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STATE-OF-THE-ART REVIEW OF PHASE EQUILIBRIA
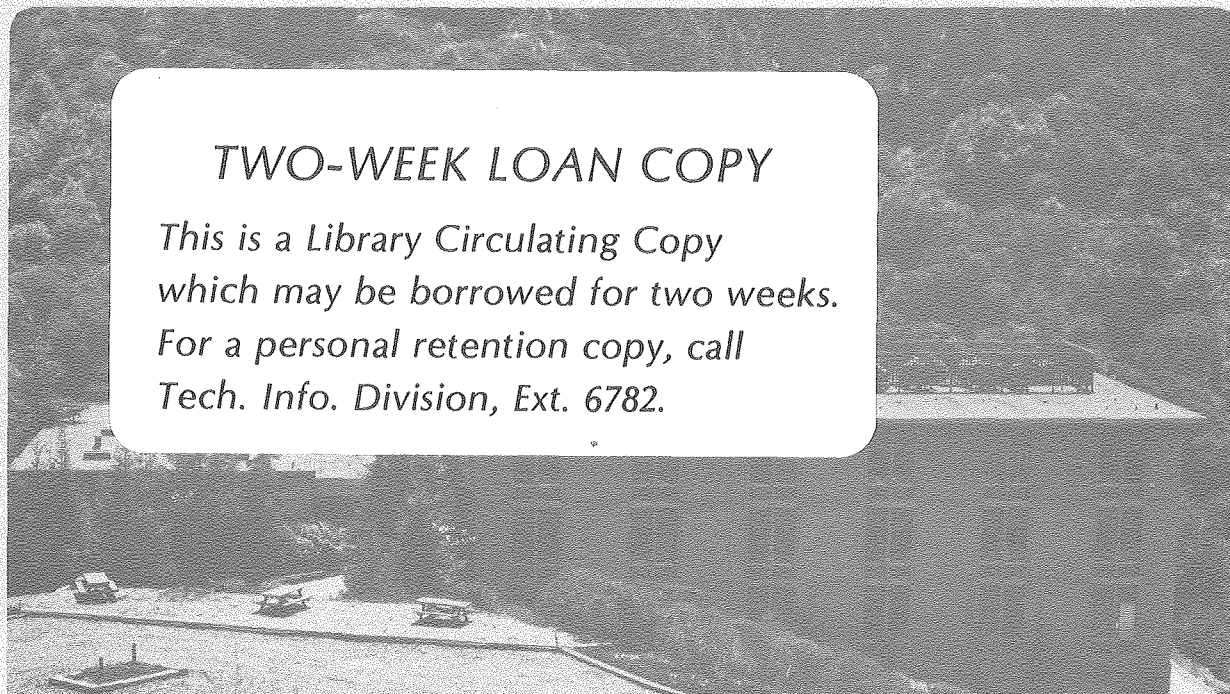
J. M. Prausnitz

March 1980

DISCLAIMER

State-of-the-Art Review of

Phase Equilibria

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Synopsis

High-pressure phase-equilibrium calculations using an equation of state are more sensitive to the mixing rules than to details in the effect of density or temperature on pressure. Therefore, calculations using any one of the currently popular equations of state are often successful provided at least one binary parameter is included in the mixing rules; in some cases, two binary parameters are required. However, for significant progress, more fundamental attention must be given to the problem of how to extend equations of state to mixtures. One possible technique is provided by perturbation theory; another by superposition of chemical equilibria.

At low or moderate pressures, vapor-phase corrections are often important. When specific intermolecular forces produce formation of molecular aggregates, strong deviations from ideal-gas behavior can be significant even at pressures well below 1 bar.

When vapor-liquid equilibrium data are reduced using conventional expressions for the excess Gibbs energy, the resulting binary parameters tend to be partially correlated and therefore, not unique. Lack of uniqueness makes it difficult, but not impossible, to calculate ternary liquid-liquid equilibria using binary parameters only.

New models for calculating properties of liquid-phase mixtures must allow for changes in free volume to give consideration to the effect of mixing on changes in rotational and vibrational degrees of freedom. Liquid-phase volumetric effects are also important in describing the solubilities of gases in solvent mixtures. Therefore, future liquid-phase models should incorporate a liquid-phase equation of state, either of the van der Waals type or, perhaps, as given by the direct-correlation function theory of liquids.

While the executive committee for this conference has honored me by requesting that I once again present a review of the state of the art of phase equilibria, this assignment presents me with a difficult conflict. On the one hand, I must be fair and perceptive but on the other, I must choose and omit. In the limited time available, I must both include and exclude, thereby unavoidably giving preferences on grounds which are based on little more than my own opinions. Therefore, let me at once apologize not so much for what I shall say, but for what I shall not say.

Phase equilibrium thermodynamics has generated a vast literature and in the space of one hour I can only mention a few topics. My choices are in no sense dogmatic; I fully recognize that in choosing particular topics, I reveal my personal preferences; others may well choose differently and, no doubt, with good reason. My position is similar to that of the late Professor Guggenheim: When his book "Thermodynamics" was published, a reviewer made a pertinent remark that surely applies to me. The reviewer said, "This book is very nice but it has an inappropriate title. It should be called Pride and Prejudice." Therefore, if in this short review I omit something dear to you, for example one of your own articles, please forgive me. At this festive ball, with so many distinguished beauties, it is not possible to dance with all the debutantes.

I should like to begin with some comments on present problems concerning equations of state. Figure 1 presents a reminder to indicate why equations of state are important to us: given the relation between pressure, volume, temperature and composition, we can calculate fugacities and thereby phase equilibria. There are two important items to remember: first, it is necessary that the equation of state apply to all phases of interest. That is obvious but the second item is not quite as evident: since the pressure is <u>integrated</u> with respect to volume, the precise volume dependence is often not very important; however, since the pressure is <u>differentiated</u> with respect to mole number, calculated K factors are very sensitive to the effect of composition. The composition effect is included in what we commonly call mixing rules and we find that small changes in the mixing rules can have large consequences on phase equilibria.

Figure 2 shows a few isotherms for methane calculated with three currently-popular equations of state: the Soave form of the Redlich-Kwong equation, the Peng-Robinson equation and the Lee-Kesler form of the Benedict-Webb-Rubin equation (1). There appears to be no major difference between the equations; all of them do well at densities below the critical but at higher densities, all show noticeable deviations from experiment. Figure 3 shows similar calculations for water and now the deviations from experiment are considerably larger. In determining the constants for these equations, for methane as well

as for water, priority has been given to the vapor-pressure data. Therefore, calculated vapor-pressures are good but calculated fluid densities, especially liquid densities, show appreciable error. Figures 2 and 3 illustrate that, after a hundred years of effort, we still do not have a satisfactory simple equation of state valid for the entire fluid-density region.

It is possible to achieve good representation with a complicated equation of state, using a large number of adjustable constants and various equations of state for this purpose have been proposed. But these are not of interest here. Complicated equations require a large body of experimental data which is rarely available. To find an equation of state which is both simple and reliable, we must look to developments in molecular theory which, I expect, will be discussed later in this meeting.

For process calculations, it is desireable to have an equation of state which is cubic in volume because it is then possible to find the roots of the equation analytically. Unfortunately, however, cubic equations are not capable of representing well the properties of real fluids over a wide density range. A comprehensive review by Martin (2) has shown convincingly that any cubic equation of state is a compromise, giving good representation in only part of the pressure-density diagram.

Fortunately, however, even an inadequate equation of state can be remarkably useful for calculating vapor-liquid

equilibria, probably because fugacities (or K-factors) depend on an integral of the equation of state; it frequently happens that errors in the integral of a function are much smaller than errors in the function itself. As suggested by Figure 1, the effect of composition on pressure is more important than the effect of volume; the important quantity is the mixing rule.

Figure 4 reviews conventional mixing rules and also reminds us that these apply to a one-fluid theory of mixtures, viz. the assumption that the properties of a mixture are equivalent to those of a hypothetical pure fluid whose characteristic constants are functions of composition. The one-fluid theory is so common that we have perhaps forgotten about alternatives such as the two-fluid theory. I shall briefly return to that alternative later.

The important feature of Figure 4 is to indicate first, that there is only limited theoretical basis for the common mixing rules and second, that a binary constant, here called k_{ij}, is introduced in one of the mixing rules. The importance of this constant is shown in Figure 5 which reports calculations by Döring (3) for the system methane-ethane. Döring calculates the binary parameter which gives minimum deviations from the experimental pressure. Two features are indicated: first, calculated phase-equilibria are sensitive to the binary parameter and second, the three equations of state studied give similar results. This figure illustrates our general experience that, at the present stage of development, the choice

of binary parameter is usually more important than the choice
of a particular equation of state.

While simple mixing rules and one binary constant are
sufficient for many mixtures, some mixtures, especially those
with at least one polar component, are better represented by
somewhat different mixing rules, as indicated in Figure 6.
One modification, particularly suitable for mixtures of small
and large molecules, introduces a binary constant into the
mixing rule for molecular-size constant b. Another modification
attempts to take polarity into account by dividing the at-
tractive-force constant a into polar and nonpolar contributions.

These modifications often help to achieve better re-
presentation but they do not solve the basic problem viz.,
that real mixtures are not random mixtures. Real molecules
have preferences in their choice of neighbors and therefore
the quadratic mole-fraction dependence of the equation-of-
state constants is meaningful only for simple mixtures where
the random-mixing approximation is a good one. I will return
to this in a moment but first I want to show two examples
showing mixing-rule modifications in practice. Figure 7
shows K factors for hydrogen in heavy hydrocarbons (4).
In this case, attractive forces are relatively unimportant;
much more important is the fluid structure when we mix small
and large molecules. In this example, calculations by El-
Twaty are based on a modified Soave equation; the modification
is due to the mixing rule for b; k_{ij} is set equal to zero.

As shown, it is also possible to fit the data using the original Soave equation but in that event, it is necessary to use unrealistically large values of k_{ij}. (When $k_{ij} > 1$, a_{ij} is negative which makes little physical sense.)

Figure 8 shows calculations for the system hydrogen sulfide-water (5) using a Soave-type equation of state and two adjustable binary parameters. The binary constants are physically reasonable but unfortunately their temperature dependence becomes appreciable, especially at lower temperatures.

Further modifications in mixing rules are likely to attract more attention in the near future. Some useful empirical suggestions toward that end have been made by Huron and Vidal (6).

The importance of binary parameters is not difficult to understand if we recall that, intermolecular forces between unlike molecules cannot, at present, be simply related to intermolecular forces between like molecules. Nevertheless, there is always the suspicion that a binary parameter is just a correction factor to hide our ignorance. Just how deep this suspicion is, was revealed to me some years ago in the men's room of Gilman Hall (University of California, Berkeley) where I found the graffiti shown in Figure 9.

Inspired by this caustic comment on k_{12}, I now want to inquire how we may improve our treatment of mixtures by relaxing the random-mixing assumption. One possible method, shown in Figure 10, is to use perturbation theory which gives an expansion of the Helmholtz energy in powers of reciprocal

temperature. The zeroth term is the hard-sphere term; the composition dependence of this term is well-known (7). The first perturbation term is the random-mixing term where the quadratic mixing rules apply. The higher terms take into account the effect of nonrandomness, also called clustering. We have some, but not much, fundamental information about these terms.

The important point in this expansion is that each term has its own mixing rule, suggested by theory. In this treatment we do not use one overall mixing rule but assign different mixing rules to different contributions to the Helmholtz energy. The Helmholtz energy is directly related to the equation of state and fugacities, as usual, are obtained by differentiation with respect to composition.

An application of these ideas is shown in Figure 11 where we see Henry's constants calculated by Liu for a variety of volatile solutes in polyethylene (8), using perturbed-hard-chain theory. Only one binary constant, independent of temperature, is used for each binary system. The effect of temperature is represented very well, probably because an attempt was made to take into account the effect of nonrandom mixing.

A more classical method to account for nonrandomness is provided by a chemical hypothesis as indicated in Figure 12. The preferences which molecules have in their choice of neighbors can be expressed quantitatively by formation of

complexes, i.e. through association and solvation equilibria. For simplicity, Figure 12 shows the general ideas for a pure fluid which can form dimers; in this view, a pure fluid is, in effect, a binary mixture consisting of monomers and dimers. The distribution of monomers and dimers is given by an equilibrium constant (a function of temperature only) and by fugacity coefficients as calculated from the partition function.

To reduce these ideas to practice, it is necessary to make some quantitative statement about the various terms in the partition function; in particular, (see bottom of Figure 12) it is necessary to specify how these terms depend on volume. The details of these dependencies are not important here; in the simplest case, the free volume leads to a function (v-b) in the equation of state; the potential leads to a function a/v^2 in the equation of state; while the rotational and vibrational contributions are assumed independent of volume. The important point is that nonrandomness is taken seriously by taking into account strong specific forces of attraction.

The chemical treatment is easily extended to mixtures but the calculations are formidable. In general, a binary mixture of components A and B contains five molecular species: monomers A and B and dimers A_2, B_2 and AB.

An application of this type of chemical theory was made by Gmehling and Liu (9) who used the perturbed-hard-chain

partition function. Figure 13 shows calculated results for the highly polar system methanol-water at moderate and high pressures. For the entire range shown, only two binary parameters are required; these are for the cross dimer: one standard enthalpy and one standard entropy of formation. Similar chemical-type calculations have been reported by various authors, notably by Wenzel and Rupp (10).

