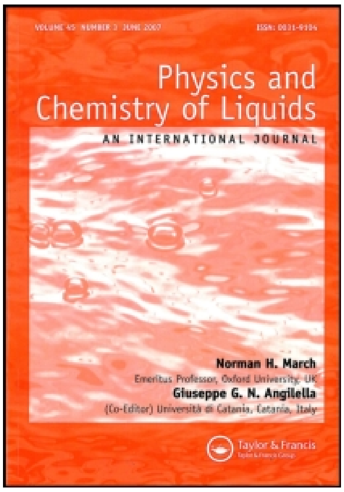

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Solubility and Enhanced Tension of Solute in Solution

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Solubility and Enhanced Tension of Solute in Solution

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In solution, solute molecules B are coupled by attractive forces between them and all other molecules present; and these other molecules enhance the tension in the coupling force between solute molecules an amount π_B, the osmotic pressure of the solution solute. Two equilibria determine the n_B^0 moles of pure solute which dissolve in n_A^{l0} moles of pure liquid solvent. If at T the solute is solid and in excess, then 1) the n_B^{lsat} moles of B in the n_A^l moles of A in a solution saturated with B are in thermodynamic equilibrium with the solid solute at the same T and p and 2) the n_B^{lsat} moles of B and n_A^l moles of A may also be in chemical equilibrium with the moles of new molecular or ionic species formed in the solution. Solute molecules dissolve until the chemical potential of the solution solute, $p_B^l(T, p, x_B^{lsat})$, equals the chemical potential of pure solid solute at the same T and p, $\mu_B^{so}(T, p)$. When the solution is saturated with B and the mole fraction of B is $x_B^{lsat} = n_B^{lsat}/\sum_j n_j^l$, then the vapor pressures of the solid solute at T and p, the solution solute at T and p, and the pure undercooled liquid solute at T and p-π_B^{sat} are identical. If at T the n_B^{l0} moles of pure solute and the n_A^l moles of pure solvent are liquids. then if molecules of B are allowed to dissolve in A while molecules of A are dissolved in B, the resulting solutions may 1) contain only molecules of A and B or 2) contain A and B which also react to form other ionic and molecular species. The two solutions may be identical or they may differ. In all cases, however, the mole ratio of $n_B^l n_A^l$ in both solutions must be identical.

INTRODUCTION

The intent of this article is to describe the ratio of solute to solvent in the solution (or solutions) formed from n_B^0 moles of pure substance B (solute) and n_A^0 moles of pure substance A (solvent). The novelty of the argument will be an absence of traditional terms such as ideal solution, fugacities and activities of solute and solvent. Instead, the altered states of the solute and solvent will be expressed as enhanced solute tension[1] and enhanced solvent tension.[2] This is an appropriate alternative to the usual treatment of solubility since it has been shown that the vapor pressure and other colligative properties and all partial molar quantities of the solute are altered by all molecules in the solution precisely as if tension in the coupling forces between solute molecules is enhanced by an amount equal to the osmotic pressure of the solute,[1] π_B. Likewise, it has been shown that the colligative properties and all partial molar quantities of the liquid solvent are altered precisely as if tension in the coupling forces between solvent molecules is enhanced by π_A, the osmotic pressure of the solvent in the solution.[2,3]

If only molecules of A and B are present in a liquid solution, then a purely thermodynamic argument is sufficient to establish the ratio of B to A in the solution, n_B^l/n_A^l, when they are in equilibrium with an excess of B; and $n_B^l/n_A^l = n_B^0/n_A^{l0}$, the ratio of the n_B^0 moles of pure solute which dissolve in the n_A^{l0} moles of pure liquid solvent. However, molecules of B and A may also react to form other ionic and molecular species in the solution. In this case molecules of B and A are in chemical equilibrium with their reaction products as well as in thermodynamic equilibrium with other phases of A and B present. Chemical and ionic reactions may profoundly increase n_B^0/n_A^{l0}. The solvent A or any other species present in the solution can affect n_B^l/n_A^l only to the extent that they couple molecules of B and enhance the tension between them.[1]

CHEMICAL POTENTIALS OF PURE SOLUTE SOLID, LIQUID AND GAS AT T AND APPLIED PRESSURE p

In this section we will review the classic thermodynamic properties of n_i^0 moles of pure species i. We shall designate species i as pure species B, the solute, although all statements about it will pertain also to pure species A, the solvent.

The molar Gibbs free energy or chemical potential of pure solute at T and applied pressure p is written $\mu_B^0(T, p)$ and it can be changed by changing T and p according to

$$d\mu_B^0 = -\bar{S}_B^0\, dT + \bar{V}_B^0\, dp, \tag{1}$$

where $\bar{S}_B^0$ and $\bar{V}_B^0$ are the molar entropy and molar volume of pure solute, respectively.

These molar quantities of pure solute, μ_B^0, $\bar{S}_B^0$ and $\bar{V}_B^0$, are complicated functions of T and p and they also depend on whether the pure solute is a solid, liquid or gas at T and p. We shall presume that pure solute means that all molecules of B are of one kind in all phases. We shall also presume that the molecules of B are monomers in all phases. Thus, the monomers of pure solid solute, pure liquid solute and pure gas solute are designated by the symbols $(\mathrm{B})_1^{so}$, $(\mathrm{B})_1^{lo}$ and $(\mathrm{B})_1^{go}$, respectively. Hereafter, however, we will delete the subscript 1 from the symbol. If the molecules of solute B cluster to form dimers, trimers and higher polymers, then the partial molar quantities and other thermodynamic properties of each polymer must be treated as if each polymer (B)n was a solution with all its other polymers.[4]

The chemical potential of pure solid solute is written $\mu_{\mathrm{B}}^{so}(T, p)$ and it changes with changing T and p applied to the solid solute as

$$\mathrm{d}\mu_{\mathrm{B}}^{so} = -\bar{S}_{\mathrm{B}}^{so}\,\mathrm{d}T + \bar{V}_{\mathrm{B}}^{so}\,\mathrm{d}p^{s}. \tag{2}$$

Likewise, the chemical potential of pure liquid solute is written $\mu_{\mathrm{B}}^{lo}(T, p)$ and it changes as

$$\mathrm{d}\mu_{\mathrm{B}}^{lo} = -\bar{S}_{\mathrm{B}}^{lo}\,\mathrm{d}T + \bar{V}_{\mathrm{B}}^{lo}\,\mathrm{d}p^{l}; \tag{3}$$

and the chemical potential of pure vapor solute is written $\mu_{\mathrm{B}}^{go}(T, p)$ and it changes as

$$\mathrm{d}\mu_{\mathrm{B}}^{go} = -\bar{S}_{\mathrm{B}}^{go}\,\mathrm{d}T + \bar{V}_{\mathrm{B}}^{go}\,\mathrm{d}p^{g} \tag{4}$$

when changing the temperature and pressure applied to the vapor.

