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THERMODYNAMICS OF ASSOCIATED SOLUTIONS. HENRY'S CONSTANTS FOR NONPOLAR SOLUTES IN WATER

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October 1983

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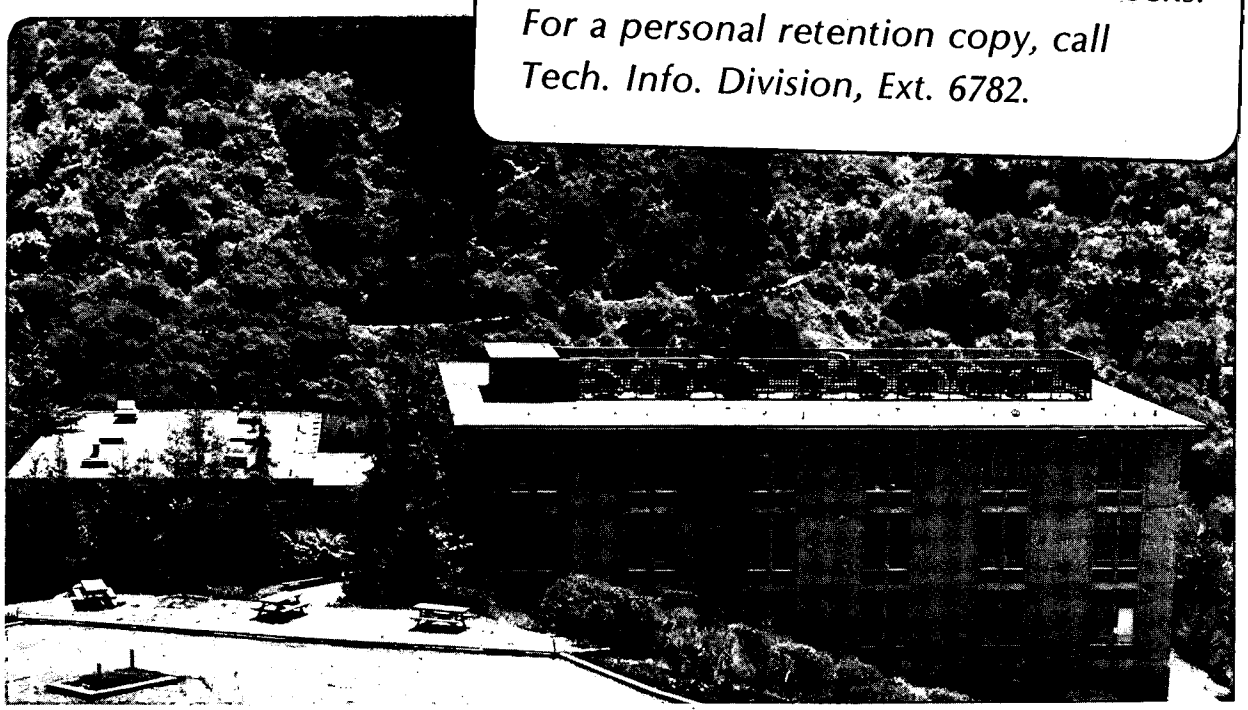

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Ying Hu†, Edmundo Azevedo*, Dorothea Lüdecke**, and John Prausnitz

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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THERMODYNAMICS OF ASSOCIATED SOLUTIONS. HENRY'S CONSTANTS FOR NONPOLAR SOLUTES IN WATER

Ying Hu,[†] Edmundo Azevedo,[*] Dorothea Lüdecke[**]
and John Prausnitz

Molecular and Materials Research Division
Lawrence Berkeley Laboratory and
Chemical Engineering Department
University of California
Berkeley, CA 94720

ABSTRACT

A systematic derivation is presented for the Helmholtz energy of a van der Waals fluid mixture whose nonideality is ascribed to both chemical and physical interactions; this derivation, applicable to all fluid densities, leads to an equation of state which contains chemical equilibrium constants in addition to the customary physical van der Waals constants a and b. Attention is given to the need for simplifying assumptions and to the variety of simplifying assumptions that can lead to useful results. A particular equation of state is used to correlate Henry's constants of nonpolar solutes in water over a wide temperature range. The correlation, however, is only partially successful because as yet we do not have a truly satisfactory theory for thermodynamic properties of mixtures containing molecules that differ appreciably in size.

† East China Institute of Chemical Technology, Shanghai, China
* Instituto Superior Tecnico, Lisbon, Portugal
** Institut für Metallphysik, Göttingen, W. Germany

Many authors have explained fluid nonideality by supposing that a fluid contains not only the apparent molecular species but, in addition, polymers of such species which are in chemical equilibrium; for example, for acetic acid vapor, deviations from ideal-gas behavior at low or moderate pressures are readily explained by assuming that acetic acid dimerizes, in part, to form acetic acid dimers in addition to acetic acid monomers. Similarly, thermodynamic properties of liquid solutions of hydrocarbons and alcohols can be correlated by postulating that alcohols polymerize, in part, to form dimers, trimers etc. in addition to alcohol monomers; finally, thermodynamic properties of liquid solutions of chloroform and acetone are readily interpreted by assuming that these two species solvate to form a 1:1 chloroform-acetone complex.

When these "chemical" theories of nonideal fluids were first proposed early in this century (Dolezalek,1908), it was customary to assume that the "true" species form an ideal solution; in other words, all deviations from ideal behavior were ascribed to chemical effects. It was not until (about) 1950 that some authors took into account also physical interactions between the true species (Scatchard, 1949; Kretschmer and Wiebe, 1954). However, theories which used both chemical and physical contributions to nonideality were confined either to gases at moderate densities (second virial coefficients) or to liquid solutions containing only subcritical components at conditions remote from critical.

It was only in 1976 that Heidemann (1976) proposed an equation of state, applicable to all fluid densities, for fluids which exhibit chemical and physical contributions to nonideal behavior. Since then, other authors, notably Gmehling and Liu (1979), Baumgaertner et al. (1980) and Wenzel et al. (1982) have proposed similar equations of state based on a variety of simplifying assumptions. However, to the best of our knowledge, for such equations of

state no systematic derivation has been presented which clearly gives the fundamental ideas and which also indicates why simplifying assumptions are necessary and what choice of assumptions may be available. In this work we present such a derivation, applicable to all fluid densities; we then illustrate the applicability of a chemical-physical equation of state toward correlation of Henry's constants of nonpolar solutes in water over a wide temperature range.

Thermodynamic Framework

Consider a binary mixture of components A and B. In the absence of any association or solvation, the number of moles of A is n_{Ao} and the number of moles of B is n_{Bo}.

