Article

Teaching Thermodynamics of Ideal Solutions: An Entropy-Based Approach To Help Students Better Understand and Appreciate the Subtleties of Solution Models

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ABSTRACT: The thermodynamic formalism of ideal solutions is developed in most of the textbooks postulating a form for the chemical potential of a generic component, which is adapted from the thermodynamics of ideal gas mixtures. From this basis, the rest of useful thermodynamic properties can be derived straightforwardly without further hypothesis. Although formally elegant, this approach to ideal solutions does not allow appreciation of subtle concepts embodied in the model such as requirements of molecular size and shape or the fact that equations that contain the universal gas constant (R) can be applied to describe liquid or solid solutions. As alternative, it is discussed here an approach centered on the behavior of the partial molar entropy of the component using the framework provided by the concept of accessible volume. It is shown that this way of presenting the topic allows a more natural flow and, particularly, analytical justification of all the hypothesis and ideas behind many fundamental solution models, including that of ideal solutions, with the extra advantage that it can almost entirely carried out from a macroscopic point of view.

KEYWORDS: *Upper-Division Undergraduate, Graduate Education/Research, Physical Chemistry, Chemical Engineering, Materials Science, Thermodynamics*

The ideal-solution model is a central concept in courses of physical chemistry and thermodynamics of chemistry, chemical engineering, and materials science curricula. The model paves the way for the understanding of the more complex behavior of real gas, liquid, or solid solutions. Many textbooks define ideal solutions as those single phase multicomponent mixtures for which the chemical potential (μ_i) has a specific form, adapted from the thermodynamics of ideal gas (ig) mixtures.[1−5] For the latter type of mixtures, it is found that

$$\mu_i^{ig} = G_i^{ig} + RT \ln y_i \qquad (1)$$

where G_i^{ig} represents the Gibbs free energy per mol of the pure i component in ideal gas state at pressure P and temperature T, y_i the molar fraction of i in the mixture, and R the gas constant. For mixtures in any state (gas, liquid, solid) that behave as ideal solutions (is), it is postulated that

$$\mu_i^{is} = G_i + RT \ln x_i \qquad (2)$$

where x_i now represents the mixture molar fraction and G_i the Gibbs free energy of the pure component in the physical state of the mixture, evaluated at P and T.[6]

Eq 2 is one of the cornerstones of ideal solution thermodynamics. This definition of ideal solution is also rather appealing from a formal point of view because of the property of G (and μ_i) as generating function effortlessly yields the rest of useful thermodynamic state functions without further hypothesis. Thus, by partial derivation or simple algebra, other partial molar properties such as entropy, volume, enthalpy, or internal energy ($\overline{S}_i^{is}$, $\overline{V}_i^{is}$, $\overline{H}_i^{is}$, $\overline{U}_i^{is}$) can be directly derived from eq 2 in terms of mixture composition and intensive (i.e., per mol) properties of the pure component (S_i,

V_i, H_i, U_i), yielding the full body of basic equations to develop the topic.[7]

However, we have noticed that this formal scheme based on postulating an expression for μ_i may be puzzling for most of the students. After years of teaching, we have indentified many reasons that (i) the concept of chemical potential may be at this point of the course somewhat elusive as the student is just starting to be familiar with it; (ii) the replacement of G_i^{ig} by G_i in eq 2, although perceived as intuitively reasonable, is actually introduced rather arbitrarily and without analytical demonstration; (iii) eq 2 contains the gas constant R while it is applied to liquid or solid mixtures, a clearly disrupting concept considering that students may not have knowledge on statistical mechanics to understand that R is actually a fundamental constant not only associated with ideal gases; (iv) despite the fact that some of the derivations of eq 2 provide a physical interpretation of the behavior of individual components in the solution in terms of energy or volume,[7] few textbooks emphasize the subtle but conceptually important physical meaning of the corresponding expression for $\overline{S}_i^{is}$ such as considerations on molecular size or shape associated with it.[8]

In the last years, we have been using a different approach to introduce the concept of ideal solution, centered on the behavior of function entropy. Instead of postulating a specific form for the chemical potential, we invest time in developing with some more detail the corresponding expression for $\overline{S}_i^{is}$. The advantage is that this development allows direct appreciation of several of the hypotheses that support several fundamental solution models. Another advantage is that the students are already familiar with the dependencies of S on natural variables P, T (or P, V), actually, much more that they

A

are with G (or μ_i). We have also pursued a macroscopic approach, avoiding the invocation of statistical thermodynamics to support concepts or equations, to fit the contents of our engineering curricula. In this article, we delineate how we present the concepts that lead to the ideal solution model under this new framework.