In superimposing chemical equilibria on an equation of state, it is usual practice to confine attention to dimerization. In principle, it is possible to include tri-merization as well as formation of higher aggregates but to do so requires much computation and, what is worse, additional adjustable parameters.

I now turn attention to phase equilibria at low or moderate pressures. Figure 14 reminds us that in vapor-liquid equilibria we must calculate vapor-phase fugacity coefficients and that in vapor-liquid and in liquid-liquid equilibria we must calculate activity coefficients. The choice of standard-state fugacity is troublesome for super-critical components; for solutions of gases in liquids, therefore, an equation-of-state method is more useful than the customary activity-coefficient method.

At moderate pressures, vapor-phase fugacity coefficients are often calculated using second virial coefficients. The main problem is to estimate the cross-coefficient B_{12} where

some surprises may occur, as illustrated in Figure 15. Experimental results for the system methanol-trimethylamine show that the second virial cross-coefficient is much more negative than the second virial coefficient for either pure fluid. There appears to be strong attraction between the different molecules which depresses the fugacity coefficients well below unity, even at pressures near 1 atm (11).

For mixtures containing organic acids, the virial equation is not applicable; a chemical theory must be used. The tendency of these acids to dimerize is so strong that large deviations from ideal-gas behavior occur, even at low pressures where ordinarily one might expect no significant deviations. Figure 16 shows results for mixtures of acetaldehyde and acetic acid. Even at 0.25 atm, fugacity coefficients for acid-rich mixtures are well removed from unity.

Turning now to activity coefficients, I want first to indicate the debt of thanks which we owe to Dr. Gmehling and Professor Onken for their exhaustive search and reduction of experimental data. Their continuing series of data books sponsored by DECHEMA provide a tremendously useful service to all who are concerned with phase equilibria. Second, I want to indicate my appreciation to Professor Fredenslund, Dr. Rasmussen and Dr. Gmehling for the vigor with which they have pursued the UNIFAC method for correlating activity coefficients. Thanks to their efforts, UNIFAC is now a common engineering tool used in many countries.

Figure 17 reminds us that activity coefficients are
directly related to the excess Gibbs energy. Numerous models
have been proposed for G^E but there is no time here to review
them. I do, however, want to call attention to a problem
common to all current models, viz. the non-uniqueness of binary
parameters obtained from data reduction. Within the un-
certainty of the experimental data and that of the model,
there are many sets of binary parameters which can be used.
If we confine attention to binaries, this non-uniqueness has
no particular practical importance but when we want to use
binary parameters to predict multicomponent equilibria, then
the results are influenced by our choice of binary parameters.
In multicomponent vapor-liquid equilibria, this influence is
often weak because in such equilibria the dominant quantities
are the pure-component vapor pressures; the activity coefficients
play only a secondary role. However, in liquid-liquid equilibria,
vapor pressures play no role at all and even small changes in the
activity coefficients can have large effects. To illustrate,
Figure 18 shows some calculations by Anderson (12) for the
ternary benzene-ethanol-water, using the UNIQUAC equation.
For the immiscible pair (benzene-water), binary parameters
are determined by mutual solubilities. For the two miscible
pairs, we have some choice of binary parameters. Those which
give best binary vapor-liquid equilibria give erroneous ternary
liquid-liquid equilibria; these results are shown by the dashed

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lines. Small adjustments in the binary parameters give very good ternary results while the corresponding binary vapor-liquid equilibria are still reasonably good. The present situation is such that for many mixtures we can calculate multicomponent liquid-liquid equilibria using only binary parameters but to do so, we need a few multicomponent data to guide us in the selection of the best binary parameters. Conclusions similar to Anderson's were reported by Nicolaides and Eckert (13).

Our simple models for the excess Gibbs energy are most likely to fail for strongly nonideal mixtures. In such cases, analogous to what I said earlier about the equation of state, we can improve representation by superimposing a chemical theory. A particularly thorough attempt in that direction was made by Nagata (14) who superimposed both associating and solvating equilibria on the UNIQUAC equation as shown in Figure 19. In this case chemical equilibria refer to continuous association, not just dimerization, with the simplifying assumption that a suitably defined equilibrium constant [See Flory (15)] is independent of the degree of polymerization. With this superposition it is possible to obtain remarkably accurate representation of mixture properties as shown in Figure 20 for propanol-carbon tetrachloride. There are four binary parameters and there are two association parameters for propanol which are independent of the other component. Nagata's treatment accurately reproduces both the excess Gibbs energy

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and the S-shaped results for the excess enthalpy.

Any method like Nagata's, based on a combined chemical-plus-physical theory, is virtually certain to give good results for binary systems of nonelectrolytes. However, scale-up to multicomponent systems is very difficult not only because of formidable computation but also because drastic simplifications are needed if one includes, as Nagata does, polymerization beyond formation of dimers. For engineering application, therefore, chemical theories have serious limitations. Nevertheless, it is clear that in some cases a chemical theory is the only one capable of representing the data. To illustrate, consider the excess enthalpy data of Munn and Svejda (16) for the system propionic acid-triethylamine, shown in Figure 21. It is evident that none of our current physical models could possibly do justice to these data. The evidence for strong complex formation is so convincing that the only reasonable way to represent these data is through a chemical equilibrium constant for the formation of a 3:1 compound.

Chemical theories of solution have a long history; they were particularly popular in the period 1905-1925. One early advocate of the chemical approach was Dolezalek who worked on such theories while he was on the faculty of our host institution, the Technical University of Berlin.

A possibly promising new model for the excess Gibbs energy has been introduced by Brandani (17) who uses a partition function of the van der Waals form, as shown in

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Figure 22. There are two important features. First, the energy is calculated not with a one-fluid theory but with a two-fluid theory using local compositions, as suggested by Maurer (18); the use of local compositions provides an attempt to allow for nonrandomness. Second, and probably more important, the partition function includes a free-volume term which allows some account to be taken of the effect of mixing on rotational and vibrational degrees of freedom. With few exceptions, our common models are more or less based on a checker-board model where the mixing process is considered to be no more than an exchange of nearest neighbors. In fact, however, mixing also changes the free space available to a molecule for exercising its rotational and vibrational motions. It is precisely this effect which is reflected in the free-volume term. The importance of that term was pointed out by Flory (19) who, however, used a one-fluid theory of random mixing. Brandani has combined Flory's insight concerning free volume with Maurer's inter-pretation of Wilson's local compositions. Note that the characteristic energy terms are per unit volume (similar to solubility parameters) to allow for changes in intermolecular separations. Such changes are not taken into account in a lattice (checker-board) model.

Figure 23 shows some calculations for the system acetone-polystyrene; contrary to simple lattice theory, the Flory parameter χ is a function of concentration. The two adjustable

parameters, used for fitting the excess Gibbs energy, also represent the enthalpy of mixing for this system.

The important feature of Brandani's work is that the excess Gibbs energy of the mixture depends not only on molecular sizes and molecular energies in addition to temperature and composition. It depends also on the volume of the mixture. That is why a van der Waals-type partition function is particularly useful for liquid mixtures: it provides us not only with the free energy but simultaneously with the liquid-phase equation of state.

The importance of volumetric effects becomes particularly evident when we consider the solubilities of gases in liquids. To illustrate, Figure 24 shows a reduced, corresponding-states plot prepared by Anderson (20) for calculating fugacities of hypothetical pure liquids at temperatures exceeding the critical. The curve is essentially arbitrary. It was chosen such that typical gas-solubility data might yield activity coefficients at infinite dilution which are in the range 1-100. Figure 25 shows such activity coefficients, based on Anderson's arbitrary curve.

When these binary results are coupled with the UNIQUAC equation, it is possible to calculate activity coefficients for gaseous solutes in solvent mixtures using only binary parameters. However, the multicomponent results are often disappointing, as illustrated in Figure 26, showing calculations by Kistenmacher and Landeck (21) for carbon dioxide in mixtures

of water and ethylene glycol. At 25^0C, carbon dioxide is nearly at its critical temperature and, therefore, a highly expanded fluid. The significant disagreement cannot be removed by adjustment of binary parameters; it must surely be attributed to the failure of UNIQUAC to allow for volumetric changes resulting from mixing. Gas solubility is strongly sensitive to the density of the liquid solvent.

It now appears that mole fraction is not enough to specify solvent composition; we must also somehow specify the density. That is exactly what Brandani's treatment does. Further, it is the calculation of density which is the key element in the important work of Mathias and O'Connell (22) who use the theory of direct correlation functions to calculate gas solubilities. An essential element in their solubility calculation is that they first calculate the volume of the gas-liquid solution. Figure 27 shows some calculations for hydrogen-benzene with one binary constant. The calculations utilize an equation of state for the liquid phase. Once the volumetric properties are estimated, it is then possible to use the equation of state for calculating chemical potentials and thereby to predict gas solubilities as shown in Figure 28. The binary constant in Figure 28 is the same as that used in Figure 27. When we use a liquid-phase equation of state to calculate the chemical potential of the solute, there is no need to use hypothetical states

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(e.g. supercritical pure "liquids") for calculating standard-state fugacities.

It is time for me to stop talking so that we may enjoy a well-earned Berliner Mittagsessen. Let me quickly conclude, therefore, by making five summarizing statements:

1 - We still do not have a truly satisfactory equation of state for mixtures covering all fluid densities. However, in many cases it appears that this is not a serious limitation because what really counts are the mixing rules.

2 - The simple mixing rules, with some modifications, often do very well. One adjustable binary constant is essential but sometimes we need two.

3 - For significant progress, we must critically re-examine the one-fluid approximation and possibly abandon the over-all mixing rule idea. It may be better to look at different contributions to a mixture's free energy and to devise specific mixing rules for each contribution.

4 - Nonideality in binary mixtures can often be represented well by chemical theory but it is difficult to generalize chemical theory for multicomponent mixtures.

5 - In liquid mixtures, especially in those containing gaseous solutes, volumetric effects are often important. We must get away from the old lattice ideas and develop models which take into account changes in volume that accompany the mixing process.

Because of time limitations, there is much important material that, with regret, I had to omit. In making my selections of what to include in this review, I was guided by a comment made by the French essayist Michel Montaigne who said that in writing his essays, he was preparing a bouquet of flowers, and like a boy on a summer meadow, picking a few flowers here and there, all he did was to provide the string that holds them together.

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Nomenclature

A	=	Helmholtz energy
a	=	attractive-force constant in equation of state
a	=	activity
a_{ij}	=	binary parameter
B	=	second virial coefficient
b	=	molecular-size constant in equation of state
C	=	third virial coefficient
c	=	speed of light
c_{ij}	=	binary size parameter
E	=	energy
$E_{(i)}$	=	potential energy of hypothetical fluid i
E_{12}	=	binary size parameter
$\mathcal{F}$	=	a function
f	=	fugacity
f^0	=	standard-state fugacity
f^{0L}	=	fugacity of pure liquid
G^E	=	excess Gibbs energy
g^E	=	molar excess Gibbs energy
H^E	=	excess enthalpy
h^E	=	molar excess enthalpy
h_A	=	enthalpy of association
h_{AB}	=	enthalpy of solvation
K_{ij}	=	binary energy parameter
K	=	K-factor = y/x
K	=	chemical equilibrium constant

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k_{ij} = binary energy parameter

k = Boltzmann's constant

m = mass

N = number of molecules

n_i = number of moles of component i

n_T = total number of moles

P = total pressure

P_c = critical pressure

Q = partition function

$q_{r,v}$ = rotational and vibrational contributions to partition function

R = gas constant

r = number of segments

T = temperature

T_c = critical temperature

Δu_{ij} = binary parameter

V = total volume

V_f = free volume

v = molar volume

x = liquid-phase mole fraction

y = vapor-phase mole fraction

z = compressibility factor

γ = true mole fraction

Nomenclature
(continued)

ϵ_{ij} = characteristic potential energy for the i-j interaction

γ = liquid-phase activity coefficient

γ_{ij}^{∞} = activity coefficient of solute i infinitely dilute in solvent j

Λ = part of ideal-gas contribution to partition function, depends on temperature, not density

