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THE CONDITIONS OF CHEMICAL EQUILIBRIUM

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ABSTRACT

Accepted thermodynamic theory assumes chemical equilibrium to require that the chemical potential μ_i of each component i be the same throughout the system. A thermodynamic theory is developed in which a more restrictive constraint is postulated. Each chemical component is assumed to be characterized by an average molar free energy content which must have the same value throughout a system at equilibrium. Subsets of a chemical component in non-ideal phases at equilibrium may have different sets of accessible energy states from those available to other subsets; as a consequence, the average molar free energies for a component i of such phases may differ from μ_i . The new theory is consistent with the laws of thermodynamics, and it predicts the same conditions of equilibrium as accepted theory for homogeneous reactions in dilute solutions, even if imperfect, and in heterogeneous equilibria of all components between perfect solutions or of solutes between dilute solutions. But conditions of heterogeneous equilibria involving one or more non-ideal solutions are predicted to be different from conditions predicted by accepted theory.

Inconsistances which have been reported between values of μ_i calculated from calorimetric data for metallic solutions and values from vapor

pressure or emf measurements are predicted by the new theory.

Introduction

The macroscopic theory of thermodynamics has been the subject of many careful studies.^{1,2} Those studies have demonstrated that equilibrium thermodynamic theory can be derived from a compact set of strongly buttressed postulates and is consistent with a large quantity of experimental data. As a consequence of the evidence, probably almost all physical scientists would agree with a statement by Peter Fong³ that "As far as a macroscopic theory of equilibrium is concerned, thermodynamics---has been developed to such a state of perfection that no more drastic new discovery is expected."

A major reason for the high level of confidence in macroscopic thermodynamic theory is the fact that it has seemed to depend upon no assumptions that can be questioned unless one questions the laws of thermodynamics themselves. Because of this apparent independence of assumptions, any discrepancy noticed between thermodynamic theory and chemical structure and bonding theory is inevitably settled in favor of the thermodynamic theory on the general grounds that arguments from models are unreliable.

But the definition of the chemical potential itself implies a model for chemical thermodynamic systems--a model that is not imposed as a requirement of the laws of thermodynamics. The definition of the chemical potential is almost certainly the most general and mathematically appealing postulate that can be formulated to describe the contribution of the chemical components of a system to its total thermodynamic properties. Nonetheless, as a postulate, it should be judged on the extent of agreement it provides with experimental data in

competition with any alternate postulate which also is compatible with the laws of thermodynamics.

The central purposes of this paper are (1) to postulate a relationship between the properties of the chemical components of a thermodynamic system and the integral thermodynamic properties of that system which differs from the relationship defined by the chemical potential and (2), to illustrate some of the consequences of the new postulate. The thermodynamic theory which results from the new postulate is consistent with the laws of thermodynamics and the Gibbs-Duhem relation and leads to the same predicted conditions of equilibrium for gas phase reactions, for partitioning of components between perfect solutions, and for homogeneous equilibria in dilute non-ideal solutions as does the accepted theory. But the new theory predicts different conditions from those now accepted as correct for heterogeneous equilibria involving a non-ideal solution and for liquid drop-vapor and crystallite-vapor equilibria.

In the present paper I say little about equilibria between drops or crystallites and their vapor because those topics seem best reserved for a separate discussion of the thermodynamics of surfaces and interfaces.

But I should mention that it was in the course of studying theories of vaporization kinetics for surfaces that I found discrepancies between concepts and predictions formulated in terms of Gibbs free energies and those formulated in terms of fugacities which led me to question the accepted theory.

Those discrepancies could be resolved by assuming fugacities to be related to the partial molal Gibbs free energies of particles at constant

molar surface area rather than at constant total surface area. That assumption conflicted with accepted theoretical proofs that surface free energies influence vapor pressure only through their effects on internal pressures of the bounded phases.^{4,5} The divergence of my analysis from accepted theory seemed to arise at a point common to more of chemical thermodynamics than to surface thermodynamics alone.

I had consciously treated small particles as if they are giant molecules. This has the effect of making the fugacity of a single component particle a function of its average molar free energy content. If this relationship is to be assumed for particles, consistency requires that a similar relationship be assumed between the fugacities of components of solutions and their free energy contents. Such a relationship is not consistent with accepted thermodynamic theory, but the studies of Elliott and co-workers encouraged me to think that thermodynamic solution theory might be imperfect.^{7,8} Elliott and co-workers have collected a considerable body of data for intermetallic solutions, some of which conflicts with accepted theory.⁸ The thermodynamic theory that has resulted from the new analysis predicts the general kind of behavior that they report and provides an explanation of the systematic disagreement that they have noticed between data obtained by different experimental methods.

