Thermodynamics of Highly Dilute Solutions and the Quest for Ultrapurity

Since very high purity is sometimes required for health-related (and other) products, it is useful to reexamine the common thermodynamic relations that describe the chemical potential of a solute at very high dilution. Because Stirling's approximation is not valid for small numbers, the usual thermodynamic relations must be reformulated for small systems, i.e., for a solute in a small bubble or drop. A simplistic analysis indicates that in a small bubble or drop, the chemical potential of a solute goes to a finite value as the mole fraction of solute goes to zero, in contrast to the conventional result, where that chemical potential goes to negative infinity. This simplistic analysis has profound implications for separation science; it implies that (in theory) ultrapurity may be attained by conventional diffusional methods. While serious objections can be raised to invalidate the simplistic analysis, it may nevertheless be useful for chemical engineers to consider separation methods using highly dispersed systems.

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Introduction

Highly dilute solutions are now of increasing interest in chemical technology because of rising expectations in pollution abatement, because of high-purity requirements for health-related products in pharmacology and biotechnology and for packaging of foods, medicines, and other items for human consumption. It is this increasing interest that prompted us to ask: What can thermodynamics tell us about dilute solutions? In particular, what can it tell us with respect to separation operations for achieving very high purity?

According to classical thermodynamics, the chemical potential μ_B of solute B in an excess of solvent A, is given by

$$\mu_B = \mu_B' + kT \ln x_B \tag{1}$$

where x_B is the mole fraction, k is Boltzmann's constant, T is the absolute temperature, and μ_B' is a constant, independent of composition.

As $x_B \rightarrow 0$, $\mu_B \rightarrow -\infty$. Therefore, Eq. 1 implies that it is not possible to remove every solute molecule B from solvent A in a finite number of separation steps. The conventional wisdom is that it is not possible to achieve perfect purity by absorption, extraction, or other diffusional operations. In any standard separation device, mole fraction x_B can be made arbitrarily small but not zero (Denbigh and Denbigh, 1985).

This work presents, first, a simplistic reexamination of Eq. 1, as suggested by the statistical thermodynamics of Boltzmann for very dilute systems. We then apply to separation science the tentative conclusions of that simplified analysis with a surprising result: it may be theoretically possible to achieve ultrapurity in a diffusional operation in a finite number of steps. Finally, we indicate some pertinent criticisms of our simplistic analysis.

We do not present any clear conclusions. Our main purpose is to illuminate and stimulate discussion on a timely subject that has long been neglected.

Chemical Potential of a Solute in a Highly Dilute Solution

Consider a homogenous phase containing N_B molecules of B and N_A molecules of A where $N_A \gg N_B$. Let $N_T = N_A + N_B$. The chemical potential (per molecule) μ_B is related to the total Gibbs energy $\underline{G}$ and to the configurational entropy of mixing $\Delta \underline{S}^c_{mix}$ by

$$\mu_B = \left(\frac{\partial \underline{G}}{\partial N_B}\right) = \mu_B' - T\left(\frac{\partial \Delta \underline{S}^c_{mix}}{\partial N_B}\right) \tag{2}$$

where μ_B' is a constant that depends on temperature and pressure but not on composition. Equation 2 assumes that the Gibbs energy and the configurational entropy of mixing are continuous functions of N_B. (See Appendix).

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For the configurational entropy of mixing we use Boltzmann's relation

$$\Delta \underline{S}^c_{mix} = -k \ln [N_A! N_B! / N_T!]. \tag{3}$$

We substitute Eq. 3 into Eq. 2. The derivative of Eq. 3 with respect to N_B is not obvious because the factorial function is discrete for integer values of N_A and N_B. As shown in the Appendix, the customary procedure is to use Stirling's approximation for large N; in that event, Eq. 1 follows from Eqs. 2 and 3. However, for N_A or $N_B < 100$, Stirling's approximation is poor. Therefore, to differentiate Eq. 3 with respect to N_B, we utilize the continuous property of the digamma function ψ, which is related to the factorial function by

$$\psi(N) = d \ln N!/dN. \tag{4}$$

From Eqs. 2, 3, and 4 we now obtain

$$\mu_B = \mu'_B + kT[\psi(N_B) - \psi(N_T)]. \tag{1a}$$

When both N_A and $N_B > 100$, Eq. 1a is essentially equivalent to Eq. 1. However, as indicated later, when $N_B \rightarrow 0$, Eq. 1a gives a finite chemical potential, unlike Eq. 1.