The chemical potentials of pure solute solid, liquid and vapor are equal at only one temperature, T_{B}^{0}, when the applied pressure is its vapor pressure at T_{B}^{0}, $p_{\mathrm{B}}^{go}(T_{\mathrm{B}}^{0})$, i.e.

$$\mu_{\mathrm{B}}^{so}(T_{\mathrm{B}}^{0}, p_{\mathrm{B}}^{go}(T_{\mathrm{B}}^{0})) = \mu_{\mathrm{B}}^{lo}(T_{\mathrm{B}}^{0}, p_{\mathrm{B}}^{go}(T_{\mathrm{B}}^{0})) = \mu_{\mathrm{B}}^{go}(T_{\mathrm{B}}^{0}, p_{\mathrm{B}}^{go}(T_{\mathrm{B}}^{0})). \tag{5}$$

T_{B}^{0} is the triple point temperature; it is also the melting temperature of pure solid solute subject only to its vapor pressure at T_{B}^{0}. At all temperatures less than T_{B}^{0},

$$\mu_{\mathrm{B}}^{so}(T, p_{\mathrm{B}}^{go}) < \mu_{\mathrm{B}}^{lo}(T, p_{\mathrm{B}}^{go})$$

where p_{B}^{go} is the vapor pressure at T.

If the pure solute is solid at T and applied pressure p, it is below its melting temperature, $T_{\mathrm{B}_m}^{0}$, at p. Only at $T_{\mathrm{B}_m}^{0}$ is

$$\mu_{\mathrm{B}}^{so}(T_{\mathrm{B}_m}^{0}, p) = \mu_{\mathrm{B}}^{lo}(T_{\mathrm{B}_m}^{0}, p). \tag{6}$$

Of course, $T_{\mathrm{B}_m}^{0} = T_{\mathrm{B}}^{0}$ when $p = p_{\mathrm{B}}^{go}(T_{\mathrm{B}}^{0})$.

The chemical potential of pure solid solute is less than the chemical potential of pure liquid solute at the same T and p when $T < T_{\mathrm{B}m}^{0}$. As the temperature increases from T to $T_{\mathrm{B}m}^{0}$ at constant p, Eq. (2) for pure solid solute becomes

$$\mu_{\mathrm{B}}^{so}(T_{\mathrm{B}m}^{0}, p) - \mu_{\mathrm{B}}^{so}(T, p) = -\int_{T}^{T_{\mathrm{B}m}^{0}} \bar{S}_{\mathrm{B}}^{So}\,\mathrm{d}t. \tag{7}$$

Likewise, for pure liquid solute at constant p, Eq. (3) becomes

$$\mu_{\mathrm{B}}^{lo}(T^0_{\mathrm{B}m}, p) - \mu_{\mathrm{B}}^{lo}(T, p) = -\int_T^{T^0_{\mathrm{B}m}} \bar{S}_{\mathrm{B}}^{lo}\,\mathrm{d}T. \tag{8}$$

By subtracting Eq. (8) from Eq. (7) and noting Eq. (6), the chemical potentials of pure liquid B and pure solid B at the same T and p differ by

$$\mu_{\mathrm{B}}^{lo}(T, p) - \mu_{\mathrm{B}}^{so}(T, p) = \int_T^{T^0_{\mathrm{B}m}} (\bar{S}_{\mathrm{B}}^{lo} - \bar{S}_{\mathrm{B}}^{so})\,\mathrm{d}T. \tag{9}$$

The molecules of solute are less ordered in the liquid phase than in the solid phase so that the molar entropy of its pure liquid is greater than the molar entropy of pure solid at the same T and p. Thus, the molar entropy increases upon melting at T and constant p, i.e.

$$\Delta\bar{S}_{\mathrm{B}}^{lso} = (\bar{S}_{\mathrm{B}}^{lo} - \bar{S}_{\mathrm{B}}^{so}). \tag{10}$$

The molar entropy of melting is related to the molar enthalpy of melting at constant p. Enthalpy is defined as $H \equiv U + pV$; so that a change in enthalpy at constant p is $\Delta H = \Delta U + p\,\Delta V$, where ΔU is the change in the internal energy, U. From the First Law of Thermodynamics, adding an amount of heat at constant pressure, $\Delta Q|p$, changes the internal energy and the pressure-volume work an amount $\Delta Q|p = \Delta U + p\,\Delta V$ so that $\Delta Q|p = \Delta H|p$. From the Second Law of Thermodynamics, adding an amount of heat at constant pressure increases the entropy an amount $\Delta S|p = \Delta Q|p/T$. Thus, it follows that $\Delta S = \Delta H/T$ at constant p and Eq. (10) becomes

$$(\bar{S}_{\mathrm{B}}^{lo} - \bar{S}_{\mathrm{B}}^{so}) = \Delta\bar{H}_{\mathrm{B}}^{lso}/T \tag{11}$$

and Eq. (9) becomes

$$\mu_{\mathrm{B}}^{lo}(T, p) - \mu_{\mathrm{B}}^{so}(T, p) = \int_T^{T^0_{\mathrm{B}m}} \frac{\Delta\bar{H}_{\mathrm{B}}^{lso}}{T}\,\mathrm{d}T, \tag{12}$$

where $\Delta\bar{H}_{\mathrm{B}}^{lso}(T, p)$ is the enthalpy increase when melting one mole of pure solid solute at T and constant p. $\Delta\bar{H}_{\mathrm{B}}^{lso}(T, p)$ is a function of T and p, but it often approximates a constant over a narrow range of temperatures.

CHEMICAL POTENTIAL OF SOLUTE IN SOLUTION

At an applied pressure p and T the chemical potential of the solute dissolved in a liquid solvent is less than the chemical potential of pure liquid solute by an amount

$$\mu_{\mathrm{B}}^{l}(T, p, x_{\mathrm{B}}^{l}) - \mu_{\mathrm{B}}^{l\mathrm{o}}(T, p) = \int_{p}^{p-\pi_{\mathrm{B}}} \bar{V}_{\mathrm{B}}^{l\mathrm{o}}\, \mathrm{d}p, \tag{13}$$

where x_{B}^{l} is the mole fraction of solute and where π_{B} is the osmotic pressure of the solute in the solution. If at T a pressure p is applied to the liquid solution of B in A and a pressure $p - \pi_{\mathrm{B}}$ is applied to the pure liquid solute, then the chemical potentials are equal, i.e.

$$\mu_{\mathrm{B}}^{l}(T, p, x_{\mathrm{B}}^{l}) = \mu_{\mathrm{B}}^{l\mathrm{o}}(T, p - \pi_{\mathrm{B}}). \tag{14}$$

In general, for any partial molar property of B in the solution, it was shown[1]

$$\bar{Z}_{\mathrm{B}}^{l}(T, p, x_{\mathrm{B}}^{l}) = \bar{Z}_{\mathrm{B}}^{l\mathrm{o}}(T, p - \pi_{\mathrm{B}}). \tag{14a}$$

The solute in the solution at T and p may be in equilibrium with solute in other phases at T and p. In this article we are considering two cases. In one case T is less than $T_{\mathrm{B}m}^{0}$; thus, pure solute is a stable solid whereas pure liquid solute is undercooled and metastable at T. In the other case, T is greater than $T_{\mathrm{B}m}^{0}$. In both cases $T > T_{\mathrm{A}m}^{0}$. In both cases the solute may also be in equilibrium with reaction products formed from the solute and solvent.

