Fluctuations in Highly Dilute Solutions

William L. Kubic, Jr.
Los Alamos National Laboratory
Los Alamos, NM 87545

Introduction

According to classical thermodynamics, the chemical potential of B in an excess of A is

$$\mu_B = \mu_B^* + kT \ln x_B. \qquad (1)$$

As the mole fraction of B approaches zero, the chemical potential becomes negatively infinite; therefore, an infinite amount of work is required to remove the last molecule from a mixture. For separation processes such as distillation and extractions, infinite work translates into infinite contacting areas and infinite flow rates. The thought-provoking paper of Sciamanna and Prausnitz (1987) suggests that Eq. 1 is incorrect when applied to very small systems. Contrary to classical thermodynamics, their analysis suggests that ultrapurity may be achievable with finite equipment and flow rates.

Sciamanna and Prausnitz correctly argue that the classic, statistical-mechanical derivation of the entropy of a mixture relies on assumptions that are not valid for small systems. By using better approximations, they derived the following expression for the chemical potential of small systems:

$$\mu_B = \mu_B^* + kT\,[\psi(n_B) - \psi(n_T)]. \qquad (2)$$

The infinite dilution limit of this expression is finite; therefore, it may be possible to achieve ultrapurity in practice. The analysis also indicates that the magnitude of the chemical potential increases with the size of the system. Hence, if the simplifictions used in deriving Eq. 2 are correct, ultrapurity can be obtained in a diffusional process by finely dispersing the impure phase.

The derivation of Eq. 2 ignores statistical fluctuations. Sciamanna and Prausnitz discuss the importance of fluctuations in small systems, but they present no analysis to quantify this effect. This research note examines the implications of fluctuations on separation processes using a simple stochastic model of an extraction process.

The single staged extraction process, Figure 1, will be examined. Impure A containing 10 ppm of B is purified by contacting it with pure S. The impure phase is dispersed into small droplets for contacting with the continuous solvent phase. The ratio of the impure-phase molar flow rate to the solvent molar flow rate is 1 to 10. The droplets of product are collected and mixed in a single product tank.

Because of statistical fluctuations, the composition of each droplet exiting the equilibrium stage is a random variable. Some droplets are ultrapure, but others contain molecules of B. Unless it is possible to inspect each droplet and isolate the ones that are ultrapure, the process engineer must be content with a mixture of all droplets as in the example process.

Equilibrium Stage

Statistical thermodynamics approximates a system of molecules as a stochastic process. For very large systems, the distribution of possible states about the mean is very narrow; therefore, the macroscopic behavior of the system is deterministic. The system averages correspond to the thermodynamic functions. In small systems, variations about the mean are significant, and equilibrium properties lose their meaning. It is more appropriate to consider the distribution of states in a small system rather than the most probable behavior.

The example process consists of three components and two phases. A and S are assumed to be completely immiscible. B is distributed between the A-rich phase, α, and the S-rich phase, β, Figure 2. To concentrate only on the entropic effects, it also will be assumed that a molecule of B has no preference for either phase α or phase β. This simplification corresponds to assuming B forms an ideal solution with both A and S in the sense of Rault's law.

The number of ways to arrange n_B particles in the system is

$$N_{n_B} = \frac{(n_A + n_B + n_S)!}{n_B!\,(n_A + n_B)!}. \qquad (3)$$

n_A and n_S are the number of molecules of A and S, respectively. The number of ways of arranging n_B molecules such that m molecules are in phase α is given as:

$$N_m^\alpha = \frac{(n_A + m - 1)!}{m!\,(n_A - 1)!}\,\frac{(n_S + n_B - m)!}{n_S!\,(n_S - m)!}. \qquad (4)$$

Because B has no preference for being in α or β, the probability

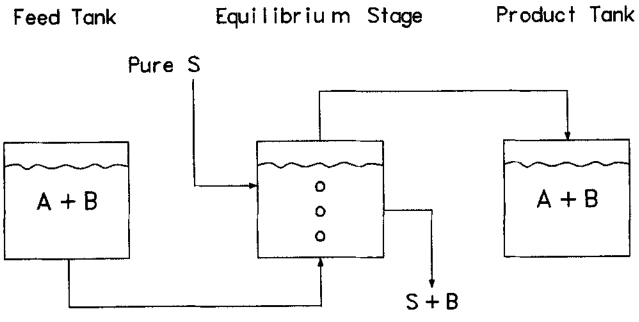

Figure 1. Single-stage extraction process.