The Chemical Potential in Thermodynamic Theory

The discussion that follows will always be in terms of the Gibbs free energy. The principal reason for this choice is that at constant temperature and pressure labile phase transformations (the melting of ice to liquid water, for example) are possible at constant Gibbs free

energy which have no counterparts when temperature or pressure is replaced by a different independent variable, such as volume. Specific consideration of labile equilibria is not necessary to a discussion of the distinctions between the new and the accepted theory, but a consideration of labile equilibria is essential to a full description of heterogeneous equilibria.

Gibbs¹ introduced the function now known as the chemical potential μ to describe the contribution of each chemical component to the thermodynamic functions of a chemical system. In multicomponent systems, the chemical potential for component i can be defined as the partial derivative of the Gibbs free energy taken with temperature T , pressure P , and the quantities of all other components n_j ---held constant:

$$\mu_i = \left[\frac{\partial G}{\partial n_i} \right]_{T,P,n_j} \quad (1)$$

When this relationship is adopted, the change in Gibbs free energy of any phase as a function of temperature, pressure, and quantities of the chemical components, if surface area is negligible, is

$$dG = VdP - SdT + \sum \mu_i dn_i \quad (2)$$

Equilibrium between two phases, α and β , at constant temperature and pressure requires that $dG^\alpha = dG^\beta$, from which it follows that the chemical potentials for each component must be the same in each phase. That is for component i , for example,

$$\mu_i^\alpha = \mu_i^\beta \quad (3)$$

As noted in the introduction, the definition of the chemical potential either by means of Eq. (1) or in the alternate forms that can be written¹ implies a model for chemical systems. Implicit in the derivation of Eq. (3) is the assumption that additional constraints are absent. The theory to be proposed in the next section assumes a stronger constraint on multi component equilibria than imposed by the requirement $dG^\alpha = dG^\beta$.

Some considerations outside accepted thermodynamic theory are cited as provisional justification for changes from accepted theory. In order to develop a model that agrees as closely as possible with our perceptions of the nature of chemical interactions, the chemical component is assigned a more prominent role than in accepted theory.

An Alternate Theory of Chemical Equilibrium

The components of a chemical system are defined, as usual, as the minimum set of elements or compounds from which the system can be formed. For simplicity in writing, this paper will usually speak of components as atoms.

A specific phase is defined as a phase for which all intensive properties are fixed. Any change in composition, temperature, pressure, structure or other intensive variables by even a differential amount, other than statistical fluctuations about an average, produces a change in specific phase.

The conclusion of accepted theory that $\mu_i^\alpha = \mu_i^\beta$ when specific phases α and β are at equilibrium is derived from the fundamental requirement that the total free energy G_T of a closed system be a minimum at constant temperature and pressure. In the new theory, a more restrictive condition of equilibrium is assumed. It is assumed that each chemical component of a multicomponent system, for example component i , has an identifiable free energy content G_i such that $G_T = G_1 + G_2 + \dots + G_i + \dots$, and each of these free energy contents of the sum must be separately minimized. This assumption has the immediate corollary that the component i in a quantity of a specific phase α sufficient to contain n_i^α moles of component i has an identifiable free energy content G_i^α . One of the intensive properties of phase α then is an average molar free energy content

$$\omega_i^\alpha = \frac{G_i^\alpha}{n_i^\alpha} \quad (4)$$

The nature of this average will be discussed in more detail later.

At this point it is important to identify the differences between ω_i^α and the chemical potential. The quantity ω_i^α is not given by Eq. (1), as is the chemical potential. The average molar free energy of component i is given by

$$\omega_i^\alpha = \left(\frac{\partial G_i^\alpha}{\partial n_i^\alpha} \right)_{T,P,c} \quad (5)$$

This differential is not for the total free energy content of phase α , G_T^α , but for the free energy content of component i in phase alpha, G_i^α , and

the subscript c is used to indicate that the differential is at constant composition of phase α rather than at constant number of moles of components other than i in phase α . When two phases, α and β , are at equilibrium there is no thermodynamic driving force for transfer of any component, say i , from one phase to the other. This condition is realized when

$$\omega_i^\alpha = \omega_i^\beta \quad (6)$$

In the new theory ω_i serves the function in determining what Lewis called the escaping tendency that μ_i serves in accepted theory.^{9,10} Accordingly, ω_i can be called the escaping potential for component i .