There are two conceivable routes for producing a system highly dilute in component B. First, consider the case where N_B is fixed and N_A rises. In this case, the mole fraction of component B decreases and the chemical potential of B, as computed by Eq. 1, becomes more negative, approaching $-\infty$ as $N_A \rightarrow \infty$. This result is not surprising when we recall that the chemical potential of component B is directly related to the work required to remove B from the system. As the size of the system increases, so does the work required for removing B from the system. An appropriate analogy is a needle in a haystack. As the size of the haystack increases, more work is required to locate the needle.

Second, consider the case where N_A is fixed and molecules of component B are removed. When only one molecule of B remains, the mole fraction of component B is small but not zero. When $N_B = 1$, the chemical potential calculated by Eq. 1 is a finite number. However, when $N_B = 0$, Eq. 1 gives $\mu_B = -\infty$. This infinite jump is intuitively unappealing.

The haystack analogy suggests that as the size of the haystack is reduced, the work to locate the needle should decline. We postulate that Eq. 1 is valid for the first route to ultrapurity but that Eq. 1a is appropriate for the second route. We do not assert that this postulate *must* be correct, but we believe it to be of sufficient interest for further study. We are particularly interested in the effect that Eq. 1a has on separations science.

Figure 1 illustrates the important difference between Eqs. 1 and 1a. Equation 1 says that as $N_B \rightarrow 0$, $\mu_B \rightarrow -\infty$, whereas Eq. 1a says that as $N_B \rightarrow 0$, μ_B approaches a finite number that depends on the number of solvent molecules N_A. As N_A declines, it becomes "easier" to remove the last molecule of B. Equation 1a suggests that the size of the system is important; in a small bubble or drop containing N_A molecules of A, the mole fraction of the *last* molecule of B increases as N_A falls.

Phase Equilibrium: Requirement for Ultrapurity

Consider a two-phase system where discontinuous phase α is in equilibrium with continuous solvent phase β. In the discontinuous phase, we have molecules A and B with an excess of A. In the continuous phase we have molecules S and B with an excess of S. We assume that A and S are totally immiscible. We now consider the thermodynamic requirement for ultrapurity ($N^\alpha_B = 0$). The essential problem is this: we need to know the chemical potential of component B when it is no longer in phase α.

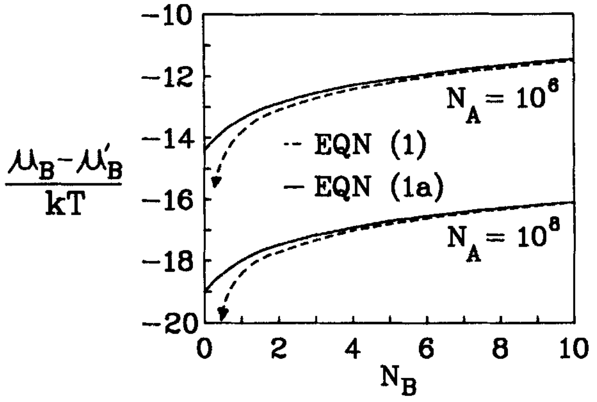

Figure 1. Comparison of Eq. 1 and Eq. 1a.

We assume that phase α can be made ultrapure provided that we can find a phase β such that

$$\mu^\beta_B \leq \mu^\alpha_B\,(N^\alpha_B = 0) \tag{5}$$

where $\mu^\alpha_B\,(N^\alpha_B = 0)$ is the chemical potential of a "virtual" molecule of B in phase α. The concept of a virtual component was discussed by Gibbs (1928); it is the limiting chemical potential of component B. Further discussions are given by Reis (1986), Kirkwood and Oppenheim (1961), and Beattie and Oppenheim (1979). According to Eq. 1a, the chemical potential of a virtual molecule of B is

$$\mu^\alpha_B\,(N^\alpha_B = 0) = \mu'^\alpha_B + kT[\psi(0) - \psi(N^\alpha_A)] \tag{6}$$

Assuming N^α_A is large ($N^\alpha_A > 100$), the digamma function and the logarithm function are equivalent and Eq. 6 becomes:

$$\mu^\alpha_B\,(N^\alpha_B = 0) = \mu'^\alpha_B + kT[\psi\,(0) - \ln\,(N^\alpha_A)] \tag{6a}$$

where $-\psi(0) =$ Euler's constant $= 0.5772156 \ldots$. Equations 5 and 6a provide a criterion for attainment of ultrapurity in terms of distribution coefficient K defined by

$$K = \exp\,[(\mu'^\alpha_B - \mu'^\beta_B)/kT] \tag{7}$$

(The usual relation $K = x^\beta_B / x^\alpha_B$ follows at once from Eq. 1, but not from Eq. 1a unless N^α_B is large.)