We assume that both components A and B can continuously associate to form linear polymers: dimers, trimers, etc. according to

$$A_1 + A_1 \rightleftarrows A_2 \qquad B_1 + B_1 \rightleftarrows B_2$$

$$A_2 + A_1 \rightleftarrows A_3 \qquad B_2 + B_1 \rightleftarrows B_3$$

$$\vdots \qquad\qquad \vdots$$

$$A_i + A_1 \rightleftarrows A_{i+1} \qquad B_i + B_1 \rightleftarrows B_{i+1}$$

where index i goes from unity to infinity. As indicated by the double arrows, we assume that the indicated molecular species are in chemical equilibrium, characterized by equilibrium constants $K_{A_2}, \ldots, K_{A_{i+1}}$ and $K_{B_2}, \ldots, K_{B_{i+1}}$ which depend only on temperature. For simplicity, we assume that, for each component, all association constants are equal, independent of i, designated by K_A and K_B, respectively.

For solvation, there are many stoichiometric possibilities: the general formula for a solvated species is $A_n B_m$ where indices n and m can be

any integer between one and infinity. To simplify, we assume that solvation equilibria are of the form

$$A_1 + B_1 \rightleftarrows AB$$

$$AB + AB \rightleftarrows (AB)_2$$

$$\vdots$$

$$(AB)_i + AB \rightleftarrows (AB)_{i+1}$$

where index i goes fron one to infinity. Further, we assume that one equilibrium constant K'_{AB}, applies to all solvation equilibria, except the first one; its equilibrium constant is K''_{AB}.

Given this physical picture, our aim is to establish an expression for the Helmholtz energy $\underline{A}$ of a mixture at temperature T and volume V containing monomers, associated species and solvated species which are in chemical equilibrium. Unlike other authors, we do <u>not</u> assume that this mixture is ideal; subject to simplifying assumptions, we take into account physical interactions (repulsion and attraction) between the chemically-equilibrated molecular species.

To obtain the desired expression for $\underline{A}$ we consider four steps, all at temperature T. Our reference states are pure component A and pure component B, each at T and 1 bar, in the ideal-gas state. In this reference state, pure components A and B exist only as monomers.

<u>Step I</u> - Formation of Pure Associated and Solvated Species in the Ideal-Gas State at T and 1 bar:

$$\Delta \underline{A}_I = \sum_{i=1}^{\infty} n_{A_{i+1}} [\Delta g^\circ_{A_{i+1}} + i\,RT]$$

$$+ \sum_{i=1}^{\infty} n_{B_{i+1}} [\Delta g^\circ_{B_{i+1}} + i\,RT]$$

$$+ \sum_{i=1}^{\infty} n_{(AB)_i} [\Delta g^\circ_{(AB)_i} + (2i-1)\,RT] \qquad (1)$$

where $\Delta g^{\circ}_{A_{i+1}}$ = standard Gibbs energy of formation of one mole of species A_{i+1} . Similar definitions hold for $\Delta g^{\circ}_{B_{i+1}}$ and $\Delta g^{\circ}_{(AB)_i}$. The number of moles of species j is designated by n_j .

Step II - The Pure Monomers and the Pure Associated and Solvated Species at T and 1 bar in the Ideal-Gas State are Mixed to Form an Ideal-Gas Mixture at T and V :

$$\Delta \underline{A}_{II} = \sum_j n_j \, RT \ln \frac{n_j RT}{V} \tag{2}$$

where gas constant R in the logarithm is chosen to give units of bars. We now introduce n_T , the total number of moles

$$n_T = \sum_{i=1}^{\infty} n_{A_i} + \sum_{i=1}^{\infty} n_{B_i} + \sum_{i=1}^{\infty} n_{(AB)_i}$$

We then obtain for $\Delta \underline{A}_{II}$

$$\Delta \underline{A}_{II} = RT \left[-n_T \ln V + n_T \ln RT + \sum_{i=1}^{\infty} n_{A_i} \ln n_{A_i} + \sum_{i=1}^{\infty} n_{B_i} \ln n_{B_i} + \sum_{i=1}^{\infty} n_{(AB)_i} \ln n_{(AB)_i} \right] \tag{3}$$

Step III - Each Molecule in the Ideal-Gas Mixture at T and V (a Point) is Inflated to a Hard Sphere to Form a Hard-Sphere Mixture :

$$\Delta \underline{A}_{III} = n_T \, RT \, \underline{A}^*(\xi) \tag{4}$$

where $\xi = \frac{n_T \hat{b}}{V}$ is the reduced density with $\hat{b}$ a size parameter for the mixture and $\underline{A}^*(\xi)$ is obtained from a suitable hard-sphere equation of state. [Equation (4) uses a one-fluid approximation. While some other approximation could be used, only the one-fluid approximation gives a

feasible algebraic form.] For example, if we use the original van der Waals equation,

$$\underline{A}^{*}(\xi) = -\ln(1-4\xi) \tag{5}$$

or, using the Carnahan-Starling equation,

$$\underline{A}^{*}(\xi) = -\frac{\xi(3\xi-4)}{(1-\xi)^2} \tag{6}$$

<u>Step IV</u> - The Hard Spheres at T and V are Charged with an Attractive Potential to Form a Real Mixture:

$$\Delta\underline{A}_{IV} = n_T \frac{\hat{a}}{\hat{b}} \underline{A}^{**}(\xi) \tag{7}$$

where $\frac{\hat{a}}{\hat{b}}$ is a parameter characterizing the attractive potential energy of the mixture and $\underline{A}^{**}(\xi)$ is obtained from a semi-empirical equation of state of the van der Waals form. For example, if the original van der Waals equation is used,

$$\underline{A}^{**}(\xi) = -\xi \tag{8}$$

If we adopt the Redlich-Kwong equation of state,

$$\underline{A}^{**}(\xi) = -\frac{1}{4}\ln(1+4\xi) \tag{9}$$

The desired Helmholtz energy $\underline{A}$ of the real mixture is given by

$$\underline{A} = n_{Ao}\,\underline{a}_A^{\circ} + n_{Bo}\,\underline{a}_B^{\circ} + \Delta A_I + \Delta A_{II} + \Delta A_{III} + \Delta A_{IV} \tag{10}$$

where $\underline{a}_A^{\circ}$ is the molar Helmholtz energy of pure A in the standard state; a similar definition holds for $\underline{a}_B^{\circ}$.

The equation of state for pressure P follows from

$$P = -\left(\frac{\partial \underline{A}}{\partial V}\right)_{T,n_j} \tag{11}$$

$$P = n_T\left[\frac{RT}{V} - RT\,\frac{\partial \underline{A}^*(\xi)}{\partial V} - \left(\frac{\hat{a}}{\hat{b}}\right)\frac{\partial \underline{A}^{**}(\xi)}{\partial V}\right] \tag{12}$$

The chemical potentials for components A and B are, respectively, equal to those for monomers A_1 and B_1. [For a simple proof of this general result see Prigogine and Defay (1954)]

$$\mu_A = \mu_{A_1} = \left(\frac{\partial \underline{A}}{\partial n_{A_1}}\right)_{T,V,n_j(j\neq A_1)} \tag{13}$$

$$\mu_B = \mu_{B_1} = \left(\frac{\partial \underline{A}}{\partial n_{B_1}}\right)_{T,V,n_j(j\neq B_1)} \tag{14}$$

For μ_A, we obtain

$$\begin{aligned}\mu_A = {} & \underline{a}_A^\circ - RT\ln(V/RT) + RT(1+\ln n_{A_1}) \\ & + RT\,\underline{A}^*(\xi) + n_T\,RT\,\frac{\partial \underline{A}^*(\xi)}{\partial \xi}\cdot\frac{\partial \xi}{\partial n_{A_1}} \\ & + \frac{\hat{a}}{\hat{b}}\,\underline{A}^{**}(\xi) + n_T\,\frac{\hat{a}}{\hat{b}}\,\frac{\partial \underline{A}^{**}}{\partial \xi}\cdot\frac{\partial \xi}{\partial n_{A_1}} + n_T\,\underline{A}^{**}(\xi)\,\frac{\partial \hat{a}/\hat{b}}{\partial n_{A_1}}\end{aligned} \tag{15}$$

There is a similar relation for μ_B.