Equation (6) may appear to be nothing more than a restatement with a change of symbols of the requirement of the accepted theory that at equilibrium $\mu_i^\alpha = \mu_i^\beta$; one interpretation of the accepted theory is that each chemical potential is itself simply a measure of an average molar free energy for one component. This interpretation is encouraged by the fact that a requirement for equilibrium in the accepted theory is that the chemical potential for each component be identical in all parts of any phase or particle at equilibrium.¹ That there is a difference between ω_i and μ_i for some chemical systems, will be apparent after the conditions for local equilibrium in condensed phases or particles have been developed.

For a phase to be at internal equilibrium, it is necessary that the average molar free energy for each component have the same value throughout the phase when the volume elements compared are large enough to be viewed as internally homogeneous after thermal fluctuations are averaged. If this requirement were not met, the phase would be unstable with respect to transfer of a component from a volume element in which its average free energy content is high to a volume element in which its average free energy content is lower.

In a condensed phase, however, local equilibrium within these homogeneous regions is postulated in the new theory to require only that the average free energy content for each component summed over the local volume be a minimum and not that all atoms or molecules of a component have a single set of accessible free energy states. The term "set of free energy states" applied to a subset of the atoms or molecules of a particular component is meant to identify atoms or molecules which

because of different chemical environments, have different zero point energies from other atoms or molecules of the same component in the same phase. The relative concentrations of component atoms belonging to these different sets cannot be described by a conventional equilibrium constant.

For molecules the existence of separate sets of free energy states for a given component when in different environments within the molecule is already at least implicitly accepted. For example, the total molecular energy of organic molecules can be calculated as the sum of the energies of the bonds present.¹¹ The energies assigned to carbon-carbon single bonds are different from those assigned to carbon-carbon double bonds or triple bonds. When the bond energies are viewed as joint contributions of the atoms bonded, this procedure amounts to summing energy contents for the component atoms, with these energy contents for any given component atom a function of the number and kind of neighboring atoms. Furthermore, an equilibrium constant cannot be written to describe the relative concentrations within a molecule of a given kind of atom in the different environments in which it is found--the atoms of any component *i* in a molecule have free energy contents that fall into different sets depending on differences in their chemical environments.

This kind of analysis for molecules when extended to condensed phase non-ideal solutions yields the expectation that the free energy content of any atom will depend upon the nature of the atoms adjacent to it. Suppose, for example, that a solute dissolves exothermally to form a dilute solution in some solvent. Then the accessible energy

states and the resultant/^{free energy} contents of solvent atoms in the first coordination sphere about each solute atom in a dilute solution are systematically lower than the accessible energy states and the resultant average free energy contents of solvent atoms at greater distances from the solute atoms. The fraction of solvent atoms that can occupy the thermodynamically favored sites of lower average free energy cannot be increased beyond a value dictated by solute concentration and particle packing considerations no matter how much lower the average free energy content of solvent atoms in the first coordination sphere may be. The relative concentration of the solvent atoms that differ in average free energy contents depends on the solute concentration, not on an independent equilibrium constant. If the overall average molar free energy content of the atoms of each component of a dilute solution is the lowest possible for the system under consideration, the phase with local differences in average free energy contents will be thermodynamically stable.

Similarly, the surface atoms or molecules in a single component liquid drop which is suspended in its equilibrium vapor are in a higher average free energy state than are atoms or molecules inside the drop. The surface atoms are in equilibrium with the atoms inside the drop when the average free energy of the drop cannot be lowered at constant n for the drop by changing the fraction of atoms of the drop that are in the surface. The equilibrium is, of course, metastable relative to condensation of vapor to form larger drops.

With this background, a more explicit definition of the escaping potential ω_i for component i of a phase α can be stated as

$$\omega_i^\alpha = \frac{n_i(I)\tau_i(I) + n_i(II)\tau_i(II) + \dots}{n_i^\alpha} \quad (7)$$

where $n_i(II)$, for example, represents the number of moles of i in phase α with a Maxwell-Boltzmann distribution of energy state such that their average molar Gibbs free energy content is $\tau_i(II)$. The new symbol τ is introduced because values of τ_i in two phases at equilibrium are not necessarily equal while the values of ω_i must be equal.

A separate term in τ must be introduced for each subset of component i which have a distinguishable set of accessible energy states. The sum in the numerator yields G_i^α the total free energy content of particles of component i in α , and $n_i^\alpha = n_i(i) + n_i(II) + \dots$, as before, is the total number of moles of component i in phase α .