It follows from Eqs. 5 and 6 that for ultrapurity in phase α:

$$K/1.781 \geq (x^\beta_B)\,(N^\alpha_A) \tag{8}$$

where 1.781 is the exponential of Euler's constant.

The important property of Eq. 8 is that the criterion for ultrapurity depends not only on x^β_B, the composition of phase β, but also on N_A, i.e., the size of phase α. For a fixed K, Eq. 8 gives a limiting value for the product of x^β_B and N^α_A. For values below or equal to that limit, the last molecule of B leaves phase α.

To facilitate illustrative calculations, we prefer to use a criterion for ultrapurity that is an equity rather than an inequality. The phase equilibrium condition for ultrapurity given in Eq. 5 becomes

$$\mu_B^\beta = \mu_B^\alpha (N_B^\alpha = 0) \qquad (5a)$$

From Eq. 8, we find that ultrapurity is attained provided that the distribution coefficient K (Eq. 7) is given by

$$K = (1.781)(x_B^\beta)(N_A^\alpha) \qquad (9)$$

Dispersed Bubbles or Drops

To give a physical picture of the equations derived above, we consider drops of α dispersed in a continuous phase β. The total number of molecules, N_T^α, in one drop is related to drop diameter D by

$$N_T^\alpha = N_{AV}(\rho/MW)(\pi D^3/6) \qquad (10)$$

where N_{AV} is Avogadro's number, ρ is the mass density, and MW the average molecular weight of the mixture in the drop. If the drop is highly dilute in solute B, the molecular weight and mass density are essentially those of component A. We now substitute Eq. 10 into Eq. 9 using the following units

D = microns (μm)
ρ = kg/m^3
MW = kg/kmol
x_B^β = parts per million (ppm)

we obtain

$$K/(\rho/MW) = 562 D^3 x_B^\beta . \qquad (11)$$

To obtain some numerical results, we consider as the dispersed phase first, a typical low-pressure gas, and second, a typical liquid. For these cases, Figure 2 (a plot of Eq. 11) shows D as a function of x_B^β. Figure 2 gives typical conditions required to attain ultrapurity in phase α.

For a low-pressure gas, ideal-gas conditions are assumed and $(\rho/MW) = P/(RT)$. Consider the case where $P = 1$ bar and $T = 300$ K; then the molar gas density $(\rho/MW) = 0.0401$ kmol/m^3. Assuming that S is a good solvent for solute B, a realistic Henry's constant is 0.2 bar/mol fraction. For this case, $K = 5$ as defined by Eq. 7. If the bubble diameter is 0.2 μm, then to attain ultrapurity the concentration of B in phase β must be below 27.78 ppm.

In the second example, consider a liquid as the dispersed phase α where $\rho = 1{,}000$ kg/m^3 and $MW = 100$ kg/kmol. Assuming that S is a good solvent for solute B, a reasonable value for the distribution coefficient defined by Eq. 7 is $K = 100$. If $x_B^\beta = 17.79$ ppm, then the drop diameter must be below 0.1 μm to attain ultrapurity in phase α.

Chemical Solvent

Drop (or bubble) sizes in the range of 0.1–0.2 μm are probably too small for realistic separation operations. However, drop (or bubble) sizes in the range 1–2 μm may be satisfactory. The technical feasibility of droplet production in this size range has been demonstrated by Scott (1986).

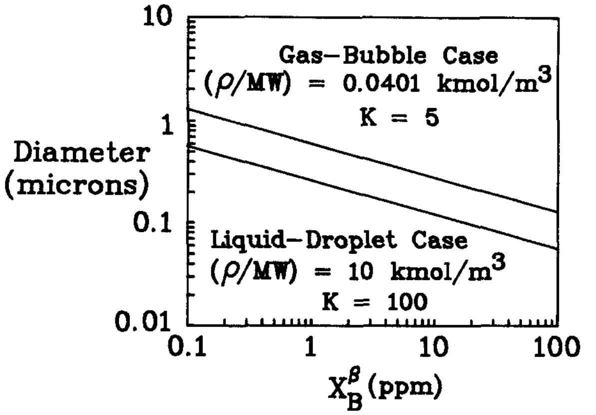

Figure 2. Dispersed-phase diameter required to obtain ultrapurity in dispersed phase α.

