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Manuscript received March 16, 1971; revision received May 6, 1971; paper accepted May 19, 1971.

Thermodynamics of Nearly-Ideal Systems

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The industrial importance of mixtures of closely similar substances is out of proportion to their relatively small numbers due to their frequent occurrence and the difficulty of their separations. A procedure specially designed for the general prediction of their properties, particularly relative volatility, over a wide range of state variables is needed.

Such a procedure is developed in this work for convenient application to multicomponent systems with the use of generalized functions. The relative volatility of a nearly ideal system is decomposed into ideal solution factors and nonideality factors. The first order perturbation theory of Longuet-Higgins is adopted for the calculation of the nonideality factor. The validity of the procedure for the quantitative description of real mixtures is demonstrated with the system propane/propylene for which extensive data are available.

The required pure fluid properties for the general application of the procedure are reviewed. System parameters are evaluated for 15 binary systems of industrial interest.

A great deal of effort has been devoted to the phase behavior and other properties of close boiling mixtures (*1* to *23*). Almost invariably the experimental work is difficult due to the closeness of the vapor and liquid compositions in an equilibrium cell. The resulting correlation of the data is usually specific for the given system over the range of variables studied (*8, 12, 15, 20*). Efforts of such lim-

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ited utility are nevertheless justified on account of the great accuracy with which relative volatilities must be known in such systems for the purpose of reliable design calculations (*15*).

Therefore a generalized procedure for the accurate prediction of relative volatilities in such systems over a wide range of state variables from a minimum of experimental data is needed. Preferably the procedure should be able to use various types of experimental data on the system of interest to include, but not to be limited to, phase equilibrium data. Perturbation analysis appears to offer a sound basis for the development of such a procedure. For each mixture system of closely similar substances the properties are considered to be perturbations of a suitable ideal mixture.

The theory of first order perturbation is well developed. According to Longuet-Higgins (*24*) and Brown (*25*), the mixture excess properties are expressed entirely in terms of the properties of pure fluids and an energy constant for each pair of unlike molecules. The development is an extension of the principle of corresponding states. The specific form of the molecular potential energy need not be known.

Brown (*25*) developed the perturbation theory to include second-order effects by representing the molecular interaction potential in the Lennard-Jones form. The additional terms in the expressions for the properties of mixtures depend on the parameters of the potential function, which must be precisely known. Wheeler and Smith (*26*), Calvin (*27*), and Calvin and Smith (*28*), developed applications of the higher order perturbation theory.

It seems apparent that the simple first-order perturbation theory should describe mixtures of closely similar components that deviate slightly from ideal solution behavior. We refer to such mixtures as being nearly ideal. By the same token, the description of mixtures containing components of great dissimilarity must take into consideration higher order perturbations.

This work demonstrates the applicability of the first order perturbation theory to real mixtures with the system propane/propylene for which experimental data are available over an extended range of conditions. To facilitate the application of the theory we report the system parameter values for 15 binaries, in most of which the components are more closely similar than propane and propylene.

The procedure we developed for the application of the theory is generally applicable as the required pure component properties are all available as generalized functions.

NEARLY-IDEAL SYSTEMS

Since the components in a nearly-ideal system are closely similar, we represent their properties as being only slightly different from those of a base component. Similarly, the real mixture is considered to be only slightly different from an ideal base mixture. In this way we obtain useful results by introducing generalized base functions and generalized deviation functions. It remains in application only to evaluate a few parameters by referring to suitable experimental data to characterize the particular system of interest.

Consider the volatility of component 2 relative to 1 in a binary mixture. The following thermodynamic identity serves as a useful basis of discussion

$$\alpha_{2,1} = \frac{y_2\, x_1}{x_2\, y_1} = \left(\frac{f_2^{0L}}{f_2^{0V}}\right)\left(\frac{f_1^{0V}}{f_1^{0L}}\right)\left(\frac{\gamma_2^{L}}{\gamma_1^{L}}\right)\left(\frac{\gamma_1^{V}}{\gamma_2^{V}}\right) \tag{1}$$

The standard state (superscript 0) refers to the pure fluid at the temperature and pressure of the two-phase system. Equation (1) shows that α may be considered as the product of the ratios of the pure fluid fugacities and the activity coefficients. Of the four fugacities in Equation (1), two are hypothetical at the T and p of interest. However, because of the similarity of the components, the hypothetical states are never far from the real states. They can be evaluated precisely in terms of series expansions starting from base points on the saturation curve. Figure 1 shows a state of interest and the base states at the same temperature. Expanding in Taylor series from such a base point

$$\ln\left(\frac{f^{0V}}{f^{0L}}\right)\Bigg|_{(p,T)} = \ln\left(\frac{f^{0V}}{f^{0L}}\right)\Bigg|_{(p^o,T)} + \left[\frac{\partial \ln\left(\frac{f^{0V}}{f^{0L}}\right)}{\partial \ln p}\right]\Bigg|_{(p^o,T)} \ln\left(\frac{p}{p^o}\right) + \frac{1}{2}\left[\frac{\partial^2 \ln\left(\frac{f^{0V}}{f^{0L}}\right)}{(\partial \ln p)^2}\right]\Bigg|_{(p^o,T)} [\ln(p/p^o)]^2 + \cdots \tag{2}$$

$$= (\Delta Z)\ln\left(\frac{p}{p^o}\right) + \frac{1}{2}(\Delta Z - \Delta Z_p)\left[\ln\left(\frac{p}{p^o}\right)\right]^2 + \cdots \tag{3}$$