Now the conditions for thermodynamic equilibrium at constant temperature and pressure with surface and external field effects negligible, can be summarized in terms of the new theory. Equilibrium within a phase requires that the escaping potential for each component be the same in each volume element large enough to be viewed as homogeneous, but does not require that the free energy content for each component be the same for each atomic environment in which it is found. For two phases to be at equilibrium with each other, each chemical component of one phase must have the same escaping potential as does that component in the second phase. Specific phases at equilibrium with other specific phases are characterized by differences in intensive properties other than their escaping potential; for example, if two regions of a closed system are each internally homogeneous and have for each

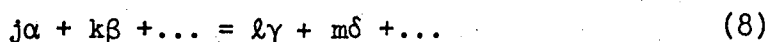
component the same escaping potential, but differ in density or average molar entropy, the two regions are parts of different specific phases.

The kinds of equilibria described above are stable equilibria in a system of fixed total composition if no reactions or rearrangements are possible that yield a new phase or phases that lower the total free energy content for the system. When such reactions or rearrangements are possible, the equilibria described above are metastable. Without experimental data or theoretical assumptions about the free energy contents of all conceivable compositional and structural arrangements of the matter in a given closed system, neither the accepted nor the new theory would allow a conclusion that an observed equilibrium state of the system is stable rather than metastable.

For most conditions in a system that is of fixed chemical composition and is initially at equilibrium, the result of a fluctuation in temperature or pressure will be, after the initial temperature and pressure are reestablished, a system that has the same specific phase or phases each present in the same quantity as before the fluctuation. Certain conditions, however, will yield a labile equilibrium in the sense that after a fluctuation each phase then present will be the same specific phase as before, but the relative quantities of phases may have changed. Such is the situation at the invariant points familiar in studies of phase equilibria, for example, at a congruent melting point, at the composition for congruent vaporization of a solid or liquid, or at a eutectic or peritectic transition.

A labile equilibrium state requires not only that the escaping potential of each component in each phase be equal to its escaping

potential in the other phases, but that there be no change in average molar free energy of any component when the labile equilibrium reaction takes place and that the compositions and properties of each phase be independent of the extent of reaction. These conditions can be expressed for the general case, say the reaction



where j, k, \dots and l, m, \dots are respectively the number of moles of reactant phases α, β, \dots and product phases γ, δ, \dots in the balanced reaction. Since G_T is unchanged by any arbitrary advancement $\Delta\eta$ of the labile equilibrium reaction

$$\begin{aligned} & - (j\sum (\omega_i^\alpha X_i^\alpha) \Delta\eta + k\sum (\omega_i^\beta X_i^\beta) \Delta\eta + \dots) \\ & + (l\sum (\omega_i^\gamma X_i^\gamma) \Delta\eta + m\sum (\omega_i^\delta X_i^\delta) \Delta\eta + \dots) = 0 \end{aligned} \quad (9)$$

where X_i^α , for example, is the mole fraction of component i in specific phase α .

Thus for the labile equilibrium reaction described by (8)

$$j\sum (\omega_i^\alpha X_i^\alpha) + k\sum (\omega_i^\beta X_i^\beta) + \dots = l\sum (\omega_i^\gamma X_i^\gamma) + m\sum (\omega_i^\delta X_i^\delta) + \dots \quad (10)$$

Predictions of the New Theory

The new theory predicts the same conditions of equilibrium for certain kinds of chemical systems as does the accepted theory. I will illustrate the application of the theory to such systems before discussing a system for which the predictions of the new theory are different.

For a single component system at constant temperature and pressure the chemical potential is in accepted theory equal to the average molar free energy content. The new theory always uses the average molar free energy as the critical parameter and consequently makes no change in predicted equilibrium for single component systems. It is worth noting, however, that even a single component phase may sometimes have subsets of atoms or molecules with different sets of available energy states. One example is β -manganese, for which the structural evidence indicates some atoms to be in different valence states than others.¹² Such a phase would have two values of τ in Eq. (7).

The average molar free energy content of any specified kind of gas molecule j in a gas mixture at low enough pressures so that the perfect gas law applies is a function only of its average internal free energy content and of its partial pressure and temperature. At constant temperature the change in its average molar free energy $\bar{\Delta}G_j$ in going from partial pressure P_1 to P_2 is $\bar{\Delta}G_j = RT \ln P_2/P_1 = RT \ln f_2/f_1$ where f_2 and f_1 are the fugacities of molecule j in the second and first state. This expression is identical to that for the change in the partial molal free energy between the same two states,¹³ so $\omega_2 - \omega_1$ is also equal to $\mu_2 - \mu_1$ for equilibria among gas/in the perfect gas range.