In the previous examples, to maintain the indicated values of x_B^β, while increasing drop (or bubble) sizes to 1–2 μm, it is necessary to increase the distribution coefficient K by a factor of 1,000. In other words, solvent S must be a highly selective solvent for solute B relative to solvent A. To attain the required large K, there must be some chemical affinity between solute B and solvent S; e.g., B might be acidic while S is basic, or else B might be a strong electron donor while S is a strong electron acceptor. To operate with drop (or bubble) sizes in the region 1–2 μm, a physical solvent will not be satisfactory because moderate values of K will lead to unacceptably low values of x_B^β, as shown in Figure 2.

For very small drops, it may be necessary to include the effect of interfacial tension in the equation of equilibrium, Eq. 5. However, for drop sizes above 0.1 μm this effect is small, as noted by Modell and Reid (1983), Defay et al. (1966), and Lewis and Randall (1961).

Gas Absorption: Bubble Column

To reduce Eq. 9 to engineering practice, we present some calculations for a continuous countercurrent gas-absorption column shown in Figure 3. Rich dispersed phase α is introduced at the bottom, while lean continuous phase β is introduced at the top.

For the column shown in Figure 3, we show in Figure 4 the equilibrium curve $EQ.$, and the operating line $(L/V)_{op}$. For ease of notation, y replaces x_B^α and x replaces x_B^β. These lines were calculated as shown elsewhere (Sciamanna 1986).

To illustrate the relations shown in Figure 4, consider the case where the gas bubbles in phase α are characterized by $D = 2$ μm, $P = 1$ bar, $T = 300$ K, and $K = 5{,}000$. The solute concentration in the inlet vapor, y_{in}, is 1,000 ppm, and the solute concentration in the inlet solvent, x_{in}, is 1 ppm. The solute concentration in the outlet vapor, y_{out}, is zero. In these calculations, the molar ratio of liquid flow to vapor flow (L/V) is 20% greater than the minimum.

We now calculate the number of transfer units (NTU) based on the α phase required to attain ultrapurity in phase α. Details are given elsewhere (Sciamanna 1986). For this case we find $\text{NTU}_\alpha = 12$, well within conventional chemical engineering practice.

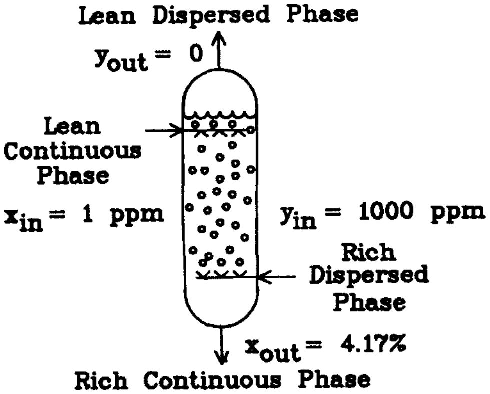

Figure 3. Gas absorption: bubble column.

Liquid-Liquid Extraction: Mixer-Settler

Consider a liquid-liquid extraction process using a staged countercurrent mixer-settler arrangement. Each mixer-settler pair approximates an equilibrium stage. The rich, dense dispersed phase α is introduced at the top of the mixer section, while the lean continuous phase β is introduced at the bottom. The dispersed phase is coalesced in the settler section, transferred to the next mixer and then redispersed. The continuous phase is separated at the top of the mixer and reintroduced countercurrently at the bottom of the next mixer. We recognize that a liquid-liquid contacting device is likely to be subject to fluid-mechanical problems when drop sizes are very small; nevertheless, with ingenuity the contemplated process may be feasible.

For the mixer-settler arrangement shown in Figure 5, we show in Figure 6 the equilibrium curve *EQ.*, and the operating line $(S/F)_{op}$. Again, for ease of notation y replaces x_B^α and x replaces x_B^β. These lines were calculated as discussed elsewhere (Sciamanna 1986).