The expansion includes terms up to the second derivative. It can be shown that the third-order term is entirely negligible. The first term on the right-hand side of Equation (2) vanishes because the fugacities of the saturated liquid and vapor are equal. The Δ symbol in Equation (3) denotes a change of property accompanying vaporization. Z_p is a derivative compressibility factor defined by Reid and Valbert (29)

$$Z_p = Z - p_r\left(\frac{\partial Z}{\partial p_r}\right)_{T_r} \tag{4}$$

Generalized correlations of p_r^0, ΔZ, and ΔZ_p therefore suffice for the calculation of the fugacity ratios. For the purposes of Equation (3), these functions need to be known for the pure saturated fluids. Available correlations of these properties are discussed in a later section in this paper.

We now turn to the nonideality factors (γ_2/γ_1) in Equa-

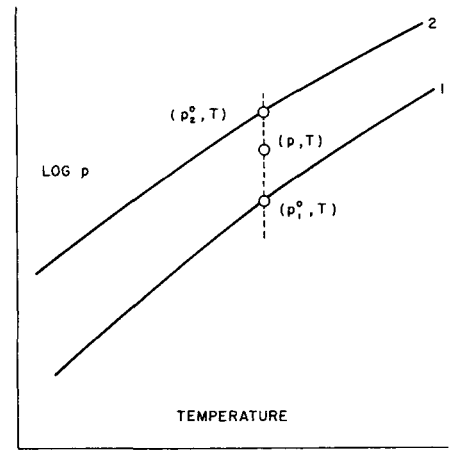

Fig. 1. Schematic showing the state of interest and the base points on the pure fluid saturation loci.

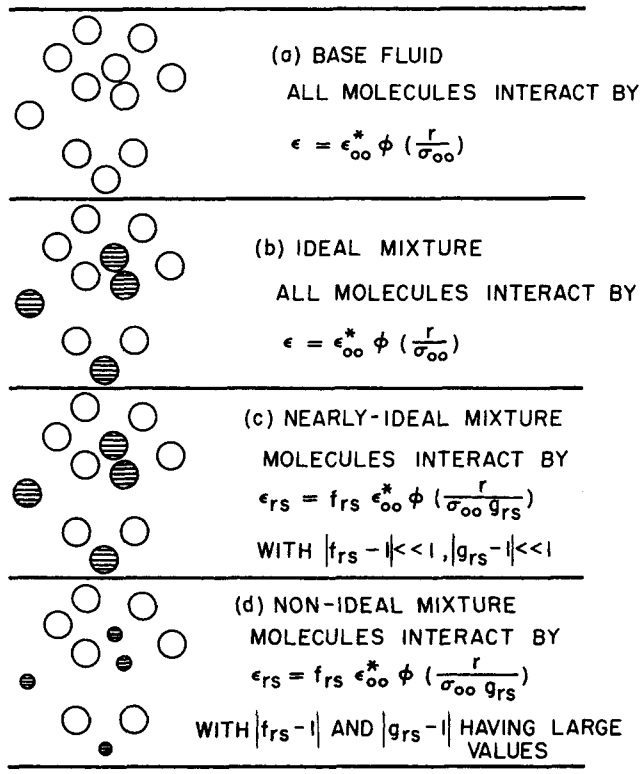

Fig. 2. Molecular interactions in mixtures.

tion (1). Let us inquire how a nearly ideal system deviates from ideal solution behavior. Figure 2 shows schematically a molecular configuration for four different fluids *a*, *b*, *c*, and *d*. In the pure fluid *a* all pairwise molecular interactions are identical and for simple fluids can be described by the same two-parameter function. In the ideal solution *b* the molecular interactions remain unchanged, even though the different species are somehow recognizable. In the nearly ideal solution *c*, the molecular interactions are slightly different, depending on the species interacting. The energy parameter f and the size parameter g are both close to 1 for all the pairs. In mixture *d* the interactions among the different types of molecules are much different whereby the parameters f and g deviate substantially from 1 for some pairs.

