

MODELS FOR THERMODYNAMIC AND PHASE EQUILIBRIA CALCULATIONS

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Models for Electrolyte Solutions

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I. MODELS FOR ELECTROLYTE SOLUTIONS

In recent years there has emerged considerable interest in models for aqueous electrolyte systems. This has been largely the result of increased concern for the environment. Aqueous-based environmental applications include gas treatment, wastewater treatment (e.g., processes involving chromatographic separations, membrane separations, pH-controlled neutralization), and chemical waste disposal in underground injection wells. In addition, aqueous chemistry is an important aspect in many other applications within the chemical industry. Typical applications occur in the areas of bioseparations, corrosion, oilfield research (e.g., scaling, enhanced oil recovery), geothermal wells, paper production, etc.

The purpose of this chapter is to provide a practical working knowledge of models of electrolyte solutions. The specific disciplines involved include:

1. Aqueous chemistry
2. Phase equilibrium
3. Thermodynamics
4. Thermodynamic property estimation
5. Mathematical modeling
6. Computer science

Creating a unified treatment of electrolyte solutions requires assimilating the contributions of researchers in the diverse areas of theory, experimentation, correlation, data compilation, computer codes, and industrial applications.

Phase equilibrium models involving an aqueous phase have generally been more difficult to produce than similar models which do not require describing an aqueous phase. The reasons for this difficulty involve describing the nonideal behavior of the aqueous solution. The conventions used in describing nonideal aqueous solution behavior, such as the mean activity coefficient, differ from those used in other phases. Another reason for the difficulty in aqueous modeling is due to the different standard state of the aqueous phase and the often complex chemistry involved. This latter issue, which refers to the detailed speciation and the associated intraphase equilibrium reactions which occur in the aqueous phase, is of crucial importance in determining the behavior of many aqueous systems. For example, in the ternary system $\text{H}_2\text{O}/\text{CO}_2/\text{NH}_3$, the vapor–aqueous phase equilibria are determined by the concentration of the molecular species $\text{H}_2\text{O}(aq)$, $\text{CO}_2(aq)$, and $\text{NH}_3(aq)$ in the aqueous phase. The concentration of these species within the aqueous phase are determined by the speciation and aqueous intraphase equilibria involving $\text{NH}_4^+(aq)$, $\text{NH}_2\text{CO}_2^-(aq)$, $\text{CO}_3^{2-}(aq)$, $\text{HCO}_3^-(aq)$, $\text{H}^+(aq)$, and $\text{OH}^-(aq)$.

The material in this chapter addresses all of these issues. Mastery of this material should allow for an understanding of the proper representation of the mathematical model of an aqueous system. In addition, it should also allow for the proper integration of these models into a larger framework involving other physical phases and, finally, a better understanding as to the workings of

the various computer codes for predicting the behavior of aqueous systems.

II. TERMS AND DEFINITIONS

The material in this chapter, as well as much of the literature on aqueous systems, is based on various terms and definitions. These generally fall into two broad categories: aqueous systems terminology and aqueous thermodynamic definitions. Each of these will be considered in more detail below.

A. Aqueous Systems Terminology

The following terms should be understood before further reading is done in this area:

Phase—The physical state of one or more chemical species.

The phases considered in this chapter and the conventional shorthand notation are gaseous (*g*), liquid (*l*), aqueous (*aq*), and solid (*s* or *cr*)

Electrolyte—A molecular or atomic species (gaseous, liquid, or solid) which has some solubility in water and reacts in water, to some significant extent, to one or more ionic (charged) species. $\text{CO}_2(g)$, and $\text{NaCl}(s)$ are examples of electrolytes.

Nonelectrolyte—A molecular or atomic species (gaseous, liquid, or solid) which has some solubility in water and remains nearly totally in the molecular form (uncharged) when dissolved in water. $\text{Ar}(g)$ and $\text{C}_6\text{H}_{14}(l)$ are examples of nonelectrolytes.

Ionic species—A species dissolved in water and possessing a charge. Charged species are either termed cations (positive charge) or anions (negative charge). $\text{Na}^+(aq)$ and $\text{Cl}^-(aq)$ are examples of ionic species.

Molecular species—A species dissolved in water and having no charge. $\text{CO}_2(aq)$ and $\text{FeCl}_3(aq)$ are examples of molecular species.

Complex, ion pair—A species composed of both cationic and anionic portions. Complexes can be charged or uncharged. $\text{FeCl}_2^+(aq)$ and $\text{FeCl}_3(aq)$ are examples of complexes.

Strong electrolyte—A molecular or atomic species which completely dissociates to its constituent base ions, leaving virtually no uncharged molecular forms of the species in water. $\text{NaCl}(s)$ and $\text{KCl}(s)$ at room temperature are examples of strong electrolytes.

Weak electrolyte—A molecular or atomic species which partially dissociates in water to its constituent ions, leaving a significant concentration of the molecular form and/or other complexes.

Aqueous electrolyte equilibrium—The thermodynamic equilibrium, described in more detail below, involving species, all of which are in the aqueous phase. An example of an electrolyte equilibrium is $\text{CO}_2(aq) + \text{H}_2\text{O}(aq) = \text{H}^+(aq) + \text{HCO}_3^-(aq)$.

Aqueous phase equilibrium—The thermodynamic description of the physical equilibrium between an aqueous phase and one other phase. The other phase can be, among others, gaseous, nonaqueous liquid, or an independent solid. $\text{Ar}(g) = \text{Ar}(aq)$ is an example of an aqueous phase equilibrium.