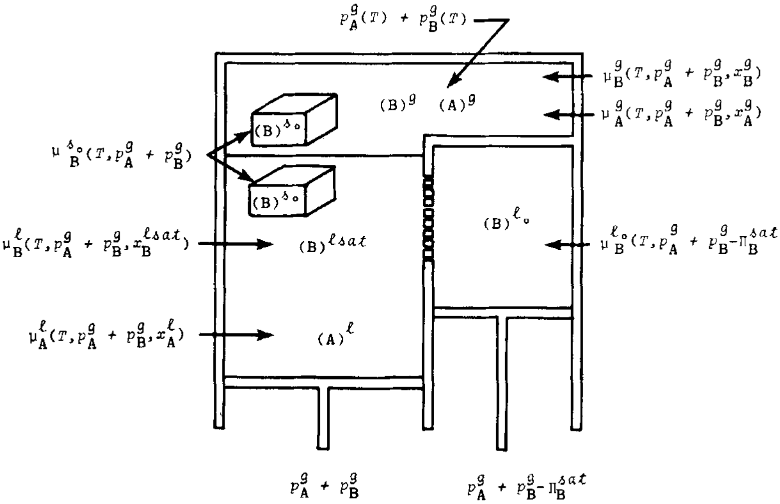

FIGURE 1 A closed system of liquid solvent A and excess solid solvent B at constant T illustrating equal chemical potentials of solute B in all phases. That is,

$$\begin{aligned}\mu_{\mathrm{B}}^{s\mathrm{o}}(T, p_{\mathrm{A}}^{g}(T) + p_{\mathrm{B}}^{g}(T)) &= \mu_{\mathrm{B}}^{g}(T, p_{\mathrm{A}}^{g}(T) + p_{\mathrm{B}}^{g}(T)) \\ &= \mu_{\mathrm{B}}^{l}(T, p_{\mathrm{A}}^{g}(T) + p_{\mathrm{B}}^{g}(T), x_{\mathrm{B}}^{lsat}) \\ &= \mu_{\mathrm{B}}^{l\mathrm{o}}(T, p_{\mathrm{A}}^{g}(T) + p_{\mathrm{B}}^{g}(T) - \pi_{\mathrm{B}}^{sat})\end{aligned}$$

Note that pure liquid solute at T is in a metastable state, i.e. supercooled, and that it is separated from the solution solute by a rigid membrane permeable only to solute molecules.

SATURATED SOLUBILITY OF SOLID SOLUTE IN LIQUID SOLVENT

Figure 1 illustrates an equilibrium between three phases of B; pure solid solute, $(\mathrm{B})^{so}$; solute dissolved to saturation in the solution with $(\mathrm{A})^{l}$ in the left cylinder, $(\mathrm{B})^{lsat}$; pure liquid solute in the right cylinder, $(\mathrm{B})^{lo}$, and solute vapor above the solution, $(\mathrm{B})^{g}$. The pressure applied to the pure solid solute and to the solution is $p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g}$ and the pressure applied to the pure liquid solute is $p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g} - \pi_{\mathrm{B}}^{sat}$ in equilibrium with the saturated solution at T. $p_{\mathrm{A}}^{g}(T)$ is the partial vapor pressure of the solution solvent at T; $p_{\mathrm{B}}^{g}(T)$ is the partial vapor pressure of solution solute at T and is also the vapor vapor pressure of pure solid solute at T. π_{B}^{sat} is the osmotic pressure of the saturated solute in the solution.

The vapors of both A and B are in equilibrium with A and B in the solution. The chemical potentials of the solute in all phases are equal, that is

$$\mu_{\mathrm{B}}^{so}(T, p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g}) = \mu_{\mathrm{B}}^{l}(T, p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g}, x_{\mathrm{B}}^{lsat}) = \mu_{\mathrm{B}}^{lo}(T, p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g} - \pi_{\mathrm{B}}^{sat})$$

$$= \mu_{\mathrm{B}}^{g}(T, p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g}, x_{\mathrm{B}}^{g}). \tag{15}$$

This statement says that when n_{B}^{lsat} moles of solute have dissolved in n_{A}^{l} moles of liquid solvent, the chemical potentials of the three phases are equal at T and at the pressures indicated and where x_{B}^{lsat} is the mole fraction of B in the saturated solution.

According to Eq. (3), the chemical potential of the pure liquid solute in the right cylinder is less than its chemical potential at $p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g}$ and the same T by an amount

$$\mu_{\mathrm{B}}^{lo}(T, p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g} - \pi_{\mathrm{B}}^{sat}) - \mu_{\mathrm{B}}^{lo}(T, p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g}) = \int_{p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g}}^{p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g} - \pi_{\mathrm{B}}^{sat}} \bar{V}_{\mathrm{B}}^{lo}\,\mathrm{d}p. \tag{16}$$

According to Eq. (12), the chemical potential of pure solid solute is less than that of pure liquid solute at the same T and pressure by an amount

$$\mu_{\mathrm{B}}^{so}(T, p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g}) - \mu_{\mathrm{B}}^{lo}(T, p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g}) = -\int_{T}^{T_{\mathrm{B}m}^{0}} \frac{\Delta\bar{H}_{\mathrm{B}}^{LSo}}{T}\,\mathrm{d}T. \tag{12a}$$

Since $\mu_{\mathrm{B}}^{so}(T, p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g}) = \mu_{\mathrm{B}}^{lo}(T, p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g} - \pi_{\mathrm{B}}^{sat})$, Eq. (15), the left sides of Eqs (16) and (12a) are identical; and, as $p_{\mathrm{A}}^{g} + p_{\mathrm{B}}^{g}$ can be replaced by p, then

$$\int_{p}^{p - \pi_{\mathrm{B}}^{sat}} \bar{V}_{\mathrm{B}}^{lo}\,\mathrm{d}p = -\int_{T}^{T_{\mathrm{B}m}^{0}} \frac{\Delta\bar{H}_{\mathrm{B}}^{lso}}{T}\,\mathrm{d}T. \tag{17}$$

This is an exact thermodynamic statement and assumes only that the solvent does not dissolve in and alter the pure solid solute. It describes the saturated solution at T and p in terms of three physical properties of the pure solute, $\bar{V}_{\mathrm{B}}^{l\circ}(T,p)$, $\Delta\bar{H}_{\mathrm{B}}^{ls\circ}(T,p)$, $T_{\mathrm{B}m}^{0}$ and in terms of the osmotic pressure of the solution solute, π_{B}^{sat}. It is a complicated description since $\bar{V}_{\mathrm{B}}^{l\circ}$ and $\Delta\bar{H}_{\mathrm{B}}^{ls\circ}$ are complicated functions of T and p and since there is a complicated relationship between π_{B}^{sat} and the mole fraction of the solute in the saturated solution, x_{B}^{lsat}. The mole fraction of solute molecules B in the saturated solution is $x_{\mathrm{B}}^{lsat} = n_{\mathrm{B}}^{lsat}/\sum_{\mathrm{j}} n_{\mathrm{j}}^{l}$ where $\sum_{\mathrm{j}} n_{\mathrm{j}}^{l} = n_{\mathrm{A}}^{l} + n_{\mathrm{B}}^{lsat} + \cdots n_{\mathrm{N}}^{l}$. When molecules and ions other than A and B are formed from A and B in the solution, then the molar amount of these new species must be included in $\sum_{\mathrm{j}} n_{\mathrm{j}}^{l}$. Moreover, the moles of pure solute, $n_{\mathrm{B}}^{s\circ}$, which dissolved are n_{B}^{lsat} plus the moles of ionic and molecular species derived from molecules of B.

