
John M. Prausnitz

Thermodynamics of Complex Fluid Mixtures

Über die thermodynamischen Eigenschaften einfacher fluider Mischungen, d. h. solcher Mischungen von Gasen oder Flüssigkeiten, die kleine nichtpolare Moleküle enthalten, ist vieles bekannt. In der Natur hingegen treten komplexe fluide Mischungen auf, die Moleküle enthalten, die eine starke Polarität und Wasserstoffbrücken aufweisen (z. B. Wasser) oder auch große nichtpolare Moleküle (z. B. Polymere).

Für die thermodynamische Beschreibung komplexer Mischungen ist es nützlich, zwei Klassen zu unterscheiden: die erste Klasse enthält identifizierbare komplexe Moleküle; die Konzentrationen dieser Moleküle können chemisch-analytisch gemessen werden. Die zweite Klasse enthält ebenfalls komplexe Moleküle, aber so viele verschiedene Arten, daß eine vollkommene quantitative und qualitative chemische Analyse nicht möglich ist (z. B. Rohöl oder Apfelsaft).

Für die erste Klasse bietet sich eine erweiterte van der Waals Theorie an, die für den ganzen fluiden Dichtebereich Geltung besitzt, doch müssen die Mischungsregeln für die charakteristischen Konstanten bei niedriger Dichte von denen bei hoher Dichte getrennt werden.

Für die zweite Klasse muß eine neue (kontinuierliche) Thermodynamik benutzt werden; diskrete Maße der Zusammensetzung (wie etwa der Molenbruch) müssen durch Verteilungsfunktionen ersetzt werden.

Diese Methoden zur Beschreibung von komplexen Mischungen werden hier mit einem Hinweis auf ihre Bedeutung für Trennverfahren in der chemischen Technik erläutert.

We live in a world of mixtures; the air we breathe, the food we eat, the blood in our veins, the petroleum in our automobiles, and the vast oceans at the shore - wherever and whatever we are, nature dislikes purity.

Speculation and discussion concerning mixtures go back to antiquity; it was a topic of particular interest to Stoic philosophers and there is evidence to suggest that large-scale, crude equipment for separating fluid mixtures was available in classical Egypt.

The current view of fluid mixtures rests squarely on the molecular theory of matter: a fluid mixture is a collection of qualitatively different molecules so arranged in space that molecules of any one type are not significantly segregated from those of other types. Just what we mean by "significantly" requires precise definition because even the simplest, most intimately mixed assembly of qualitatively different molecules shows some segrega-

tion or order. For our purposes here, however, it is sufficient to define a fluid mixture such that there is no long-range segregation (or order), where long-range means at least one order of magnitude larger than that of a molecular dimension.

While the molecular theory of matter helps us to understand what we mean by a mixture, and while it enables us to draw mental pictures [e. g. a box containing black and white billiard balls], it is not - or at least not yet - sufficient to give us a quantitative theory for mixture properties. Toward that end an additional construct is required; it is provided by thermodynamics.

One may - indeed, one should - wonder why thermodynamics (the science of heat engines) is relevant to the problem of understanding properties of fluid mixtures. It was one of the great leaps of intellectual history when J.W. Gibbs (about 1874) saw the connection; essentially, he saw that the methodology for analyzing heat engines could also be used to analyze chemical phenomena provided that an abstract mathematical function could be defined for chemical phenomena which would be analogous to that used in mechanical (heat-work) phenomena. The key idea of Gibbs was to extend thermodynamics from closed to open systems, where open refers to the transfer of matter; based on that idea, Gibbs defined the chemical potential

which is now the heart of chemical thermodynamics. The chemical potential is the essential quantity in the science of mixtures or, more precisely, in a quantitative description of mixture properties at equilibrium, appropriately called thermodynamic properties. In essence, thermodynamic properties of a mixture are those properties which give information concerning the chemical potential of a mixture, including its dependence on temperature, pressure (or density) and, most important, composition *).

A quantitative understanding of fluid mixtures is important not only for chemistry but also for biology (including medicine) and for geology (including meteorology). Since our animate and inanimate world abounds with mixtures, those who would understand the world must include a study of mixtures in their program of comprehension.