ϕ = volume fraction or segment fraction

Φ = potential

ϕ = fugacity coefficient

θ = surface fraction

θ_{ij} = local surface fraction

ρ = density

ρ_c = critical density

ν = characteristic energy density

χ = Flory interaction parameter

η = association factor

K-FACTORS FROM AN EQUATION OF STATE

$$K_i \equiv y_i / x_i = \frac{\varphi_i (\text{Liquid})}{\varphi_i (\text{Vapor})}$$

x = Mole fraction of liquid
y = Mole fraction of vapor
φ = Fugacity coefficient

$$\ln \varphi_i = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - \ln \frac{PV}{n_T RT}$$

n_i = No. of moles of i
n_T = Total No. of moles
V = Total volume

Require Equation of state

$$P = \mathscr{F}(T, V, n_1, n_2, \cdots)$$

Valid for both liquid phase and vapor phase

Figure 1
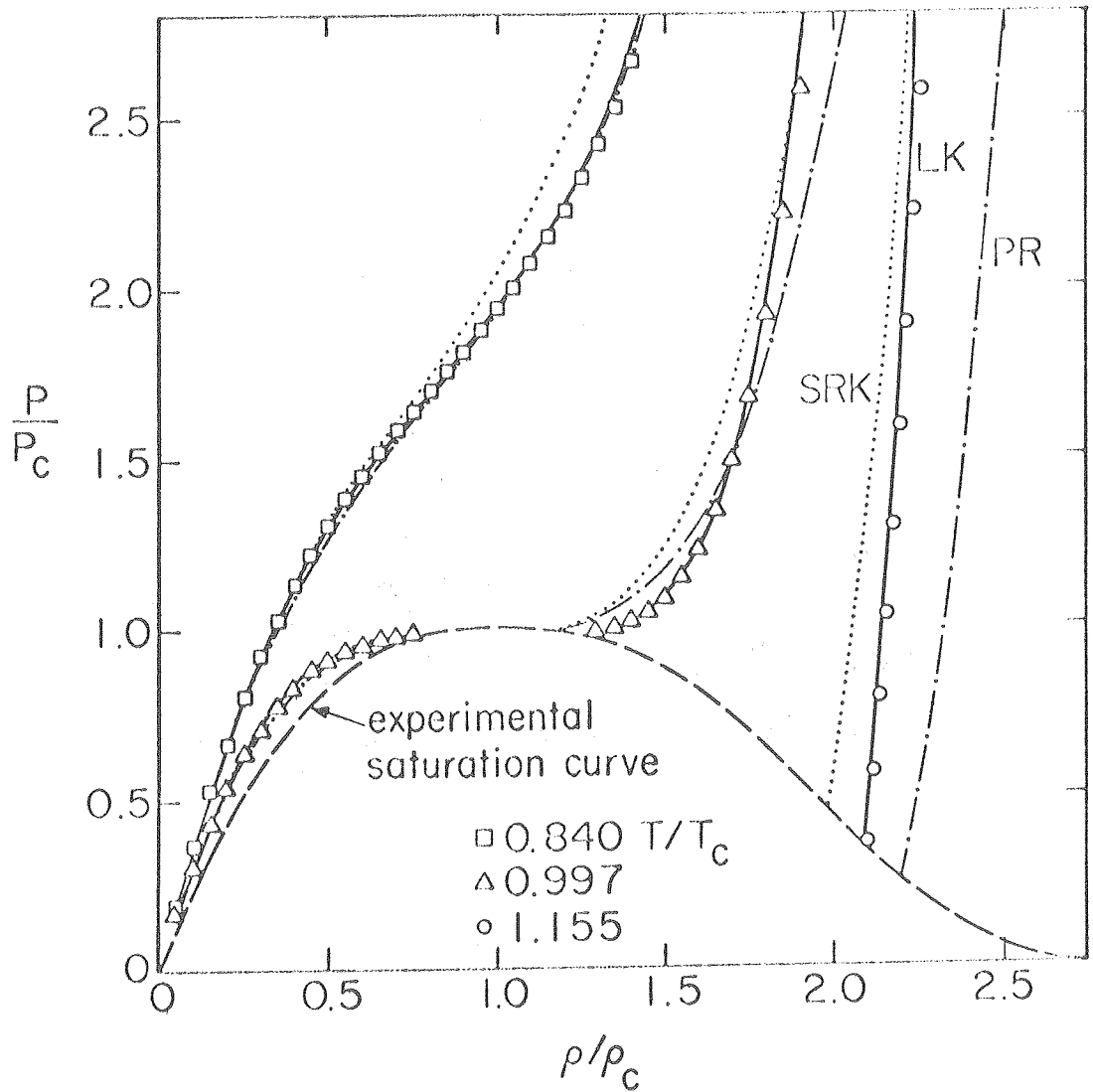
CALCULATED AND EXPERIMENTAL ISOTHERMS FOR
METHANE (SRK = Soave-Redlich-Kwong, PR =
Peng-Robinson, LK = Lee-Kesler.)

Figure 2
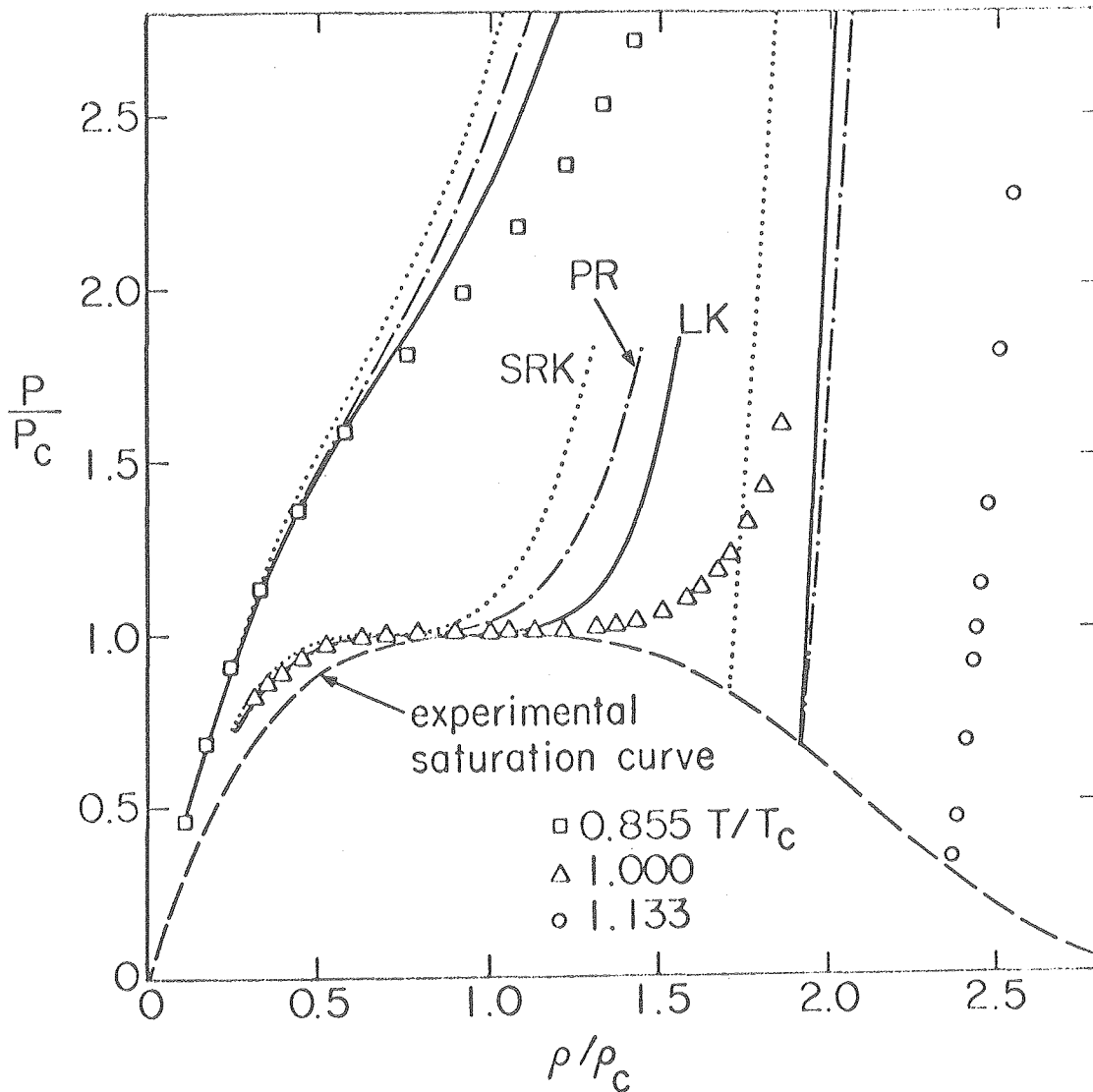
CALCULATED AND EXPERIMENTAL ISOTHERMS FOR
WATER (SRK = Soave–Redlich–Kwong, PR =
Peng–Robinson, LK = Lee–Kesler.)

Figure 3

ONE-FLUID THEORY OF MIXTURES: MIXING RULES

Size Parameter b_M

Usual assumption: $b_M = \sum_i x_i b_i$ M = mixture

Strictly valid only if $b_1 = b_2 =$ etc.

Another assumption $b_M = \sum_i \sum_j x_i x_j b_{ij}$

where $b_{ij} = \left[\left(b_i^{1/3} + b_j^{1/3} \right)/2 \right]^3$

Strictly valid only for spheres at low density

Energy-size Parameter a

Usual assumption: $a_M = \sum_i \sum_j x_i x_j a_{ij}$ k_{ij} is a binary parameter

$a_{ij} = (a_i a_j)^{1/2} (1 - k_{ij})$

Quadratic dependence on composition strictly valid only for random mixture.
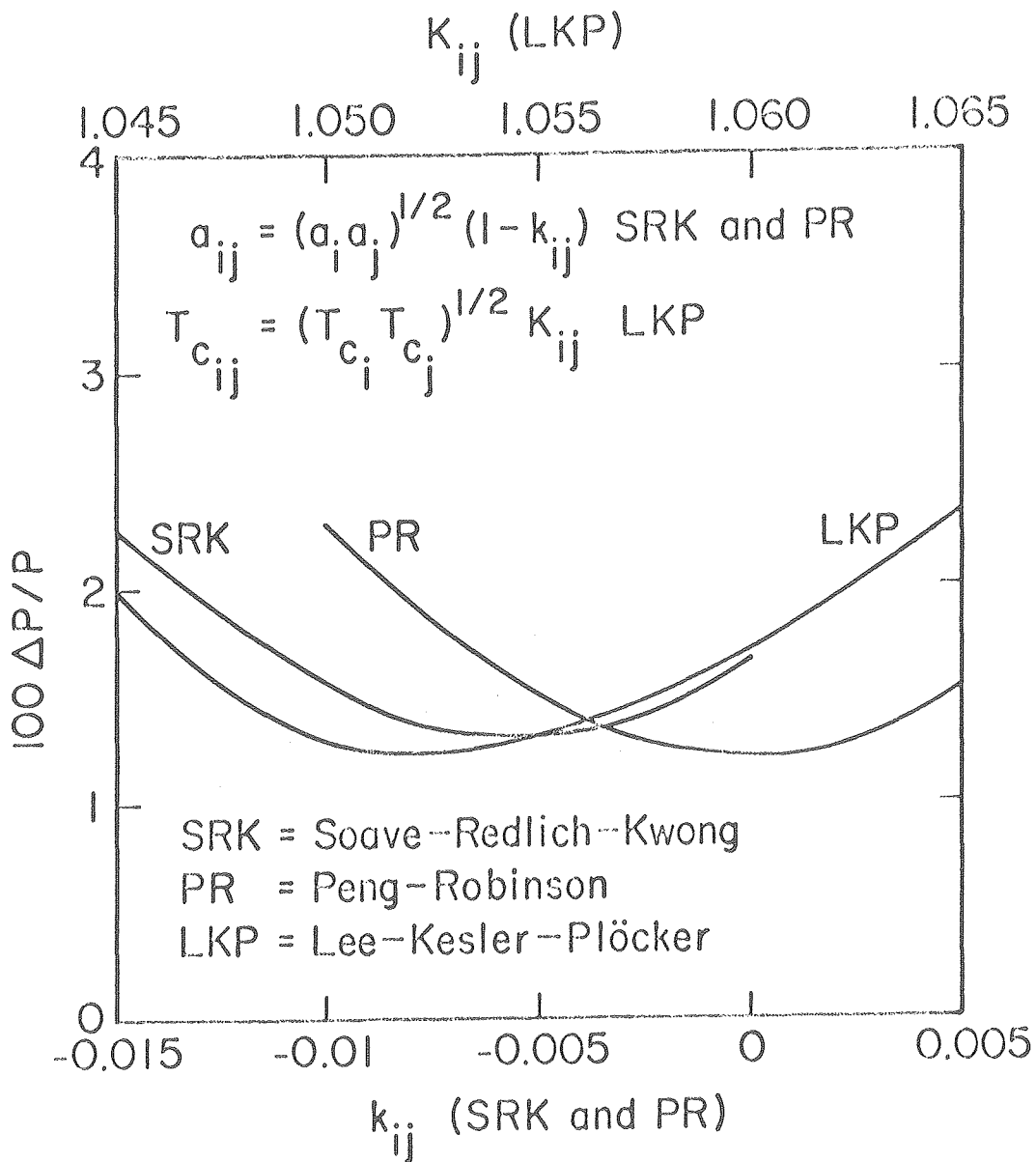
Figure 4

OPTIMUM BINARY PARAMETER FOR FITTING
ETHANE—METHANE VLE DATA (From Döring *et al.*)

Figure 5

AD HOC MODIFICATIONS IN SIMPLE (ONE-FLUID) MIXING RULES

e.g.

