

A thermodynamic framework for solutions based on the osmotic equilibrium concept –

1. General formulation

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Abstract

In this article a novel approach, based on the concept of osmotic equilibrium, is presented for the calculation of thermodynamic properties of solutions. This thermodynamic framework is inspired on the parallelism between the "solute-solvent" and "gas-vacuum" systems, initially established by the McMillan-Mayer theory (Hill [1]). The proposed formalism is developed within the context of the Legendre Transformation of the internal energy with respect entropy, volume and mole numbers of solvent species. Therefore, the equation of state express a mathematical relationship among osmotic pressure, temperature, volume, mole numbers of solute species, and chemical potentials of solvent species. In the traditional approach the equation of state relates pressure, temperature, volume and mole numbers of all species.

INTRODUCTION

There is a great number of semi-empirical models that can be used for modeling electrolyte solutions. These models are mostly based on the assumption that the excess Gibbs free energy of an electrolyte system can be written as follows (Cardoso et al. [2]) :

$$G^E = G_{LR}^E + G_{SR}^E \quad (1)$$

The long-range contribution (G_{LR}^E) is generally taken into account by means of the Debye - Hückel expression. For the short-range term (G_{SR}^E) several types of models have been used (e.g. NRTL and UNIQUAC models).

As previously remarked by Cardoso and O'Connell [3], there are some difficulties in establishing a rigorous theoretical justification for adding up LR and SR contributions due to different solution theories used in their derivations. The LR term is in general derived from the McMillan-Mayer Theory (T,V, solvent chemical potentials, solute mole numbers), while the SR contribution is obtained in the Lewis-Randall system (T,P, species mole numbers).

This article discusses a new methodology for calculating thermodynamic properties of non-ideal solutions, based on osmotic equilibrium (Π framework). The proposed approach lies on the parallelism between the "solute-solvent" and "gas-vacuum" systems, initially established by McMillan-Mayer theory (Hill [1], Friedman [4]).

II FRAMEWORK

The internal energy for a multicomponent system can be written as follows :

$$U = U(S, V, N_n, N_i) \quad (2)$$

where,

- S, V : system entropy and volume
- N_n : solvent mole numbers ($n = 1, \dots, \text{NSOLV}$)
- N_i : solute mole numbers ($i = 1, \dots, \text{NSOLU}$)

The Legendre Transformation of the internal energy with respect to S , V and all N_n allows us to define a new thermodynamic potential :

$$\Psi = \Psi(T, P, \mu_n, N_1) = U - TS + PV - \sum_n \mu_n N_n \quad (3)$$

which is equivalent to

$$\Psi = \Psi(T, P, \mu_n, N_1) = \sum_i \mu_i N_i \quad (4)$$

where,

T, P : system temperature and pressure

μ_n : chemical potential of solvent n

μ_1 : chemical potential of solute i

The differential form of (3) or (4) is expressed as

$$d\Psi = -SdT + VdP - \sum_n N_n d\mu_n + \sum_i \mu_i dN_i \quad (5)$$

which explicitly shows the dependence of Ψ on its natural coordinates (T, P, μ_n, N_1) .

In order to introduce the concept of osmotic pressure we must attach to the system a finite solvent compartment. The compartment communicates with the system through a suitable wall perfectly permeable to all solvent species and impermeable to all solute species. We assume that both system and solvent compartment are thermodynamically equilibrated with respect to temperature and the chemical potentials of the solvent species.

This combined system (system + solvent compartment) has its internal temperature and chemical potential of solvent species firmly established by means of equilibrated contacts with reservoirs of heat and solvent species (Callen [5]). Each one of these reservoirs is a very large system with uniform temperature and chemical potential for an individual solvent. It communicates with the combined system through an appropriate wall permeable only to heat and to that solvent.

The intensive properties of the solvent compartment are kept constant due the contact with the reservoirs and do not depend on the state of the original system. By denoting with an index "o" the state of the solvent compartment, we can express the correspondent Gibbs-Duhem equation as :

$$-S_0 dT + V_0 dP_0 - \sum_n N_n^0 d\mu_n = 0 \quad (6)$$

Therefore the solvent compartment pressure P_0 is only dependent of the external fields (T, μ_n) .

The osmotic pressure (Π) is the difference between the system equilibrium pressure (P) and P_0 . Thus

$$\Pi = P - P_0 \quad (7)$$

The differential form of the thermodynamical potential can be recasted by using eqs (5), (6) and (7) as

$$d\Psi = \left[-S + (V/V_0)S_0 \right] dT + Vd\Pi + \sum_n \left[-N_n + (V/V_0)N_n^0 \right] d\mu_n + \sum_i \mu_i dN_i \quad (8)$$

where it turns out that the osmotic pressure has now the status of a system independent coordinate. It is possible to write, by means of eq (8), the following partial derivatives :

$$\left(\frac{\partial \Psi}{\partial T} \right)_{\Pi, N_1, \mu_n} = -S + (V/V_0)S_0 \quad , \quad \left(\frac{\partial \Psi}{\partial \Pi} \right)_{T, N_1, \mu_n} = V \quad (9)$$

$$\left(\frac{\partial \Psi}{\partial \mu_n} \right)_{T, \Pi, N_1, \mu_m} = -N_n + (V/V_0)N_n^0 \quad , \quad \left(\frac{\partial \Psi}{\partial N_1} \right)_{T, \Pi, N_j, \mu_n} = \mu_1 \quad (10)$$