In either a single component or a polycomponent gas phase at equilibrium, the relative concentrations of the various molecules and atoms can always be expressed in terms of equilibrium constants, and the average molar free energy of each kind of atom will at equilibrium be the same in each kind of molecule in which that atom is present. For example, the gas phase equilibrium $\text{PCl}_5 = \text{PCl}_3 + \text{Cl}_2$ can be described at any temperature by an equilibrium constant, and at equilibrium the average molar free energy of chlorine atoms is the same in each of the three molecules. The new theory does not require that the molar free energy content of all the chlorine atoms within a PCl_5 molecule be the same, but only that their average be the same in PCl_5 as in PCl_3 and Cl_2 . Predictions of the new theory for compositions and concentrations in homogeneous/^{perfect} gas phase equilibria are thus unchanged from those of accepted theory.

For ideal condensed phase solutions, if the standard states for each component is taken as the pure component in the same state of matter as the solution, the integral free energy of formation of the solution is $\Delta G = \sum_i n_i RT \ln X_i$. Then ΔG_i is $n_i RT \ln X_i$ and $\bar{\Delta G}_i = \omega_i - \omega_i^0 = RT \ln X_i$, which is identical to $\mu_i - \mu_i^0$. Consequently, homogeneous equilibria in ideal solutions and the partition function for a solute between two ideal solutions are unchanged in the new theory.

The prediction of equilibrium conditions for reactions in dilute non-ideal solutions are also unchanged in the new theory, although the values of μ_i and ω_i should differ in such solutions. Suppose, for

example, that equilibrium for the reaction $aA + bB = A_a B_b$ is established in a solvent C. The free energy of the reaction ΔG_r can be written as

$$\Delta G_r = 0 = \Delta G_r' + \Delta G_r^c \quad (11)$$

where $\Delta G_r'$ is the free energy change in the reaction exclusive of the configurational entropy contributions and ΔG_r^c is the configurational contribution. But the configurational free energy change in the new theory is just $RT \ln(X_{A_a B_b}) - aRT \ln X_A - bRT \ln X_B$, which is the same value obtained in accepted theory. Solving Eq. (11) for the equilibrium constant K yields

$$\exp(-\Delta G_r'/RT) = K = \frac{X_{A_a B_b}}{X_A^a X_B^b} \quad (12)$$

$\Delta G_r'$ is a quantity that may be viewed as the sum $a\overline{\Delta G}_A' + b\overline{\Delta G}_B' + m\overline{\Delta G}_C'$ where $\overline{\Delta G}_A'$, for example, is ω_A' (in $A_a B_b$) - ω_A' (in A), and ω_A' (in $A_a B_b$), for example is the non-configurational part of the average molar free energy content of A atoms in $A_a B_b$, and m is the number of solvent atoms that undergo the average molar non-configurational free energy change $\overline{\Delta G}_C'$ as a result of formation of 1 mole of $A_a B_b$. In dilute solutions the configurational free energy change for the solvent can be neglected.

For comparison $\Delta G_r'$ can be expressed in terms of the non-configurational contributions to the chemical potentials: $\Delta G_r' = a\overline{\Delta G}_A' + b\overline{\Delta G}_B'$ where $\overline{\Delta G}_A'$, for example, is μ_A' (in $A_a B_b$) - μ_A' (in A). But only the sum $\Delta G_r'$ is required in order to relate the equilibrium constant to concentrations. This sum $\Delta G_r'$ is independent of our choice of chemical

potential or escaping potential as the parameter which determines the conditions of heterogeneous equilibrium, so that as long as attention is restricted to homogeneous reactions in solutions dilute enough to make $\Delta G_r'$ independent of concentrations, predictions of equilibrium are unaltered by the new theory.

This conclusion should apply both to such reactions as dissociation of weak acids or bases in a solvent such as water and to formation of thermally created substitutional defects such as vacancies in solids.

The conditions of heterogeneous equilibrium predicted by the new theory are different from those of accepted theory if one or more of the phases in the equilibrium is a non-ideal solution. Consider as an illustration a rather general model for a substitutional binary solution for which accepted theory would predict the solute B to obey Henry's law and the solvent A to obey Raoult's law. For simplicity the components will be described as atoms, but the discussion would apply equally to systems with molecular components.