In Equation (15), the first three terms are ideal-gas contributions; the fourth and fifth terms are hard-sphere contributions; the remaining terms are contributions from attractive forces.

We consider four types of chemical equilibria:

Association of A:

$$K_A = \frac{\phi_{A_{i+1}}}{\phi_{A_i}\ \phi_{A_1}\ P} \cdot \frac{\mathfrak{z}_{A_{i+1}}}{\mathfrak{z}_{A_i}\ \mathfrak{z}_{A_1}} \tag{16}$$

Association of B:

$$K_B = \frac{\phi_{B_{i+1}}}{\phi_{B_i}\ \phi_{B_1}\ P} \cdot \frac{\mathfrak{z}_{B_{i+1}}}{\mathfrak{z}_{B_i}\ \mathfrak{z}_{B_1}} \tag{17}$$

Solvation:

$$K'_{AB} = \frac{\phi_{AB}}{\phi_{A_1}\ \phi_{B_1}\ P} \cdot \frac{\mathfrak{z}_{AB}}{\mathfrak{z}_{A_1}\ \mathfrak{z}_{B_1}} \tag{18}$$

$$K''_{AB} = \frac{\phi_{(AB)_{m+i}}}{\phi_{(AB)_m}\ \phi_{AB}\ P} \cdot \frac{\mathfrak{z}_{(AB)_{m+1}}}{\mathfrak{z}_{(AB)_m}\ \mathfrak{z}_{AB}} \tag{19}$$

Here $\mathfrak{z}$ is the true mole fraction $(\mathfrak{z}_j = n_j/n_T)$, and ϕ is the fugacity coefficient given by the well-known thermodynamic relation

$$RT \ln \phi_k = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_k}\right)_{T,V,n_j\ (j\neq k)} - \frac{RT}{V}\right] dV - RT\ln z \tag{20}$$

where $z = PV/n_TRT$ is the compressibility factor.

The four chemical equilibria [Equations (16), (17), (18) and (19)] contain ratios of fugacity coefficients. In general, these ratios depend on temperature, density and composition. In that event, we have tremendous mathematical complexity. However, as shown by Heidemann (1976), this complexity can be greatly reduced by a proper choice of mixing rules for $\hat{a}$ and $\hat{b}$. Several choices are available such that the ratio of fugacity coefficients is independent of i (the degree of association and/or solva-

tion) and further, is the same for all four equilibria, as shown below.

For example, Heidemann assumed

$$a_i = i^2 a_1 \qquad\qquad b_i = i b_1 \tag{21}$$

and then derived the mixing rules

$$\hat{a} = \left(\frac{n_o}{n_T}\right)^2 \left(x_A^2\, a_{A_1} + 2x_A x_B \sqrt{a_{A_1} a_{B_1}} + x_B^2\, a_{B_1}\right) \tag{22}$$

and

$$\hat{b} = \left(\frac{n_o}{n_T}\right)\left(x_A\, b_{A_1} + x_B\, b_{B_1}\right) \tag{23}$$

where $n_o = n_{Ao} + n_{Bo}$. However, experimental values of a_i for normal alkanes indicate that Eq. (21) overestimates the effect of i on a_i .

In this work, we suggest a generalized mixing rule to replace Eq. (22):

$$\hat{a} = \left(\frac{n_o}{n_T}\right)^{1+w} \left(x_A^2\, a_{A_1} + 2x_A x_B \sqrt{a_{A_1}\, a_{B_1}}(1+k_{AB}) + x_B^2\, a_{B_1}\right) \tag{24}$$

where $o \leq w \leq 1$ and k_{AB} is a binary interaction parameter. Eq. (23) is unchanged.

With these mixing rules, we obtain

$$\alpha = \frac{P\phi_{A_i}\,\phi_{A_1}}{\phi_{A_{i+1}}} = \frac{P\phi_{B_i}\,\phi_{B_1}}{\phi_{B_{i+1}}} = \frac{P\phi_{A_1}\phi_{B_1}}{\phi_{AB}} = \frac{P\phi_{(AB)_i}\phi_{AB}}{\phi_{(AB)_{i+1}}}$$

$$= \frac{\xi RT}{\hat{b}} \exp \int_o^{\xi} \left(-\frac{\partial \underline{A}^*(\xi)}{\partial \xi} - \frac{(1-w)}{RT} \cdot \frac{\hat{a}}{\hat{b}} \frac{\partial \underline{A}^{**}(\xi)}{\partial \xi}\right) d\xi \tag{25}$$

The detailed derivation is presented in Appendix I. Note that when $w = 1$ (as in Heidemann's work), only repulsive forces contribute to α .

To obtain n_{A_1} , n_{B_1} and n_o/n_T , we must simultaneously solve the chemical equilibria and material balances, as discussed in Appendix II.

Henry's Constant for a Nonassociating Solute in an Associated Solvent

The most sensitive test for a theory of solutions is in the dilute region. Therefore, we now turn attention to Henry's constants. To obtain an expression for $H_{A,B}$, Henry's constant of nonassociating solute A in associated solvent B , we first recall the definition

$$H_{A,B} = \lim_{x_A \to o} (f_A/x_A) \tag{26}$$

where f_A , the fugacity of the solute, is related to the residual chemical potential $\mu_A{}^r$ by

$$\ln f_A = \frac{\mu_A^r + RT\ln (Px_A/z)}{RT} \tag{27}$$

where z is the compressibility factor of the liquid mixture; the residual chemical potential is defined by

$$\mu_A^r = \mu_A(T,x,V) - \mu_A^{\text{ideal gas}}(T,x,V) \tag{28}$$

For Henry's constant, we obtain

$$H_{A,B} = \lim_{x_A \to o} [P \exp (\frac{\mu_A^r}{RT} - \ln z)]$$

In the limit $x_A \to o$, z is the compressibility factor of pure liquid B .

Because A is nonassociating, $K_A = 0$, and the general formula for solvated species is AB_i .