$$b_M = \sum_i \sum_j x_i x_j b_{ij}$$

$$b_{ij} = \frac{1}{2}(b_i + b_j)(1 - c_{ij})$$

c_{ij} = binary parameter

Useful for mixtures of small and large molecules

or

$$a_i = a_i^{np} + a_i^p(T)$$

np = nonpolar

p = polar

$$a_M = \sum_i \sum_j x_i x_j a^{np} + \sum_i \sum_j x_i x_j a^p(T)$$

$$a_{ij}^{np} = (a_i^{np} a_j)^{1/2}(1 - k_{ij})$$

k_{ij} is now more nearly independent of temperature

$$a_{ij}^p = (a_i^p a_j^p)^{1/2}$$

Useful for mixtures with polar components

These modifications do <u>not</u> solve the non-randomness problem

Figure 6
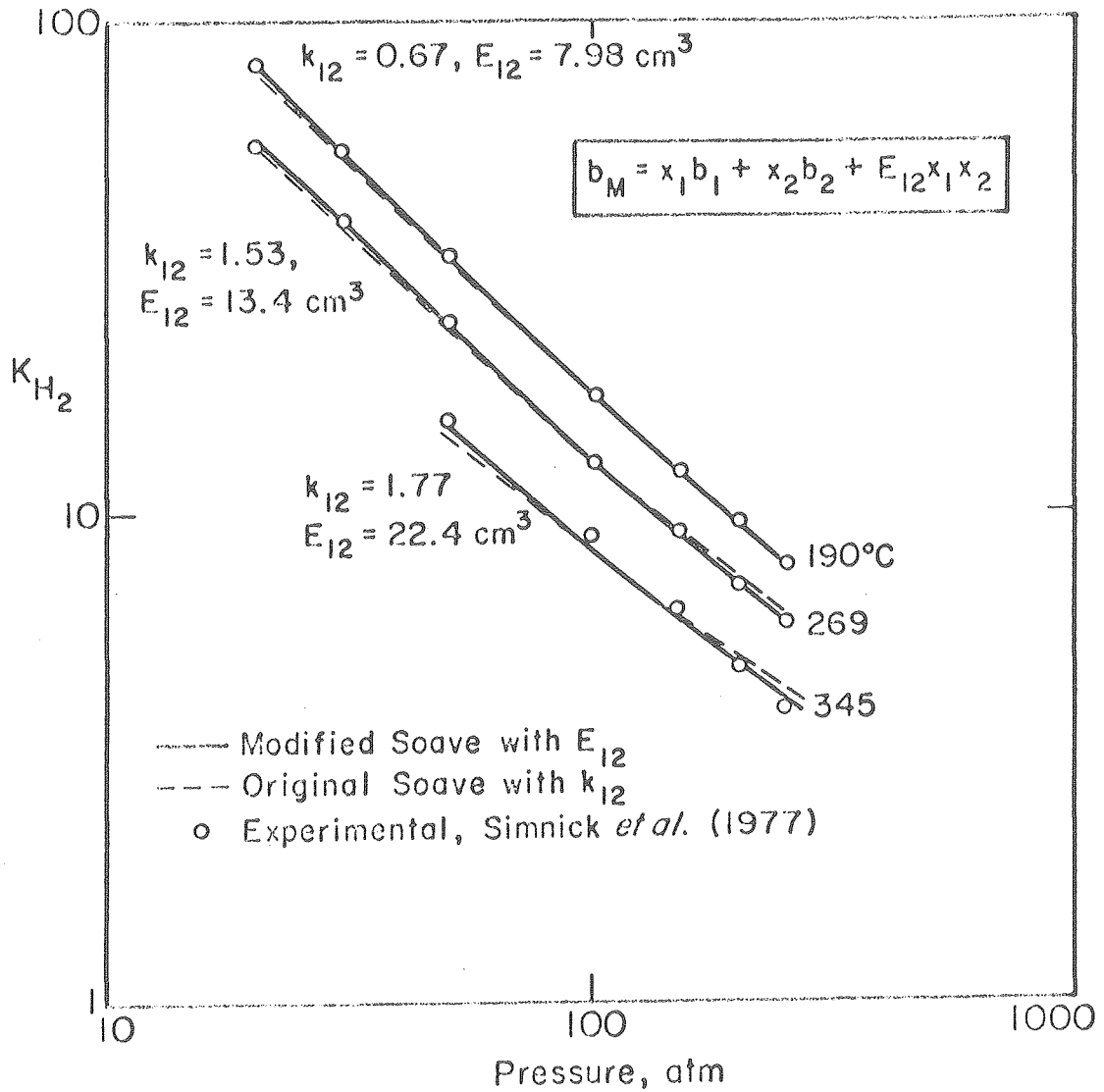
K Factors for Hydrogen in Tetralin. Using the Original Soave Equation, Physically Meaningless Binary Parameter k_{12} are required.

Figure 7
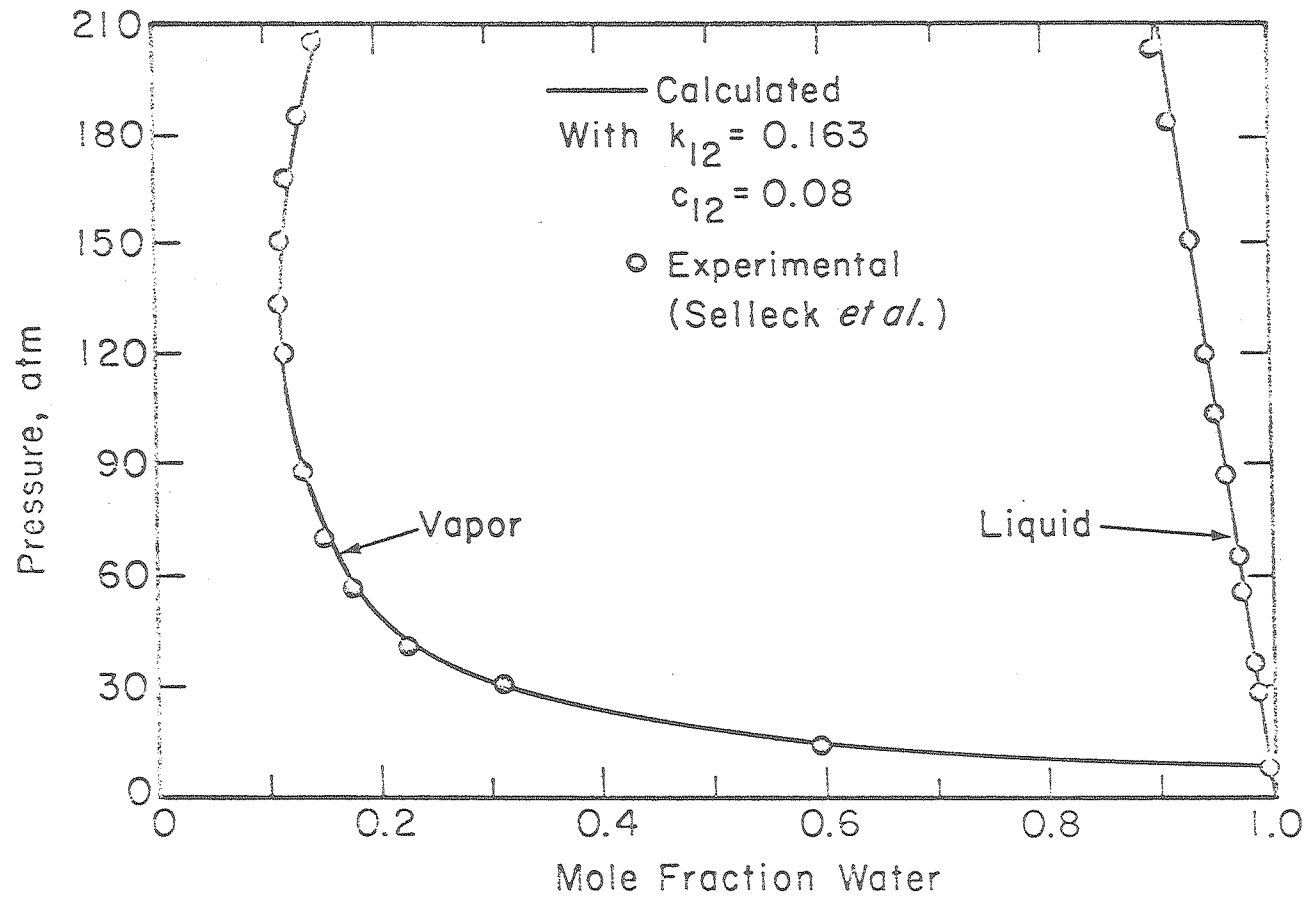
PHASE EQUILIBRIA FOR THE SYSTEM HYDROGEN
SULFIDE—WATER AT 340°F (From Evelein, Moore,
and Heidemann)

Figure 8

GRAFFITI IN GILMAN HALL (BERKELEY)

Einstein was wrong! It should be

$$E = mc^3(1 - k_{12})$$

Figure 9

EFFECT OF NONRANDOM MIXING: EXPANSION
OF HELMHOLTZ ENERGY A

$$A = A^{(0)} + \frac{A^{(1)}}{T} + \frac{A^{(2)}}{T^2} + \cdots$$

$A^{(0)}$ = Hard-sphere term

$A^{(1)}$ = Uniform-field (random) first perturbation term

$A^{(2)}, A^{(3)} \cdots$ Corrections for nonrandomness

$A^{(i)} = \mathcal{F}^{(i)}(x, \rho)$ x = Mole fraction

ρ = Density

$\mathcal{F}^{(i)}$ depends on i.

Analogy to Virial Equation for Mixtures

$$z = P/\rho RT = 1 + B\rho + C\rho^2$$

$$B = \mathcal{F}^{(B)}(x, T)$$
$$C = \mathcal{F}^{(C)}(x, T)$$

} Mixing rules for B and C are not the same
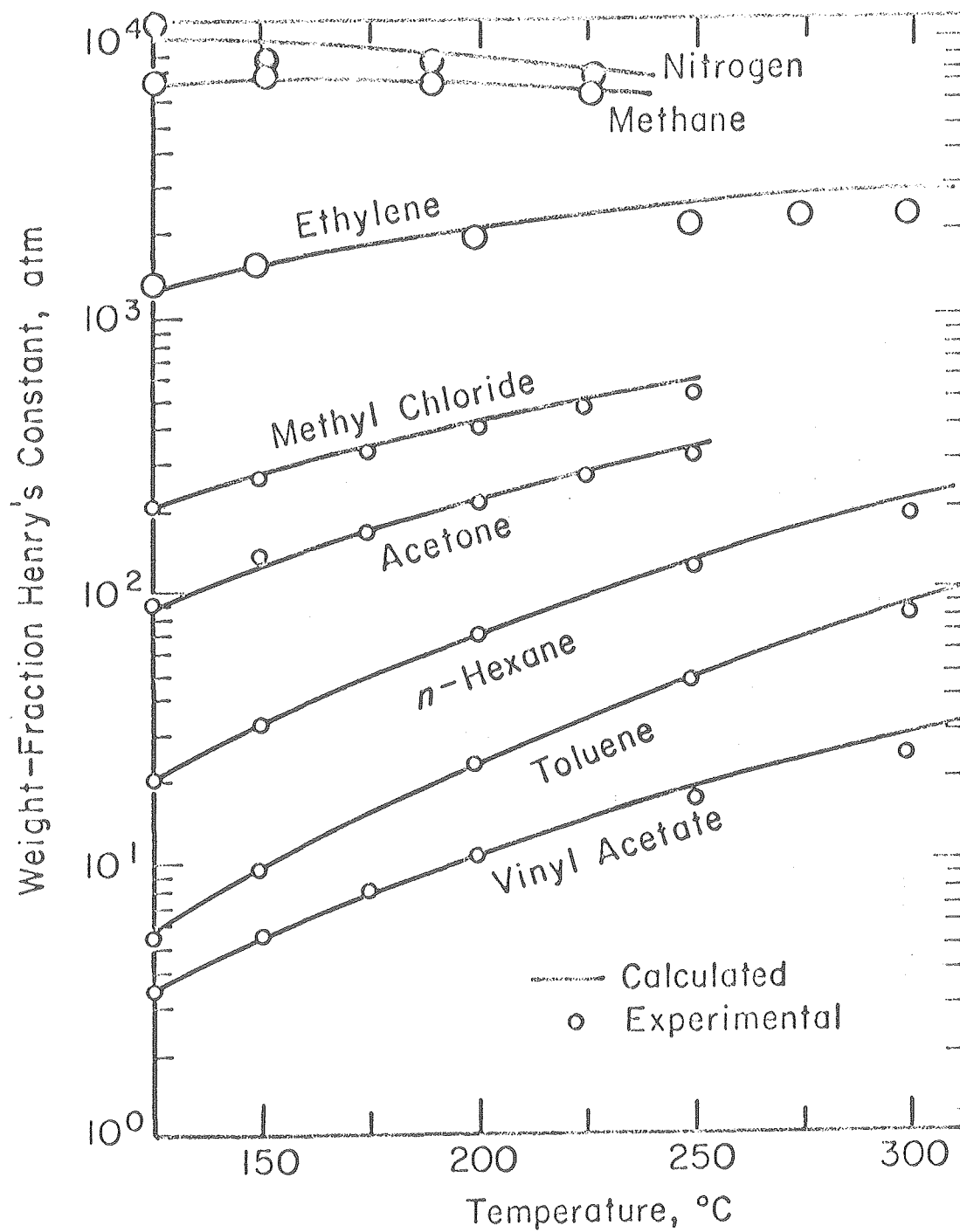
Figure 10

WEIGHT-FRACTION HENRY'S CONSTANTS
IN LOW-DENSITY POLY(ETHYLENE)

Figure 11

NONRANDOMNESS: SUPERPOSITION OF CHEMICAL EQUILIBRIA ON GENERALIZED VAN DER WAALS' PARTITION FUNCTION Q

Dimerization ① + ① ⇌ ②

$$Q = \frac{1}{N_1! \, N_2!} \langle V_f \rangle \left[\exp - \frac{\langle \Phi \rangle}{2kT} \right]^N \left[\frac{q_{r,v}}{\Lambda} \right]_1^{N_1} \left[\frac{q_{r,v}}{\Lambda} \right]_2^{N_2}$$