Table 1. Probability Distribution for the Number of Molecules of B in a Drop of A Contacted with Pure S: $N_B/(N_A + N_B) = 0.02$, $N_S/(N_A + N_B) = 10$

m (Molecules of B in A)	Drop Size (molecules)		
	50	100	200
0	0.9109	0.8297	0.6857
1	0.0891	0.1623	0.2643
2	0	0.0080	0.0397
3	0	0	0.0052
4	0	0	0.0001

that there are m molecules of B in phase α given n_B molecules of B in the system is the ratio of N_m^α to N_{n_B}:

$$P^\alpha(m|n_B) = N_m^\alpha/N_{n_B}. \tag{5}$$

To illustrate the distribution of states, consider a droplet of A containing 2.0% B. This droplet is contacted with pure S. The number of molecules of S used is ten times the number of molecules in the initial droplet. The probability distribution for the number of molecules in the droplet after contacting is given in Table 1 for various droplet sizes.

The table shows that the most probable state of the droplet after contacting is pure A. The probability of ultrapurity also increases with decreasing droplet size. These calculations are consistent with the results of Sciamanna and Prausnitz. However, the calculations also show that there is a small, but significant, probability that the droplet will contain at least one molecule of B.

Process Model

The extraction process, Figure 1, consists of three steps: dispersing the impure A into small droplets; contacting the droplets with the solvent; and collecting the droplets. Dispersing the impure A into droplets containing N_d molecules is a stochastic process. The process consists of selecting N_d molecules at random from the feed reservoir. The contacting step also is a stochastic process, which is described by the probability distribution given in Eq. 5. The collection of the droplets is an averaging step.

The probability that a droplet of N_d molecules taken from the feed tank contains N_B molecules of B is given as:

$$P(n_B) = x_B^{n_B}(1 - x_B)^{n_d - n_B}\binom{n_d}{n_B}, \tag{6}$$

where x_B is the mole fraction of B in the bulk phase.

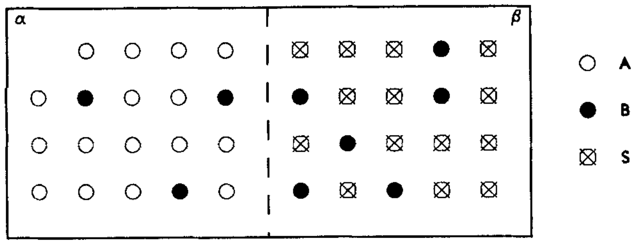

Figure 2. Idealized two-phase system.

The probability given by Eq. 5 is a conditional probability, which gives the probability that a droplet of N_d molecules entering the equilibrium stage with n_B molecules exits the process with m molecules of B. The probability that any droplet of n_d molecules exits the process with m molecules of B can be obtained from Bayes theorem:

$$P^\alpha(m) = \sum_{n_B=0}^{n_d} = P(n_B)\,P^\alpha(m|n_B). \tag{7}$$

Assuming that all of the droplets are of equal size, the probability distribution for the composition of droplets exiting the equilibrium stage can be computed. The results for various sizes of droplets are summarized in Table 2. The most probable state for a droplet after contacting is ultrapurity, and this probability increases with decreasing droplet size. However, the average composition, which is the true measure of process performance, is independent of droplet size.