IDEAL GAS MIXTURES

We start by reminding the students that the differential equation that relates S with V and T for ideal gases is

$$dS^{ig} = C_v^{ig}\frac{dT}{T} + R\frac{dV}{V} \tag{3}$$

We then introduce the archetypical mixture of two ideal gas components at P, T that produce a solution at the same P, T, see Figure 1. Integration of eq 3 for the $i = 1$ component
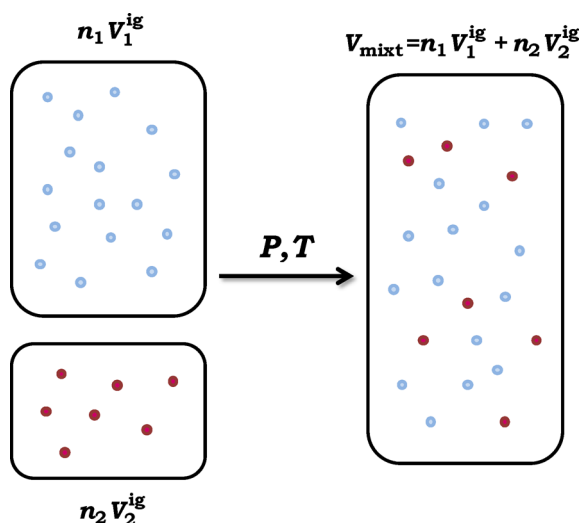

Figure 1. Schematics of a mixture of two ideal gases.

between the pure state at P, T and its state in the mixture at the same P, T implies that

$$\int_{pure}^{mixt} dS_1^{ig} = R\int_{pure}^{mixt}\frac{dV}{V} \tag{4}$$

Integration limits for the right-hand term should reflect the volumetric changes experienced by the component from its initial state at $n_1V_1^{ig}$ to the final volume of the mixture $n_1V_1^{ig} + n_2V_2^{ig}$, see Figure 1, which gives

$$\overline{S}_1^{ig} - S_1^{ig} = R\ln\frac{n_1V_1^{ig} + n_2V_2^{ig}}{n_1V_1^{ig}} \tag{5}$$

or

$$\overline{S}_1^{ig} = S_1^{ig} + R\ln\frac{n_1V_1^{ig} + n_2V_2^{ig}}{n_1V_1^{ig}} \tag{6}$$

where $\overline{S}_1^{ig}$ and S_1^{ig} are evaluated at the same P and T.

Since the volume of the reservoir for the mixture is larger than that containing any of the gases in the pure state, eq 5 predicts that $\overline{S}_i^{ig} > S_i^{ig}$. At this point, the student can certainly start to visualize that the increase in entropy perceived by the component in this mixing process at constant P and T is only due to the larger space accessible in the mixture compared with that in the pure state.[9,10] This macroscopic perspective of the

entropy in mixing processes along with the idea of accessible volume, revisited and emphasized in recent publications of this Journal,[10] becomes an essential concept here, as it will be discussed further.

ENTROPY AND ACCESIBLE VOLUME

The interpretation of the results of eqs 5 and 6 in terms of the concept of accessible volume is a key point in our attempt to describe entropy changes in mixing processes that involves phases other than ideal gases. As a first step, we should identify what would be this available or accessible volume in a real gas, liquid, or solid phase. It can be seen as the space available for translation of a single molecule while the positions of the others are fixed, a concept closely related with the so-called free volume in molecular theories of liquids.[11,12] Free volume is an elusive quantity, too complex to be fully addressed in introductory courses as it requires a detailed description of the phase at the molecular level. Despite its complexity, the students are able to rationalize it and recognize its direct connection with the volumetric behavior of pure components developed in early stages of a course of macroscopic thermodynamics.

