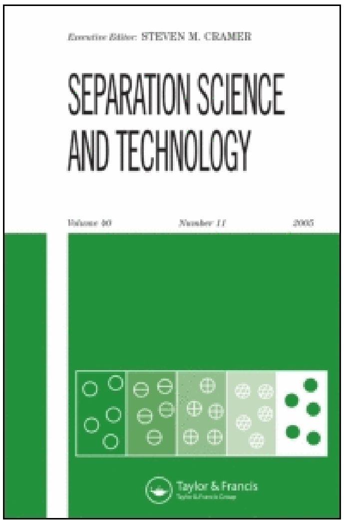

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A Theory of Chemical Separations: Thermodynamic Relationships in Linear Multistate Chemical Systems

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Summary

A simple relationship between the over-all thermodynamic equilibrium constant and the thermodynamic equilibrium constants for the individual partition states that occur within a linear multistate chemical system is derived. The interrelationships between the various parameters that characterize gas–liquid systems—the symmetrical activity coefficient at infinite dilution, Henry's constant, and the partition coefficient—are treated in detail to demonstrate the application of the theoretical results.

INTRODUCTION

This is the third in a series of articles whose purpose is to provide a more general approach to the discussion and characterization of equilibrium separation systems. A previous paper has shown that the fundamental linear partial differential equation for equilibrium chemical systems is

$$\frac{\partial c_{is}}{\partial t} - D_{ieff}\nabla c_{is}^2 + V_{ieff}\nabla c_{is} + k_{ieff}c_{is} = 0 \tag{1}$$

where the passive parameters D_{ieff}, V_{ieff}, and k_{ieff} are the effective dispersion coefficient, molar velocity, and pseudo-first-order rate constant, respectively,

$$D_{ieff} = \sum_{s=1}^{n} Y_{is}D_{is} \tag{2}$$

$$V_{i\text{eff}} = \sum_{s=1}^{n} Y_{is} v_{is} \tag{3}$$

$$k_{i\text{eff}} = \sum_{s=1}^{n} Y_{is} k_{is} \tag{4}$$

the subscript i represents component i—one of the distinct atomic, molecular, ionic, or aggregative species composing a mixture, the subscript s represents environment s—the immediate physical or chemical environment of a specific component i, Y_{is} is the fraction of component i in environment s,

$$Y_{is} = \frac{n_{is}}{n_i^0} = \frac{n_{is}}{\sum_{s=1}^{n} n_{is}} \tag{5}$$

and n_{is} is the number of moles of component i in environment s (*1*). Equations (1) through (5) are significant in that no assumptions regarding the chemical nature of either the component i or the environments $s = 1, 2, \ldots, n$ were made in the original derivation. The equations therefore apply to a wide variety of chemical systems (*2*).

A second paper in this series has demonstrated that the fundamental chemical entity in any equilibrium chemical system is the chemical state formed by the reversible physical or chemical reaction between a component i and an environment s (*3*). Such a state is called a *partition state* and is designated by the notation $\boxed{i{:}s}$ and by the subscript *is*. The customary statement of phase equilibrium (*4*),

> If two phases are in equilibrium, all components capable of passing from one to the other must have the same chemical potential in the two phases

can therefore be modified to incorporate *both* physical (i.e., phase) and chemical equilibria (*3*),

> If two partition states are in equilibrium, a component capable of passing from one to the other must have the same chemical potential in the two partition states.

In the present paper, we would like to pursue further the concept of a partition state and demonstrate a simple relationship between the *over-all* thermodynamic equilibrium constant for a linear multistate chemical system and the thermodynamic equilibrium constants for the *individual* physical and chemical equilibria that occur within the system. The interrelationships between the various parameters that characterize gas–liquid systems (such as the symmetrical activity coefficient at infinite dilution, the partition coefficient, Henry's constant, and the thermodynamic equilibrium constant) will be treated in some detail to demonstrate the application of the above concepts.