But in addition to its intellectual position, a study of mixtures is a necessity for those who make useful products from the raw materials that nature provides, especially for those who do so on a large scale: engineers, in particular, chemical engineers, who use air, petroleum, minerals, agricultural produce, sea water, coal, etc. etc. to make gasoline, paints, soaps, automobile tires, pesticides, plastics, fibers, and so on, including aspirin, cortisone and hundreds of other life-sustaining pharmaceuticals. A study of mixtures

*) We omit here dependence on time; we confine our discussion to equilibrium properties.

is essential for economic reasons because nature's raw materials are inevitably mixtures; if chemical products are to be made, it is necessary first, to separate from a naturally-occurring mixture those parts (components) that are the desired reactants for the proposed chemical reaction and second, once the proposed reaction is achieved, to separate from the reacted mixture those products that are desired from those that are not (side products) and from the reactants that have failed to react. (Chemical reactions often fail to achieve 100% completion.) Economic separation of liquid mixtures for large-scale production is most often achieved by distillation or extraction, although other methods (notably chromatography) are becoming important.

The brief discussion below concerns recent progress in our understanding of complex fluid mixtures; in this context, a complex mixture is one where either

1. the molecules are significantly asymmetric in their geometric or electronic structure, as found for example in aqueous mixtures of nonelectrolytes (hydrogen bonding, dipole moments) or in mixtures containing alcohols, nitriles, carboxylic acids, etc.

or

2. the number of components in the mixture is so large, that ordinary chemical analysis cannot be used to obtain a complete quantitative or even qualitative analysis of the mixture. Examples are provided by heavy petroleum, coaldersived liquids (tars) and vegetable oils. For such mixtures, it is often not possible to identify all of the molecular types that are present or to measure their concentrations.

It is not possible here to discuss complex mixtures in sufficient detail for engineering applications; details can be obtained by the interested reader upon writing to the author *). The discussion here is confined to an exposition of some new ideas which have already found a few applications and which are now under active development.

Mixtures of Asymmetric (Especially Polar) Molecules: Semi Empirical Mean Field Theory

Since we are interested in vapor-liquid and liquid-liquid equilibria (VLE and LLE) for mixtures that may contain one or more supercritical components, we do not use the activity-coefficient concept because, unfortunately, that concept requires standard-state fugacities which, in the liquid phase, create numerous difficulties, especially for ternary and higher mixtures. Instead,

*) Gilman Hall, University of California, Berkeley, CA 94720, USA

we use fugacity coefficients ϕ_i . If we designate two phases at equilibrium by ' and " respectively, then for every component i the equilibrium condition is

$$p_i' = \phi_i p_i'' \quad (1)$$

or

$$(\phi_i; x_i)' = (\phi_i; x_i)'' \quad (1a)$$

where x_i is the mole fraction.

Fugacity coefficient ϕ_i is obtained from chemical potential μ_i , and that, in turn, is obtained from Helmholtz energy A (for the mixture) according to

$$\left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_j} = \mu_i \quad (2)$$

where n_i is the number of moles of component i . The differentiation in Equation (2) is performed at constant temperature T , constant total volume V and constant mole number n_j ($j \neq i$).

We divide A into two contributions: the first holds only for a mixture of ideal gases and the second gives the contribution from intermolecular forces. The second is called the residual contribution designated by superscript r .

The ideal-gas contribution is well known as a function of T , V and x_i .

The residual Helmholtz energy (per mole of mixture), designated by a^r , is given by

$$a^r = a^{ref} + a^{pert} \quad (3)$$

where ref designates a well-characterized reference system and $pert$ designates a perturbation. For the reference system we use a mixture of hard spheres. For that system, we calculate a^{ref} using Percus-Yevick theory as given by the equation of Carnahan and Starling, extended to mixtures as described by Boublik and Mansoori. This equation gives us a^{ref} as a function of molar density $\rho = \frac{n_T}{V}$ [where n_T is the total number of moles] as well as

temperature T and mole fraction x_i . The molecular parameters required are molecular diameters σ_i , for every component i .

For the perturbation we use an expression of the van der Waals form

$$a^{pert} = \frac{a}{RT} \quad (4)$$

where, however, "constant" a depends not only on composition and temperature (as in previous discussions) but also weakly on density. It is this density dependence which provides a crucial improvement in representation of mixture properties because, as shown below, it enables us to separate the composition dependence of a at low densities from that at high densities.

For a pure fluid, we use an exponential decay function for a to give the density dependence such that at constant temperature

$$a \rightarrow r a^{(0)} \text{ as } Q \rightarrow 0 \quad (5a)$$

$$a \text{ (asymptotically)} \rightarrow a^{(1)} \text{ as } Q \rightarrow \infty \quad (5b)$$

The details of the decay function are not of importance for our purposes. We use a universal function such that the average of $a^{(0)}$ and $a^{(1)}$ is attained near the critical density.