Data Reduction

To apply Eq. (29), we take water for solvent B in the temperature range 20-300°C . At any temperature, we must obtain parameters a and b and

association constant K_B . To do so, we use experimental data for vapor pressures and for liquid densities over a range of temperature (Bain,1964). Since it is difficult to obtain 3 unique parameters, we use in addition, experimental Henry's constants for a particular nonassociating solute A , viz. methane (Crovetto et al.,1982) and experimental PVT and vapor-pressure data for pure methane (IUPAC, 1976). We use mixing rules Eqs. (23) and (24) with $w = o$ and for methane-water we arbitrarily set $k_{AB} = 0$.

Table 1 shows results of data reduction for water. True mole fractions (up to $\mathcal{Z}_6$) are also shown at each temperature for saturated liquid water. Figures 1 and 2 indicate that, with the parameters indicated, we obtain an excellent fit. To facilitate calculations, the parameters for pure water are represented by

$$a = (-612.42 + 67.545T)/T^{1.4} \quad (\mathrm{bar \cdot l^2 \cdot mol^{-2}}) \tag{30}$$

$$b = (0.13672 + 2.7457.10^{-5}T^{1.2})/T^{0.5} \quad (\mathrm{l \cdot mol^{-1}}) \tag{31}$$

$$\ln K = -\frac{\Delta H}{RT} + \frac{S}{R} \tag{32}$$

where $H/R = -5.890 \times 10^3 K$ and $\Delta S/R = -18.22$ for temperatures below 200°C . (For temperatures greater than 200°C , we use the association constants shown in Table 1.) Parameters a and b for methane (and other nonassociating solutes) are given in Appendix III.

Figure 3 shows calculated and experimental Henry's constants for methane in water. Also shown are Henry's constants calculated with the Carnahan-Starling-van der Waals model (no association) and different values of k_{AB} . It is evident that if this latter model is used to fit Henry's constants, it is necessary to assign a large empirical temperature dependence to k_{AB} . In this model, a single value of k_{AB} cannot reproduce the observed maximum when Henry's constant is plotted against temperature.

Table 1

PARAMETERS AND TRUE MOLE FRACTIONS OF ASSOCIATED SPECIES IN SATURATED LIQUID WATER

$t/^{o}C$	$a/bar \cdot l^{2} \cdot mol^{-2}$	$b/l \cdot mol^{-1}$	K/bar^{-1}	$\mathfrak{z}_1$	$\mathfrak{z}_2$	$\mathfrak{z}_3$	$\mathfrak{z}_4$	$\mathfrak{z}_5$	$\mathfrak{z}_6$
20	6.757	0.00946	6.511	$7.27 \cdot 10^{-1}$	$1.99 \cdot 10^{-1}$	$5.42 \cdot 10^{-2}$	$1.48 \cdot 10^{-2}$	$4.04 \cdot 10^{-3}$	$1.10 \cdot 10^{-3}$
50	6.507	0.00917	0.9830	$7.67 \cdot 10^{-1}$	$1.79 \cdot 10^{-1}$	$4.16 \cdot 10^{-2}$	$9.68 \cdot 10^{-3}$	$2.25 \cdot 10^{-3}$	$5.24 \cdot 10^{-4}$
100	6.168	0.00881	0.08563	$8.20 \cdot 10^{-1}$	$1.48 \cdot 10^{-1}$	$2.66 \cdot 10^{-2}$	$4.79 \cdot 10^{-3}$	$8.63 \cdot 10^{-4}$	$1.55 \cdot 10^{-4}$
150	5.884	0.00853	0.01357	$8.60 \cdot 10^{-1}$	$1.21 \cdot 10^{-1}$	$1.69 \cdot 10^{-2}$	$2.38 \cdot 10^{-3}$	$3.33 \cdot 10^{-4}$	$4.68 \cdot 10^{-5}$
200	5.641	0.00831	0.002881	$9.00 \cdot 10^{-1}$	$9.00 \cdot 10^{-2}$	$9.01 \cdot 10^{-3}$	$9.01 \cdot 10^{-4}$	$9.02 \cdot 10^{-5}$	$9.03 \cdot 10^{-6}$
250	5.426	0.00814	0.0007025	$9.38 \cdot 10^{-1}$	$5.84 \cdot 10^{-2}$	$3.64 \cdot 10^{-3}$	$2.27 \cdot 10^{-4}$	$1.41 \cdot 10^{-5}$	$8.79 \cdot 10^{-7}$
300	5.244	0.00805	0.0001998	$9.64 \cdot 10^{-1}$	$3.50 \cdot 10^{-2}$	$1.27 \cdot 10^{-3}$	$4.62 \cdot 10^{-5}$	$1.68 \cdot 10^{-6}$	$6.11 \cdot 10^{-8}$

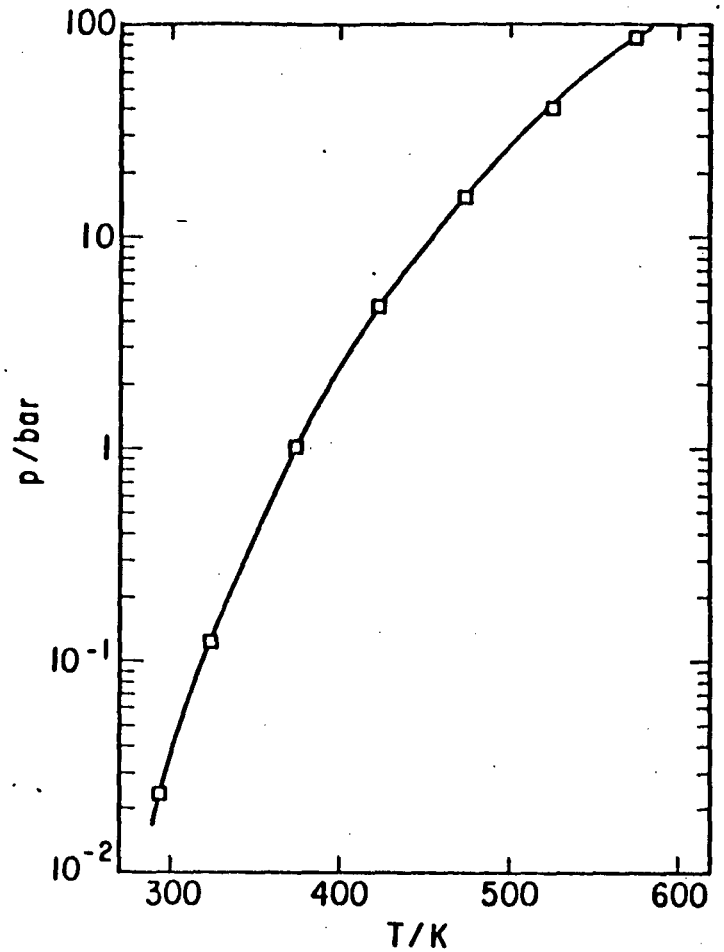

Fig. 1 Vapor Pressure of Water
—— Calc.
□ (Bain, 1964)