$N_1 + N_2 = N \qquad \langle \; \rangle = $ Average

$V_f = $ Free volume $\qquad \Phi = $ Potential

$\Lambda = $ (Part of) ideal-gas contribution

$q_{r,v} = $ Contributions from rotation and vibration

$k = $ Boltzmann's constant

$$K(T) = g_2 \varphi_2 / g_1^2 \varphi_1^2 P$$

$g_1 = $ Mole fraction monomer

$g_2 = $ Mole fraction dimer

Fugacity coefficients φ_1 and φ_2 from Equation of State

$$P = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N}$$

Figure 12
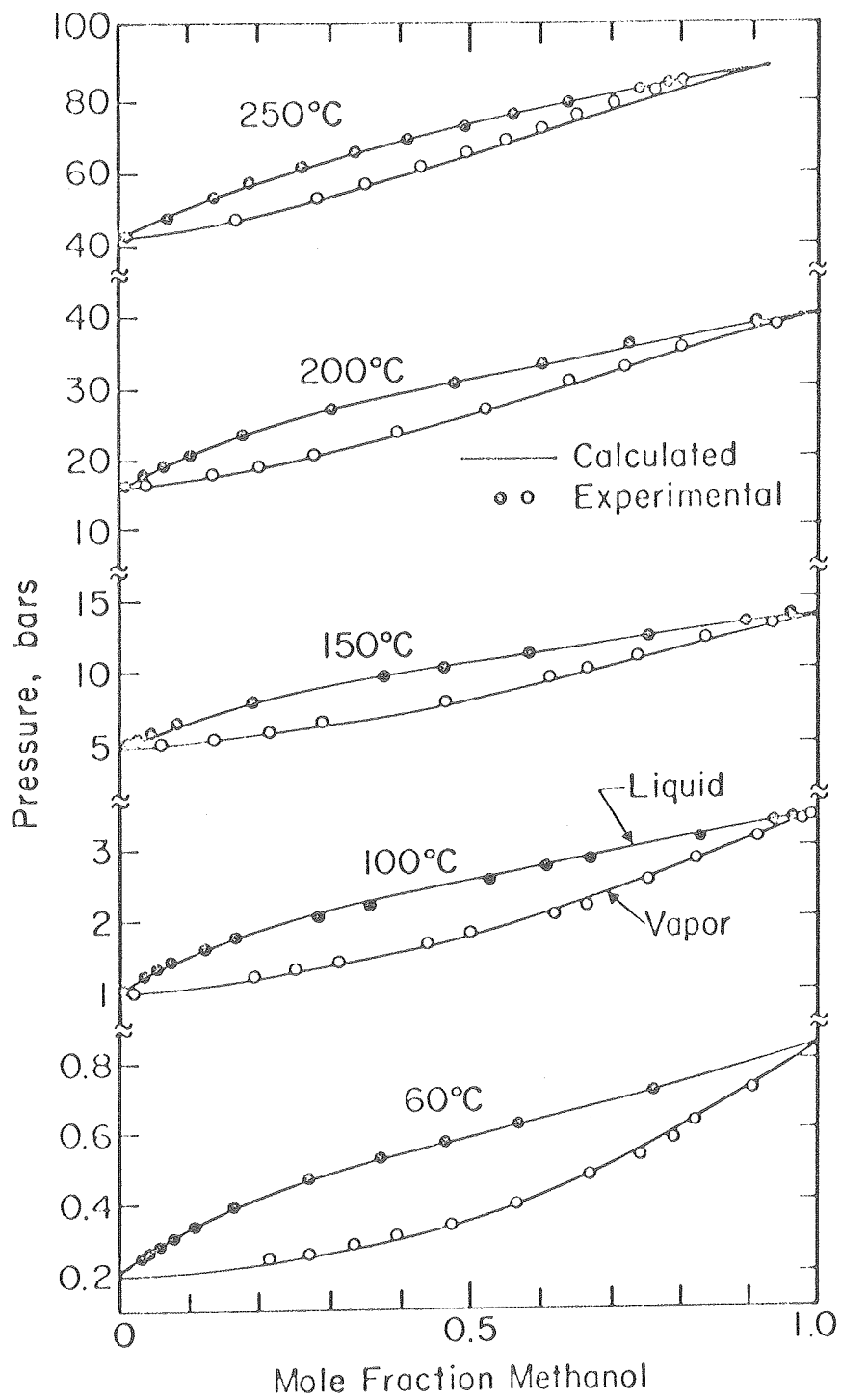
Vapor-Liquid Equilibria for Methanol-Water

Figure 13

PHASE EQUILIBRIA AT LOW OR MODERATE PRESSURES

Vapor-Liquid: $\varphi_i \, y_i P = \gamma_i x_i f_i^0$

Liquid-Liquid: $(\gamma_i x_i)' = (\gamma_i x_i)''$

φ = Fugacity coefficient; calculated from truncated virial equation, or chemical theory (dimerization).
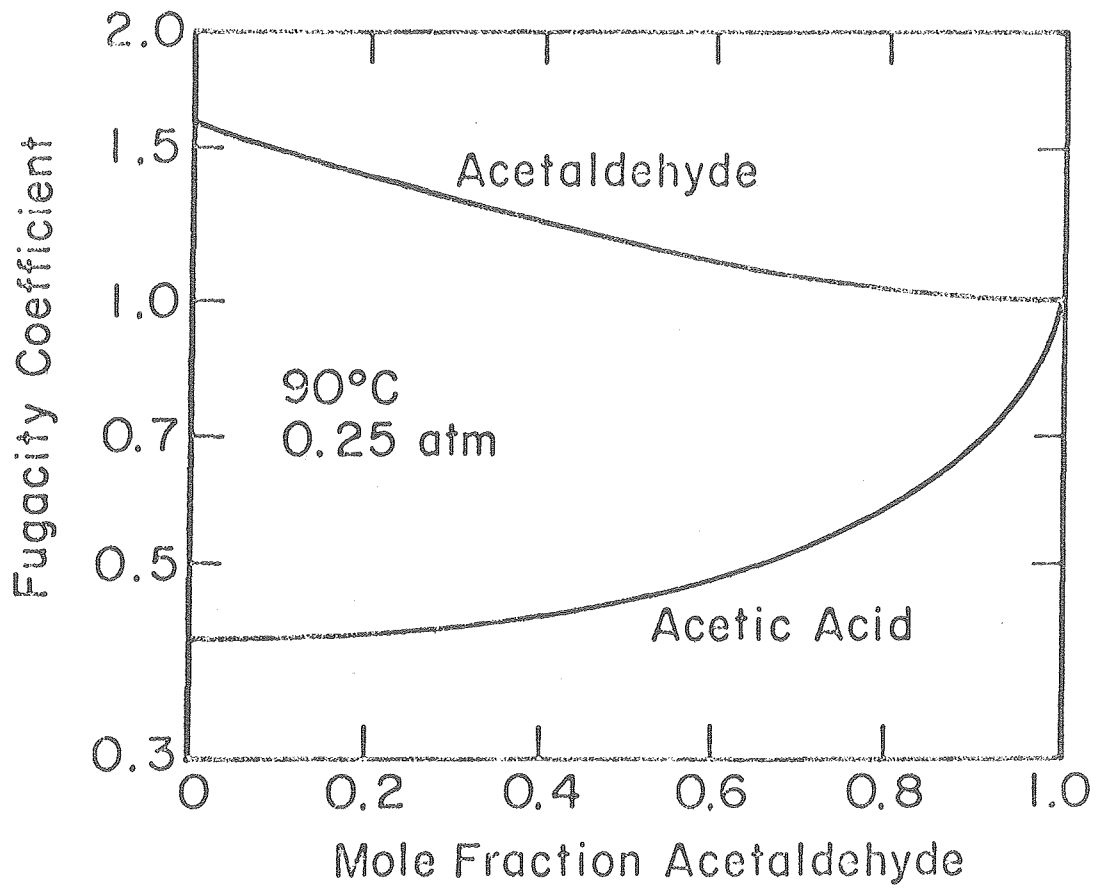
γ = Activity coefficient; usually calculated from model for excess Gibbs energy.

f^0 = Standard-state fugacity; simple for liquids but big headache for super-critical components.
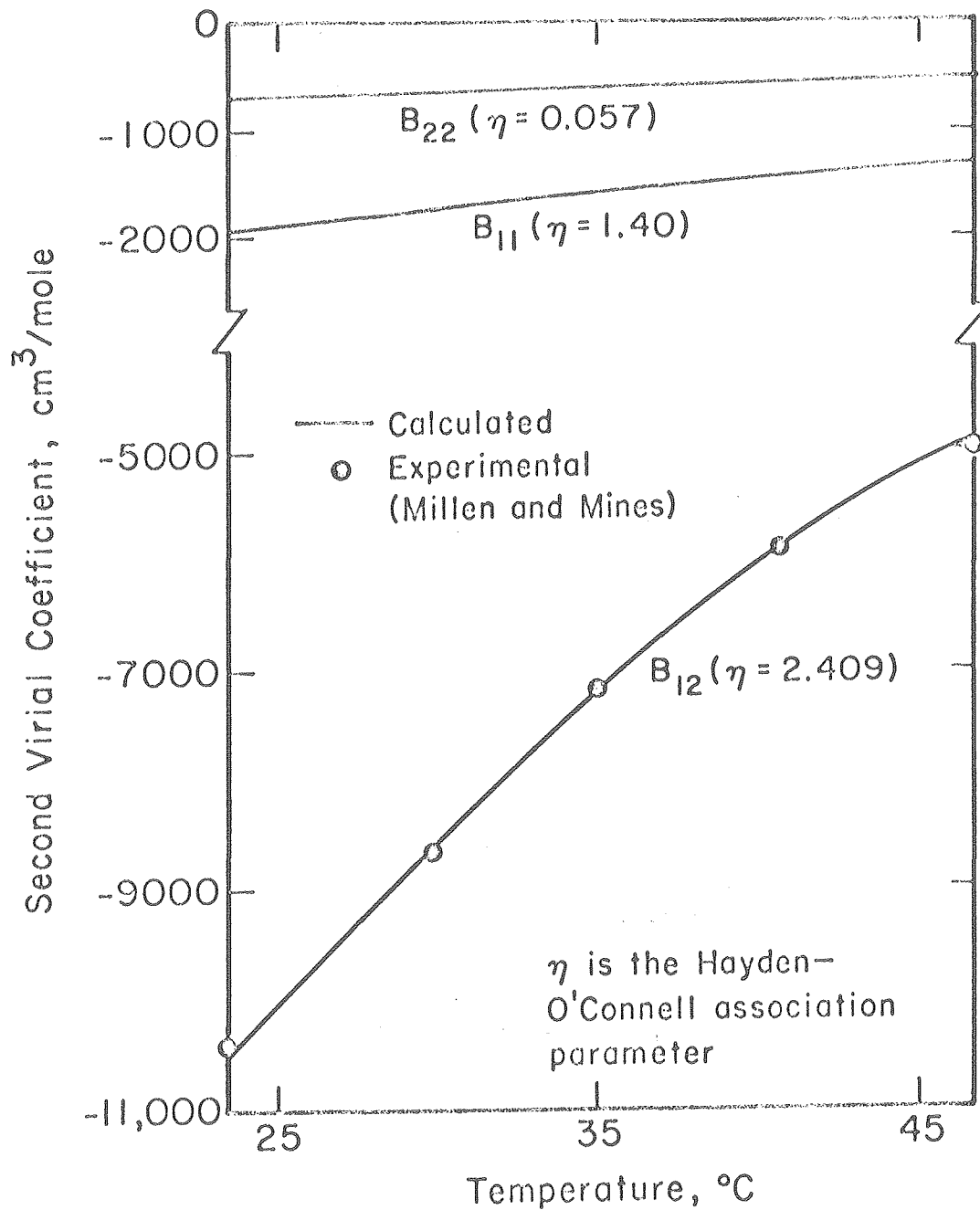
Figure 14

SECOND VIRIAL COEFFICIENTS FOR METHANOL
(I)—TRIMETHYLAMINE (2). (From E.Miller)

Figure 15

Fugacity Coefficients for the System
Acetaldehyde—Acetic Acid

Figure 16

NON-UNIQUENESS OF BINARY PARAMETERS

IN MODELS FOR EXCESS GIBBS ENERGY G^E

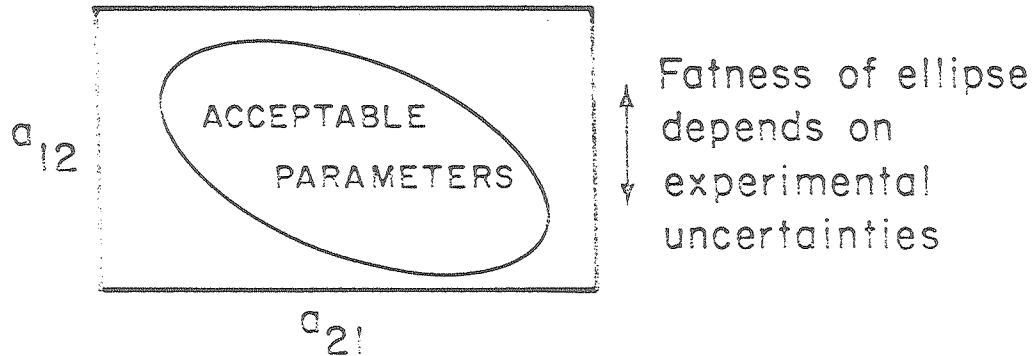$$RT \ln \gamma_i = \left(\frac{\partial G^E}{\partial n_i} \right)_{T, P, n_j}$$

n_i = No. of moles of component i

For a binary mixture:

$$G^E = \mathcal{F}(n_1, n_2, T, a_{12}, a_{21})$$

a_{12} and a_{21} are binary parameters

From data reduction:

Fatness of ellipse depends on experimental uncertainties

Parameters are correlated.