For a pure fluid, for a given temperature, we require three constants; these are b ($b = 2/3 n^{NAV} a^3$ where NAV is Avogadro's number) and $a^{(0)}$ and $a^{(1)}$. We obtain $a^{(1)}$ primarily from experimental second-virial-coefficient data because the second virial coefficient B is given by

$$B = b - a / RT \quad (6)$$

where R is the gas constant.

We obtain b and $a^{(1)}$ from experimental data for liquid densities and vapor pressures or, for supercritical components, from data for high-pressure densities and fugacities. We find that, typically, $a^{(1)}$ is about 10 or 20% lower than am .

The composition dependence for am is uniquely fixed by molecular physics: it must be quadratic in mole fraction x . In general

$$a^{(0)} = \sum_i \sum_j x_i x_j a_{ij} \quad (7a)$$

or, for a binary mixture,

$$a^{(0)} = x_1^2 a_{11} + x_2^2 a_{22} + 2 x_1 x_2 (a_{12})^{1/2} (1 - k_{12}) \quad (7b)$$

where x refers to the mole fraction in the vapor phase and where adjustable binary parameter k_{12} is determined from experimental second-virial-coefficient data (B_{12}).

For complex mixtures, molecular physics tells us little about the composition dependence of $a^{(1)}$. However, experience tells us that for such mixtures a quadratic composition dependence (such as Equations 7a and 7b) is too simple. We therefore adopt the next highest approximation, viz. a cubic relation which, for a binary mixture, has the form

$$a^{(1)} = x_1^3 a_{111} + x_2^3 a_{222} + 3 v_{112} x_1^2 x_2 + 3 v_{122} x_1 x_2^2 \quad (8)$$

where x now refers to the mole fraction in the liquid phase.

At a fixed temperature, we obtain adjustable binary parameter v_{112} from experimental (VLE or LLE) data near $x_2 = 0$ and v_{122} from similar data near $x_2 = 1$, where x refers to the liquid phase. (If component 2 is supercritical, we never reach the state $x_2 = 1$. In that event we obtain v_{122} from experimental data where x_2 is large, i. e. as large as experimental data provide.)

We find that the methods described above give a good representation of experimental VLE and LLE data for a variety of strongly nonideal binary mixtures, including high-pressure aqueous mixtures of polar and nonpolar electrolytes, provided that all molecules are not very large. (For mixtures containing very large molecules we have developed an alternate mixture theory, based on a variation of Flory-Huggins theory, employing one binary entropic and one binary enthalpic parameter. It works well for concentrated aqueous mixtures of "nasty" solutes such as polyethylene glycol.)

As expected, the method outlined above is not accurate in the critical region. Our method is only an extension of the much-studied mean-field theory of fluids which is known to be inadequate at conditions close to critical. However, exploratory work suggests that our extension can be useful remarkably close to the critical point (although not at the exact critical point) by introducing into our expression for a' corrections arising from fluctuations in density and composition. We do not elaborate on this here but merely indicate that, for engineering applications, the use of such corrections may be more promising than the switching-function method which uses an interpolation between the mean-field theory (applicable remote from critical conditions) and the scaled non-analytic theory (applicable at the critical point).

The mean-field theory given above is also useful for those binary mixtures where the molecular size ratio is well removed from unity. Good fits of experimental data were obtained for such asymmetric mixtures as n-hexane / hydrogen and n-decane / methane; for these binaries, the size ratio is about 8, i. e. $a_1/r_2 = 2$. For these systems, good agreement follows primarily from using the Boublik-Mansoori form of the Carnahan-Starling equation. One-fluid van der Waals theory is not applicable to such asymmetric mixtures, especially in the dilute region, as shown by computer-simulation calculations of Shing and Gubbins.

Generalization of Equation (8) to a ternary system requires one ternary parameter while generalization to a quaternary system requires three ternary parameters but no quaternary parameter.

Early calculations indicate that for ternary VLE, satisfactory results are often obtained upon using a reasonable approximation for the ternary parameter based only on binary data. However, an adjustable ternary parameter is almost always required for ternary LLE wherein two binaries are completely miscible while the third exhibits only partial miscibility.