As long as the concentration of B atoms is sufficiently low that the interactions between B atoms can be neglected, the non-configurational part of the free energy of formation of the solution is directly proportional to the number of moles of B in the solution n_B so that

$$\Delta G_t = n_B \Delta G_f' + n_B RT \ln X_B + n_A RT \ln X_A \quad (13)$$

where $\Delta G_f'$ is the non-configurational part of the free energy of formation of enough solution to contain one mole of B. But

$(\partial \Delta G_t / \partial n_B)_{T,P,n_A} = \Delta G_f' + RT \ln X_B = \mu_B - \mu_B^{\circ}$. In accepted theory it is assumed that at equilibrium the chemical potential of B in the solution is equal to its chemical potential in the vapor, μ_B^v . Since $\mu_B^v - \mu_B^{\circ} = RT \ln(f_B/f_B^{\circ})$ it then follows that the activity of the solute $a_B = f_B/f_B^{\circ} = X_B \exp(\Delta G_f'/RT)$, which is one form of Henry's law, with the Henry's law constant identified as $f_B^{\circ} \exp(\Delta G_f'/RT)$. When μ_A for the A in solution is assumed equal to μ_A^v , either direct differentiation of Eq. (12) with respect to n_A or application of the Gibbs-Duhem relation leads to Raoult's law, $f_A = f_A^{\circ} X_A$, for the solvent in the range over which the solute obeys Henry's law.¹³

In the new theory the non-configurational free energy is a consequence of a change in free energy content not only of solute atoms, but also of solvent atoms in a sphere about each solute atom. Whether the sphere that includes those solvent atoms that undergo a significant change in free energy content includes only the nearest neighbors to each solute atom or includes solvent atoms at greater distances would depend upon the particular system. The analysis to follow does not require that the diameter of the sphere of influence be known, but the analysis is valid only for the concentration range over which the overlapping of spheres of influence on free energy content of solvent atoms can be neglected.

The configurational free energy contribution to ω_A or ω_B in a substitutional solution is the same as it is to μ_A or μ_B ; the fact that some of the A atoms are conceived in the new theory to have different non-configurational free energy contents than do others does not

alter this conclusion since an exchange of A atoms between positions of different free energy contents produces configurations indistinguishable from the configuration before the exchange.

If the non-configurational free energy content of the pure solvent is described by $G'_A = \omega'_A n_A$ the non-configurational free energy content of the solvent after solution of n_B moles of B would be

$$G'_A = \omega'_A n_A(0) + \tau'_A(I) n_A(I) + \tau'_A(II) + \dots \quad (14)$$

Here $n_A(0)$ is the number of solvent atoms far enough from all solute atoms to be unaffected by their presence in solution and $n_A(II)$, for example, is the number of solvent atoms that have changed in non-configurational free energy content from ω'_A to $\tau'_A(II)$ as a result of solution formation. But $n_A(II)$ must be proportional to n_B and $\tau'_A(II) - \tau'_A(0)$ can be called $\Delta\tau'_A(II)$ so the changes in non-configurational free energy content of the solvent atoms is

$$\Delta G'_A = n_B [k_I \Delta\tau'_A(I) + k_{II} \Delta\tau'_A(II) + \dots] \quad (15)$$

where k_{II} , for example, is the ratio of $n_A(II)$ to n_B .

The sum inside the brackets is the contribution of the change in solvent free energy content to $\Delta G'_f$. This sum can be called $k \Delta G'_f$ where k is a constant.

Thus

$$\Delta G'_A = n_B k \Delta G'_f \quad (16)$$

and by difference

$$\Delta G'_B = n_B(1-k)\Delta G'_f \quad (17)$$

The change in escaping potential of the solute is $\omega_B - \omega_B^0 = (1-k)\Delta G'_f + RT \ln X_B$ and since $\omega_B = \omega_B^v$ at equilibrium, $\omega_B - \omega_B^0 = RT \ln f_B / f_B^0$. When the definition of the activity of B is made $a_B = f_B / f_B^0$, not only for the vapor but for a condensed phase at equilibrium with its vapor,

$$a_B = \frac{f_B}{f_B^0} = X_B \exp[(1-k)\Delta G'_f / RT] \quad (18)$$

This equation is Henry's law with the Henry's law constant identified as $f_B^0 \exp[(1-k)\Delta G'_f / RT]$ instead of as $f_B^0 \exp(\Delta G'_f / RT)$, the value in accepted theory.

For the solvent, $\omega_A - \omega_A^0 = Z_B k \Delta G'_f + RT \ln X_A$ where $Z_B = n_B / n_A$, the mole ratio of solute to solvent. It follows since $\omega_A = \omega_A^v$ that

$$a_A = \frac{f_A}{f_A^0} = X_A \exp(Z_B k \Delta G'_f / RT) \quad (19)$$

This expression reduces to Raoult's law only if the exponent is zero.