To illustrate the relations shown in Figure 6, consider the case where the liquid droplets in phase α are characterized by $D = 1$ μm, $MW = 100$ kg/kmol, $\rho = 1{,}000$ kg/m^3, and $K = 10^5$. The solute concentration in the inlet feed, y_{in}, is 1,000 ppm, and the solute concentration in the inlet solvent, x_{in}, is 1 ppm. The solute concentration in the outlet raffinate, y_{out}, is zero. The molar solvent-to-feed ratio (S/F) is 20% greater than the minimum.

Finally, we calculate the number of equilibrium stages N_{eq} required to attain ultrapurity in phase α. For this case we find $N_{eq} = 2$, well within conventional chemical engineering practice.

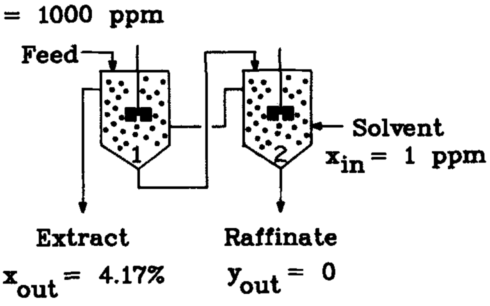

Figure 5. Liquid-liquid extraction: mixer-settler cascade.

If the initial thermodynamic assumptions are valid, and neglecting significant mechanical problems, these illustrative calculations suggest that ultrapurity may be attained, at least in principle, by a diffusional operation under conditions that resemble those encountered in conventional chemical engineering technology.

Critique

Continuous or discrete?

The optimistic calculations given in the previous section are based on Eq. 6a, which in turn follows from Eq. 4 applied to Boltzmann's configurational entropy of mixing. Are these equations valid for calculating the chemical potential of a vanishing dilute solute? A claim for validity may be criticized as unduly simplistic.

To maintain our usual practice of differentiating a continuous function, we introduced the digamma function in Boltzmann's equation to evaluate the chemical potential of component B as $N_B \rightarrow 0$. However, there is an alternate way to find μ_B from Boltzmann's equation for small N_B. For a solution highly dilute in B, a possibly more appropriate definition may be obtained by assuming that $\underline{G}$ is a discrete function of N_B. In that event,

$$\mu_B = \left(\frac{\delta \underline{G}}{\delta N_B}\right) = \mu_B' - T\left(\frac{\delta \Delta \underline{S}^C_{mix}}{\delta N_B}\right) \qquad (2a)$$

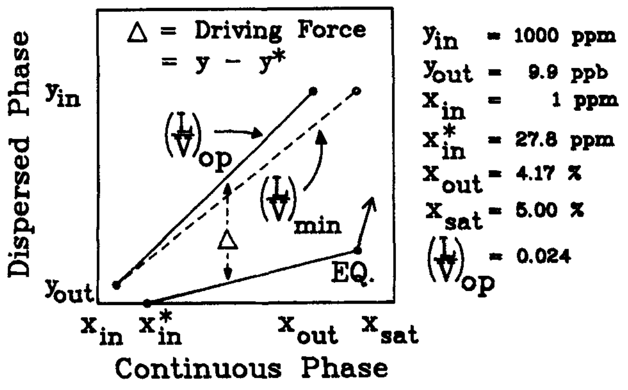

Figure 4. Operating diagram for continuous absorption column.

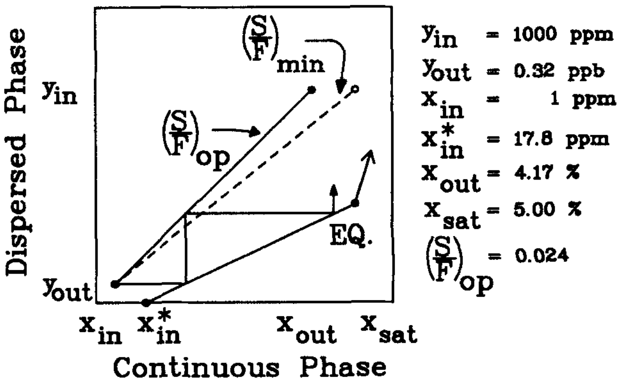

Figure 6. Operating diagram for staged mixer-settler cascade.

In Eq. 2, ∂ designates the usual differential operator, while in Eq. 2a, δ designates a finite-difference operator.