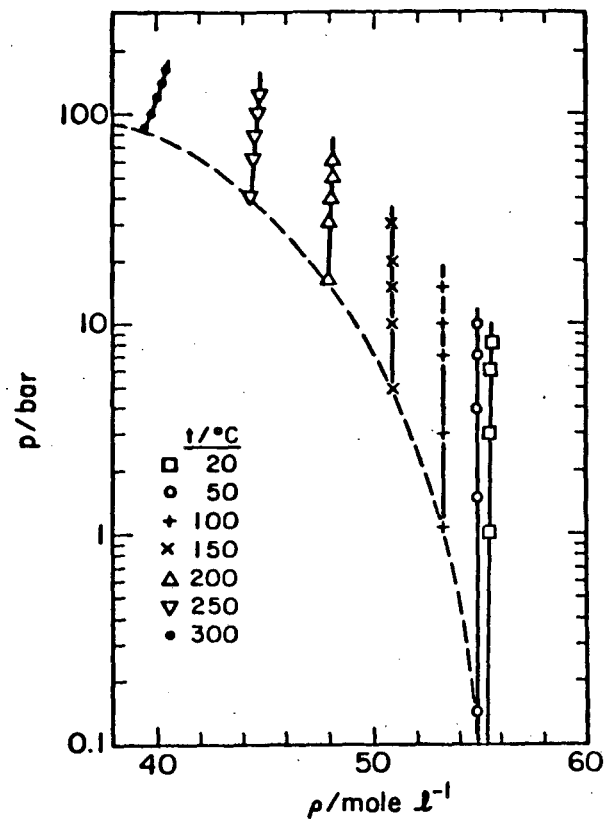

Fig. 2 Pressure-Liquid Density Diagram of Water
—— Calc.
Symbols: (Bain, 1964)

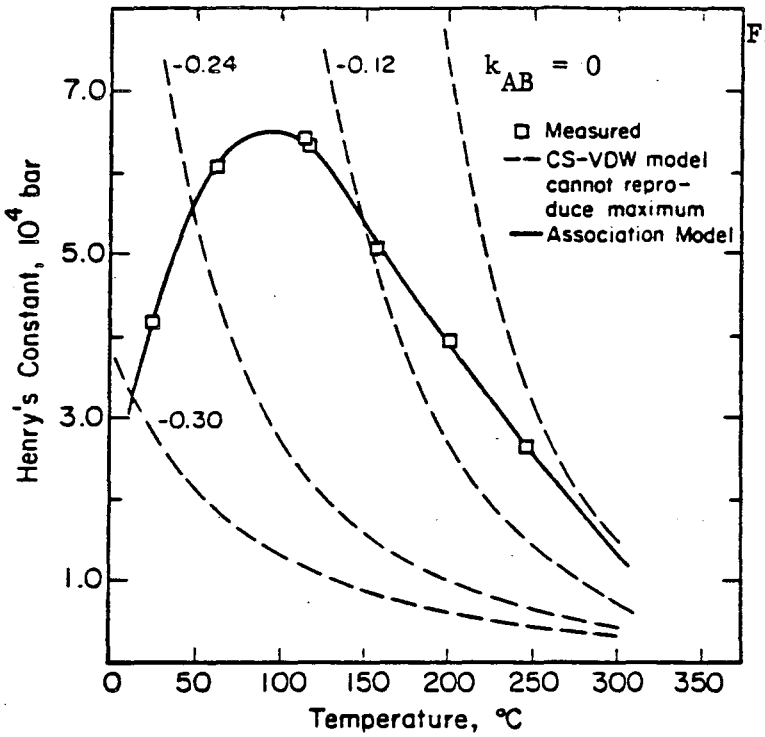

Fig. 3 Henry's Constant for Methane in Water.
Methane is used as a probe to determine the chemical equilibrium constant for water. (k_{AB} is arbitrarily set equal to zero.)
□ (Crovetto et al.,1982)

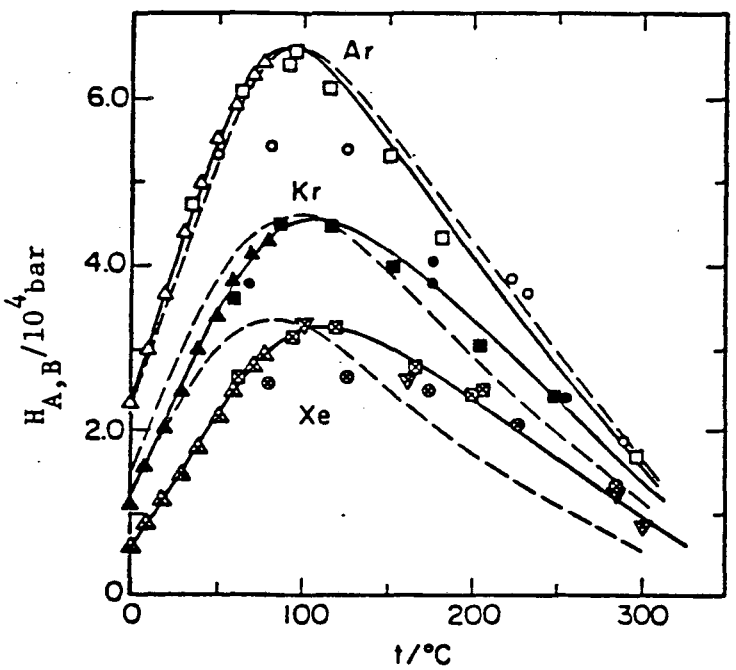

Fig. 4 Henry's Constants for Ar, Kr, Xe in Water.
○ ● ⊗ (Potter and Clynne,1978)
△ ▲ ▽ (Wilhelm et al.,1977)
□ ■ ⊠ (Crovetto et al.,1982)
◬ (Benson and Krause,1976)

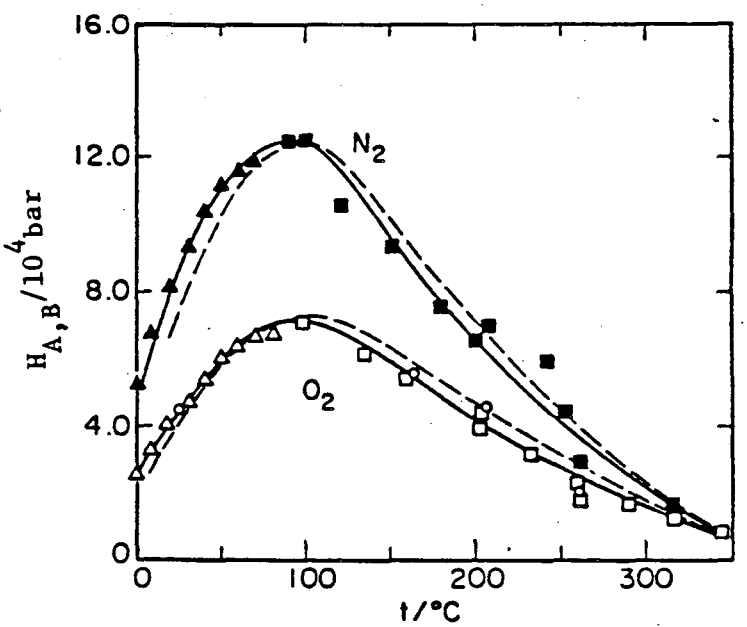

Fig. 5 Henry's Constants for O_2 and N_2 in Water.
△ ▲ (Wilhelm et al.,1977)
□ ■ (Himmelblau,1960)
○ (Pray et al.,1952)