If the exponent is expressed as a series, Eq. (19) becomes

$$a_A = \frac{f_A}{f_A^0} = X_A \left[1 + \frac{Z_B k \Delta G'_f}{RT} + \frac{1}{2!} \left(\frac{Z_B k \Delta G'_f}{RT} \right)^2 + \dots \right] \quad (20)$$

At solute concentrations low enough so that the difference between X_A and 1 and between Z_B and X_B can be neglected, the first three terms of the series expansion have the functional form of the equation which Elliott, Lemons, and Swofford⁷ deduced for the solvent in its concentrated solution by analogy with Henry's law. In Elliott's equation

$$a_A = f_A/f_A^0 = 1 - k_A X_B + k_B X_B^2 \quad (21)$$

the terms k_A and k_B are introduced as proportionality constants that reflect respectively interactions of solute atoms with solvent atoms and interactions between solute atoms, and k_A is explicitly expected to differ from unity--the value required by Raoult's law--unless the solute also obeys Raoult's law. Terms in $k_B X_B^2$ can arise either from solute-solute interactions as envisioned in Elliott's equation or from solute-solvent interactions as demonstrated in the derivation of Eq. (20). This point should be kept in mind when the predictions of Eq. (20) are compared to experimental data.

The original impetus to the solution studies of Elliott and his co-workers was Elliott's identification of an inconsistency between the models for chemical solutions from which Henry's law can be derived and the conclusion reached by application of the Gibbs-Duhem equation--that the solvent obeys Raoult's law in the range of concentrations over which the solute obeys Henry's law.¹⁴ Because macroscopic thermodynamic theory has been generally perceived as employing no assumptions except the laws of thermodynamics, most physical chemists have rejected the arguments that led to Elliott's equation and have discounted

experimental data which Elliott and co-workers collected in support of the equation on the general grounds that measurements of variation of solvent activities as a function of very low solute concentrations is exceptionally difficult. And Elliott and co-workers have themselves been led to question the laws of thermodynamics in a privately circulated monograph.¹⁵

In the present paper it is argued that accepted solution theory has implicitly employed a model that is not imposed as a necessary consequence of the laws of thermodynamics. The alternate theory which has been proposed has been shown above to be consistent with the laws of thermodynamics and with the Gibbs-Duhem equation, so long as that equation is applied to relate the chemical potentials of a particular phase, and yet to yield an expression for the relationship between solvent fugacities and compositions in the Henry's law range for the solute which is approximated by Elliott's equation.

A partition function between two immiscible solvents can be obtained immediately for a solute in dilute solutions by eliminating f_B from the Henry's law equations (18) for the two solutions. The result

$$\frac{x_B^B}{x_B^\alpha} = \exp\{[(1-k^\alpha)\Delta G_f^{\alpha'} - (1-k^\beta)\Delta G_f^{\beta'}]/RT\} \quad (22)$$

has the same form as the partition function of accepted theory, but the exponential is no longer $(\Delta G_f^{\alpha'} - \Delta G_f^{\beta'})/RT$ as it is in accepted theory.

Discussion

In this paper the accepted conditions of heterogeneous chemical equilibrium, that each component have the same chemical potential in each phase present, has been identified as dependent on an implied model for chemical interactions. A thermodynamic theory has been described which depends upon a more restrictive assumption--that in a system at equilibrium each chemical component has an average free energy content that must be the same in all parts of the system, with the parts chosen just large enough to be treated as homogeneous with respect to any inherent structural discontinuities or thermal fluctuations. The equilibrium is labile if the conditions of Eq. (10) are met or metastable if some alternate arrangement of the components can lower the escaping potentials of the system components from their values in the established equilibrium.

A second difference from accepted theory is that the new theory explicitly assumes that atoms of a given component can belong to subsets which have different sets of accessible energy states and therefore different average free energy contents. A system can be stable with some atoms in higher average free energy states than are other atoms of the same component if the structural sites at which the atoms have lower accessible energy states are fully occupied. A consequence derived in accepted theory is that atoms of a given component must all have the same chemical potentials if the system is at equilibrium.

The new theory has been shown to yield the same predicted equilibria as does accepted theory in several circumstances--in homogeneous reactions in gas or condensed phase dilute solutions, even if

imperfect, and for all components in heterogeneous equilibria between perfect solutions or of solutes between dilute solutions. But for partitioning of solutes between dilute solutions the partition constant is not in the new theory a simple function of the integral free energies of formation of the two solutions as it is in the accepted theory.

The Henry's law constant for a solute in the new theory includes an exponential term, $(1-k)\Delta G_f'$ where the accepted theory has $\Delta G_f'$. Here k is a constant that must be determined by experiment or assumption if the fugacity of the solute in dilute solution is to be related to $\Delta G_f'$, the non-configurational part of the integral free energy of formation of enough solution to contain one mole of solute.