Figure 17

Vapor-Liquid and Liquid-Liquid Equilibria

in the System Benzene-Ethanol-Water
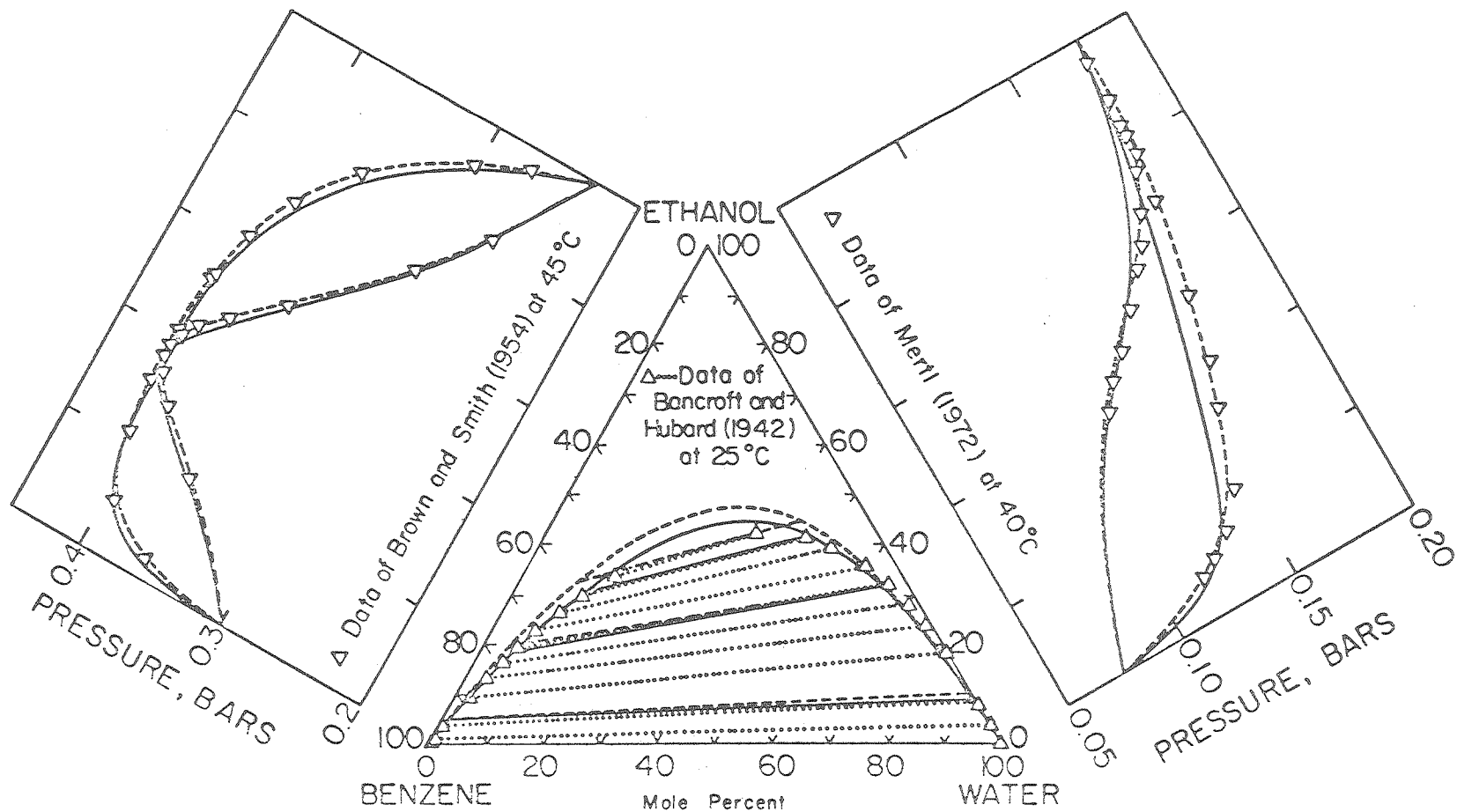
Figure 18

UNIFICATION OF ASSOCIATION AND SOLVATION CHEMICAL EQUILIBRIA WITH UNIQUAC

$$g^E = g^E(\text{combinatorial}) + g^E(\text{residual})$$

$$g^E(\text{residual}) = \text{usual UNIQUAC term} = \mathscr{F}(\theta, T, \Delta u_{12}, \Delta u_{21})$$

θ = surface fraction

$\Delta u_{12}, \Delta u_{21}$ = binary interaction parameters

$g^E(\text{combinatorial})$ = Flory–Huggins term for <u>all</u> species

Associating Equilibrium	$A_1 + A_i \rightleftharpoons A_{i+1}$	$K_A = \dfrac{\Phi_{A_{i+1}}}{\Phi_{A_1}\Phi_{A_i}}\left(\dfrac{i}{i+1}\right)$
Solvating Equilibrium	$A_i + B \rightleftharpoons A_i B$	$K_{AB} = \dfrac{\Phi_{A_i B}}{\Phi_{A_i}\Phi_B}\left(\dfrac{i\, r_B/r_{A_1}}{i + r_B/r_{A_1}}\right)$

Φ = segment fraction r = No. of segments
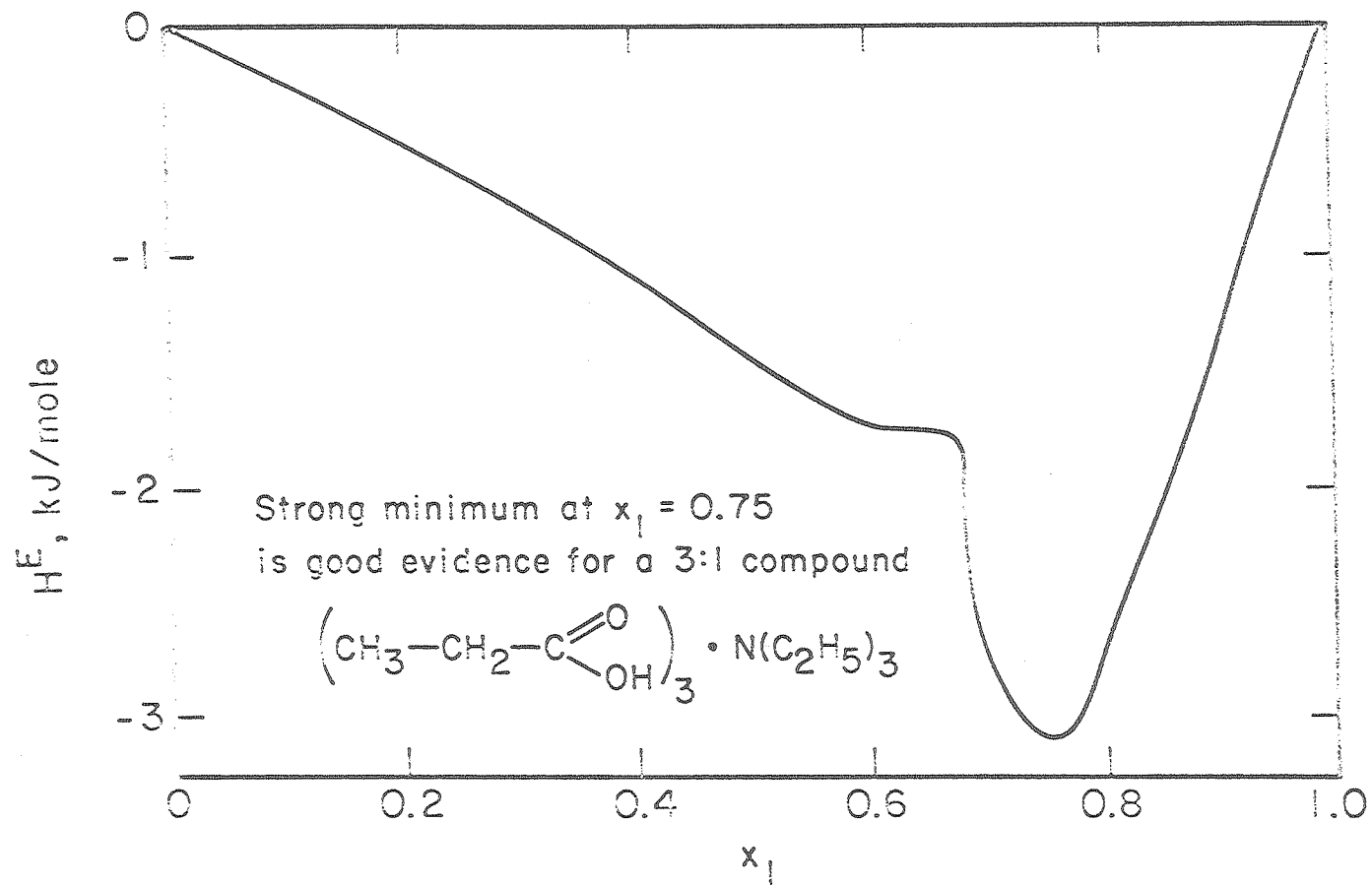
Figure 19
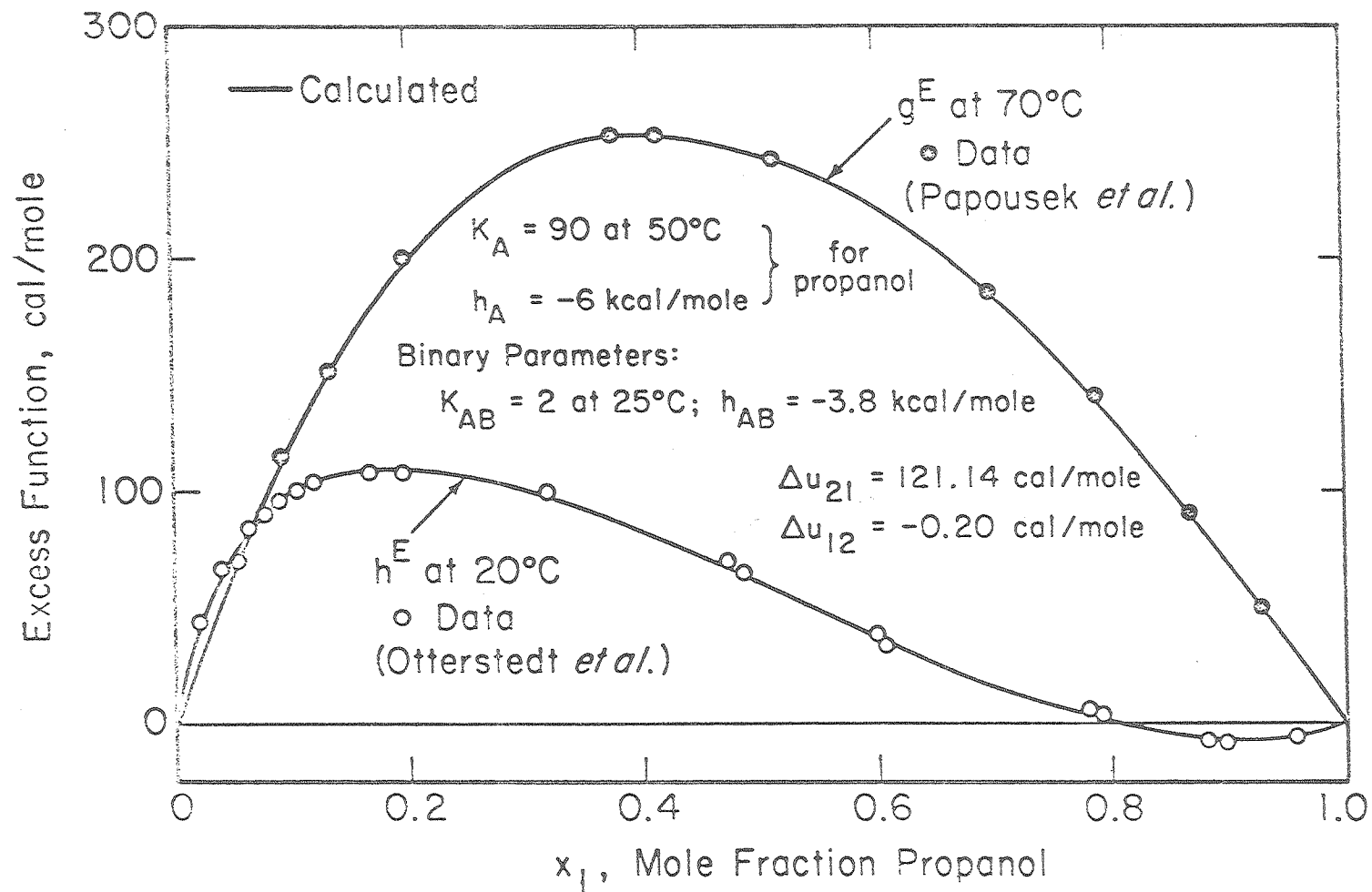
EXCESS FUNCTIONS FOR *n*-PROPANOL (1)—CARBON TETRACHLORIDE(2)
(From Nagata)

Figure 20

Strong minimum at $x_1 = 0.75$
is good evidence for a 3:1 compound

$$\left(CH_3-CH_2-C{\overset{\textstyle O}{\underset{\textstyle OH}{\big\langle}}}\right)_3 \cdot N(C_2H_5)_3$$