In its simplest form, free volume is defined as the difference between the actual volume of the phase (n_iV_i), temperature- and pressure-dependent, and the volume occupied by the molecules themselves, not available for molecular translations.[12] We can define the accessible volume (V_i^{acc}) in similar fashion. The volume occupied by the molecules themselves is referred to as hard-core, close-packed, or excluded volume and can be seen as an structural parameter related for instance with the b parameter of the van der Waals equation.[12] Figure 2 shows this
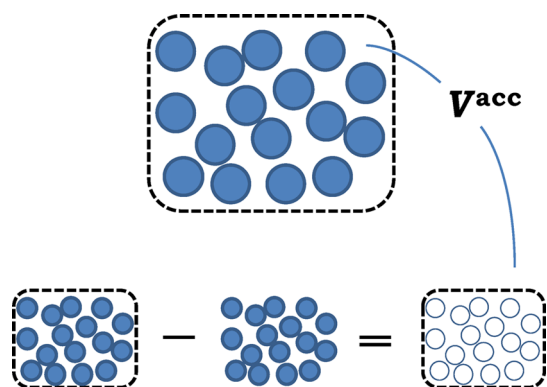

Figure 2. Schematics of the concept of available space or accessible volume (V^{acc}) in a pure component. It can be seen as the difference between the total volume of the phase and the volume occupied by the molecules themselves.

conceptualization, where we have envisioned our generic phase as composed by finite-sized entities, in opposition to the punctual, infinitesimally sized, ideal gases species. At this point, we will assume that species are rigid spheres and ignore details of their molecular structures to simplify the treatment. We can analyze some boundary conditions of this simple definition of V_i^{acc}. In the ideal gas-limit, the volume of the molecules themselves tends to zero, and the accessible volume is that of the whole reservoir, that is, $V_i^{acc} \to V_i$. At $T = 0$ K, considering that the phase is in the solid state, the available volume for molecular motions vanishes and $V_i^{acc} \to 0$.[13]

In the context of an introductory course, two important dependencies of V_i^{acc} need to be highlighted. One of them is its temperature (eventually pressure) dependency, embodied in that of V_i and related with the compressibility of the phase, as described by its corresponding state equation. Figure 3 shows that an increase in available space is directly connected with an decrease in phase density if we assume that core volumes are essentially rigid spheres.
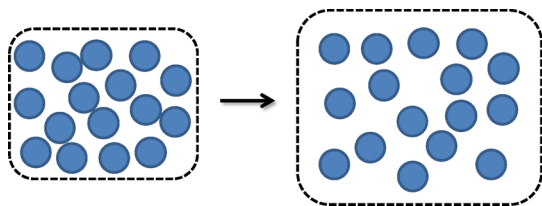

Figure 3. Connection between the increase in available space and the decrease in phase density.

The other one is the not so obvious molecular-size dependency. Figure 4 is presented to clarify the connection
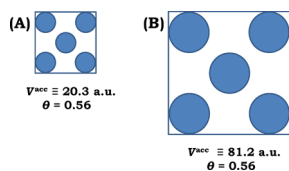

Figure 4. A 2-D representation to differentiate concepts of accessible volume (V^{acc}) and fraction of accessible volume (θ). (A) Circles have radii equal to unity, which implies that the square has a length side of 6 units; (B) the radii of the circles have been duplicated so the square side has a length of 12 units.

between molecular size and available space using a 2-D representation of packed spheres where the latter parameter is quantified in terms of areas. The array shows five circles representing chemical units surrounded by empty space. Notice that while molar volumes (V_i) are evidently different between examples A and B, circles representing chemical units are similarly packed so we may anticipate comparable density values in mass per unit volume for either A or B cases. In the first case, the circles have unity radii so the square has sides of 6 units in length. Calculation of the free or available space as square minus circles areas yields a value of 20.3 area units. Increasing the molecular size by duplicating the circles' radii yields a much larger amount of accessible space, equivalent to 81.2 area units.