Longuet-Higgins (*24*) developed the statistical theory of the thermodynamic properties of solutions in which the parameters f and g are close to 1. Only linear terms of $(f-1)$ and $(g-1)$ were retained in the perturbation calculations. He succeeded in expressing the excess properties entirely in terms of the thermodynamic properties of the pure base fluid and an interaction parameter for each pair of species

$$d_{12} = 2f_{12} - (f_{11} + f_{22}) \tag{5}$$

Longuet-Higgins' perturbation theory, called the conformal solution theory, is applied in this work for the description of the nonideal behavior of nearly ideal solutions. Description of the conformal solution theory can be found in standard references (*30* to *32*).

The assumptions made by Longuet-Higgins in the development of the conformal solution theory are:

1. The solutions obey classical statistical mechanics—there are no "quantum effects."
2. The *intra*molecular contributions to the energy of the fluid are the same as for the ideal gas. The intermolecular environment does not appreciably affect the energies of the internal motions.
3. The intermolecular potential energy of the mixture in any configuration is the sum of all pairwise interactions.
4. The pair potential between two species r and s is given by

$$\epsilon_{rs} = f_{rs}\,\epsilon^*_{oo}\,\phi\left(\frac{r}{g_{rs}\,\sigma_{oo}}\right)$$

where $\epsilon^*_{oo}\,\phi\left(\frac{r}{\sigma_{oo}}\right)$ is the potential energy between two molecules of the reference species, separated by a distance r, and f_{rs} and g_{rs} are constants depending only on the identity of r and s.

5. The components are so closely similar that with a suitable choice of reference species f_{rs} and g_{rs} are close to 1.0.
6. For every pair of species $g_{rs} = \frac{1}{2}\,(g_{rr} + g_{ss})$.
7. The mixture is assumed to be random in the sense that the potential energy U of a mixture for each spatial configuration of molecules is the average over all assignments of the different species to all positions in proportion to the mole fractions.

Other than these assumptions, the development is rigorous. For instance the existence of any lattice structures is not postulated. The results are equally applicable to liquid and gas mixtures.

For the purposes of engineering calculations we are mainly interested in the excess Gibbs free energy. According to the conformal solution theory

$$\tilde{G}^E = \sum_{r<s}\sum x_r x_s\,\tilde{U}^o\,d_{rs} \tag{6}$$

For binary mixtures Equation (6) simplifies to

$$\tilde{G}^E = \tilde{U}^o\,d_{12}\,x_1\,x_2 \tag{7}$$

Also

$$\tilde{V}^E = \left(\frac{\partial \tilde{U}^o}{\partial p}\right)_T \sum_{r<s}\sum x_r x_s\,d_{rs} \tag{8}$$

$$\tilde{H}^E = \left[\tilde{U}^o - T\left(\frac{\partial \tilde{U}^o}{\partial T}\right)_p\right] \sum_{r<s}\sum x_r x_s\,d_{rs} \tag{9}$$

From Equation (6) we derive

$$RT\ln\gamma_i = \sum_r x_r\,\tilde{U}^o\,d_{ir} - \sum_{r<s}\sum x_r x_s\,\tilde{U}^o\,d_{rs} \tag{10}$$

For binary mixtures Equation (10) simplifies to

$$RT\ln\gamma_1 = \tilde{U}^o\,d_{12}\,x_2^2 \tag{11}$$

$$RT\ln\gamma_2 = \tilde{U}^o\,d_{12}\,x_1^2 \tag{12}$$

Therefore, for use in Equation (1), we have

$$\frac{\gamma_2}{\gamma_1} = \exp\left[\left(\frac{\tilde{U}^o}{RT_c{}^o}\right)\frac{d_{12}}{T_r{}^o}\,(x_1 - x_2)\right] \tag{13}$$

In Equations (6) to (13) $\tilde{U}^o$ represents the molal configurational energy of the pure reference substance; that is, the negative of the molal internal energy deviation (*31*). They permit the evaluation of the binary interaction constant d_{12} from a variety of data. A small amount of reliable data suffices for this purpose. The binary interaction constant then allows reliable prediction of the nonideality factor according to Equation (13) over a wide range of state conditions for use in Equation (1).

There is considerable flexibility in the selection of a base fluid for a particular mixture system. Obviously the base fluid should be as close as possible in properties to the com-

ponents of interest in order for the parameters f and g to be close to 1. The simplest choice would probably be one of the actual components in the mixture. Whatever the choice it is important to realize that the interaction constant d_{rs} is associated with a base fluid and must be applied in a manner consistent with its evaluation. We have always chosen the heavy component to be the base fluid in this work.

PURE-FLUID PROPERTIES

The pure-fluid property values required in the procedure described here are known with a high degree of accuracy for some components from specific experimental determinations or direct derivations therefrom. Common examples are accurately measured vapor pressures and liquid densities. Such values should be used when available. In the absence of such values, estimation can be made from generalized correlations. The following discussion concerns the procedure for making the estimates. Available generalized correlations are reviewed. We should point out at the outset that satisfactory accuracy is obtainable for the critically important properties from available correlations.