Mixtures Containing Very Many Components: Continuous Thermodynamics

If a mixture contains hundreds (or thousands) of components, ordinary chemical analysis cannot be used to identify all molecules and their concentrations. For such mixtures it has been customary to use the pseudocomponent concept wherein a mixture containing very many components is assumed to have thermodynamic properties very similar to those of a hypothetical mixture containing only a small number (perhaps 6 or 8) of fictitious components; these are called pseudocomponents. Properties of the highly multicomponent mixture are then obtained by estimating properties of the mixture of pseudocomponents, using standard procedures wherein pseudocomponents are treated as if they were real components. The key to success lies on proper identification of the pertinent pseudocomponents and their concentrations. Unfortunately, such identification is often arbitrary and, also unfortunate, some thermodynamic properties are sensitive to the details of that identification. The pseudo component concept, therefore, has serious deficiencies.

An alternate description is provided by considering the mixture to have an infinite number of components, that is, as a continuous mixture rather than as a mixture of a finite number of discrete components. The pertinent thermodynamics for such continuous mixtures, called continuous thermodynamics, was developed only recently. It is one of the few topics in chemical thermodynamics which was not foreseen by J.W. Gibbs.

In continuous thermodynamics, discrete mole fractions x_i are replaced by a continuous distribution function $F(I)$ where I is a continuous variable for characterizing the components in the mixture (e. g. normal boiling point or molecular weight). In general, distribution function F may depend on two or more independent continuous variables but, for our limited purposes here, we consider only one independent variable.

In a typical case, the continuous variable I ranges from some lower limit I_0 to infinity. The normalization condition

$$\int_{I_0}^{\infty} F(I) dI = 1 \quad (9)$$

corresponds to the discrete-thermodynamic condition

$$\sum x_i = 1 \quad (10)$$

It is also possible to use a semi-continuous description by allowing the concentrations of some identified components (typically those present in large concentrations) to be represented by discrete mole fractions while those of others are represented by a continuous distribution function. For example, suppose we have a homologous series such as normal paraffins beginning with methane and extending to high-molecular-weight polyethylene. We might decide to consider methane (1), ethane (2), propane (3) and butane (4) as discrete components and everything higher as continuous components. Suppose we use molecular weight for I . Noting that the molecular weight of butane is 58, the normalization condition becomes

$$\sum_{i=1}^4 x_i + \int_{58} f F(I) dI = 1 \quad (11)$$

In this case $F(I)$ would be such that $F(I)$ is zero when $I = 58$.

If two fluids phases ' and ' are at equilibrium, the equilibrium condition (Equation (1)) is now rewritten

$$u(I)' = u(I)'' \quad (1b)$$

or, in terms of fugacity coefficients,

$$[O(I) F(I)]' = [O(I) F(I)]'' \quad (1c)$$

For discrete components, chemical potentials (or fugacity coefficients) can be calculated from an equation of state using standard thermodynamics, as given in numerous text-books. Analogous relations have recently been established for continuous components provided that the equation-of-state parameters (so-called constants) are expressed as functions of I .

For a mixture of discrete components, the equation of state is of the form

$$P = f(T, V, n_j, x_1, x_2, \dots) \quad (12a)$$

where P is the pressure. For a continuous mixture, the equation of state is of the form

$$P = f(T, V, n_T, F(I)). \quad (12b)$$

In effect, to reduce Equation (12 b) to practice, it is necessary to express the pure-component constants in the equation of state as a function of/and, for the mixture, to write mixing rules in terms of $F(I)$ rather than in terms of x . For example, if we use a quadratic rule for van der Waals constant a , we have for the mixture of discrete components

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (7c)$$

where the summation is over all discrete components in the mixture.

But for a continuous mixture, van der Waals constant a is given by

$$a = \int F(I) \cdot F(I)^* dI I^* \quad (7 d)$$

where the integral is over all values of I present in the mixture.

Continuous thermodynamics has been applied to petroleum technology.

To represent the properties of a high-boiling oil, the perturbed-hard-chain equation of state was used. This equation contains three molecular constants for each molecular species. To use this equation of state, we require

- a characteristic potential energy designated by $e q/k$ where e is the largest (negative) potential energy between a pair of chain segments (where one segment comes from one molecule and the other from another molecule) and q is the external molecular surface area; k is Boltzmann's constant.

- a characteristic molecular size v^* representing the hardcore volume of one chain segment. (v^* is similar to u^3 where Q is the segment diameter.)