THEORETICAL

Consider a multistate chemical system (*1*) containing the following physical and chemical equilibria:

$$\underset{\text{in G}}{\boxed{i}} + s \rightleftharpoons \underset{\text{in L}}{\boxed{i{:}s}} \qquad s = 1, 2, \ldots, n \tag{6}$$

For simplicity of argument, we will assume that (a) the system has two phases (designated by the superscripts G and L) and (b) partition state $\boxed{i}$ is the only partition state within phase G (thus, all of the remaining partition states $\boxed{i{:}s}$ are in phase L).

The condition of over-all phase equilibrium is (*4–8*)

$$\mu_i^{\mathrm{G}} = \mu_i^{\mathrm{L}} \tag{7}$$

where μ_i is the over-all chemical potential of component i. According to a previous publication (*3*), we can write the condition of physical or chemical equilibrium for reactions (6) as

$$\mu_i^{\mathrm{G}} = \mu_{is} - \mu_s \equiv \mu'_{is} \qquad s = 1, 2, \ldots, n \tag{8}$$

where μ'_{is} is, *by definition* (*3*), the chemical potential of partition state $\boxed{i{:}s}$. Note that μ'_{is} is equal to the over-all chemical potential for component i in phase L,

$$\mu'_{is} = \mu_i^{\mathrm{L}} \qquad s = 1, 2, \ldots, n \tag{9}$$

We now define the activity, a, of component i in phases G, L, and environment s as

$$\mu_i^{\mathrm{G}} \equiv \mu_i^{\mathrm{G}\dagger} + RT \ln a_i^{\mathrm{G}} \tag{10}$$

$$\mu_i^{\mathrm{L}} \equiv \mu_i^{\mathrm{L}\dagger} + RT \ln a_i^{\mathrm{L}} \tag{11}$$

$$\mu_{is} \equiv \mu_{is}^{\dagger} + RT \ln a_{is} \tag{12}$$

respectively, where the superscript † represents the standard state chemical potential, a quantity which is dependent only on temperature and pressure. Rearranging Eqs. (8) and (10) through (12), we obtain

$$a_i^{\mathrm{L}} = a_i^{\mathrm{G}} \exp\left[\frac{\mu_i^{\mathrm{G}\dagger} - \mu_i^{\mathrm{L}\dagger}}{RT}\right] \equiv \mathbf{K}_i a_i^{\mathrm{G}} \tag{13}$$

$$a_{is} = a_i^{\mathrm{G}} \exp\left[\frac{\mu_i^{\mathrm{G}\dagger} + \mu_s - \mu_{is}^{\dagger}}{RT}\right] \equiv \mathbf{K}'_{is} a_i^{\mathrm{G}} \tag{14}$$

Equations (13) and (14) define the thermodynamic equilibrium constants $\mathbf{K}_i$ and $\mathbf{K}'_{is}$.

The mole fraction of component i in phase L, X_i^{L}, and in partition state $\boxed{i{:}s}$, X_{is}, are related by the formula,

$$X_i^{\mathrm{L}} \equiv \sum_{s=1}^{n} X_{is} \tag{15}$$

Recasting Eqs. (13) through (15), we can write the following equality,

$$\mathbf{K}_i \equiv \frac{a_i^{\mathrm{L}}}{a_i^{\mathrm{G}}} = \left(\frac{a_i^{\mathrm{L}}}{X_i^{\mathrm{L}}}\right)\left(\frac{X_i^{\mathrm{L}}}{a_i^{\mathrm{G}}}\right) = \left(\frac{a_i^{\mathrm{L}}}{X_i^{\mathrm{L}}}\right) \sum_{s=1}^{n} \left(\frac{X_{is}}{a_{is}}\right) \mathbf{K}'_{is} \tag{16}$$

In the limit as X_{is} approaches zero, the chemical system becomes progressively more ideal in component i and

$$\lim_{X_{is}\to 0} \left(\frac{a_i^{\mathrm{L}}}{X_i^{\mathrm{L}}}\right) = 1 \tag{17}$$

$$\lim_{X_{is}\to 0} \left(\frac{a_{is}}{X_{is}}\right) = 1 \qquad s = 1, 2, \ldots, n \tag{18}$$

Therefore,

$$\mathbf{K}_i^{\infty} \equiv \lim_{X_{is}\to 0} \mathbf{K}_i = \sum_{s=1}^{n} \mathbf{K}'^{\infty}_{is} \tag{19}$$

where the superscript ∞ represents the value of the thermodynamic equilibrium constant at infinite dilution.