Vapor pressure must be known in the use of Equation (3). Several general correlations of reduced vapor pressure are available, including those of Lydersen, Greenkorn, and Hougen (*33*), Riedel (*34*), and Pitzer and co-workers (*35*). We have used the table values of Pitzer et al. in a Langrangian interpolation routine in this work, except where specific data were available.

For the change in compressibility factor with vaporization ΔZ we have similarly used the table values of Pitzer et al. in Langrangian interpolation calculations. To calculate ΔZ_p we take Z_p from Reid and Valbert's table (*29*) and extrapolate to the saturation states. We then calculate Z_p of the saturated liquid from Chueh and Prausnitz' (*36*) correlation of isothermal compressibility β_T. The definition of β_T is

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{14}$$

It is related to Z_p by

$$Z_p = p\ Z\ \beta_T \tag{15}$$

The calculation of nonideal solution behavior according to Equation (13) requires the configurational energy to be known. Ellis, Lin, and Chao (*37*) developed a generalized correlation of this property for saturated liquids. For liquids not at their saturation states, an isothermal correction can be added to the saturation value

$$\tilde{U}(p, T) = \tilde{U}(p^o, T) + \left(\frac{\partial \tilde{U}}{\partial p}\right)_T (p - p^o) \tag{16}$$

Equation (16) expresses $\tilde{U}$ as a series expansion about the saturation state including terms up to the linear. In view of the pressure insensitivity of $\tilde{U}$, Equation (16) should give an excellent approximation at conditions of interest in nearly-ideal solution calculations. The derivative at the right-hand side of Equation (16) is given by

$$\left(\frac{\partial \tilde{U}}{\partial p}\right)_T = \tilde{V}(p\beta_T - T\alpha_p) \tag{17}$$

The equation is to be evaluated at the saturation state. The β_T of saturated liquids correlated by Chueh and Prausnitz (*36*) is useful here. The coefficient of thermal expansion α_p defined by

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{18}$$

has been correlated for saturated liquids by Ellis, Lin, and Chao (*37*). We estimate the error in the calculated values of $\tilde{U}$ of liquids to be about 1 to 2%.

The configurational energy of vapors can be calculated in a similar manner. However, since no correlation is available for the saturated vapor, we calculate it from the corresponding liquid value

$$\left(\frac{\tilde{U}}{RT_c}\right)^V = \left(\frac{\tilde{U}}{RT_c}\right)^L + \frac{T_R\,\Delta\tilde{S}}{R} - T_R\,\Delta Z \tag{19}$$

The Δ symbol denotes a change with vaporization. We have used values of $\Delta\tilde{S}$ and ΔZ from Pitzer et al. (*35*).

For making pressure corrections to $\tilde{U}$ of vapors we make use of the derivative compressibility factors Z_p and Z_T of Reid and Valbert (*29*).

The configurational energy of vapors is much smaller in value than that of the liquids. Much larger relative errors of estimate can be tolerated. The calculated nonideal solution behavior of the vapor mixture is usually negligible for the systems we studied.

THE PROPANE/PROPYLENE SYSTEM

To demonstrate that the thermodynamics of nearly-ideal systems validly describes the behavior of real mixture systems we have made extensive computations for the system propane/propylene. Comparisons of our calculations with the experimental values of relative volatility over a wide range of state variables are made. The experimental data on this system are very extensive, covering temperatures from −56.9 to 190.0°F., pressures from 10 to 600 lb./sq.in.abs., and compositions from pure propane to pure propylene.

Reamer and Sage (*19*) determined volumetric data for the superheated gas mixtures. We analyzed the data in terms of Equations (8) and (17) and Reid and Valbert's derivative compressibility factors (*29*). With an interaction constant $d_{12} = -0.0167$ we obtained excellent fitting of the data. Figure 3 shows the results at 220°F. and 600 lb./sq.in.abs. This is the condition at which the two mixtures studied showed maximum values of excess volume.

The recent phase equilibrium data determined by Hirata et al. (*13*) were at low temperatures and pressures. Analysis of mixture composition was by means of gas chroma-

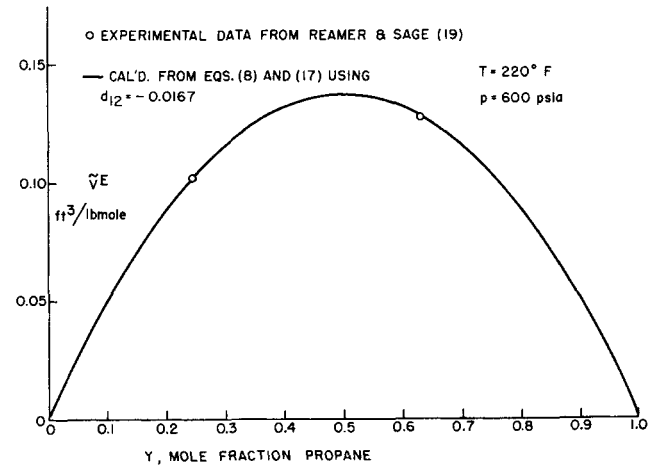

Fig. 3. Excess volume of propane/propylene gas mixtures.