We now consider the chemical potential as defined by Eq. 2a with the configurational entropy given by Eq. 3. The result is surprising. As shown in the Appendix, we find that Eq. 1 follows directly with no mathematical approximations. Unfortunately, however, the chemical potential defined by Eq. 2a is not unique for a small value of N_B because it then depends on the initial state of the system. For instance, suppose we desire $\Delta\mu_B$ at $N_B = 2$. We can obtain this $\Delta\mu_B$ by allowing N_B to increase from 1 to 2 or else by allowing N_B to decrease from 3 to 2. Hence, there is ambiguity in calculating $\Delta\mu_B$ when N_B is small. On the other hand, the continuous derivative is unambiguous; it is the slope of the tangent line at a particular N_B.

At large values of N_B, both methods produce identical results but at small values of N_B they do not. It is appealing to give priority to the continuous form, Eq. 2, consistent with our conventional view that in classical thermodynamics, the value of a state function should be independent of the path.

Fluctuations

Our thermodynamic analysis indicates that attainment of ultrapurity is only possible if the chemical potential of "virtual" component B at $N_B = 0$ is finite. This is the crucial requirement. If this requirement is not met, there is no advantage to reducing the size of phase α to increase the chemical potential of component B.

Consider two chemically identical two-phase systems side by side where the α phase contains components A and B and the β phase contains components B and S. As before, A and S are totally immiscible. In case I, the α phase is dispersed as finely divided droplets in the β phase, while in case II the α and β phases are separated by a single interface. We assume that we can lower the chemical potential of component B in the β phase and correspondingly extract B from the α phase. At some low value of μ_B^β, there is only one molecule of B in each droplet in the dispersed phase. The mole fraction corresponding to the last molecule of B in the dispersed case is identical to that in the nondispersed case.

Suppose now that the chemical potential of B in the β phase is the same in both cases, I and II. We can now speculate that if μ_B^β is lowered further, the dispersed phase becomes ultrapure while the nondispersed phase does not. However, because of fluctuations, it seems unlikely that all droplets are ultrapure.

When N_B is small, the usual thermodynamic equations need modification because fluctuations are then significant. We do not here discuss this subject in the detail that it deserves. However, we present a simple, pertinent calculation based on the Poisson distribution that is appropriate for random events for small numbers.

Consider an ensemble of small bubbles or drops α, each containing a large number of molecules A. These bubbles or drops are in a continuous phase β containing some molecules B. At a given moment, we determine the number of molecules B in every bubble or drop. We designate by $\overline{N}_B^\alpha$ the average number of B molecules per bubble or drop. What is the probability p that a given bubble or drop contains N_B^α molecules of B? It is given by

$$p(N_B^\alpha) = \frac{(\overline{N}_B^\alpha)^{N_B^\alpha}}{N_B^\alpha!} \exp(-\overline{N}_B^\alpha). \qquad (12)$$

When $N_B^\alpha = \overline{N}_B^\alpha = 0$, Eq. 12 is satisfied; in that event $p(0) = 1$. This is necessary because N_B^α is never negative. However, suppose $\overline{N}_B^\alpha = 1$. In that event,

$$p(0) = 1/e = 0.36788\ldots$$

$$p(1) = 1/e = 0.36788\ldots$$

$$p(2) = 1/2e = 0.18394\ldots$$

When, on the average, there is one molecule of B per bubble or drop, there are indeed some bubbles and drops that are ultrapure ($N_B^\alpha = 0$). Unfortunately, however, there are others that contain 1, 2, etc., molecules of B. Is it possible somehow to identify and remove those bubbles or drops where $N_B^\alpha = 0$?

Chemical potential in an open system

The grand partition function provides a suitable method for studying the equilibrium composition of a bubble or drop α in a continuous medium β. Phase α is an open system with respect to B; chemical potential μ_B is the same in both (continuous and discontinuous) phases. Neglecting effects of nonideality, the probability of having at least one molecule B in α is given by

$$p(N_B^\alpha \geq 1) = 1 - \exp\left[(-\nu/\Lambda_B^3)\exp(\mu_B/kT)\right] \qquad (13)$$

Where ν is the volume of the bubble or drop and Λ is the de Broglie wavelength (Hill, 1960). For p to go to zero, it is necessary that $\mu_B \rightarrow -\infty$, consistent with Eq. 1. However, one wonders about the various assumptions that are made in the usual application of the grand partition function; are these assumptions valid for small numbers?