There is no simple exact relationship between π_{A}^{sat} and x_{B}^{lsat}. However, the solution solute differs from pure liquid solute under all circumstances exactly as if tension in the coupling force between solute molecules B in the solution is enhanced by π_{B}. This fact requires a mechanism which enhances the solute tension and which relates x_{B}^{l} to π_{B}. A relationship was derived[1] by recognizing that the thermal pressure exerted by the internal reflection of all molecules at the boundary of the solution is opposed by a tension τ_{B} in the coupling force between the molecules of solute. Each molecular species in the solution contributes to the thermal pressure in proportion to its molar concentration in the solution of volume V^{l}, i.e. in proportion to n_{j}^{l}/V^{l}, where the proportionality factor is RT. Thus, the total thermal pressure is $RT\sum_{\mathrm{j}} n_{\mathrm{j}}^{l}/V^{l}$. The coupling force between the molecules of each species must oppose the entire thermal pressure.[1] Thus, the tension in the solution solute B is the force exerted by all the molecules on a unit area of solution boundary divided by the fraction of the unit area consisting of solute molecules, $n_{\mathrm{B}}^{l}\bar{V}_{\mathrm{B}}^{l}/V^{l}$. That is,

$$\tau_{\mathrm{B}} = \frac{RT\sum_{\mathrm{j}} n_{\mathrm{j}}^{l}}{V^{l}} \div \frac{n_{\mathrm{B}}^{l}\bar{V}_{\mathrm{B}}^{l}}{V^{l}},$$

or

$$\tau_{\mathrm{B}} = \frac{RT}{x_{\mathrm{B}}^{l}\bar{V}_{\mathrm{B}}^{l}}. \tag{18}$$

For pure liquid solute $x_{\mathrm{B}}^{l\circ} = 1$ so that the internal tension between its molecules is $\tau_{\mathrm{B}}^{0} = RT/\bar{V}_{\mathrm{B}}^{l\circ}$. The osmotic pressure of the solution solute is the amount by which τ_{B} exceeds τ_{B}^{0}, namely

$$\pi_{\mathrm{B}} = \tau_{\mathrm{B}} - \tau_{\mathrm{B}}^{0} = RT\left(\frac{1}{x_{\mathrm{B}}^{l}\bar{V}_{\mathrm{B}}^{l}} - \frac{1}{\bar{V}_{\mathrm{B}}^{l\circ}}\right), \tag{19}$$

where $\bar{V}^{l}_{B}(T, p, x^{l}_{B})$ and $\bar{V}^{lo}_{B}(T, p)$ are the partial molar volume of the solution solute and the molar volume of pure solute at the same T and p. Since it was shown that $\bar{V}^{l}_{B}(T, p, x^{l}_{B}) = \bar{V}^{lo}_{B}(T, p - \pi_{B})$, Eq. (19) may be written

$$\pi_{B} = RT\left[\frac{1}{x^{l}_{B}\bar{V}^{lo}_{B}(T, p - \pi_{B})} - \frac{1}{\bar{V}^{lo}_{B}(T, p)}\right]. \qquad (19a)$$

If the pure liquid solute is only slightly compressible then

$$\pi_{B} = \frac{RT}{\bar{V}^{lo}_{B}}\left(\frac{1}{x^{l}_{B}} - 1\right). \qquad (19b)$$

Equations (19) and (19a) are exact relationships between π_{B} and x^{l}_{B} when all molecules in the solution are internally reflected and when they exert only a thermal force at the solution boundary where they change momentum as they are reflected.[5]

Equation (19a) describes the relationship between π^{sat}_{B} and x^{lsat}_{B} so that Eq. (17) describes the amount of the dissolved solute, n^{lsat}_{B}, with respect to the moles of solvent plus any other molecules or ions that may have formed in the solution. Clearly, the solubility of the solute is determined by the physical properties of the pure solute, namely, $\bar{V}^{lo}_{B}$, $\Delta\bar{H}^{lso}_{B}$, T_{Bm} and by the solution temperature T. When only molecules A and B are in the solution, the only role of the solvent is that it enhances the tension in the coupling forces between solute molecules by the amount π^{sat}_{B}. On the other hand, if other species are also formed, then the role of the solvent is two fold: 1) it reacts with solute molecules to form these other species and thereby increases the moles of solute entering the solution and 2) it contributes to the enhanced tension in the coupling force between solute molecules, π^{sat}_{B}.

SOLUTIONS OF LIQUID SOLUTE AND LIQUID SOLVENT

In this case both pure solute and pure solvent at applied pressure p are at a temperature T which exceeds their melting temperatures T^{0}_{Bm} and T^{0}_{Am}, respectively, so that both are liquids. Figure 2A illustrates n^{lo}_{A} moles of pure liquid solvent in equilibrium with its vapor at T and vapor pressure $p^{go}_{A}(T)$. Figure 2A also illustrates n^{lo}_{B} moles of pure liquid solute in equilibrium with its vapor at T and vapor pressure $p^{go}_{B}(T)$. The chemical potentials of the pure liquid solvent and pure liquid solute prior to removing the barrier are $\mu^{lo}_{A}(T, p^{go}_{A})$ and $\mu^{lo}_{B}(T, p^{go}_{B})$, respectively. At time $t = 0$, the barrier was removed so that the vapor of B began to dissolve in the liquid of A while the vapor of A began to dissolve in the liquid of B. In equilibrium at $t = \infty$, the vapor pressure of A decreased from $p^{go}_{A}(T)$ to a partial vapor pressure $p^{g}_{A}(T)$ as the vapor pressure of B decreased from $p^{go}_{B}(T)$ to a partial vapor pressure $p^{g}_{B}(T)$. Also when equilibrium was attained, the number of moles