For the linear system treated, Eq. (19) states that the effect of each partition state $\boxed{i{:}s}$ upon the distribution of component i between phases G and L is additive. This relationship is particularly valuable in chromatography (all types), where the infinite dilution approximation usually applies. Note that no assumptions regarding the physical or chemical nature either of component i or the environments s have been made in deriving Eq. (19).

The equilibrium constant, $\mathbf{K}'_{is}$, is somewhat unusual in the fact that it is dependent upon the chemical potential of environment s (rather than upon the *standard state* chemical potential of s). We can eliminate this feature by employing the equation

$$\mu_s \equiv \mu_s^{\dagger} + RT \ln a_s \tag{20}$$

and rewriting Eq. (19) as

$$\mathbf{K}_i^{\infty} = \sum_{s=1}^{n} \mathbf{K}_{is}^{\infty} a_s \tag{21}$$

where $\mathbf{K}_{is}^{\infty}$ is now a true thermodynamic equilibrium constant,

$$\mathbf{K}_{is}^{\infty} \equiv \exp\left[\frac{\mu_i^{G\dagger} + \mu_s^{\dagger} - \mu_{is}^{\dagger}}{RT}\right] \tag{22}$$

By employing arguments similar to the above, we can also derive a relationship between the partition *ratio* at infinite dilution, κ_i,

$$\kappa_i \equiv \lim_{X_{is} \to 0} \frac{c_i^{L}}{c_i^{G}} \tag{23}$$

and the partition *coefficients* (at infinite dilution) for the individual partition states $\boxed{i{:}s}$,

$$\kappa_{is} \equiv \lim_{X_{is} \to 0} \frac{c_{is}}{c_i^{G}} \tag{24}$$

This relationship is

$$\kappa_i = \sum_{s=1}^{n} \kappa_{is} \tag{25}$$

GAS–LIQUID DISTRIBUTION

The distribution of a component i in gas–liquid systems is characterized, at high dilutions, by a number of different parameters: (a) Henry's constant, H_i (for noncondensable gases),

$$H_i \equiv P \lim_{X_{is} \to 0} \frac{a_i^{G}}{a_i^{L}} \tag{26}$$

(b) the symmetrical activity coefficient at infinite dilution, γ_i^∞ (for condensable gases),

$$\gamma_i^\infty \equiv \frac{P}{p_i^0} \lim_{X_{is}\to 0} \frac{a_i^G}{a_i^L} \tag{27}$$

(c) the thermodynamic equilibrium constant at infinite dilution, $\mathbf{K}_i^\infty$ (for any type of gas),

$$\mathbf{K}_i^\infty \equiv \lim_{X_{is}\to 0} \frac{a_i^L}{a_i^G} \tag{19}$$

and (d) the partition ratio at infinite dilution, κ_i (for any type of gas),

$$\kappa_i \equiv \lim_{X_{is}\to 0} \frac{c_i^L}{c_i^G} \tag{23}$$

These four equations provide a clue as to how we can redefine the thermodynamic equilibrium constants, $\mathbf{K}_{is}'^\infty$, in terms of *equivalent Henry's constants, H_{is}, and equivalent symmetrical activity coefficients* (at infinite dilution), γ_{is}^∞. Thus,

$$H_{is} \equiv P \lim_{X_{is}\to 0} \frac{a_i^G}{a_{is}} \tag{28}$$

$$\gamma_{is}^\infty \equiv \frac{P}{p_i^0} \lim_{X_{is}\to 0} \frac{a_i^G}{a_{is}} \tag{29}$$

$$\mathbf{K}_{is}'^\infty \equiv \lim_{X_{is}\to 0} \frac{a_{is}}{a_i^G} \tag{30}$$