Table 1. Accuracy Study on the Propane-Propylene System With $d_{12} = -0.0167$

T°F.	% absolute deviation in relative volatility	% average deviation in relative volatility	Number of smoothed points
−56.9 (*13*)*	1.6	−1.4	9
−48.1 (*13*)	0.8	−0.6	9
−39.5 (*13*)	0.7	+0.6	9
−28.8 (*13*)	0.7	+0.7	9
10.0 (*8*)	2.2	1.5	9
10.0 (*19*)	2.5	−1.8	9
25.5 (*8*)	2.7	−2.5	9
40.0 (*8*)	2.6	−2.3	9
40.0 (*19*)	3.6	−3.5	9
82.7 (*8*)	1.4	−1.1	9
100.0 (*8*)	2.3	+1.1	9
100.0 (*19*)	2.6	−0.9	9
134.9 (*8*)	0.7	−0.4	9
160.0 (*8*)	1.0	+0.4	9
160.0 (*19*)	1.5	−0.7	9

* The numbers in parentheses refer to sources of data.

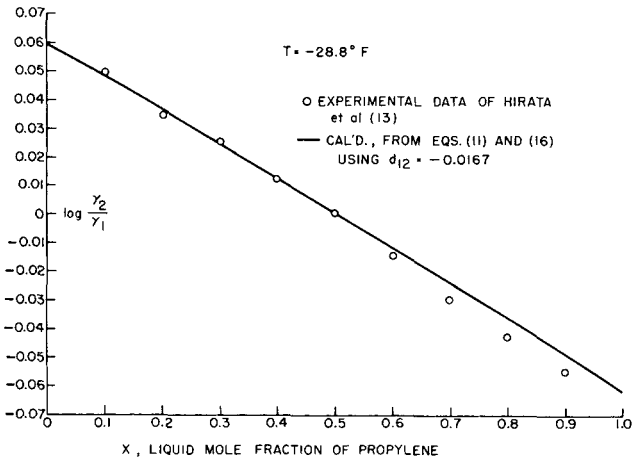

Fig. 4. Activity coefficients of propane/propylene liquid solutions.

tography. The accuracy appeared excellent with the least uncertainty associated with the thermodynamic analysis of their data. We analyzed their activity coefficient of the liquid solutions in terms of Equation (11) and our configurational energy correlation with the result $d_{12} = -0.0167$. Figure 4 shows the agreement of our calculations with experimental data at − 28.8°F. The pressure of the system ranges from 21 to 28 lb./sq.in.abs. at this temperature.

Since excellent agreement in the value of the interaction constant d_{12} was obtained from such diverse sources, we used this value of d_{12} to make extensive calculations of relative volatility for comparison with the large number of data points in the literature. A total of 99 smoothed points were compared covering 11 isotherms including all the experimental conditions except the temperature of 190°F. which exceeded $T_r = 0.98$ for propane. The correlations α_p and β_T were inapplicable at that temperature. The absolute average deviation from the smoothed α values amounted to 1.5%. Table 1 gives a summary of the results at the various temperatures. Figures 5, 6, 7, and 8 show the comparisons at −56.9, 25.5, 70 and 100°F. respectively. Each figure is meant to show data from a different source. The lowest temperature data is from Hirata et al. (*13*), the middle temperatures from Hanson et al. (*8*) and Manley (*15*), and the highest temperature from Reamer and Sage (*19*). The figures show that the calculated values agree with the data generally within the experimental uncertainties.

The data from the different sources appear to vary in quality. Reamer and Sage (*19*) obtained their five isotherms in 1950 and stated that composition determinations involved significant uncertainties, since they used a catalytic hydrogenation procedure to determine olefin concentration. This would be especially true in the dilute region of the composition spectrum. A year or so later Hanson et al. (*8*) obtained three more isotherms and correlated both sets of data. They determined unsaturates concentration by means of volumetric absorption with an aqueous nitrate solution. The comparisons in Table 1 are with respect to the smoothed data (*19*) and Hanson's correlation (*8*).

Very recently, Manley (*15*) carried out a detailed experimental study of the thermodynamic properties of the propane/propylene system for five isotherms (−20, 10, 40, 70, 100°F.) with pressures from 20 to 1600 lb./sq.in. abs. These data consist of: vapor pressure and density for the pure liquids and three liquid mixtures at various temperatures, and vapor compressibility factors for the pure

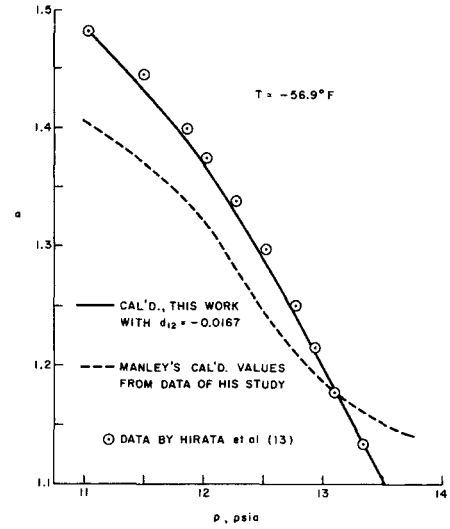

Fig. 5. Relative volatility of propane/propylene at −56.9°F.