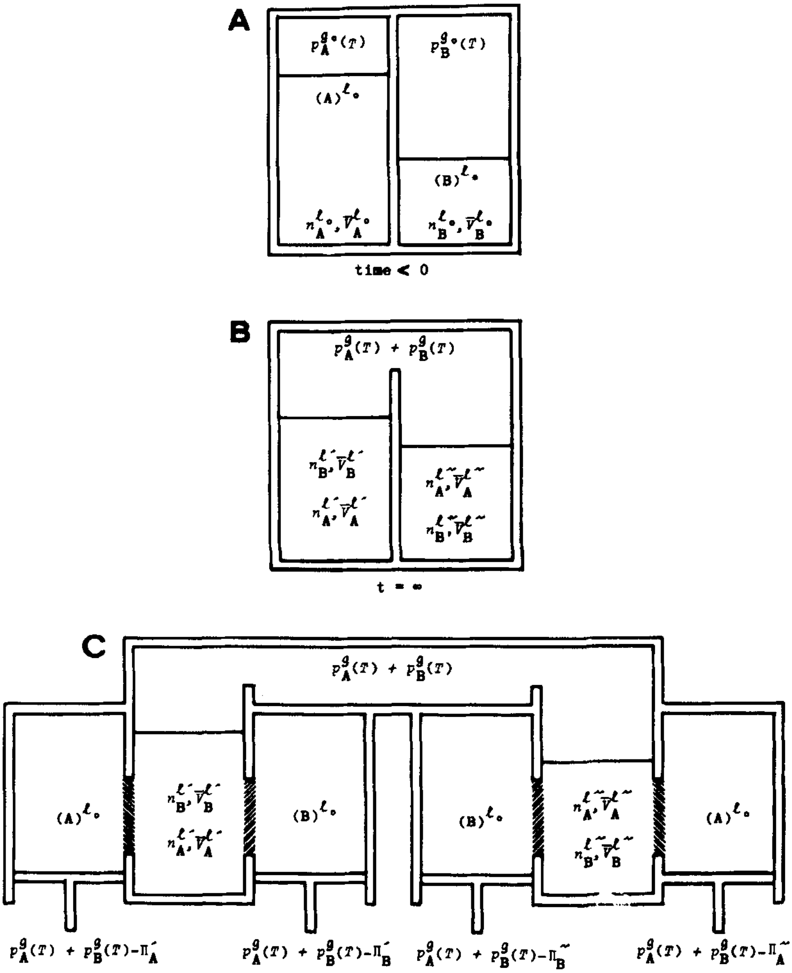

FIGURE 2 Closed systems of liquid solvent A and liquid solute B at constant T. A: pure solvent and pure solute before barrier separating them was removed. B: primary solution formed by vapor of B dissolving in liquid A (left) and secondary solution formed by vapor of A dissolving in B after barrier separating vapors was removed. C: the same primary and secondary solutions as in B are also in equilibrium with pure liquid $(A)^{l\circ}$ and pure liquid $(B)^{l\circ}$. Since the chemical potentials of the solvent in both solutions must be equal and the chemical potentials of the solute must be equal, it is shown in the text that $\pi'_A = \pi''_A$ and $\pi'_B = \pi''_B$. It is also shown that $n_B^{l'}/n_A^{l'} = n_B^{l''}/n_A^{l''}$. Note that a rigid membrane permeable only to molecules of A separates pure liquid A from the primary and secondary solutions and a rigid membrane permeable only to molecules of B separates pure liquid B from the primary and secondary solutions.

of solvent in the solution in the left compartment of Figure 2B decreased from $n_A^{l\circ}$ to $n_A^{l'}$ as the moles of solute increased from 0 to $n_B^{l'}$. This solution is arbitrarily designated the primary solution. At the same time, the moles of solvent dissolved in the secondary solution in the right compartment increased from 0 to $n_A^{l''}$ as the moles of solute decreased from $n_B^{l\circ}$ to $n_B^{l''}$. At T the combined pressures applied to both solutions is $p_A^g(T) + p_B^g(T)$. The chemical potential of the solvent in the primary solution decreased from $\mu_A^{l\circ}$ to $\mu_A^{l'}(T, p_A^g + p_B^g, x_A^{l'})$ and it became equal to the chemical potential of the solvent in the secondary solution, i.e.

$$\mu_A^{l'}(T, p_A^g + p_B^g, x_A^{l'}) = \mu_A^{l''}(T, p_A^g + p_B^g, x_A^{l''}); \qquad (20)$$

where $x_A^{l'}$ is the mole fraction of solvent in the primary solution and where $x_A^{l''}$ is its mole fraction in the secondary solution. Likewise, the chemical potential of the solute in the secondary solution decreased from $\mu_B^{l\circ}$ to $\mu_B^{l''}(T, p_A^g + p_B^g, x_B^{l''})$ and it became equal to the chemical potential of the solute in the primary solution, i.e.

$$\mu_B^{l''}(T, p_A^g + p_B^g, x_B^{l''}) = \mu_B^{l'}(T, p_A^g + p_B^g, x_B^{l'}). \qquad (20a)$$

Later in this section we will conclude that $x_A^{l'}$ must always equal $x_A^{l''}$ and $x_B^{l'} = x_B^{l''}$ not only when the primary and secondary solutions consist only of molecules of A and B but also when new ionic or molecular species are formed from A and B in the primary and secondary solutions.

The primary and secondary solutions in Figure 2B are illustrated again in Figure 2C where $n_B^{l'}$ moles of solute are dissolved in $n_A^{l'}$ moles of solvent on the left and where $n_A^{l''}$ moles of solvent are dissolved in $n_B^{l''}$ moles of the solute on the right. In addition, in Figure 2C, the solution on the left is shown to be in equilibrium with pure liquid solvent and with pure liquid solute. Of course, the pressure applied to the pure liquid solvent must be $p_A^g + p_B^g - \pi'_A$, and the pressure applied to the pure liquid solute must be $p_A^g + p_B^g - \pi'_B$, where π'_A is the osmotic pressure of the solvent in the primary solution and π'_B is the osmotic pressure of its solute. Likewise, the secondary solution on the right is shown to be in equilibrium with pure liquid solvent at T and applied pressure $p_A^g + p_B^g - \pi''_A$ and also in equilibrium with pure liquid solute at T and applied pressure $p_A^g + p_B^g - \pi''_B$, where π''_A and π''_B are the osmotic pressures of the solvent and solute in the secondary solution.

For the solvent of the primary solution, we may write that

$$\mu_A^{l'}(T, p_A^g + p_B^g, x_A^{l'}) - \mu_A^{l\circ}(T, p_A^g + p_B^g) = \int_{p_A^g + p_B^g}^{p_A^g + p_B^g - \pi'_A} \bar{V}_A^{l\circ}\, dp; \qquad (21)$$

and for its solute that

$$\mu_B^{l'}(T, p_A^g + p_B^g, x_B^{l'}) - \mu_B^{l\circ}(T, p_A^g + p_B^g) = \int_{p_A^g + p_B^g}^{p_A^g + p_B^g - \pi'_B} \bar{V}_B^{l\circ}\, dp; \qquad (22)$$

For the solvent of the secondary solution in Figure 2B and C, we may write that

$$\mu_A^{l''}(T, p_A^g + p_B^g, x_A^{l''}) - \mu_A^{l0}(T, p_A^g + p_B^g) = \int_{p_A^g + p_B^g}^{p_A^g + p_B^g - \pi_A''} \bar{V}_A^{l0}\,\mathrm{d}p; \tag{23}$$

and for its solute that

$$\mu_B^{l''}(T, p_A^g + p_B^g, x_B^{l''}) - \mu_B^{l0}(T, p_A^g + p_B^g) = \int_{p_A^g + p_B^g}^{p_A^g + p_B^g - \pi_B''} \bar{V}_B^{l0}\,\mathrm{d}p. \tag{24}$$

Of course, the applied pressure ($p_A^g + p^g$) in Eqs (20) through (24) may be replaced with any pressure p.