- a flexibility parameter c where $3c$ is the number of external degrees of freedom, that is, those degrees of freedom which are affected by density in the normal fluid range (barring unusually high densities where all degrees of freedom become external). For atoms (argon) or small molecules (methane), $c = 1$ but for more complex molecules, $c > 1$.

For a pure fluid, the equation of state is of the form

$$P^* = \int I T^* v^{*,c} l \quad (13)$$

where y is the volume per chain segment and where

$$P^* = \frac{eq}{kv^*} \quad \text{and} \quad T^* = \frac{eq}{ck}$$

The high-boiling oil is considered to be a mixture of three classes (or ensembles): paraffinic, naphthenic and aromatic.

Upon fitting to the equation of state experimental vapor-pressure and density data for a large number of hydrocarbons, the molecular constants were correlated as linear functions of $I =$ molecular weight:

$$e q i k = 1^{(1)} + m^{(1)} I \quad (14a)$$

$$v^* = 1^{(2)} + m^{(2)} I \quad (14b)$$

$$c = 1^{(3)} + m^{(3)} I \quad (14c)$$

To use $e q/k$ within the framework of continuous thermodynamics, three sets of constants $^{(1)}$, $^{(2)}$, $^{(3)}$ were obtained, one each for paraffinic, naphthenic and aromatic hydrocarbons. Similarly, to use v^* and c within the framework

of continuous thermodynamics, three sets of constants $j^{(2)}$, $m^{(2)}$ and $j^{(3)}$, $m^{(3)}$ were obtained.

To characterize the oil, experimental measurements are required to determine the relative amounts of paraffins, naphthenes and aromatics and, for each ensemble, the distribution of molecular weights. These experimental data, coupled with the correlated equation-of-state constants, give a good description of the heavy oil within the framework of continuous thermodynamics.

However, for practical applications in chemical process design, a molecular-thermodynamic description of the material of interest is not sufficient because, for design of separation equipment, it is necessary to perform flash calculations; these calculations combine thermodynamic relations (Equation 1 b) with material balances. This combination of relations produces a set of strongly nonlinear equations that can be solved only by iteration with a sophisticated computer program.

A flash calculation corresponds to the following situation: A fluid mixture of known composition at advanced pressure flows continuously into a chamber maintained at some fixed lower pressure. When the entering fluid experiences the lower pressure, some of the fluid evaporates from a liquid to a gaseous phase (that is, it flashes). A gaseous flow G and a liquid flow L leave the chamber so that no material accumulates in the chamber (steady-state operation). In an isothermal flash, both temperature and pressure of the chamber are specified.

The problem is to calculate the ratio G/L and to find the compositions of G and L .

Flash calculations constitute the first major step for designing large-scale separation equipment such as distillation columns.

To solve the equations that describe a realistic flash, analytical mathematics cannot be used. A numerical procedure has been developed using the method of Gaussian quadrature. Using this method and a powerful computer, it is now possible to make flash calculations for high-boiling oils using continuous thermodynamics and the perturbed-hard-chain equation of state. Similarly, it is now possible to make flash calculations for vegetable oils and for polydisperse polymer solutions.

For complex mixtures, the advantage of continuous thermodynamics follows from its independence of the pseudocomponent method, thereby avoiding arbitrary assignment of pseudocomponents.

Conclusion

Thanks to intensive efforts in molecular physics (especially in computer simulation), we now have a reasonable understanding of simple fluid mixtures, i. e. mixtures whose molecules are spherically symmetric in shape and electric charge; slowly we are beginning to understand somewhat more complicated mixtures where the molecules deviate slightly from spherical symmetry.

Knowledge is advancing quickly but we are still many years removed from an adequate understanding of complex mixtures, where complex is defined as early in this article. It is therefore necessary for application in chemical technology to devise semi-theoretical, phenomenological methods for describing complex mixtures quantitatively. Progress in that development requires contributions from classical and statistical thermodynamics, from molecular physics and physical chemistry and from an understanding of both engineering needs and experimental limitations.

It is not possible to obtain all desired mixture properties from experiment since the required effort would be hopelessly tedious and prohibitively expensive. It is also not as yet possible to calculate desired properties from first principles, even when the latest computers are available. It has become customary, therefore, to use a compromise, often called molecular thermodynamics, which follows from the American pragmatic tradition: to attain a practical goal, synthesize, interpolate, invent; do the best you can with whatever limited intellectual resources are available. The brief discussion given here illustrates that tradition as applied to the vast domain of complex fluid mixtures.