According to classical thermodynamics, the ideal solution assumption implies that the mole fractions of B in the α and β phases are equal at equilibrium. The exit composition computed by the classical approach equals the average composition obtained from the stochastic model. This result contradicts the assertion of Sciamanna and Prausnitz that small systems behave differently than large systems.

Discussion

Resolving the conflict between the results of this study and the results of Sciamanna and Prausnitz requires careful interpretation of thermodynamics and statistical mechanics. Sciamanna and Prausnitz approached the problem by extending chemical potential to small systems. Within the formalisms of the grand cannonical ensemble, chemical potential arises as a Lagrange multiplier in the process of determining the most probable distribution of states. Therefore, chemical potential is

Table 2. Probability Distribution for the Number of Molecules in a Droplet Exiting the Extraction Process

m (Molecules of B in A)	Drop Size (molecules)		
	100	1,000	10,000
0	0.999910	0.999092	0.990952
1	0.000090	0.000907	0.009006
2	0	0.000001	0.000041
3	0	0	0
Avg. Comp., ppm	0.909	0.909	0.909

characteristic of only part of the total ensemble. The usefulness of chemical potential for systems that exhibit significant fluctuations must be questioned. The method used by Sciamanna and Prausnitz to evaluate chemical potential in small systems requires taking a derivative with respect to a discrete variable. The meaning of this operation for small systems is not clear.

The probabilistic approach used in this study avoids any problems with applying the concept of chemical potential to a single droplet. This approach considers all possible states of the system and requires no differentiation. The most probable state of the system predicted by the stochastic model is consistent with the results of Sciamanna and Prausnitz, but the average behavior of an ensemble of droplets is identical to the classical behavior. This agreement with the classical results is the result of a subtle assumption used in deriving Eq. 5. This assumption is that the positions of the phases are fixed. From a combinatorial point of view, the number of states available to an ensemble of droplets, in which droplet positions are fixed, is identical to the number of states in a bulk phase. Hence, the ideal entropy of these two systems should be the same. In the simplistic system considered in this study, only combinatorial effects need be considered, so the agreement with classical behavior is not surprising.

In real dispersed systems, droplet positions are not fixed. The number of possible droplet arrangements contributes to the overall entropy of the system, but this should not affect the phase equilibrium of the simple system used in this study. The average compositions of a dispersed system can be obtained by averaging over all possible positions. However, the average behavior of an ensemble of droplets with fixed positions is independent of the actual positions. Therefore, all configurations behave identically, and averaging over all configurations yields the same results as a single configuration.

The equilibrium properties of small systems and finely dispersed systems present special problems to chemical engineers. This study illustrates the danger of extending thermodynamic properties to a single droplet and extrapolating the results to an ensemble of droplets. This study suggests that ensembles of droplets, which are more important to chemical processing than single droplets, can be described by statistical averages. The results also suggest that differences between the behavior of a finely dispersed phase and a bulk phase do not arise from differences in the ideal entropy of mixing but from the complex molecular interactions.

Notation

k = Boltzmann constant
m = number of molecules of B in α phase after contacting
n_i = number of molecules of i
n_T = total number of molecules in a given phase
N_{N_A} = number of ways of arranging m molecules of B in the system
N_m^α = number of ways of arranging m molecules of B in the α phase for a system containing n_B molecules of B
$P(n_B)$ = probability that a droplet contains n_B molecules of B
$P\alpha(m)$ = probability that the α phase contains m molecules of B
$P\alpha(m|n_B)$ = probability that the α phase initially containing n_B molecules of B contains m molecules of B
T = temperature
x_B = mole fraction of B
μ_B = chemical potential of B
μ_B^* = reference chemical potential of B
$\psi(n)$ = diagamma function

Literature Cited

Sciamanna, S. F., and J. M. Prausnitz, "Thermodynamics of Highly Dilute Solutions and the Quest for Ultrapurity," *AIChE J.*, **33**, 1315 (1987).

Manuscript received Jan 21, 1988, and revision received Apr. 12, 1988