We can characterize the amount of accessible volume in terms of another useful parameter, the fraction of available or accessible volume, θ, defined as the ratio between V_i^{acc} and V_i. The advantage of a description in terms of θ is that its value becomes under certain circumstances independent of molecular size. For instance, packing theories predict that objects of similar shape but different size, packed in a similar arrangement, yield equal fractions of free or accessible space. The concept is simply demonstrated in Figure 4, where θ values calculated as the ratio between free to total (square) areas is about 0.56 in both cases, despite the duplication in circle diameter. We then may expect that components with dissimilar size but comparable molecular shape and density can be described in terms of a common value of θ, despite the fact they contribute

to the eventual mixture with very different amounts of accessible volume. Notice that the boundary limits for θ are 0 for solids at $T = 0$ K ($V_i^{acc} \rightarrow 0$) and 1 for the ideal gas state ($V_i^{acc} \rightarrow V_i$).

■ PARTIAL MOLAR ENTROPY IN GENERIC MIXTURES

With these elements, we can rationalize the behavior of $\bar{S}_i$ in a generic homogeneous mixture carried out at constant P and T, as shown in Figure 5. A generic phase, either pure components
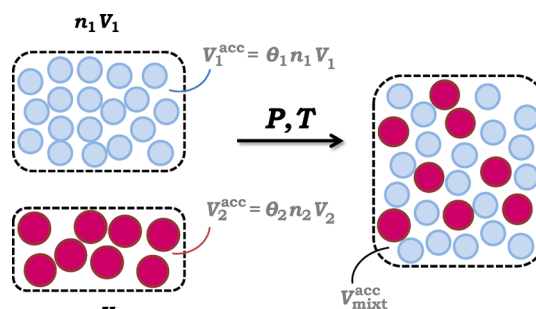

Figure 5. Schematics of a generic mixture.

or mixture, differentiates from ideal gases in two structural factors: the presence of molecular interactions and the above-addressed differences in the amount of accessible volume. At this point, we will assume that any change in intermolecular interactions when passing from pure component to mixture in our generic phase does not affect entropy. The thermodynamics of van der Waals fluids provides an adequate framework to reinforce this concept: we can remind the students that for a van der Waals pure fluid, changes in S at constant T do not depend on a, the intermolecular attraction parameter, and it happens because a is a temperature-independent parameter.[14] We then formalize our assumption by stating that any molecular interaction either in pure components or mixture is considered temperature- and composition-independent, so entropy does not depend on them. By applying this condition, we are actually ignoring subtle changes in the entropy of the mixture due to nonrandom distributions of species produced by molecular interactions, well described by models with a mechanical statistical basis.[11]

By leaving aside the problem of molecular interactions, we focus on how to integrate the concept of accessible volume to our calculations. We first recognize that the accessible volume in the mixture is larger than that of the component in the pure state and that these changes can be quantified with the elements developed in the previous section. Then, we assume that the increase in entropy of a given component in the generic mixture is quantitatively similar to that experienced by a component in an ideal gas mixture, if expressed in terms of the accessible volume. Once again, the thermodynamics of van der Waals pure fluids can be helpful to reinforce the concepts as it predicts that S at constant T only depends on the difference $V - b$, that is, the concept of accessible volume we are pursuing to develop here.[14] Therefore, $\bar{S}_i$ in our generic mixture can be described in terms of the eq 6 but considering variations in accessible volume between pure and solution states:

$$\bar{S}_1 = S_1 + R \ln \frac{V_{mixt}^{acc}}{\theta_1 n_1 V_1}$$

$$(7)$$

where the terms $\overline{S}_1$ and S_1 are now evaluated at the same P, T and at the physical state of the mixture, that is, real gas, liquid, or solid. Notice that the presence of terms evaluated at the state of the mixture, instead of as ideal gases, or the presence of the R constant, is a natural consequence of the extension of the concepts embodied in eqs 5 and 6 to generic mixtures. The calculation of accessible volume in the individual component has simply been performed in terms of θ_i, although that of the mixture (V_{mixt}^{acc}) requires some extra considerations about the solution that will be developed in the next section.