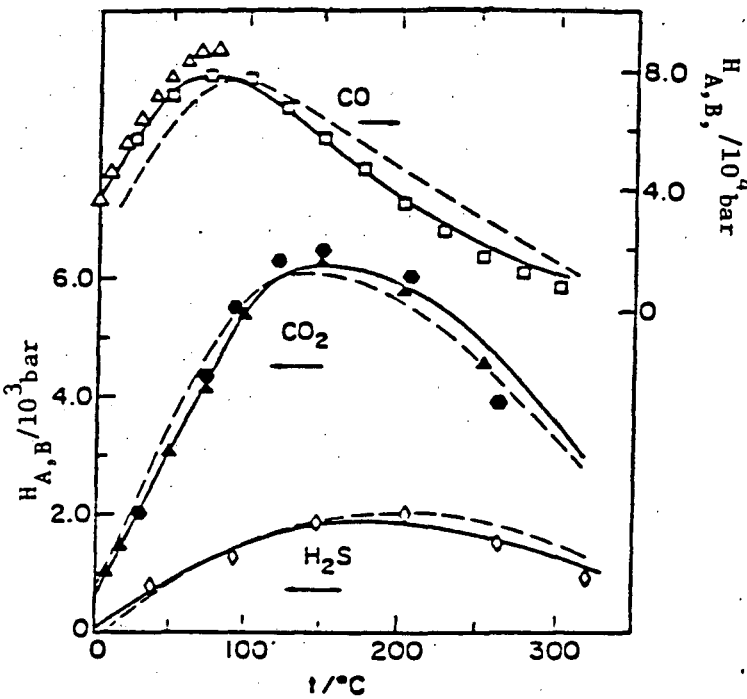

Fig. 6 Henry's Constants of CO, CO_2 H_2S in Water

△ (Winkler, 1901)
□ (Jung et al., 1971)
▲ (Schulze and Prausnitz, 1981)
● ◇ (Gas Processors Association, 1982)

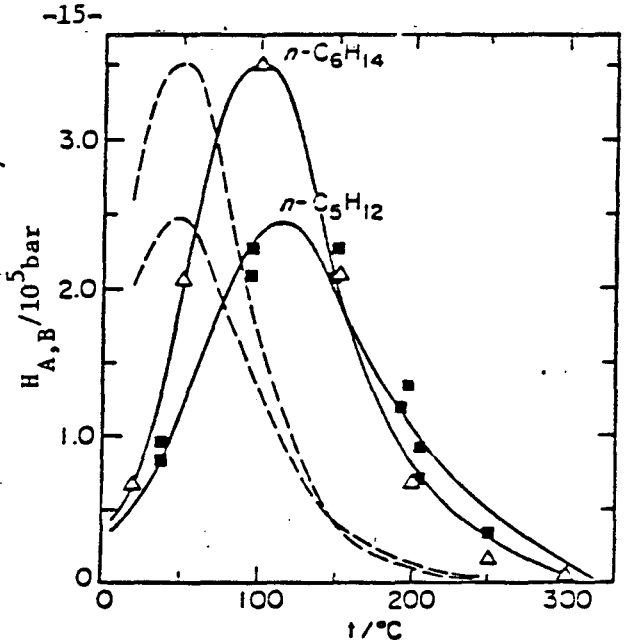

Fig. 7 Henry's Constants of n-C_5H_{12}, n-C_6H_{14} in Water

■ (Gas Processors Association, 1982)
△ (Tsonopoulos and Wilson, 1983)

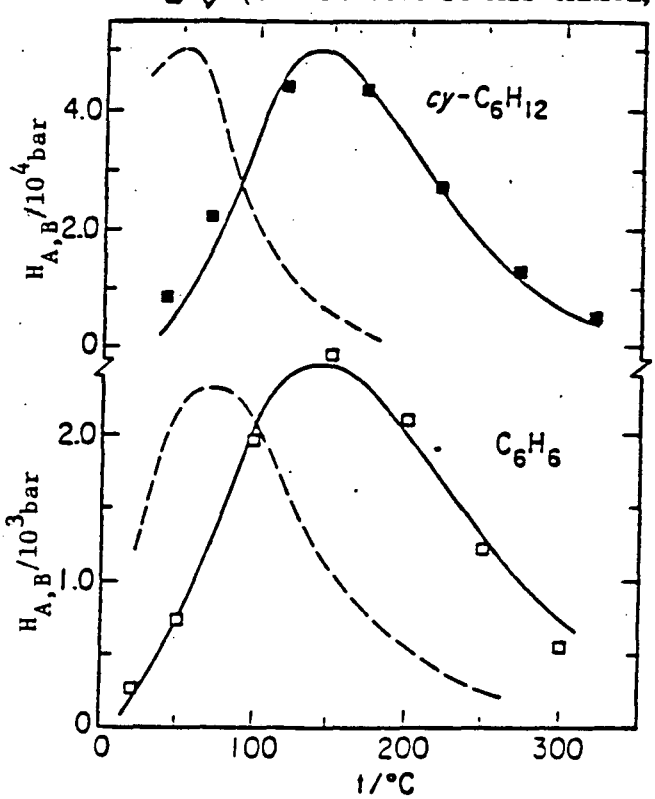

Fig. 8 Henry's Constants of C_6H_6, Cyclo-C_6H_{12} in Water

□ (Tsonopoulos and Wilson, 1983)

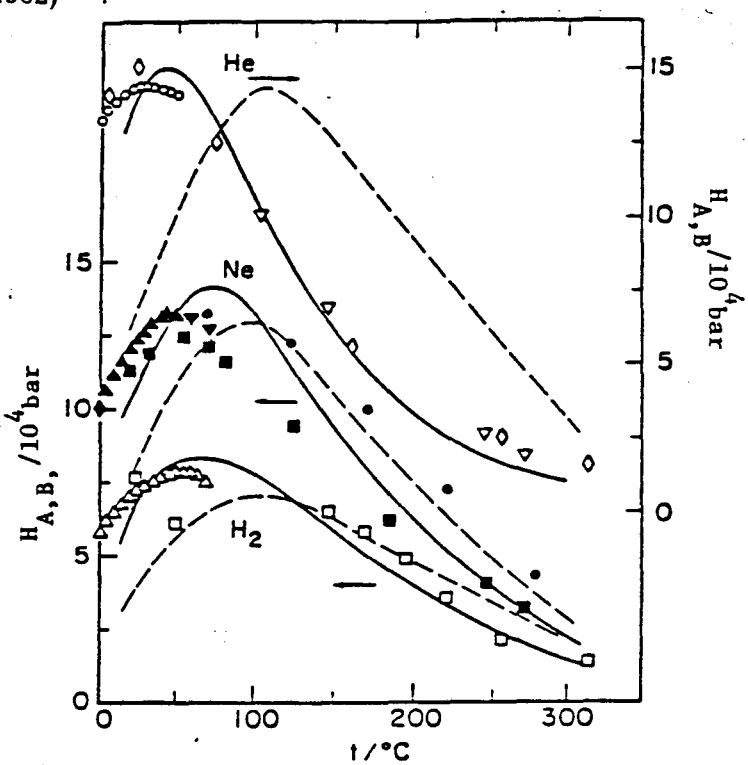

Fig. 9 Henry's Constants of He, Ne, H_2 in Water

○ ▲ (Benson and Krause, 1976)
◇ □ (Pray et al., 1952)
▽ (Potter and Clynne, 1978)
▼ △ (Wilhelm et al., 1977)
(Crovetto et al., 1982)