Conclusion

This work reexamines the conventional wisdom which claims that, using standard diffusional operations, ultrapurity cannot be attained because it is impossible, in a finite number of operations, to remove the last molecule of a solute from a solvent. A simplistic reexamination, based on Boltzmann's equation for the entropy of mixing, suggests that the last molecule can be removed under special conditions. When that simplistic analysis is accepted, it may be possible—at least in theory—to achieve ultrapurity by dispersing the phase to be purified into small bubbles or drops and then contacting these with a favorable immiscible solvent.

However, a more careful analysis tends to discredit the simplistic analysis because it neglects fluctuations.

Nevertheless, the discussion given here indicates that in conceiving separation operations for high purity, it may be advantageous to give attention not only to temperature, pressure, and concentration, but also to phase size. While the usual textbook thermodynamic relations are applicable to traditional separation operations, they may require important modifications for small systems, (Hill, 1963). Future work must be directed toward establishing details of such modifications.

Acknowledgment

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Notation

D = diameter of gas bubble or liquid droplet
G = Gibbs energy per molecule
H = enthalpy per molecule
K = distribution coefficient, Eq. 7
k = Boltzmann's constant
MW = molecular weight of dispersed phase
N = number of molecules
N_{AV} = Avogadro's number, 6.022×10^{26} molecule/kmol
p = Probability, Eq. 12 or 13
S = entropy per molecule
$\Delta \underline{S}^c_{mix}$ = total configurational entropy of mixing
T = absolute temperature
! = factorial function

Greek letters

Γ = gamma function
Λ = de Broglie wavelength
μ = chemical potential per molecule
ν = volume of a bubble or drop
ρ = mass density of dispersed phase
ψ = digamma function

Superscripts

E = excess property of mixing
α = dispersed phase
β = continuous phase
$'$ = standard state for dilute solution
o = conventional standard state
$\bar{\ }$ = overbar: an average

Subscripts

A = solvent in dispersed phase
B = solute in dispersed and continuous phases
T = total number of A and B molecules in dispersed phase
$\underline{\ }$ = underbar: an extensive property

Appendix: Derivation of an Expression for the Chemical Potential of a Solute at High Dilution

Consider a binary system containing N_A solvent molecules A and N_B solute molecules B. The Gibbs energy $\underline{G}$ is related to enthalpy $\underline{H}$ and entropy $\underline{S}$ by

$$\underline{G} = \underline{H} - T\underline{S} \tag{A1}$$

where the underbar refers to the total extensive property. For the purposes of this discussion, all derivatives with respect to N_B are taken with N_A, temperature, and pressure held constant. The chemical potential per molecule is defined by

$$\mu_B = \left(\frac{\partial \underline{G}}{\partial N_B}\right) = \left(\frac{\partial \underline{H}}{\partial N_B}\right) - T\left(\frac{\partial \underline{S}}{\partial N_B}\right) \tag{A2}$$

At system temperature and pressure, the enthalpy of the mixture is

$$\underline{H} = N_A H_A^o + N_B H_B^o + \underline{H}^E \tag{A3}$$

where H_A^o and H_B^o are enthalpies per molecule of the pure components and $\underline{H}^E$ is the total excess enthalpy of mixing. The enthalpic contribution to the chemical potential is

$$\left(\frac{\partial \underline{H}}{\partial N_B}\right) = H_B^o + \left(\frac{\partial \underline{H}^E}{\partial N_B}\right) \tag{A3a}$$

Similarly, the total mixture entropy at the system temperature and pressure is given by

$$\underline{S} = N_A S_A^o + N_B S_B^o + \Delta \underline{S}^c_{mix} + \underline{S}^E \tag{A4}$$

where S_A^o and S_B^o are entropies per molecule of the pure components, $\Delta \underline{S}^c_{mix}$ is the total configurational entropy of mixing, and $\underline{S}^E$ is the total excess entropy of mixing. The entropic contribution to the chemical potential is

$$\left(\frac{\partial \underline{S}}{\partial N_B}\right) = S_B^o + \left(\frac{\partial \Delta \underline{S}^c_{\rm mix}}{\partial N_B}\right) + \left(\frac{\partial \underline{S}^E}{\partial N_B}\right) \tag{A4a}$$

Substituting Eqs. A3a and A4a into Eq. A2 yields

$$\mu_B = \mu_B^o + \mu_B^E - T\left(\frac{\partial \Delta \underline{S}^c_{\rm mix}}{\partial N_B}\right) \tag{A5}$$

where

$$\mu_B^o = H_B^o - TS_B^o \tag{A5a}$$

and

$$\mu_B^E = \left(\frac{\partial \underline{H}^E}{\partial N_B}\right) - T\left(\frac{\partial \underline{S}^E}{\partial N_B}\right) \tag{A5b}$$

For dilute dystems, μ_B^E is independent of composition.