PARTIAL MOLAR ENTROPY IN SPECIFIC SOLUTION MODELS

The generic eq 7 can be further elaborated to describe the thermodynamics of a series of relevant solution models, including ideal solutions. To derive these expressions, we simply need to address the calculation of V_{mixt}^{acc} in eq 8. We start considering those mixtures that are additive in terms of volume, that is, $V_{mixt} = n_1V_2 + n_2V_2$. If we additionally assume that core volumes of individual components are also additive, it follows from the above conditions that accessible volumes are also additive, that is, $V_{mixt}^{acc} = V_1^{acc} + V_2^{acc} = \theta_1 n_1 V_1 + \theta_2 n_2 V_2$. Therefore, eq 7 can be rewritten as

$$\overline{S}_1 = S_1 + R \ln \frac{\theta_1 n_1 V_1 + \theta_2 n_2 V_2}{\theta_1 n_1 V_1} \tag{8}$$

Remarkably, eq 8 has also been derived from statistical mechanics arguments, and it has been proposed to describe the thermodynamics of athermal (zero mixing enthalpy) solutions of molecules with markedly different sizes, fractions of accessible volume, or phase density, but that follow the additive rule of volumes.[15] Entropy in mixtures of polymers with solvents or monomers chemically similar have been successfully described with this equation. However, other important types of mixtures that are not additive in terms of volumes, for instance, interstitial solutions in metallic alloys, do not fit to this description.

Additional considerations about molecular shape and size can simplify eq 8 even more. We may now consider that molecules of both components have a similar shape and mass density, but not necessarily similar size, for example, the situation shown in Figure 4. In those cases, although components may differ in amounts of accessible volume, their fractions can be considered similar ($\theta_1 = \theta_2$), and eq 8 reduces to

$$\overline{S}_1 = S_1 + R \ln \frac{n_1 V_1 + n_2 V_2}{n_1 V_1} \tag{9}$$

or

$$\overline{S}_1 = S_1 - R \ln \frac{n_1 V_1}{n_1 V_1 + n_2 V_2} \tag{10}$$

The argument of the natural logarithm is the volume fraction of the 1 component (Φ_1), so eq 10 can be rewritten generically for the i component as

$$\overline{S}_i = S_i - R \ln \Phi_i \tag{11}$$

Eq 11 is identical to the entropic form of the Flory−Huggins theory, widely used to describe polymer solutions and mixtures between molecules with dissimilar size. Strictly, it does describe molecular mixtures between species that provide similar fractions of accessible volume, that is, similar densities in mass per unit volume, a more stringent condition than that

embodied in eq 8. Besides its well-known application in polymer thermodynamics, eq 11 has served as a basis for several other model solutions widely used in several branches of chemical engineering.[16] In a strict way, it could be used for instance to describe mixtures between two hydrocarbons with different numbers of carbon atoms or two real gases with comparable critical properties.

If we now assume in eq 10 that molecular sizes are identical ($V_1 = V_2$), volume fractions reduce to molar fractions, thus yielding the equation that defines ideal solutions:

$$\overline{S}_i^{is} = S_i - R \ln x_i \tag{12}$$

In summary, the assumptions needed to obtain eq 12 from eq 6 have flown rather naturally: molecular interactions were assumed temperature- and composition-independent so entropy is only dictated by changes in accessible volume, in a similar fashion to that of ideal gas mixtures; molecular size and shape of species are assumed to be comparable to yield expressions that contain the molar fraction of the mixture instead of individual accessible volume contributions. The description of ideal solutions can be completed in the traditional fashion, assuming that when components are mixed, each of them is subjected to the same molecular interactions that are in the pure state, that is, the condition $\overline{H}_i^{is} = H_i$ holds. The additive rule in terms of volume, $V_{mixt}^{is} = n_1V_1 + n_2V_2$, leads to $\overline{V}_i^{is} = V_i$, whereas the combination of the two above conditions yields $\overline{U}_i^{is} = U_i$. Eq 12, along with the condition $\overline{H}_i^{is} = H_i$ and the relationship $\mu_i^{is} = \overline{H}_i^{is} - T\overline{S}_i^{is}$, finally yields eq 2, thus completing the full body of equations used to describe ideal-solution thermodynamics.