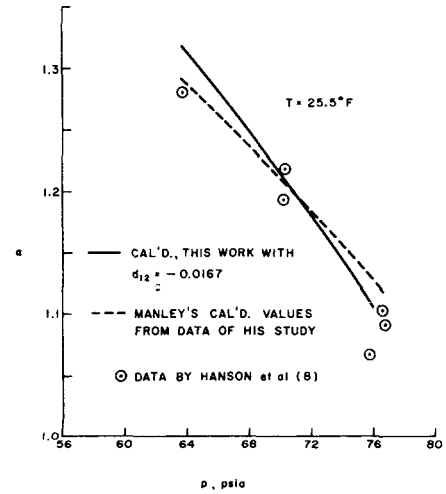

Fig. 6. Relative volatility of propane/propylene at 25.5°F.

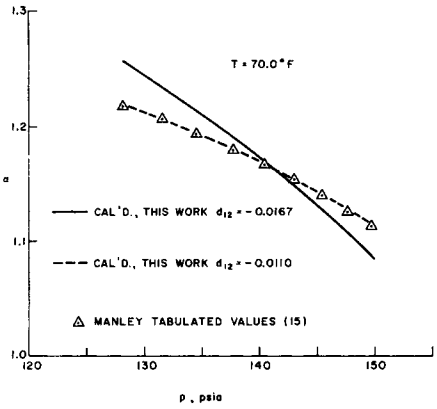

Fig. 7. Relative volatility of propane/propylene at 70°F.

components. He integrated the Gibbs-Duhem equation to calculate equilibrium vapor compositions. Our method with $d_{12} = -0.0110$ reproduced his calculations to within 0.3% average absolute deviation in α. However, there appears to be some inconsistency between Manley's and Hirata's equilibrium values as shown in Figure 5 at the temperature −56.9°F. Similar comparisons with the same conclusion were made by Manley (*15*) at higher temperatures up to −28.8°F.

Our calculated results with $d_{12} = -0.0167$ appear in Figures 6, 7, and 8 to be slightly steeper than indicated by the experimental data toward the terminals of the composition range. We have therefore examined the trends of the data in the terminal composition ranges in light of a thermodynamic condition for the terminal slopes

$$\lim_{x_2 \to 0} \left[\left(\frac{\partial x_2}{\partial p} \right)_{T,S} (1 - K_2) \right] = \frac{-\Delta \tilde{V}_1}{RT} \quad (20)$$

We derived this equation in a manner similar to the derivation of the thermodynamic conditions for isobaric systems given by Rowlinson (*31*). The derivative $(\partial x_2/\partial p)_{T,S}$ was determined graphically from the isothermal data upon smoothing and extrapolating to $x_2 = 0$. The subscript S denotes saturation conditions along the phase boundary. K_2 was likewise determined at the same time upon extrapolating the smoothed data to $x_2 = 0$. $\Delta \tilde{V}_1$ denotes the volume of vaporization of the pure liquid 1 and is well known.

The results of the calculations are shown in Table 2, in

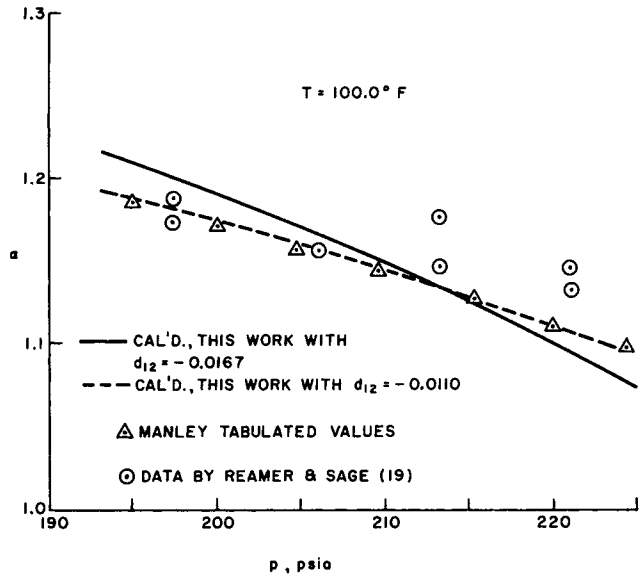

Fig. 8. Relative volatility of propane/propylene at 100°F.

which the lack of equality of the two sides of Equation (20) is given as a relative deviation. The Table shows significant deviations at the propylene-rich end at the three temperatures 10, 40, and 100°F. that we studied with Reamer and Sage's data. At the propane-rich end, a significant deviation is observed for the 40°F. data. These deviations indicate that the terminal slopes of α ($= K_2$ or $1/K_1$) should be somewhat higher in the propane-rich end and should be lower in the propylene-rich end, which is in the direction of our calculations. Funk and Prausnitz (*4*) made a similar observation for the propylene-rich end based on their correlation.