Maxwell relations can be straightforwardly derived. For example :

$$\left(\frac{\partial \mu_1}{\partial \Pi}\right)_{T, N_1, \mu_n} = \left(\frac{\partial V}{\partial N_1}\right)_{T, \Pi, N_j, \mu_n} = \bar{V}_1 \quad (11)$$

$$\left(\frac{\partial \mu_1}{\partial T}\right)_{\Pi, N_1, \mu_n} = \left(\frac{\partial(-S + (V/V_0)S_0)}{\partial N_1}\right)_{T, \Pi, N_j, \mu_n} = -\bar{S}_1 + (S_0/V_0)\bar{V}_1 \quad (12)$$

In these formulae the second derivatives are essentially analogous to the so defined partial molar property operator (Van Ness and Abott [6]). The properties \bar{V}_1 and \bar{S}_1 embody the same features of the familiar partial molar properties. For instance, by means of eqs (4),(9),(11) and (12) one can easily show that

$$V = \sum_1 N_1 \bar{V}_1 \quad , \quad S = \sum_1 N_1 \bar{S}_1 \quad (13)$$

AN IDEAL GAS SOLUTE MODEL

In the present context, we define an ideal solution by the following relationship for the solute species chemical potential :

$$\mu_i^{ID} = \mu_i^*(T, l, \mu_n) + RT \ln(\Pi z_i) \quad (14)$$

where $\mu_i^*(T, l, \mu_n)$ is the chemical potential of solute species i at system temperature T , solvent chemical potentials μ_n , and unity osmotic pressure, z_i is the solvent free solute mole fraction and R is the gas constant. Equation (14), written for the solute species in a solvent medium, is in close analogy with the chemical potential of a gas species belonging to an ideal gas mixture in a "vacuum medium".

With formulae (11) and (13) one gets the well known Van't Hoff equation for the osmotic pressure in dilute multisolute systems :

$$\bar{V}_1^{ID} = RT/\Pi \quad , \quad V^{ID} = \left(\sum_1 N_i\right) RT/\Pi \quad (15)$$

It also can be derived from this model the following properties of mixing for solute mixtures prepared at constant T, Π and μ_n :

$$\Delta V^{MIX} = 0 \quad , \quad \Delta S^{MIX} = -R \sum_1 N_i \ln z_i \quad (16)$$

These results are identical to the familiar property changes of mixing for "conventional" ideal gases [6].

THE REAL SOLUTION CASE

A real solution framework may now be defined in close analogy with the classical approach adopted for non-ideal gas mixtures [6]. Differentiating (14) at constant T, μ_n one arrives :

$$d\mu_1^{ID} = RT d \ln(\Pi z_1) \quad (\text{const. } T, \mu_n) \quad (17)$$

Relationship (17) can then be used to evaluate μ_1^{ID} changes for processes carried on at constant T and μ_n . This practical feature can now be readily extended to real systems by

introducing a fugacity function in the Lewis sense :

$$d\mu_1 = RTd\ln f_1^{\text{os}} \quad (\text{const. } T, \mu_n) \quad (18)$$

For the sake of completeness, we have to choose the value of an integration constant in the fugacity definition. We set this constant such that

$$f_1^{\text{os, ID}} = \Pi z_1 \quad (19)$$

Using eq (11) and (18) we can write

$$\bar{V}_1 d\Pi = RTd\ln f_1^{\text{os}} \quad (\text{const. } T, \mu_n, z_1) \quad (20)$$

By standard algebraical manipulations, integrating from $\Pi=0$ to $\Pi=\Pi$ at constant T, μ_n, z_1 , and assuming ideal behavior (eq (19)) at $\Pi=0$, one gets

$$\ln(f_1^{\text{os}}/\Pi z_1) = \int_0^\Pi \left(\frac{\bar{V}_1}{RT} - \frac{1}{\Pi} \right) d\Pi \quad (21)$$

Relationship (21) can be used for calculating osmotic fugacity (f_1^{os}) provided an equation of state for the osmotic pressure is given in terms of V, T, μ_n and z_1 . In this way, it is remarkable that all formalisms for calculating fugacity in gas mixtures, can be readily extended for modeling non-ideal solutions. Therefore the proposed approach allows one to avoid the more traditional formalism based on the excess Gibbs free energy.

Based on the Π framework it is possible to do calculations of thermodynamic properties of electrolyte systems by means of a semi-empirical model for the osmotic pressure as follows

$$\Pi = \Pi_{\text{LR}} + \Pi_{\text{SR}} \quad (22)$$

where Π_{LR} and Π_{SR} stand for Debye-Hückel and a Van der Waals type equation of state contributions. Experimental osmotic pressure data can be used to fit necessary model parameters.

The present framework is similar with the so called ISAC theory (Isoactive-Solvent) proposed by Myers and Myers [7] in the sense that the same thermodynamic potential is used. Nevertheless, ISAC theory adopts a excess free energy approach which leads to activity coefficient as basic functions.

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