EXCESS ENTHALPY FOR PROPIONIC ACID (1)–TRIETHYLAMINE (2)

AT 25°C (From Munn and Svejda)

Figure 21

ACTIVITY COEFFICIENTS FROM A VAN DER WAALS-TYPE PARTITION FUNCTION Q

$$Q = [Q_{COMB}][FV][\exp E/kT]$$

FV = Free-Volume Term

E = Energy

k = Boltzmann's Constant

Q_{COMB} = Combinatorial Term, e.g. Flory-Huggins

N = No. of molecules

For a Binary

$$E = N_1 E_{(1)} + N_2 E_{(2)}$$

$$E_{(1)} = \mathcal{F}(\theta_{11}, \theta_{21}, \nu_{21})$$

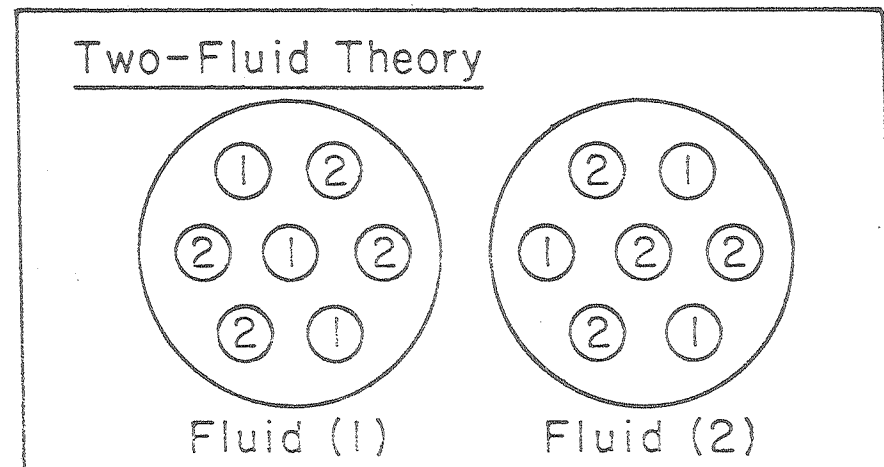$$E_{(2)} = \mathcal{F}(\theta_{22}, \theta_{12}, \nu_{12})$$

θ_{ij} = <u>Local</u> Composition

$$\nu_{ij} = \frac{\epsilon_{ij} - \epsilon_{jj}}{v}$$

Two-Fluid Theory

Fluid (1)   Fluid (2)

Note that ν_{ij} is energy <u>per unit volume</u>

Figure 22

○ Experimental

— Calculated from two-fluid van der Waals-type partition function using:

$$\nu_{12} = 0.68 \text{ cal/cm}^3$$
$$\nu_{21} = -5.04$$

$$\ln a_1 = (\text{Flory-Huggins Term}) + \chi \Phi_2^2$$
$$a_1 = \text{activity of acetone}$$
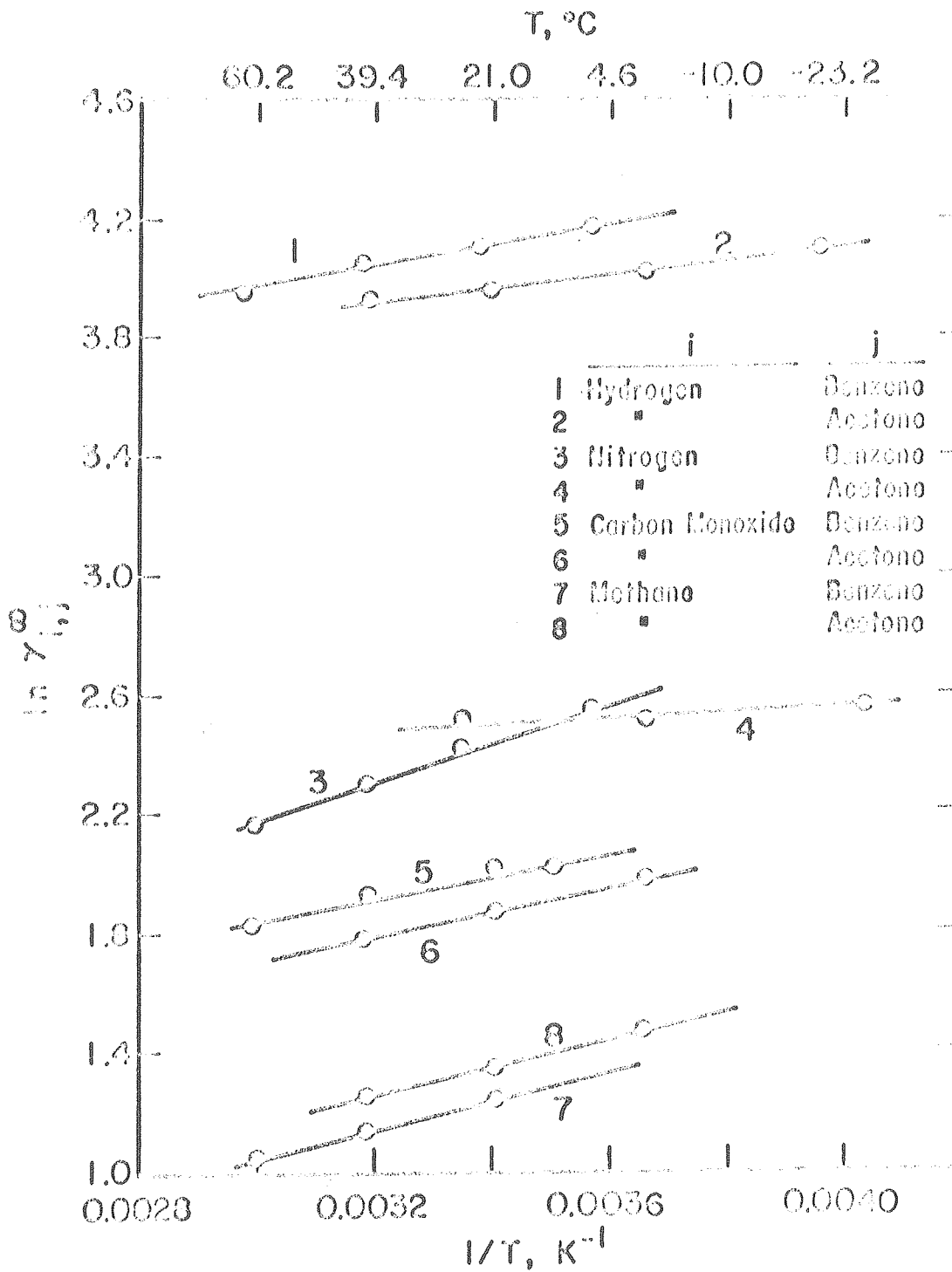
Φ_2, Volume Fraction Polymer
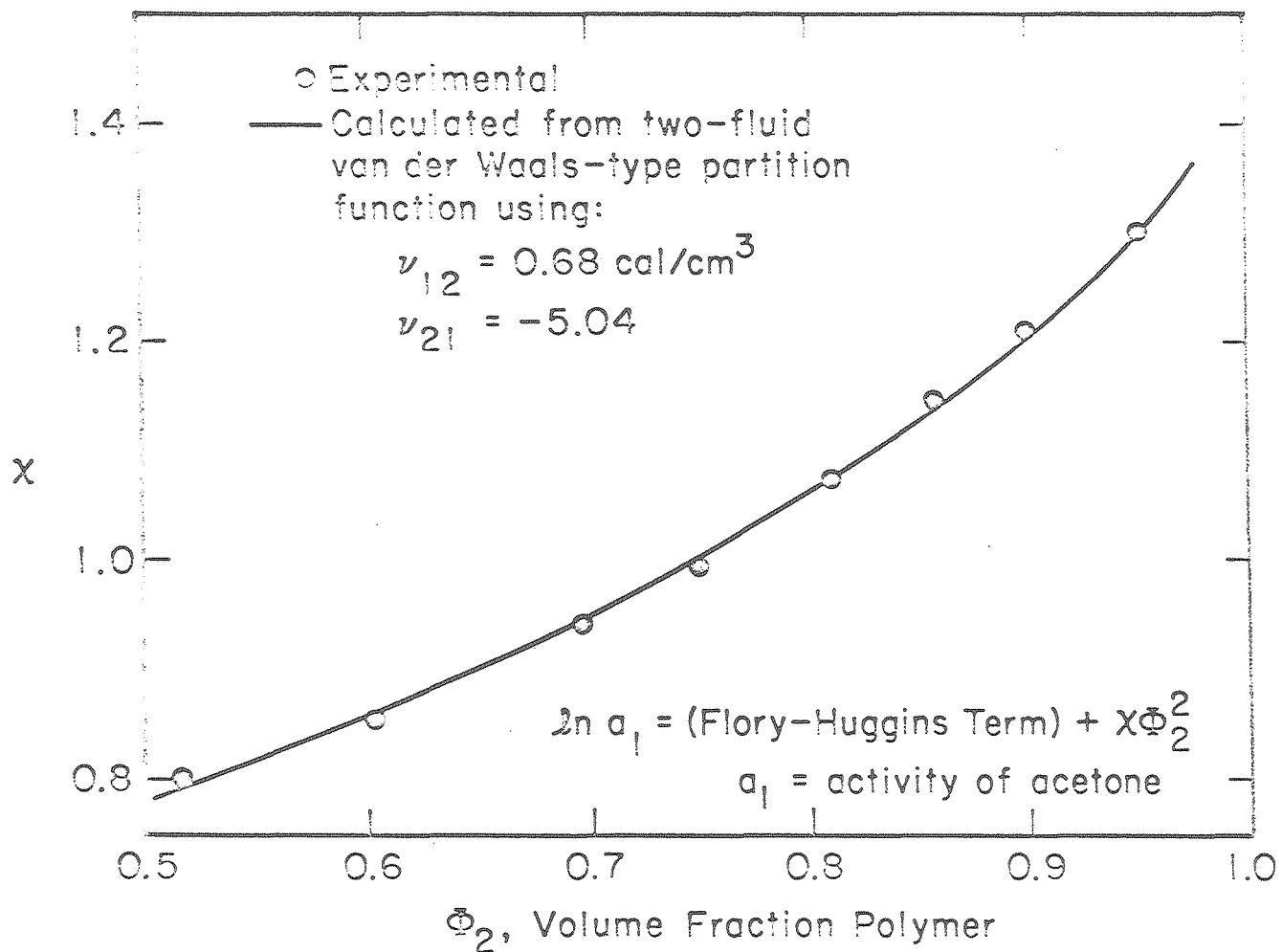
FLORY χ PARAMETER FOR ACETONE (1) – POLYSTYRENE (2) AT 25°C (From Brandani)

Figure 23
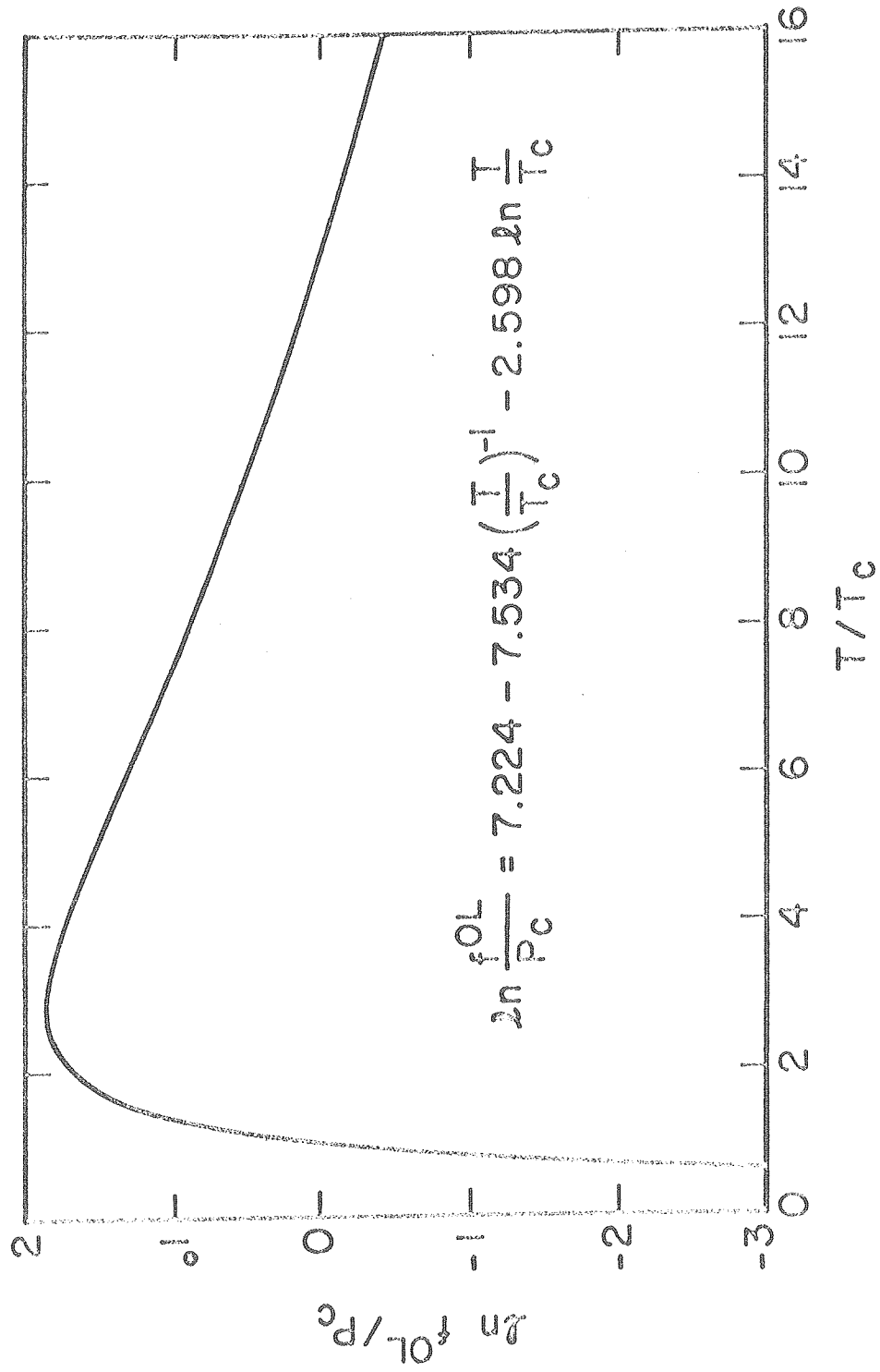
Generalized Fugacities for Noncondensable Fluids