Two relationships which can be derived from Eq. (19) and Eqs. (26) through (30) are

$$\frac{1}{H_i} = \sum_{s=1}^{n} \frac{1}{H_{is}} \tag{31}$$

$$\frac{1}{\gamma_i^\infty} = \sum_{s=1}^{n} \frac{1}{\gamma_{is}^\infty} \tag{32}$$

Pitzer and Brewer have stated (*9*): "We frequently have to deal with solutions in which, for one reason or another, it is assumed that the solute forms compounds with the solvent. These are known in general as *solvates*. . . . Until the present time, however, it has been difficult to determine with any degree of certainty the relative amounts of [unsolvated] substances and of the various possible [solvates]. How, then, are we to treat such compounds in our thermodynamic work? The simplest method of disposing of this question would be to ignore the existence of such [solvates], and this would be entirely justifiable, since *thermodynamics is not compelled to take cognizance of the various molecular species which may exist in a system, particularly when the existence of such species cannot be absolutely demonstrated*" [author's emphasis].

The key point in the above quote is the question of *identity*, i.e., can we independently determine the various partition states of a distributing component i? If we can (and if it is possible to measure distinct thermodynamic equilibrium constants for each partition state), our theoretical description of a chemical system can be more detailed than Eq. (7). On the other hand, if the existence of many partition states cannot be demonstrated experimentally, there is usually little sense to further complicate the theoretical description with unmeasurable parameters such as $\mathbf{K}'^{\infty}_{is}$ in Eq. (19). The latter situation frequently occurs when mixed solvents are employed [each solute molecule is solvated simultaneously by molecules of each solvent, so no simple arithmetic relationship such as Eq. (19) exists].

CONCLUSIONS

The foregoing equations may prove useful for predicting and correlating gas solubilities in chemical systems where chemical interactions are prominent. Four gas–liquid systems for which there is detailed evidence for the existence of solvates or complexes are (a) the dissolution and ionization of ammonia in water (*9*), (b) the dissolution of iodine in benzene (*10, 11*), (c) the dissolution of acetone in chloroform (*4, 12, 13*), and (d) the dissolution of olefins in a solution of silver nitrate in ethylene glycol (*14*). Karger gives many other example of gas–liquid systems in which chemical interactions are important in determining separation efficiency (*15*).

While a gas–liquid equilibrium system has been employed as a model for the above calculations, the derived equations are generally applicable to liquid–liquid, solid–liquid, chemical, and other types of equilibria. This paper demonstrates that Eq. (7) is a relatively "ignorant" mathematical statement. There can be numerous hidden physical and chemical equilibria within a chemical system. The relative contributions of such equilibria to the solubility of a solute cannot be obtained from a knowledge only of the over-all equilibrium constant $\mathbf{K}_i$. To quote Locke, "the activity coefficient, γ_i^{∞}, represents the condition rather than the cause of solution non-ideality" (*16*).

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List of Symbols

a	activity
c	concentration (moles/cm^3)
D	diffusion coefficient (cm^2/sec)
H	Henry's law constant (atm)
k	pseudo-first-order rate constant (sec^{-1})
$\mathbf{K}$	thermodynamic equilibrium constant [Eqs. (13) and (22)]
$\mathbf{K}'$	modified thermodynamic equilibrium constant [Eq. (14)]
n	number of moles (moles)
n_i^0	total number of moles
P	total pressure (atm)
p_i^0	partial pressure of pure component i (atm)
R	gas constant (1.987 Gibbs/mole)
T	temperature (°K)
V	velocity (cm/sec)
X	mole fraction
Y	segregation fraction

Greek Letters

γ	activity coefficient (symmetrical convention)
κ	partition coefficient or partition ratio at infinite dilution (moles/cm^3:moles/cm^3)
μ	chemical potential
μ'	chemical potential of a partition state

Superscripts

G	gas phase (or any phase designated G)
L	liquid phase (or any phase designated L)
∞	infinite dilution
†	standard state

Subscripts

i	component i
$i\mathrm{eff}$	effective value for component i

is	component i in environment s $\left(\text{partition state } \boxed{i{:}s}\right)$
s	environment s
1, 2	specific environments

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