Hill and co-workers (*12*) developed a correlation for this system, based on regular solution theory. However, it was originally intended only for the temperature range between 50 and 140°F. Ellis (*38*) extended the correlation outside of this range, but the accuracy of its performance deteriorated.

DISCUSSION

Our study of the propane/propylene system has demonstrated that this system is nearly ideal for practical purposes. The thermodynamics of nearly ideal systems described here can be expected to describe similar systems.

TABLE 2. CONSISTENCY TEST FOR PROPYLENE/PROPANE VAPOR-LIQUID EQUILIBRIUM DATA (*19*)

(a)

T, °F.	$\lim_{x_1 \to 0} \left[\left(\frac{\partial x_1}{\partial p} \right)_{T,S} (1 - K_1) \right]$, lb./sq.in.abs.$^{-1}$	$-\frac{\Delta \tilde{V}_2}{RT}$, lb./sq.in.abs.$^{-1}$	% deviation
10	−0.01841	−0.0155	−18.8
40	−0.01031	−0.00873	−16.1
100	−0.00435	−0.00308	−41.0

(b)

T, °F.	$\lim_{x_2 \to 0} \left[\left(\frac{\partial x_2}{\partial p} \right)_{T,S} (1 - K_2) \right]$, lb./sq.in.abs.$^{-1}$	$-\frac{\Delta \tilde{V}_1}{RT}$, lb./sq.in.abs.$^{-1}$	% deviation
10	−0.01978	−0.01941	+1.9
40	−0.00985	−0.01078	−8.6
100	−0.00383	−0.00388	+1.3

To facilitate the application of the theory we report in Table 3 the interaction constants for 15 binaries. Literature values of activity coefficients were used in the determinations for systems 1-11 and 13. Vapor-liquid equilibrium data for systems 14 and 15 were directly compared with our calculated values for adjustment of d_{12} until the best agreement was obtained. The degree of fitting of data is highly sensitive to the value of d_{12}. For instance, the calculated $\tilde{V}^E$ in Figure 3 is directly proportional to d_{12} according to Equation (8). The sensitive dependence of the calculated relative volatility on d_{12} is illustrated in Figure 7 in which the two calculated curves correspond to values of d_{12} that are only slightly different.

There are insufficient number of known d_{12}'s for any reliable correlation to be developed for predictive purposes. The prediction of binary mixture behavior from pure fluid properties appears to be in general an unpromising endeavor. Rowlinson (*31*) stressed that binary systems, not the pure components, must be the basis for the quantitative discussion of multicomponent systems. Our present work agrees with this viewpoint.

Most of the binaries in Table 3 are as closely similar as, or more similar than, propane/propylene. It appears certain that the behavior of systems in this category should be accurately described by the present theory. The deviations from ideal solution behavior of several such systems are small but not negligible, since their relative volatilities differ only slightly from 1. The nonideality factor makes a substantial contribution to the difference from 1 of the relative volatility. This contribution should be accounted for in engineering studies of superfractionation systems. Examples may be cited in the C_8 aromatics. The relative volatility can be as low as 1.02-1.03, while the ratio of activity coefficients may amount to 1.004. The ratio (γ_1/γ_2) makes up a significant part of α.

Several binaries included in Table 3 do show substantial dissimilarity between the two components. We refer to propane/propyne, propane/propadiene, propylene/propyne, and propadiene/propyne. Their values of d_{12} are large. They should not be expected to accurately follow the thermodynamics of nearly ideal systems. They are nevertheless included in Table 3 in view of their occurrence in industrial systems together with propane and propylene.

We have made studies of the relative volatilities of the multicomponent C_3 system based on the binary constants reported in Table 3 for comparison with experimental data by Hill et al. (*12*). They used a six-stage equilibrium unit in their work, and as a result, their phase compositions were not completely reported and had to be estimated in the course of our calculations. Hill's data cover a temperature range from 50 to 140°F. and a wide range of compositions. The average deviations of our calculated α-values from Hill's data for 26 experimental conditions are: 2.2% for propylene/propane, 2.7% for propadiene/propane, 2.3% for propyne/propane. Table 4 presents comparisons of the calculated and experimental equilibrium conditions. These examples are chosen to illustrate the best, the average, and the worst comparisons. The accuracy of the calculations is probably acceptable for some engineering applications.