Subtracting Eq. (23) from Eq. (21) and noting Eq. (20), it follows that

$$\int_{p}^{p - \pi_A'} \bar{V}_A^{l0}\,\mathrm{d}p = \int_{p}^{p - \pi_A''} \bar{V}_A^{l}\,\mathrm{d}p. \tag{25}$$

Therefore, it follows that $\pi_A' = \pi_A''$. That is, the osmotic pressure of the solvent in the primary and secondary solutions must be the same. Subtracting Eq. (24) from Eq. (22) and noting Eq. (20a), it follows that

$$\int_{p}^{p - \pi_B'} \bar{V}_B^{l0}\,\mathrm{d}p = \int_{p}^{p - \pi_B''} \bar{V}_B^{l0}\,\mathrm{d}p. \tag{26}$$

and that $\pi_B' = \pi_B''$.

It has been shown[2] that solute dissolved in a solution alters the solution solvent exactly as if the tension in the coupling force between solvent molecules, τ_A, exceeds the tension in pure solvent, τ_A^0, at the same T and p by an amount π_A. Since $\pi_A' = \pi_A''$, it also follows that $\tau_A' = \tau_A''$. It was shown in the preceding section and elsewhere,[1] that the solvent in a solution alters the solute exactly as if the tension in the coupling force between solute molecules, τ_B, exceeds the tension in pure solute, τ_B^0, at the same T and p by an amount π_B. Therefore, since $\pi_B' = \pi_B''$, it follows that $\tau_B' = \tau_B''$. If the solute tensions in the primary and secondary solutions may be attributed entirely to the thermal pressure exerted by the solution molecules, then according to Eq. (18) it follows that

$$x_B^{l'} \bar{V}_B^{l'}(T, p, x_B^{l'}) = x_B^{l''} \bar{V}_B^{l''}(T, p, x_B^{l''}). \tag{27}$$

Since for any solution $\bar{V}_B^{l}(T, p, x_B^{l}) = \bar{V}_B^{l0}(T, p - \pi_B)$ and since $\pi_B' = \pi_B''$, so that $\bar{V}_B^{l0}(T, p - \pi_B') = \bar{V}_B^{l0}(T, p - \pi_B'')$, it follows also that $\bar{V}_B^{l'}(T, p, x_B^{l'}) = \bar{V}_B^{l''}(T, p, x_B^{l''})$ and Eq. (27) becomes

$$x_B^{l'} = x_B^{l''}. \tag{28}$$

By a similar argument, it also follows that at the same T and p,

$$x_{\mathrm{A}}^{l'}\bar{V}_{\mathrm{A}}^{l'}(T,p,x_{\mathrm{A}}^{l'}) = x_{\mathrm{A}}^{l''}\bar{V}_{\mathrm{A}}^{l''}(T,p,x_{\mathrm{A}}^{l''}) \tag{29}$$

and that

$$x_{\mathrm{A}}^{l'} = x_{\mathrm{A}}^{l''}. \tag{29a}$$

Therefore, for any solutions formed from solute B and solvent A, their mole ratios must also equal, i.e.

$$n_{\mathrm{B}}^{l'}/n_{\mathrm{A}}^{l'} = n_{\mathrm{B}}^{l''}/n_{\mathrm{A}}^{l''}. \tag{30}$$

Equation (30) does not necessarily require that both solutions be identical. If they are, the two constituents are miscible i.e. can mix with any ratio. If they are not identical, then the two liquids A and B are only partially miscible. These cases will be considered separately.

PRIMARY AND SECONDARY SOLUTIONS IDENTICAL AND CONSISTING ONLY OF A AND B

When n_{B}^{lo} and n_{A}^{lo} moles of pure liquid solute B and solvent A are allowed to mix, if no molecules of B were changed as they dissolved in A and no molecules of A were changed by B then

$$n_{\mathrm{A}}^{l'} + n_{\mathrm{A}}^{g} + n_{\mathrm{A}}^{l''} = n_{\mathrm{A}}^{lo} + n_{\mathrm{A}}^{go}, \tag{31}$$

and

$$n_{\mathrm{B}}^{l'} + n_{\mathrm{B}}^{g} + n_{\mathrm{B}}^{l''} = n_{\mathrm{B}}^{lo} + n_{\mathrm{B}}^{go}. \tag{32}$$

No new species of ions or molecules were formed or lost in either the primary or secondary solutions. Since the mole ratios in the primary or secondary solutions must always be equal when in equilibrium with each other, Eq. (30), then with Eq. (31) it follows that

$$\frac{n_{\mathrm{B}}^{l'}}{n_{\mathrm{A}}^{lo} - n_{\mathrm{A}}^{l''} + (n_{\mathrm{A}}^{go} - n_{\mathrm{A}}^{g})} = \frac{n_{\mathrm{B}}^{l''}}{n_{\mathrm{A}}^{l''}}, \tag{33}$$

and with Eq. (32) that

$$n_{\mathrm{B}}^{l'}n_{\mathrm{A}}^{l''} = n_{\mathrm{B}}^{l''}(n_{\mathrm{A}}^{lo} + n_{\mathrm{A}}^{go} - n_{\mathrm{A}}^{g}) + n_{\mathrm{A}}^{l''}n_{\mathrm{B}}^{l'} - n_{\mathrm{A}}^{l''}(n_{\mathrm{B}}^{lo} + n_{\mathrm{B}}^{go} - n_{\mathrm{B}}^{g}). \tag{34}$$

Subtracting $n_{\mathrm{B}}^{l'}n_{\mathrm{A}}^{l''}$ from both sides of Eq. (34) then

$$\frac{n_{\mathrm{B}}^{l''}}{n_{\mathrm{A}}^{l''}} = \frac{n_{\mathrm{B}}^{lo} + (n_{\mathrm{B}}^{go} - n_{\mathrm{B}}^{g})}{n_{\mathrm{A}}^{lo} + (n_{\mathrm{A}}^{go} - n_{\mathrm{A}}^{g})}, \tag{35}$$

or since the amount of gas in the vapor phase can be made vanishingly small,

$$\frac{n_B^{l''}}{n_A^{l''}} = \frac{n_B^{l_o}}{n_A^{l_o}} = \frac{n_B^{l'}}{n_A^{l'}}; \tag{35a}$$

that is, the primary and secondary solutions not only have the same mole ratio, the mole ratio in the solution is exactly the same as the mole ratio of the pure liquids B and A. In other words, the solutions are identical and miscible, i.e. they can be mixed with any ratio.

The unequal heights of the upper surfaces of the primary and secondary solutions in Figure 2B implies no gravitational field. If gravity were to act on the vapor of the solute and solvent, their vapor pressures above the primary solution on the left would be less than the vapor pressures of solute and solvent of the primary solution. Both solute and solvent would distill over from the left to the right solution until their upper surfaces were at the same height.