We now change the standard state from pure fluid to an ideal dilute solution at unit mole fraction; this standard state is designated by a superscript prime ($'$):

$$\mu'_B = \mu_B^o + \mu_B^E + \text{constant} \tag{A6}$$

Substituting Eq. A6 into Eq. A5 yields Eq. 2.

Boltzmann's relation for the ideal entropy of mixing is given by $\Delta \underline{S}^c_{mix}$, Eq. 3. The continuous derivative of Eq. 3 with respect to N is not obvious because the factorial function is discrete for integer values of N; it is not continuously differentiable. The usual procedure assumes large values of N such that Stirling's approximation is valid. Stirling's approximation is

$$\ln N! \approx N \ln (N) - N. \tag{A7}$$

From Eq. 3, the partial molar entropy of solute B is

$$\left(\frac{\partial \Delta \underline{S}^c_{\rm mix}}{\partial N_B}\right) = -k\,(\ln N_B - \ln N_T) = -k \ln x_B \tag{A8}$$

For $N < 100$, Stirling's approximation is poor; therefore, we use the continuous property of the gamma function. The digamma function ψ (Abramowitz and Stegun, 1970) is defined by

$$\psi(N) = d \ln \Gamma(N + 1)/dN \tag{A9}$$

where Γ is the gamma function:

$$\Gamma(N+1) = \int_0^\infty e^{-z} z^N \, dz \qquad \text{(A10)}$$

The gamma function, sometimes called the generalized factorial function, is equal to the factorial function for all positive integer values of N. Equation A9 can therefore be rewritten as shown in Eq. 4. For positive integer values of N, the digamma function is equal to

$$\psi(N) = \psi(0) + \sum_{i=1}^{N} 1/i \qquad \text{(A11)}$$

where $-\psi(0)$ = Euler's constant = 0.5772156649 . . . is defined by the limit

$$-\psi(0) = \lim_{N\to\infty} \left[\left(\sum_{i=1}^{N} 1/i \right) - \ln N \right]. \qquad \text{(A12)}$$

Using the gamma function, Boltzmann's entropy of mixing is

$$\Delta \underline{S}^c_{mix} = -k \ln \left[\Gamma(N_A + 1)\Gamma(N_B + 1)/\Gamma(N_T + 1) \right] \qquad \text{(A13)}$$

where $\Gamma(N+1)$ is the gamma function and equal to $N!$ for integer values of N. The partial molar entropy of solute B follows from using the digamma function defined in Eq. A9; it is

$$\left(\frac{\partial \Delta \underline{S}^c_{\text{mix}}}{\partial N_B} \right) = -k[\psi(N_B) - \psi(N_T)] \qquad \text{(A14)}$$

Substituting Eq. A14 into Eq. 2 yields Eq. 1a. For larger values of N, i.e., as $N \longrightarrow \infty$,

$$\psi(N) \approx \ln N \qquad \text{(A15)}$$

In Eq. A14, the quantity in brackets approaches $\ln x_B$, the classical thermodynamics value, only when both N_B and N_A becomes large (N_A and $N_B > 100$).

An alternate method for calculating the partial molar entropy is to compute the discrete derivative of Boltzmann's relation with respect to N_B. The partial molar entropy for solute B is found from

$$\left(\frac{\delta \Delta \underline{S}^c_{\text{mix}}}{\delta N_B} \right) = -k\,[\ln N_B! - \ln (N_B - 1)! - \ln N_T! + \ln (N_T - 1)!] \qquad \text{(A16)}$$

where $\delta N_B = -1$ (molecule). It follows from the recursive property of factorials [i.e., $N! = N(N-1)!$] that

$$\left(\frac{\delta \Delta \underline{S}^c_{\text{mix}}}{\delta N_B} \right) = -k\,(\ln N_B - \ln N_T) = -k \ln x_B \qquad \text{(A17)}$$

where $x_B = N_B/N_T$. Discrete differentiation yields the same result as that based on Stirling's approximation.

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