Table 3. Binary Interaction Constant d_{12} for Several Systems

System	d_{12}
1. ethylbenzene-o-xylene (*20*)	−0.00083
2. m-xylene-o-xylene (*20*)	−0.00050
3. ethylbenzene-p-xylene (*20*)	−0.00079
4. p-xylene-o-xylene (*20*)	−0.00048
5. ethylbenzene-m-xylene (*20*)	−0.00084
6. p-xylene-m-xylene (*20*)	−0.00008
7. isopentane-n-pentane (*20*)	+0.0002
8. propane-propadiene (*12*)	−0.0510
9. propane-propyne (*12*)	−0.1260
10. propylene-propadiene (*12*)	−0.0136
11. propylene-propyne (*12*)	−0.0660
12. propane-propylene (*13, 19*)	−0.0167
(*15*)	−0.0110
13. propadiene-propyne (*12*)	−0.0331
14. ethane-ethylene (9)	−0.0101
15. n-butane-1-butene (*22*)	−0.0080

Table 4. Phase Equilibria in the System Propane/Propylene/Propadiene/Propyne

(a)

$T = 140.0°F.$ $p = 344.0$ lb./sq.in.abs.

i	x	y	$\alpha_{i,1}$ (calc.)	$\alpha_{i,1}$ (exp.)	deviation
Propylene	0.4690	0.4907	1.1057	1.0958	−0.9
Propadiene	0.0100	0.0095	0.9873	0.9929	0.6
Propyne	0.0100	0.0099	1.0350	1.0347	0.0

(b)

$T = 90.0°F.$ $p = 183.0$ lb./sq.in.abs.

i	x	y	$\alpha_{i,1}$ (calc.)	$\alpha_{i,1}$ (exp.)	deviation
Propylene	0.4940	0.5242	1.1422	1.1288	−1.2
Propadiene	0.0120	0.0109	0.9459	0.9663	2.1
Propyne	0.0120	0.0118	1.0217	1.0461	2.3

(c)

$T = 50.0°F.$ $p = 95.0$ lb./sq.in.abs.

i	x	y	$\alpha_{i,1}$ (calc.)	$\alpha_{i,1}$ (exp.)	deviation
Propylene	0.1250	0.1419	1.2559	1.1621	−8.1
Propadiene	0.0280	0.0273	1.0001	0.9999	0.0
Propyne	0.0250	0.0277	1.1621	1.1359	−2.3

In conclusion, we have shown that with generalized pure component saturation properties and one binary interaction constant for each pair it is possible to describe the phase behavior of nearly-ideal systems. As a result of these studies we make the following observations regarding nearly-ideal solution theory: 1. The significant (though small) deviations from ideality are adequately accounted for. 2. The computation is completely generalized and can be used on a variety of systems. 3. Volumetric data on a system can be used to characterize the nonidealities of mixing. 4. The results are suitable for engineering calculations on systems of closely similar components.

ACKNOWLEDGMENT

J. A. Ellis was supported on a NEDA Fellowship. The authors thank Michael Moranville for assistance in the calculations.

NOTATION

d_{rs} = constant characterizing binary interaction between components r and s

f_{rs} = energy intensity factor describing the interaction between species r and s
f_r^{0L} = standard state fugacity of component r in the liquid phase
f_r^{0V} = standard state fugacity of component r in the vapor phase
G = Gibbs free energy
g_{rs} = size parameter describing interaction between species r and s
H = enthalpy
K = y/x = equilibrium ratio
k = Boltzmann's constant
N_r = number of molecules of component r
p = absolute pressure
p^o = vapor pressure
p_r = p/p_c = reduced pressure
p_c = critical pressure
R = molal gas constant
r = distance of separation between two molecules
S = entropy
T = absolute temperature
T_r = T/T_c = reduced temperature
T_c = critical temperature
U = configurational energy
V = volume
x_r = mole fraction of component r in the liquid phase
y_r = mole fraction of component r in the vapor phase
Z = compressibility factor
Z_p = derivative compressibility factor function, see Equation (4)
Z_c = critical compressibility factor

Greek Letters

α_p = thermal expansion coefficient = $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$
$\alpha_{r,s}$ = relative volatility of component r with respect to s
β_T = isothermal compressibility = $-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$
γ_r^L = activity coefficient of component r in the liquid phase
γ_r^V = activity coefficient of component r in the vapor phase
ϵ_{rs} = potential energy between two molecules separated by a distance r
ϵ^*_{oo} = minimum potential energy between two molecules of the base fluid
ϵ = interaction potential between two molecules
σ_{oo} = collision diameter between two molecules of the base fluid
ϕ = potential energy function, a function of the distance of separation between two molecules
ω = $-1.000 - \log (P_R^o)|_{T_R=0.7}$ = acentric factor

Superscripts

E = an excess function
Id = ideal solution property
L = liquid
o = property of the reference substance
V = vapor
$\sim$ = a molal property

Subscripts

mix = a mixture property
P = constant pressure
r, s = mixture components
S = along the saturation locus
T = constant temperature
1, 2 = binary mixture components

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Manuscript received March 3, 1971; revision received June 22, 1971; paper accepted June 24, 1971.