PRIMARY AND SECONDARY SOLUTIONS IDENTICAL AND CONTAINING A AND B PLUS REACTION PRODUCTS

When $n_A^{l_o}$ moles of A and $n_B^{l_o}$ moles of B are allowed to mix as illustrated in Figure 2B, $n_A^{l'_o}$ moles of A and $n_B^{l'_o}$ moles of B become the primary solution while $n_A^{l''_o}$ moles of A and $n_B^{l''_o}$ moles of B become the secondary solution. Thus, $n_A^{l_o} = n_A^{l'_o} + n_A^{l''_o}$ and $n_B^{l_o} = n_B^{l'_o} + n_B^{l''_o}$.

Some or most of the molecules of B may solvate with molecules of A according to the reaction

$$\mathrm{aA} + \mathrm{B} \rightleftharpoons \mathrm{BA_a}$$

where the extent of the reaction is characterized by its equilibrium constant

$$\mathrm{K} = \frac{[n_{BA_a}^{l}]}{[n_A^{l}]^{a}[n_B^{l}]}.$$

Each mole of BA_a is made from 1 mole of B and a moles of A so that $n_B^{l'_o}$ moles of the initial B which became the primary solution is

$$n_B^{l'_o} = n_B^{l'} + n_{BA_a}^{l'}$$

and

$$n_A^{l'_o} = n_A^{l'} + a n_{BA_a}^{l'}.$$

Similarly for the secondary solution

$$n_{\mathrm{B}}^{l''_0} = n_{\mathrm{B}}^{l''} + n_{\mathrm{BA_a}}^{l''}$$

and

$$n^{l''_0} = n_{\mathrm{A}}^{l''} + \mathrm{a}n_{\mathrm{BA_a}}^{l''}.$$

In these terms, the mole fractions of A and B in the primary solution are

$$x_{\mathrm{A}}^{l'} = \frac{n_{\mathrm{A}}^{l'}}{\sum_{\mathrm{j}} n_{\mathrm{j}}^{l'}} \tag{36}$$

where $\sum_{\mathrm{j}} n_{\mathrm{j}}^{l'} = n_{\mathrm{A}}^{l'} + n_{\mathrm{B}}^{l'} + n_{\mathrm{BA_a}}^{l'}$ and

$$x_{\mathrm{B}}^{l'} = \frac{n_{\mathrm{B}}^{l'}}{\sum_{\mathrm{j}} n_{\mathrm{j}}^{l'}}. \tag{37}$$

Likewise, the mole fractions of A and B in the secondary solution are

$$x_{\mathrm{A}}^{l''} = \frac{n_{\mathrm{A}}^{l''}}{\sum_{\mathrm{j}} n_{\mathrm{j}}^{l''}}, \tag{38}$$

$$x_{\mathrm{B}}^{l''} = \frac{n_{\mathrm{B}}^{l''}}{\sum_{\mathrm{j}} n_{\mathrm{j}}^{l''}}, \tag{39}$$

where $\sum_{\mathrm{j}} n_{\mathrm{j}}^{l''} = n_{\mathrm{A}}^{l''} + n_{\mathrm{B}}^{l''} + n_{\mathrm{BA_a}}^{l''}$.

Since $x_{\mathrm{A}}^{l'}$ must equal $x_{\mathrm{A}}^{l''}$ and $x_{\mathrm{B}}^{l'}$ must equal $x_{\mathrm{B}}^{l''}$, the right sides of Eqs (36) and (38) are equal and the right sides of Eqs (37) and (39) are equal, i.e.

$$\frac{n_{\mathrm{A}}^{l'}}{\sum_{\mathrm{j}} n_{\mathrm{j}}^{l'}} = \frac{n_{\mathrm{A}}^{l''}}{\sum_{\mathrm{j}} n_{\mathrm{j}}^{l''}} \tag{40}$$

$$\frac{n_{\mathrm{B}}^{l'}}{\sum_{\mathrm{j}} n_{\mathrm{j}}^{l'}} = \frac{n_{\mathrm{B}}^{l''}}{\sum_{\mathrm{j}} n_{\mathrm{j}}^{l''}} \tag{41}$$

Dividing Eq. (40) by Eq. (41), again it follows that

$$n_{\mathrm{A}}^{l'}/n_{\mathrm{B}}^{l'} = n_{\mathrm{A}}^{l''}/n_{\mathrm{B}}^{l''}.$$

The mole ratio of pure solvent and pure solute which formed the two solutions is

$$n_{\mathrm{A}}^{l_0}/n_{\mathrm{B}}^{l_0} = \frac{n_{\mathrm{A}}^{l'} + \mathrm{a}n_{\mathrm{BA_a}}^{l'} + n_{\mathrm{A}}^{l''} + \mathrm{a}n_{\mathrm{BA_a}}^{l''}}{n_{\mathrm{B}}^{l'} + n_{\mathrm{BA_a}}^{l'} + n_{\mathrm{B}}^{l''} + n_{\mathrm{BA_a}}^{l''}}, \tag{42}$$

when the vapor phase is vanishingly small. Of course, $n_{\mathrm{A}}^{l'}$ may differ from $n_{\mathrm{A}}^{l''}$. Suppose $n_{\mathrm{A}}^{l'}/n_{\mathrm{A}}^{l''}$ is the fraction F, then also $n_{\mathrm{B}}^{l'}/n_{\mathrm{B}}^{l''} = \mathrm{F}$. According to Eq. (40) or Eq. (41), the ratio

$$\frac{n_{\mathrm{A}}^{l'} + n_{\mathrm{B}}^{l'} + n_{\mathrm{BA_a}}^{l'}}{n_{\mathrm{A}}^{l''} + n_{\mathrm{B}}^{l''} + n_{\mathrm{BA_a}}^{l''}} = \mathrm{F} \tag{43}$$

Since $n_{\mathrm{A}}^{l'} = \mathrm{F}n_{\mathrm{A}}^{l''}$ and $n_{\mathrm{B}}^{l'} = \mathrm{F}n_{\mathrm{B}}^{l''}$, Eq. (43) requires also that $n_{\mathrm{BA_a}}^{l'}/n_{\mathrm{BA_a}}^{l''} = \mathrm{F}$. In terms of F, Eq. (42) can also be written

$$n_{\mathrm{A}}^{lo}/n_{\mathrm{B}}^{lo} = \frac{n_{\mathrm{A}}^{l''}(1 + \mathrm{F}) + \mathrm{a}(1 + \mathrm{F})n_{\mathrm{BA_a}}^{l''}}{n_{\mathrm{B}}^{l''}(1 + \mathrm{F}) + (1 + \mathrm{F})n_{\mathrm{BA_a}}^{l''}}.$$

No matter what F is, then,

$$n_{\mathrm{A}}^{lo}/n_{\mathrm{B}}^{lo} = \frac{n_{\mathrm{A}}^{l''} + \mathrm{a}n_{\mathrm{BA_a}}^{l''}}{n_{\mathrm{B}}^{l''} + n_{\mathrm{BA_a}}^{l''}}$$

Equation (42) can also be written

$$n_{\mathrm{A}}^{lo}/n_{\mathrm{B}}^{lo} = \frac{n_{\mathrm{A}}^{l'} + \mathrm{a}n_{\mathrm{BA_a}}^{l'}}{n_{\mathrm{B}}^{l'} + n_{\mathrm{BA_a}}^{l'}}.$$

Thus, again the primary and secondary solutions are identical, only their volumes may differ. By similar argument, the same conclusion can be drawn if the solute B dissociates in solvent A. Such solutions are miscible since $n_{\mathrm{B}}^{lo}/n_{\mathrm{A}}^{lo}$ may have any value and the two solutions will always be identical.