Figure 24

$$\ln \frac{f^{OL}}{P_c} = 7.224 - 7.534 \left(\frac{T}{T_c}\right)^{-1} - 2.598 \ln \frac{T}{T_c}$$
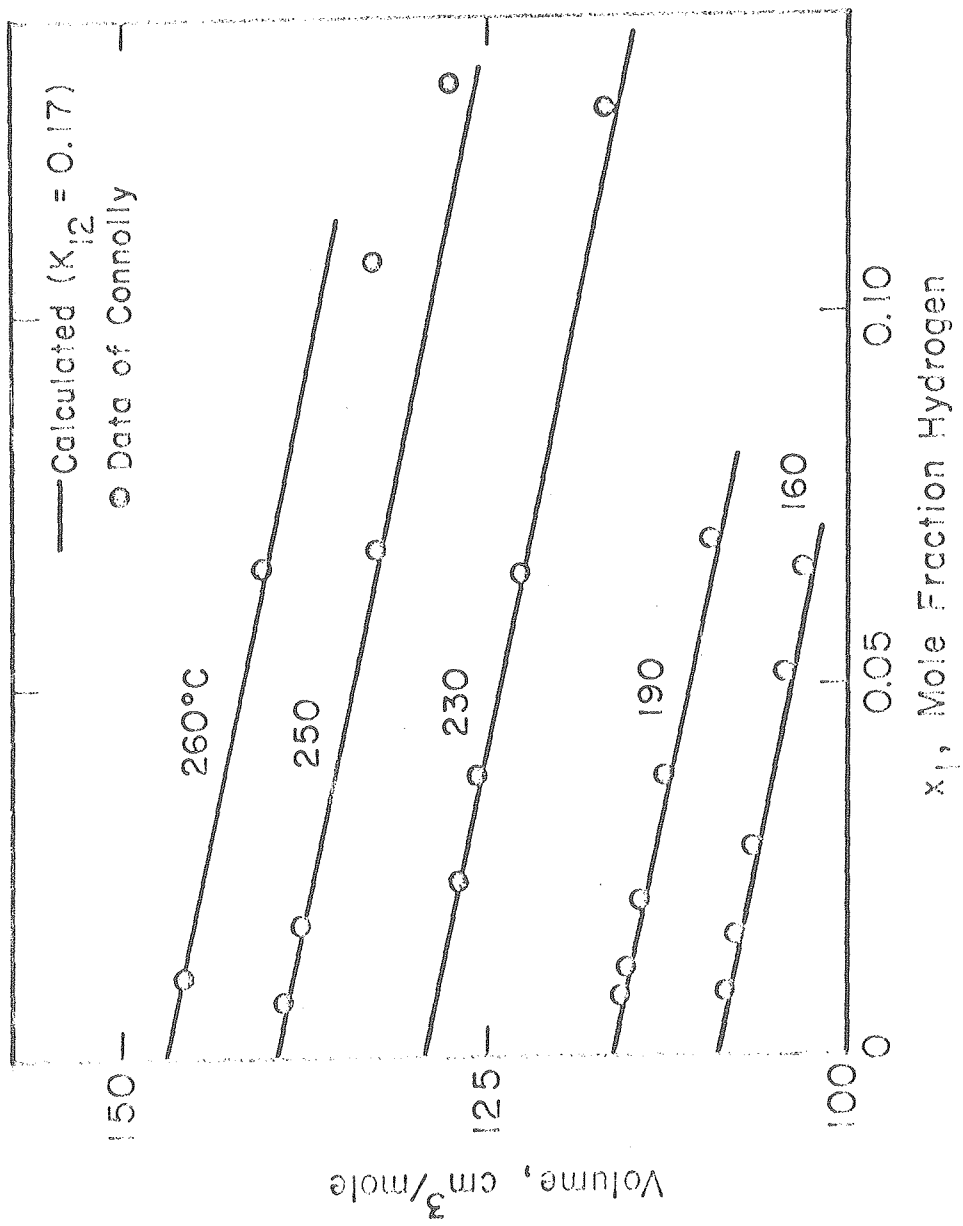
Activity Coefficients for Noncondensable Solutes at Infinite Dilution
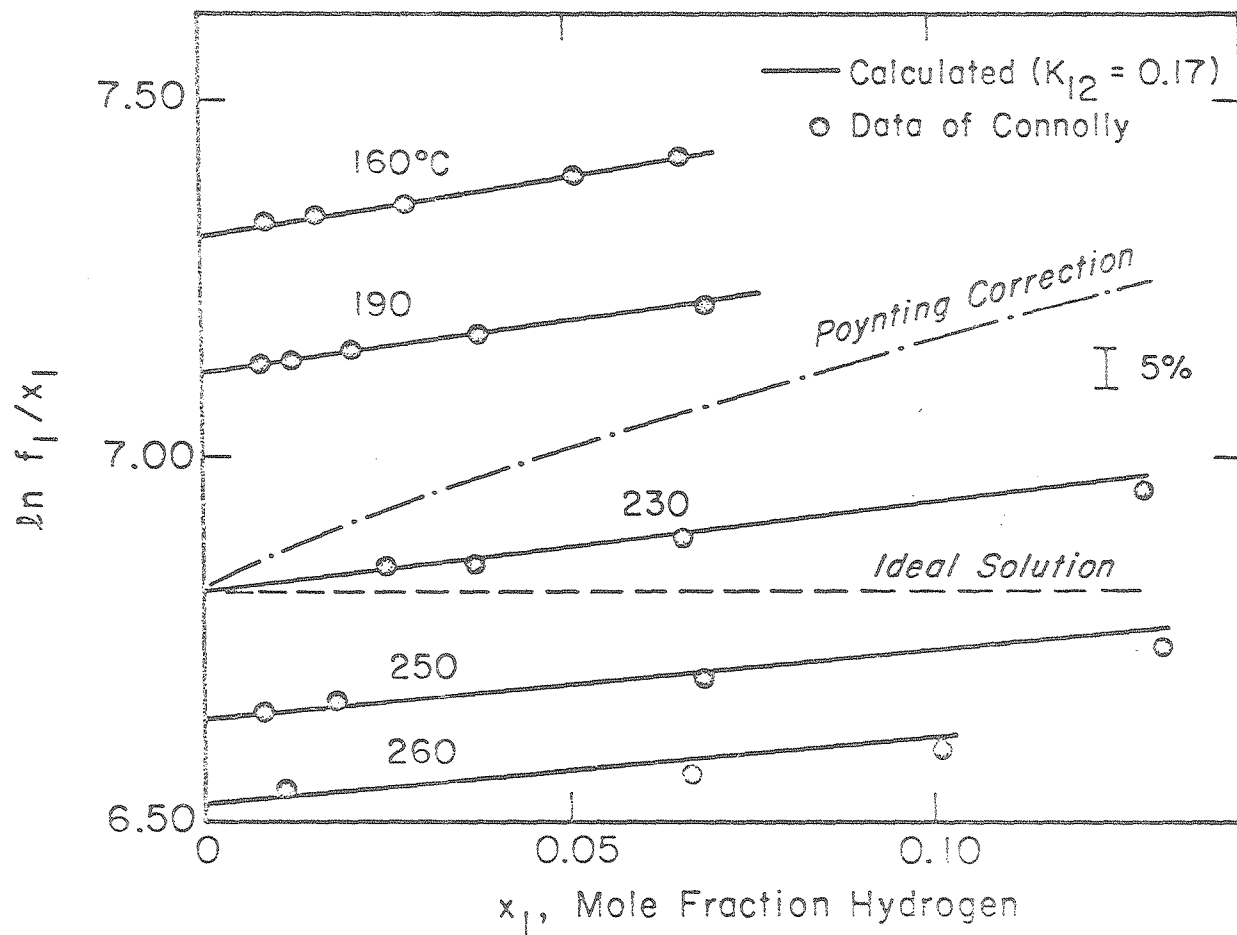
Figure 25
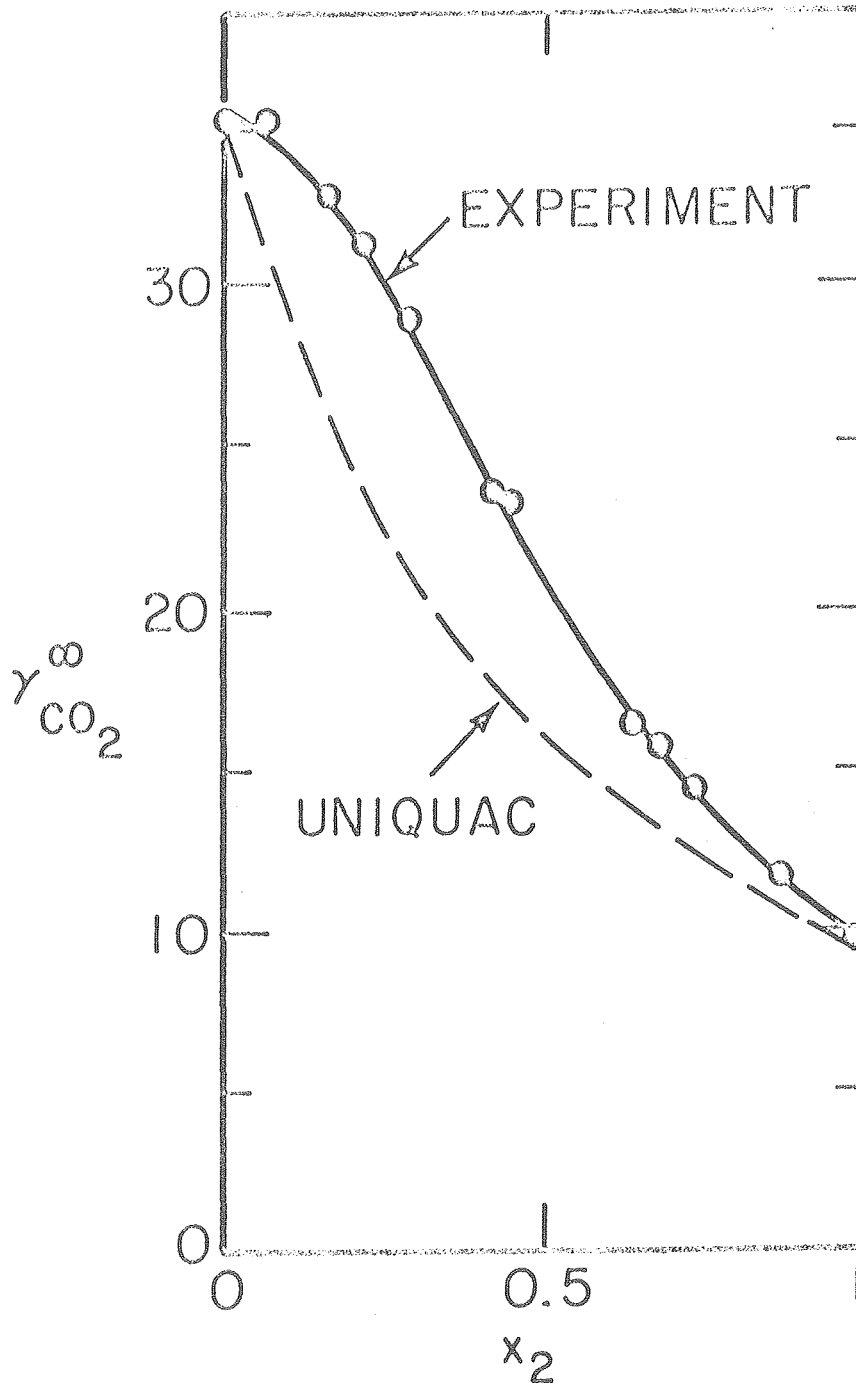
ACTIVITY COEFFICIENT AT INFINITE
DILUTION FOR CARBON DIOXIDE IN
MIXTURES OF WATER (1) — ETHYLENE
GLYCOL (2) AT 25°C (From Landeck
and Kistenmacher).

Figure 26

VOLAR VOLUME OF HYDROGEN (1) – BENZENE (2)
MIXTURES (From Mathias and O'Connell)

Figure 27

50

FUGACITIES OF HYDROGEN (I) — BENZENE (2) MIXTURES
(From Mathias and O'Connell)

Figure 28