We also reduced experimental Henry's-constant data in water for 14 non-associating solutes in addition to methane. Results are shown in Figures 4-9. Good fits are obtained for argon, krypton, nitrogen, oxygen, carbon monoxide, carbon dioxide and hydrogen sulfide using a single value of k_{AB}, as given in Table 2. We note that the molecular sizes of these solutes are close to that of water. However, results are not good for xenon, pentane, hexane, cyclohexane and benzene whose molecular sizes are appreciably larger than that of water; results are also not good for hydrogen, helium and neon whose molecular sizes are appreciably smaller than that of water. Our inability to fit Henry's constants for these asymmetric systems is probably due to the use of a one-fluid approximation (Equation 4) and also due to the inadequacy of mixing rules Eqs. (23) and (24). It appears that, while the chemical theory of associated fluids takes into account the effect of strongly oriented intermolecular forces, the one-fluid approximation with simple mixing rules fails to take into account normal intermolecular forces (repulsion and attraction) in mxtures where the molecules differ significantly in size. Our mixing rules are, essentially, generalizations of the van der Waals one-fluid theory of mixtures; the work of Shing and Gubbins (1983) has shown that a one-fluid theory leads to significant error for asymmetric mixtures, especially in the dilute region. To improve the chemical theory of solutions, it will be necessary to focus attention on better relations for calculating $\underline{A}^*(\xi)$, $\hat{a}$ and $\hat{b}$.

Proceeding empirically, we can very much improve our fits of Henry's constants by assigning a small linear temperature dependence to k_{AB} as shown in Table 2. We note that for large solutes, k_{AB} increases with temperature while for small solutes, k_{AB} decreases with temperature.

Figures 4 to 9 show calculated results using a temperature-independent k_{AB} (dashed lines) and using a slightly temperature-dependent k_{AB} (solid

lines) according to Table 2. This empirical procedure is clearly not satisfactory but may have some utility for estimating solubilities in water when no experimental data are available.

Table 2

k_{AB} FOR AQUEOUS BINARIES

Solute	k_{AB} at 100°C	$\frac{d\,k_{AB}}{dT}$
Ne	0.277	-0.00096
He	0.082	-0.00284
H_2	-0.104	-0.00125
O_2	-0.089	-0.00023
Ar	0.082	-0.00010
N_2	-0.100	-0.00019
Kr	0.070	0.00018
CO	-0.246	-0.00069
CO_2	-0.007	0.00009
H_2S	0.002	-0.00011
Xe	0.010	0.00032
C_6H_6	-0.170	0.00057
n-C_5H_{12}	-0.221	0.00078
cyclo-C_6H_{12}	-0.309	0.00112
n-C_6H_{14}	-3.323	0.00061

Conclusion

For associated fluids and their mixtures, it is possible, as shown here, to develop a generalized expression for the Helmholtz energy as a function of temperature, volume and composition. The generalized expression leads to an equation of state for an assembly of molecules that interact chemically to form dimers, trimers, etc., all at chemical equilibrium; this chemical interaction reflects strong orientational forces such as hydrogen bonding. Normal forces of repulsion and attraction are taken into account by application of the classical van der Waals theory of fluids.

If complete generality is to be maintained, mathematical complexity is hopelessly large. To reduce the theory to practice, simplifying assumptions must be made, as discussed here. While the introduction of chemical equilibria is useful for taking into account strong orientational forces of attraction, the chemical theory of real fluids is nevertheless limited at present by our inadequate understanding of mixtures containing molecules of different size. The conventional procedure for such mixtures is to use a one-fluid van der Waals approximation but that is insufficiently precise, especially in the dilute region. Future progress in mixture thermodynamics can only be attained if we can replace the customary one-fluid approximation by a theoretically significant expression for the potential energy and for the configurational entropy of mixtures containing molecules of different size.

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Appendix I. Derivation of Equation (25)

We rearrange Eq.(12) as follows:

$$P = n_T \frac{RT}{V} - n_T RT \frac{\partial \underline{A}^*(\xi)}{\partial V} - n_T^{1-w} \quad (n_T \hat{b})^w \frac{\hat{a}}{\hat{b}^{1+w}} \frac{\partial \underline{A}^{**}(\xi)}{\partial V} \tag{I-1}$$

According to Eqs. (23) and (24), $n_T\hat{b}$ and $\hat{a}/\hat{b}^{1+w}$ are functions of n_{Ao} , n_{Bo} and parameters of monomers only, and $\partial n_{Ao}/\partial n_{Ai}$, $\partial n_{Bo}/\partial n_{Bi}$, $\partial n_{Ao}/\partial n_{(AB)i}$, $\partial n_{(Bo)}/\partial n_{(AB)i}$ all equal i . We obtain the following equations through differentiating Eq. (I-1);

$$\left(\frac{\partial P}{\partial n_{A_i}}\right)_{T,V,n_j(j\neq A_i)} = \frac{RT}{V} - RT \frac{\partial \underline{A}^*(\xi)}{\partial V} - (1-w) \cdot \frac{\hat{a}}{\hat{b}} \frac{\partial \underline{A}^{**}(\xi)}{\partial V} - F_A i \tag{I-2}$$

$$\left(\frac{\partial P}{\partial n_{B_i}}\right)_{T,V,n_j(j\neq B_i)} = \frac{RT}{V} - RT \frac{\partial \underline{A}^*(\xi)}{\partial V} - (1-w) \frac{\hat{a}}{\hat{b}} \frac{\partial \underline{A}^{**}(\xi)}{\partial V} - F_B i \tag{I-3}$$

$$\left(\frac{\partial P}{\partial n_{(AB)_i}}\right)_{T,V,n_j(j\neq (AB)_i)} = \frac{RT}{V} - RT \frac{\partial \underline{A}^*(\xi)}{\partial V} - (1-w) \frac{\hat{a}}{\hat{b}} \frac{\partial \underline{A}^{**}(\xi)}{\partial V} - F_{AB} \tag{I-4}$$

where

$$F_A = n_T RT \partial \left[\frac{\partial \underline{A}^*(\xi)}{\partial V}\right] / \partial n_{Ao} + n_T^{1-w} \partial \left[(n_T \hat{b})^w \frac{\hat{a}}{\hat{b}^{1+w}} \cdot \frac{\partial \underline{A}^{**}(\xi)}{\partial V}\right] / \partial n_{Ao} \tag{I-5}$$