PRIMARY AND SECONDARY SOLUTIONS DIFFER

Many liquids are only partially miscible in each other. For such liquids the primary and secondary solutions may differ greatly in composition depending on the ratio $n_{\mathrm{B}}^{lo}/n_{\mathrm{A}}^{lo}$ in Figure 2A, which may be any value between 0 and ∞. Nevertheless, the thermodynamic argument requires that the chemical potentials of A in the primary and secondary solutions be equal, Eq. (20), and similarly the chemical potential of B must be equal in the primary and secondary solutions. These requirements further require that $x_{\mathrm{A}}^{l'} = x_{\mathrm{A}}^{l''}$ and $x_{\mathrm{B}}^{l'} = x_{\mathrm{B}}^{l''}$ and that $n_{\mathrm{B}}^{l'}/n_{\mathrm{A}}^{l'} = n_{\mathrm{B}}^{l''}/n_{\mathrm{A}}^{l''}$ at the same T and p. Thus, the primary and secondary solutions differ because other species or other forms of B and A must be present in differing ratios in the primary and secondary solutions. In partially miscible solutions molecules of A are affected by B differently in the primary and secondary solutions. For example, suppose that n_{A}^{lo} was 55.410 moles of water so that its volume at 20°C would be 1000 ml. Suppose also that n_{B}^{lo} was 9.633 moles of diethyl ether so that its volume at 20°C would also be 1000 ml. The solubility of ether vapor in water is 7.5 gm in 100 gm water for a mole ratio of ether to water of 0.01823. On the other hand, 100 gm of water vapor will dissolve in 5588 gm ether for a mole ratio of ether to water of 13.606. Thus, the primary solution of ether dissolved in water would occupy a volume of

1092.39 ml in the left cylinder of Figure 2B and the secondary solution of the right side would be 907.61 ml of water dissolved in ether.

In equilibrium, the chemical potentials of ether in the primary and secondary solutions must be equal. Likewise, the chemical potentials of water in the primary and secondary solutions must be equal. Similarly the partial vapor pressures of ether and water must be the same for both solutions. Also, $\pi'_{\text{ether}} = \pi''_{\text{ether}}$ and $\pi'_{\text{water}} = \pi''_{\text{water}}$. Finally it is also essential that

$$n^{l'}_{\text{ether}}/n^{l'}_{\text{water}} = n^{l''}_{\text{ether}}/n^{l''}_{\text{water}}.$$

On the other hand, the facts are that the ratio of moles of ether to water is 0.01826 when ether dissolves in water whereas the ratio is 13.606 when water dissolves in ether. This apparent inequality of $n^{l}_{\text{ether}}/n^{l}_{\text{water}}$ is resolved by recognizing that most of the water in the primary solution must be polymerized as ether molecules dissolved in it according to

$$nH_2O \rightleftharpoons (H_2O)_n$$

where the equilibrium constant is $K_n = n(H_2O)_n/[nH_2O]^n$ and where the average polymer consists of n water molecules.[6] Similarly, most of the ether in the secondary solution must be polymerized when water molecules dissolve in it according to

$$m(C_2H_5)_2 \rightleftharpoons [(C_2H_5)_2O]_m$$

where the average polymer size is m and the equilibrium constant is

$$K_m = \frac{n[(C_2H_5)_2O]_m}{[n(C_2H_5)_2O]^m}$$

Thus, the 986.80 gm of water in the primary solution consists of $n^{l'}_{H_2O} + n^{l'}_{(H_2O)_A}$. Similarly, the 639.86 gm of ether in the secondary solution consists of $n^{l_0}_{\text{ether}} + n^{l''}_{(\text{ether})_m}$. In this way, $n^{l'}_{\text{ether}}/n^{l'}_{H_2O}$ equals $n^{l''}_{\text{ether}}/n^{l''}_{H_2O}$ and the thermodynamic properties of the primary and secondary solutions are identical with regard to the molecules of water and the molecules of ether, even as this ratio differs from $n^{l_0}_{\text{ether}}/n^{l_0}_{H_2O}$.

CONCLUSIONS

In a liquid solution, the chemical potential of the solute is lowered by the tension in the coupling force between its molecules and this tension is induced by the thermal motion of all randomly moving ions, molecules or polymers within the solution. The internal tension for solute B in solution,

τ_B, is inversely proportional to the mole fraction of B in the solution, i.e. τ_B is proportional to $\sum_j n_j^l/n_B^l$. If at T pure substance B is a solid and if pure B is in excess, then the moles of B in solution increase to n_B^{lsat} and until $\mu_B^l(T, p, x_B^{lsat}) = \mu_B^{so}(T, p)$. The moles of B in the saturated solution may also be in chemical equilibrium with ions derived from B by dissociation in solvent A or with molecules formed by reaction of B with A or by any alteration of the molecular form of B in the solution. These reaction products of B may greatly increase the solubility of B in A. They also increase the sum of all species present in the solution $\sum_j n_j^l$, and thereby affect the chemical potential of B, $\mu_B^l(T, p, x_B^{lsat})$.

If at T pure substances B and A are liquids then, of course, B can never dissolve in A in sufficient amount to increase its chemical potential to equal that of pure liquid B. However, at the same time, molecules of A are dissolving in liquid B to form a secondary solution and they lower the chemical potential of B in the secondary solution. When thermodynamic equilibrium is attained, the chemical potential of B must be the same in both primary and secondary solutions and all colligative properties of B must be the same in both solutions. As molecules of B dissolve in liquid A they may react to alter the ionic or molecular form of the molecules of pure B or to alter the ionic or molecular form of the molecules of pure A. When thermodynamic and chemical equilibria are attained the primary and secondary solutions may be identical or they may differ greatly. Nevertheless, the chemical potential of B must be the same in both solutions and less than in pure liquid B; and the chemical potential of A must be the same in both solutions and less than in pure liquid A. All colligative properties of A must be the same in both solutions and all colligative properties of B must be the same in both solutions. The mole fraction of B, x_B^l, the mole fraction of A, x_A^l, and the mole ratio n_B^l/n_A^l must be the same in both solutions in equilibrium with each other.

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5. Large solute molecules, colloidal in size, also exert an increasing mechanical pressure in addition to the thermal pressure as their concentration increases. Thus, Eqs (18), (19) and (19a) require an additional term expressing the effect of this increasing mechanical pressure on the tension between the solute molecules in solution.
6. A polymer of n water molecules is more likely to be formed by a combination of smaller polymers which sum to a polymer of $(H_2O)_n$, c.f. reference 4.