APPLICATION EXAMPLES

The examples presented are used to highlight the conceptual differences between eqs 8, 11, and 12 in several contexts. The first example proposes the calculation of the total change of entropy of mixing ($\Delta S^{MIX,TOT}$) involved in the formation of the three liquid solutions described in Figure 6. It is assumed that
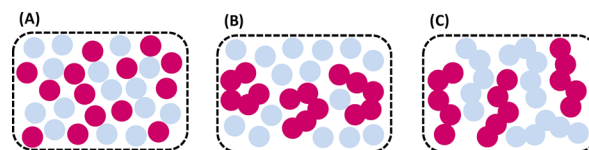
Figure 6. Binary solutions of: (A) 15 red species and 15 blue species with similar size; (B) 15 blue small species and three 5-sphere chains of red species; (C) three blue 5-sphere chains with three red 5-sphere chains.

we start from pure components that mix at constant P and T. Figure 6, panel A, corresponds to a solution formed by 15 blue and 15 red species, small molecules of the same size. Figure 6, panel B, shows a solution formed by 15 blue species with three red larger molecules, with a length equivalent to 5 spheres. The third case, Figure 6, panel C, shows a solution of three red and three blue species, both 5 spheres long.

Expressions for $\Delta S^{MIX,TOT} = \Sigma\, n_i(\overline{S}_i - S_i)$ can be derived from the respective solution model used for $\overline{S}_i$. From eq 11, we can write

$$\Delta S^{MIX,TOT} = -R(n_{red} \ln \Phi_{red} + n_{blue} \ln \Phi_{blue}) \tag{13}$$

whereas eq 12 gives

$$\Delta S^{\mathrm{MIX,TOT}} = - R(n_{\mathrm{red}} \ln x_{\mathrm{red}} + n_{\mathrm{blue}} \ln x_{\mathrm{blue}}) \quad (14)$$

In the calculations, we assume that molar volumes for the 5-sphere length molecules are five-times that of the single-sphere molecules. Case A corresponds to a random mixture of molecules with similar size, so we should use eq 14, corresponding to ideal solutions, for the calculation. Eq 13 should yield the same results as the condition $V_{\mathrm{red}} = V_{\mathrm{blue}}$ holds. Case B can be approached via eq 13 since red molecules differ markedly in size from those blue. To use eq 13, we consider that $V_{\mathrm{red}}/V_{\mathrm{blue}} = 5$. Case C can be indistinctly solved via eq 13 or 14 as molecules are actually large, but they have similar sizes. Table 1 summarizes the results obtained.

Table 1. Change in the Total Entropy by Mixing for the Three Situations Shown in Figure 6[a]

Mixture	$n_{\mathrm{red}} N_A$	$n_{\mathrm{blue}} N_A$	x_{red}	Φ_{red}	$\Delta S^{\mathrm{MIX,TOT}} N_A/R$
A	15	15	0.5	0.5	20.79
B	15	3	0.167	0.5	12.48
C	3	3	0.5	0.5	4.16

[a]N_A, Avogadro's number.

Results from Table 1 show that $\Delta S^{\mathrm{MIX,TOT}}$ decreases with the increase in molecular size of the species. Eventually, the students will be able to rationalize that this value approaches zero as molecular length increases, considering that very long molecules, such as polymers, are composed of hundreds of what we have idealized here as spheres, joined consecutively. We should also remark that for very long molecules, the driving force for mixing is dramatically reduced, and this explains why polymers do not mix with each other unless they have specific attractive interactions.

The second example is the calculation of the solid–liquid equilibrium curves for a mixture of two chemically similar molecules, heptane (C_7H_{16}) and hexatriacontane ($C_{36}H_{74}$), but that differ in molecular size. We will assume that those molecules mutually excluded in the crystal state, that is, C_7H_{16} and $C_{36}H_{74}$ solids are immiscible. The solid–liquid phase diagram expected is that of eutectic type, where typically temperature versus liquid composition in equilibrium conditions are represented. The standard treatment of the solid–liquid equilibrium yields the equation that relates x_i and T as

$$\ln x_i = \frac{\Delta H_i^{\mathrm{m}}}{R}\left(\frac{1}{T_i^{\mathrm{m}}} - \frac{1}{T}\right) - \ln \gamma_i \quad (15)$$