$$F_B = n_T RT \partial \left[\frac{\partial \underline{A}^*(\xi)}{\partial V}\right] / \partial n_{Bo} + n_T^{1-w} \partial \left[(n_T \hat{b})^w \frac{\hat{a}}{\hat{b}^{1+w}} \cdot \frac{\partial \underline{A}^{**}(\xi)}{\partial V}\right] / \partial n_{Bo} \tag{I-6}$$

$$F_{AB} = F_A + F_B \tag{I-7}$$

Substituting Eqs. (I-2), (I-3), (I-4) into Eq. (20), we obtain

$$\alpha = \frac{P\phi_{Ai}\phi_{A1}}{\phi_{A_{i+1}}} = \frac{P\phi_{Bi}\phi_{B1}}{\phi_{B_{i+1}}} = \frac{P\phi_{A1}\phi_{B1}}{\phi_{AB}} = \frac{P\phi_{(AB)i}\phi_{AB}}{\phi_{(AB)_{i+1}}}$$

$$= P \exp \left[\int_V^\infty \left(- \frac{\partial \underline{A}^*(\xi)}{\partial V} - \frac{1-w}{RT} \frac{\hat{a}}{\hat{b}} \frac{\partial \underline{A}^{**}(\xi)}{\partial V}\right) dV\right] / z$$

$$= \frac{\xi RT}{\hat{b}} \exp \int_o^\xi \left(\frac{\partial \underline{A}^*(\xi)}{\partial \xi} + \frac{1-w}{RT} \cdot \frac{\hat{a}}{\hat{b}} \cdot \frac{\partial \underline{A}^{**}(\xi)}{\partial \xi}\right) d\xi \tag{25}$$

Appendix II. Solution for n_{A1} , n_{B1} and n_o/n_T .

Substituting Eqs. (25) into Eqs. (16), (17), (18) and (19), we get

$$\alpha = \frac{\mathcal{Z}_{Ai+1}}{\mathcal{Z}_{Ai}\mathcal{Z}_{A1}K_A} = \frac{\mathcal{Z}_{Bi+1}}{\mathcal{Z}_{Bi}\mathcal{Z}_{B1}K_B} = \frac{\mathcal{Z}_{AB}}{\mathcal{Z}_{A1}\mathcal{Z}_{B1}K'_{AB}} = \frac{\mathcal{Z}_{(AB)i+1}}{\mathcal{Z}_{(AB)i}\mathcal{Z}_{AB}K''_{AB}} \qquad \text{(II-1)}$$

Then we can write the following equations from material balance.

$$\sum_{i=1}^{\infty} \mathcal{Z}_{Ai} + \sum_{i=1}^{\infty} \mathcal{Z}_{Bi} + \sum_{i=1}^{\infty} \mathcal{Z}_{(AB)i} = \frac{\mathcal{Z}_{A1}}{1-K_A\alpha\mathcal{Z}_{A1}} + \frac{\mathcal{Z}_{B1}}{1-K_B\alpha\mathcal{Z}_{B1}} + \frac{\mathcal{Z}_{AB}}{1-K''_{AB}\alpha\mathcal{Z}_{AB}} = 1 \qquad \text{(II-2)}$$

$$n_T\left(\sum_{i=1}^{\infty} i\mathcal{Z}_{Ai} + \sum_{i=1}^{\infty} i\mathcal{Z}_{(AB)i}\right) = n_T\left[\frac{\mathcal{Z}_{A1}}{(1-K_A\alpha\mathcal{Z}_{A1})^2} + \frac{\mathcal{Z}_{AB}}{(1-K''_{AB}\alpha\mathcal{Z}_{AB})^2}\right] = n_o x_A \qquad \text{(II-3)}$$

$$n_T\left(\sum_{i=1}^{\infty} i\mathcal{Z}_{Bi} + \sum_{i=1}^{\infty} i\mathcal{Z}_{(AB)i}\right) = n_T\left[\frac{\mathcal{Z}_{B1}}{(1-K_B\alpha\mathcal{Z}_{B1})^2} + \frac{\mathcal{Z}_{AB}}{(1-K''_{AB}\alpha\mathcal{Z}_{AB})^2}\right] = n_o x_B \qquad \text{(II-4)}$$

Solving Eqs. (II-2), (II-3) and (II-4) together with

$$\mathcal{Z}_{AB} = K'_{AB}\,\alpha\mathcal{Z}_{A1}\mathcal{Z}_{B1} \qquad \text{(II-5)}$$

from Eq. (II-1), we get $\mathcal{Z}_{A1}$, $\mathcal{Z}_{B1}$, $\mathcal{Z}_{AB}$ and n_o/n_T Also n_{A1}/n_o and n_{B1}/n_o.

Appendix III.

PARAMETERS a , $b^{(o)}$ AND $b^{(1)}$ FOR PURE COMPONENTS

$$\left(b = \frac{b^{(o)} + b^{(1)} T_r^2}{1 + T_r^2}\right.$$ where $T_r = T/T_c$, T_c is critical temperature)

SOLUTE	$a/\mathrm{bar \cdot l^2 \sqrt{K} \cdot mol^{-2}}$	$b^{(o)}/\mathrm{l \cdot mol^{-1}}$	$b^{(1)}/\mathrm{l \cdot mol^{-1}}$
Ne	3.916	0.03594	0.00433
He	6.470	0.01119	0.00609
H_2	4.228	0.08378	0.00507
O_2	20.73	0.01529	0.00780
Ar	22.24	0.01685	0.00789
N_2	21.77	0.02067	0.01023
Kr	43.26	0.01900	0.00970
CO	17.84	0.01940	0.00990
CO_2	71.95	0.01967	0.01004
H_2S	105.6	0.02052	0.01047
Xe	86.97	0.02458	0.01254
C_6H_6	454.7	0.05371	0.01559
n-C_5H_{12}	419.5	0.06041	0.02693
cyclo-C_6H_{12}	621.9	0.07835	0.01735
n-C_6H_{14}	598.9	0.07587	0.03359

List of symbols

A	symbol of component
$\underline{A}$	Helmholtz energy
a	van der Waals attraction parameter
$\underline{a}$	molar Helmholtz energy
B	symbol of component
b	van der Waals size parameter
f	fugacity
$\underline{g}$	molar Gibbs energy
H	enthalpy
$H_{A,B}$	Henry's constant of A in B
K	equilibrium constant
k	binary parameter
n	number of moles
P	pressure
R	gas constant
S	entropy
T	temperature
V	volume
x	liquid phase mole fraction
z	compressibility factor
$\mathfrak{z}$	true mole fraction
α	fugacity coefficient ratio
Φ	fugacity coefficient
ξ	reduced density
μ	chemical potential

Superscripts:

°	standard state
*	hard-sphere contribution
**	attractive potential contribution
^	mixture
r	residual

Subscripts:

A,B	component index
i,n,m	degree of association
I,II,III,IV	step of model construction
r	reduced property
T	total
°	absence of any association or solvation

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