnitz J. M.: Chem. Eng. Sci. *19*, 775 (1964).
19. Wichterle I.: *Vapor–Liquid Equilibria in Methane–Ethane–Propane Systems*. Monograph, Chem. Eng. Dept. Rice University, Houston 1970.

20. Prausnitz J. P., Chueh P. L.: *Computer Calculations for High Pressure Vapor–Liquid Equilibria*. Prentice Hall, Englewood Cliffs 1968.
21. Davalos J., Anderson W. R., Phelps R. E., Kidnay A. J.: J. Chem. Eng. Data *21*, 81 (1976).
22. Gunn R.: Proc. Fifty Third Annual Convention, Gas Process. Ass., *53*, 5 (1974).
23. Grausø L., Fredenslund A., Mollerup J.: Fluid Phase Equilibria *1*, 13 (1977).
24. Stryjek R., Chappelear P. S., Kobayashi R.: J. Chem. Eng. Data *19*, 340 (1974).