where ΔH_i^{m} and T_i^{m} are the melting enthalpy and melting temperature of the pure i component and γ_i the Lewis-Randall activity coefficient of i in the liquid solution that corrects from deviations from ideal-solution behavior. Since the species are chemically similar, we neglect enthalpic effects and assume that any deviation from ideality is entirely ascribed to the entropic contribution. In this case, and because of the dissimilar molecular size between components, we can use as a first approach the Flory–Huggins model, eqs 11 and 13. Derivation of the corresponding expressions for γ_i can be found in several textbooks as[2,8,9]

$$\ln \gamma_i = \ln\left(\frac{\Phi_i}{x_i}\right) + 1 - \frac{\Phi_i}{x_i} \quad (16)$$

Eq 16 predicts that deviations from ideal solution behavior increases with the increase in molecular size dissimilarity, as Φ_i

departs from x_i. If i represents the larger molecule, $\Phi_i > x_i$ and $\ln \gamma_i < 0$, so eq 15 predicts, for a given equilibrium temperature, larger values of x_i than those obtained assuming ideal liquid solutions ($\ln \gamma_i = 0$).

Figure 7 shows solid–liquid equilibrium data (black circles) in the form of equilibrium temperature versus molar fraction of
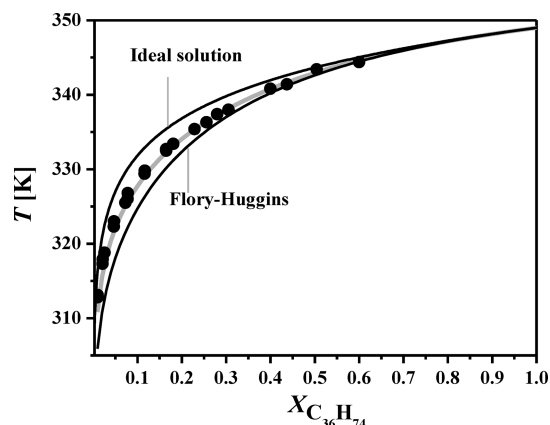
Figure 7. Solid–liquid equilibrium for the binary mixture C_7H_{16} and $C_{36}H_{74}$. Only the right branch of the eutectic-type diagram is shown, see text. Symbols represent experimental data taken from ref 17, whereas lines represent calculations performed with ideal solutions (upper black), Flory–Huggins (lower black), and a solution model that accounts for differences in fraction of accessible volume between components based on eq 18 (gray).

$C_{36}H_{74}$ in the liquid phase, in mixtures with C_7H_{16}, as taken from ref 17. Notice that only one branch of the phase diagram is shown, that on the right-hand of the eutectic point, corresponding to the solubility curve of the $C_{36}H_{74}$ component. The left-hand branch in this system occurs at very low mole fraction of $C_{36}H_{74}$ (less than 0.005) and at a lower temperature, as C_7H_{16} has a low melting point (183 K). Primary data necessary for the calculations of the equilibrium curve are ΔH^{m} and T^{m} of pure $C_{36}H_{74}$, 129.16 kJ/mol and 349 K, respectively.[17,18] Molar volumes in the liquid state for C_7H_{16} and $C_{36}H_{74}$ were taken as 147.5 and 620.20 cm^3/mol and assumed temperature-invariant.[17] Densities calculated from molar volumes are 0.678 g/cm^3 for C_7H_{16} and 0.816 g/cm^3 for $C_{36}H_{74}$. Figure 7 shows the predicted solid–liquid equilibrium curve (upper black line) calculated assuming ideal liquid solutions ($\gamma_i = 1$; $\ln \gamma_i = 0$). It can be seen that the ideal solution model underestimates solubility when compared with the experimental evidence. Flory–Huggins-type behavior (lower black line), calculated via eqs 15 and 16, correctly predict a right-shift of the equilibrium curve toward higher values of molar fraction of the larger molecule. However, the model overcorrects nonideality, yielding similar departures from experimental data to those computed from ideal solutions.