The solvent activity change with composition in a binary solution is predicted to be approximated by Eq.(19) or (20) rather than Raoult's law in the general range of applicability of Henry's law for the solute. The most obvious means of testing the alternate theories is by determining whether the experimental data for solvents in binary solutions are better fit by Raoult's law or by Eq. (19) or (20) in the range in which the solute obey Henry's law. Unfortunately, this approach presents serious experimental difficulties. It has seldom been possible to obtain good experimental data for both a solute in dilute solution and for the solvent in the same composition range. Ralph Hultgren, who with his co-workers is just completing a new compilation of data for binary intermetallic solutions and related substances,¹⁶ considers that Elliott's data⁸ are not precise enough to disprove the accepted relationship, but considers that data for metals which prove the relationship are not available either.¹⁷

Fortunately, other approaches to testing the theory are possible. The new theory challenges the relationship $\mu_i^c = \mu_i^v$, where μ_i^c is the chemical potential for a component of a condensed phase and μ_i^v is its chemical potential in the vapor. However, the new theory includes the relationship $\mu_i^v - \mu_i^o = \omega_i^v - \omega_i^o = RT \ln f_i / f_i^o$, when the gas phase obeys the perfect gas law, and $\mu_i^c - \mu_i^o$ can be obtained from calorimetric determinations of heats of solution as a function of composition which are corrected for the entropy of solution formation. If accepted theory is correct, the value of $\mu_i^c - \mu_i^o$ calculated from the integral solution data will always be equal to $RT \ln f_i / f_i^o$, when this latter quantity is determined by direct measurements of partial pressures. But if the new theory is correct, the two values will differ for some non-ideal solutions by more than expected from experimental errors.

An important reason for withholding judgment on whether solvent behavior in metallic solution is described in the Henry's law range by Raoult's law or not has been the observation, remarked on by Elliott et al. as not yet explainable, that calorimetric results usually show good correlations with regular solution theory, while results from vapor pressure and electromotive force (emf) measurements do not.⁸ This systematic difference in behavior is predicted by the new theory. As noted in the preceding paragraphs, calorimetrically determined data yield chemical potentials which obey the Gibbs-Duhem relationship while emf measurements for binary solutions, as well as vapor pressure measurements, yield escaping potentials for individual components, which do not.

It must be remembered in testing the theory by comparing calorimetric data to emf or vapor pressure data that non-ideal solutions in some composition ranges may have escaping potentials with values close

to their chemical potentials. Binary quasi-chemical regular solutions¹⁸ near equimolar concentrations, for example, would be unsuitable for tests of the theory because for such solutions the escaping potentials are equal to the chemical potentials when $X_A = X_B = 0.5$.

Tests of the theory with solutions that show more extreme departure from ideality than do intermetallic solutions are desirable. In our laboratory, we will attempt to determine the fugacities of both oxygen and titanium in the solid solutions of oxygen in titanium metal. Calorimetric measurements by Mah and co-workers¹⁹ are available as a function of composition which show the oxygen-titanium solution to be highly exothermic.

This paper has necessarily been restricted to a discussion of only a few of the relationships involving the Gibbs free energy, and has included almost nothing about other thermodynamic functions. But it is implicit in the discussion which has been given that other average molar thermodynamic properties play the role in the new theory that the corresponding partial molal quantities do in accepted theory. Usually the required relationships are obvious from the discussion that has been given. But it is necessary to question whether any reported value of the partial molal enthalpy of solution, for example, was calculated from measurements of the composition dependence of integral enthalpies of solution or was derived from determination of the temperature dependence of a fugacity or emf measurement. If the reported value was derived from measurements of integral enthalpies of solution, it is a partial molal enthalpy, but if from fugacities it is a measure of the average molar enthalpy of solution. The temperature dependence of emf

measurements if for one component of a polycomponent system are measures of average molar enthalpies of solution.

My next paper will describe implications of the new theory to the thermodynamics of surfaces. The formulations of surface thermodynamic relationships⁶ which I mentioned at the beginning of this paper can be derived as consequences of the theory.

In conclusion, it may be well to emphasize one particular distinction between the chemical thermodynamic theory presented here and accepted theory. The new theory does not permit the general use of the Gibbs-Duhem relation to determine the change in fugacity of one component of a non-ideal binary solution with composition from a known change in fugacity of the second component with composition. Consequently, the range of predictions that can be made without resort to chemical models is reduced in the new theory in comparison to accepted theory. This same loss in predictability arises, of course, also in polycomponent systems.

To take a more positive view, the new theory stresses the relationship between the changes in average free energy content and the changes of chemical bonding forces acting on each component when it is transferred from one specific phase to another. We can hope to obtain increased insight into the nature of chemical bonding by developing and exploiting our understanding of the relationships.

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