Looking for a reason for the failure of the Flory–Huggins model, we should revise the basis for the validity of eq 11: in its derivation, it was assumed that components had similar density and accessible volume fractions. Examination of density data indicates that some of these conditions may not be met. C_7H_{16} is actually rather less dense than $C_{36}H_{74}$, despite their similar chemical structures, which may lead to differences in fractions of accessible volume. To confirm this hypothesis, we need the support of some calculations. On the basis of the method of group contributions proposed by Bondi (refs 12 and 19), hard-

core volumes for C_7H_{16} and $C_{36}H_{74}$ can be readily estimated: 94.2 cm³/mol and 450 cm³/mol, respectively. Accessible volumes can be obtained by subtracting the hard-core volume from the actual molar volume of liquid phase, which yields 53.3 cm³/mol for C_7H_{16} and 170.2 cm³/mol for $C_{36}H_{74}$. Fractions of accessible volume (θ_i) can then be calculated: 0.36 for C_7H_{16} and 0.27 for $C_{36}H_{74}$. Clearly, the assumption of similar fractions of accessible volumes between components does not strictly meet in this liquid solution.

To incorporate those differences in θ_i in our calculations, we need to resort to the more rigorous eq 8, which can be rewritten as

$$\overline{S}_1 = S_1 - R \ln \frac{\theta_1 n_1 V_1}{\theta_1 n_1 V_1 + \theta_2 n_2 V_2} \tag{17}$$

The argument of the natural logarithm can be simply seen as a fraction of accessible volume of component 1 in the mixture (Φ_1^{acc}), so for the i component, eq 17 leads to

$$\overline{S}_i = S_i - R \ln \Phi_i^{acc} \tag{18}$$

Eq 18 has the same form as eq 11, except for the different meanings of Φ_i^{acc} and Φ_i. The corresponding expression for γ_i is identical to eq 16, but expressed in terms of Φ_i^{acc}.[15] Calculations based on eq 18 yield the gray solid line in Figure 7, in much better agreement with the experimental data: the smaller θ_i value of $C_{36}H_{74}$ counterbalances its larger V_i, see eq 17, thus predicting Φ_i^{acc} values that lie between Φ_i (Flory−Huggins) and x_i (ideal solutions). The example highlights the subtle molecular aspects that we need to consider for correctly predicting solution behavior.

CONCLUSIONS

It has been shown that an approach based on the behavior of $\overline{S}_i$ allows a logical flow of the several hypotheses that built up the thermodynamics of several fundamentals solution models. In the context of ideal solutions, the specific form used to describe $\overline{S}_i^{is}$ or the requirements of similar molecular shape and size between components, usually enunciated without demonstration,[1−5] arise naturally. We have found that the students are able to much better grasp subtle concepts behind the application of eqs 11, 12, or 18 that they usually lose in explanations entirely based on postulating a specific form for the chemical potential, developing at the same time a wider perspective of the topic. Another major advantage of this approach is that it is mostly macroscopic, which avoids the development of concepts of statistical mechanics, absent in our engineering curricula. For instance, derivations of expressions such as eq 11 or 18 provide a valuable connection with the Flory−Huggins theory of thermodynamics of polymer mixtures, particularly useful in materials science programs, and as a general framework to deeply understand the behavior of real mixtures between molecules with dissimilar size or shape.

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Notes

The authors declare no competing financial interest.

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(7) $\overline{S}_i^{is} = -(\partial \mu_i^{is}/\partial T)|_{P,xi} = -(\partial G_i/\partial T)|_P - R \ln x_i = S_i - R \ln x_i$. Similarly, $\overline{V}_i^{is} = -(\partial \mu_i^{is}/\partial P)|_{T,xi} = (\partial G_i/\partial P)|_T = V_i$. Finally, $\overline{H}_i^{is} = \mu_i^{is} + T\overline{S}_i^{is} = G_i + TS_i = H_i$ and that $\overline{U}_i^{is} = \overline{H}_i^{is} - P\overline{V}_i^{is} = H_i - PV_i = U_i$.

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(13) In the conceptualization shown by Figure 2, at 0 K, when species are firmly packed in contact, there may be some empty space between them. However, that volume is not available for molecular motions, so it does not contribute to entropy. This explains why the excluded volume is actually larger that the so-called van der Waals volume, on average, by about 1.2 times, see ref 19.

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