B. Aqueous Thermodynamic Definitions

A reasonable study of aqueous systems requires the mastering of the following definitions and concepts:

Solvent—For aqueous systems, this refers to water.

Solute—A substance dissolved in water. NaCl , present in water as $\text{Na}^+(aq)$ and $\text{Cl}^-(aq)$, is an example of a solute.

Molality—The customary unit of concentrations for all species in the aqueous phase other than $\text{H}_2\text{O}(aq)$. Molality (abbreviated *m*) is defined as the moles of an aqueous phase species per kilogram (approximately 55.508 mol) of water. Molality is a more convenient unit of concentration than other con-

centration units (such as molarity), in that molality is independent of temperature.

Thermodynamic properties—Aqueous-phase thermodynamic properties for all species other than water are usually expressed on a partial molal basis. This means that the property is per mole of solution. The principal properties we will be most concerned with are partial molal Gibbs free energy, enthalpy, entropy, heat capacity, and volume. Each species in solution possesses a value for each of these properties. Each of the partial molal thermodynamic properties is the sum of a standard-state term and an excess term. Thus, the general relationship for these properties can be expressed as

$$\bar{P}_i = \bar{P}_i^0 + \bar{P}_i^E \quad (1)$$

where \bar{P}_i represents any partial molal thermodynamic property and the superscripts 0 and *E* represent the standard state and the excess terms, respectively.

Standard-state (term)—This refers to the thermodynamic value (\bar{P}_i^0) at a defined state (a specified concentration, temperature, and pressure). The nonideal (excess) contributions (\bar{P}_i^E) are departures from this state. For aqueous systems, the standard state refers to a hypothetical 1 m solution of the species extrapolated to infinite dilution. For simplicity, this state is simply referred to as one of infinite dilution. It is quite important to realize that the standard state, as in most nonaqueous standard states, is a continuous function of temperature and pressure but not a function of composition. As we shall see below, the difference between the sum of standard-state values for the products of a chemical reaction multiplied by their stoichiometric coefficients and the sum of standard-state values for the reactants multiplied by their stoichiometric coefficients is related directly to the thermodynamic equilibrium constant for the reaction.

Reference state—This is the thermodynamic value (\bar{P}_i^R) at a specific standard state of 298.15 K and 1 atm. As noted above, the standard state is a continuous function of tem-

perature and pressure. That means that for any choice of temperature and pressure there is a standard-state value.

The reference state, on the other hand, refers to a specific temperature and pressure, as noted above. One of the principal purposes for a reference state is that this state becomes the most common condition for experimental measurements. Compilations of experimental data for aqueous systems are usually comprised of measurements of the reference-state partial molal free energy, enthalpy, entropy, heat capacity, and volume.

Excess (term)—This measures the departure of a partial molal thermodynamic property from the standard state. This term is customarily a function of temperature, pressure, and composition. As we shall see below, this term is related directly to the activity, and in turn, to the activity coefficient and concentration of the species in question.

Activity—The activity of a species (a_i), is a thermodynamic property of the species which relates directly to the excess Gibbs free energy (G_i^E). Specifically,

$$\overline{G}_i^E = RT \ln(a_i) \quad (2)$$

where R is the gas constant and T is the absolute temperature.

Activity coefficient—The activity coefficient of a dissolved species (γ_i), is defined as the thermodynamic property of the species which relates directly to the activity by

$$a_i = \gamma_i m_i \quad (3)$$

where m_i is the concentration of the species in units of molality. Defined this way, the aqueous activity coefficient is said to conform to the asymmetric convention. The asymmetric convention means that the activity coefficient of the species approaches unity as the concentration of the species approaches zero (infinite dilution). This is quite different from the more familiar symmetric conventions, utilized in other chapters of this text, in which the species activity coefficient approaches unity as the species mole fraction ap-

proaches unity. The asymmetric convention is far more suitable in aqueous systems, since if the solute were to approach a mole fraction of unity, the mole fraction of the water would approach zero and the molality would go infinite and the system would hardly be aqueous. A typical activity coefficient plot for each convention is shown in Fig. 1. It is important to point out that with respect to the solvent, water, the activity coefficient cannot be defined, since the molality of a solvent with respect to itself has no meaning. The operative quantity used herein is the activity which for pure water is 1.0. A typical plot of water activity is shown in Fig. 2.

We can now put some of these concepts into the form of equations. For the five principal thermodynamic functions described in general form in Eq. (1) above, we get:

$$\text{Gibbs free energy} \quad \overline{G}_i = \overline{G}_i^0 + \overline{G}_i^E \equiv \mu \quad (4)$$

$$\text{Enthalpy} \quad \overline{H}_i = \overline{H}_i^0 + \overline{H}_i^E \quad (5)$$

$$\text{Heat capacity} \quad \overline{Cp}_i = \overline{Cp}_i^0 + \overline{Cp}_i^E \quad (6)$$

$$\text{Entropy:} \quad \overline{S}_i = \overline{S}_i^0 + \overline{S}_i^E \quad (7)$$

$$\text{Volume} \quad \overline{V}_i = \overline{V}_i^0 + \overline{V}_i^E \quad (8)$$

The partial molal Gibbs free energy, shown above, is also known as the chemical potential. Using the definitions (2) and (3), developed earlier, an important relationship which pertains to every equilibrium reaction involving the aqueous phase can now be developed.

Combining Eqs. (2), (3), and (4), we get:

$$\overline{G}_i = \overline{G}_i^0 + RT \ln(\gamma_i m_i) \quad (9)$$

Consider a general, stoichiometrically balanced, aqueous-phase equilibrium reaction involving R different aqueous-phase reactant

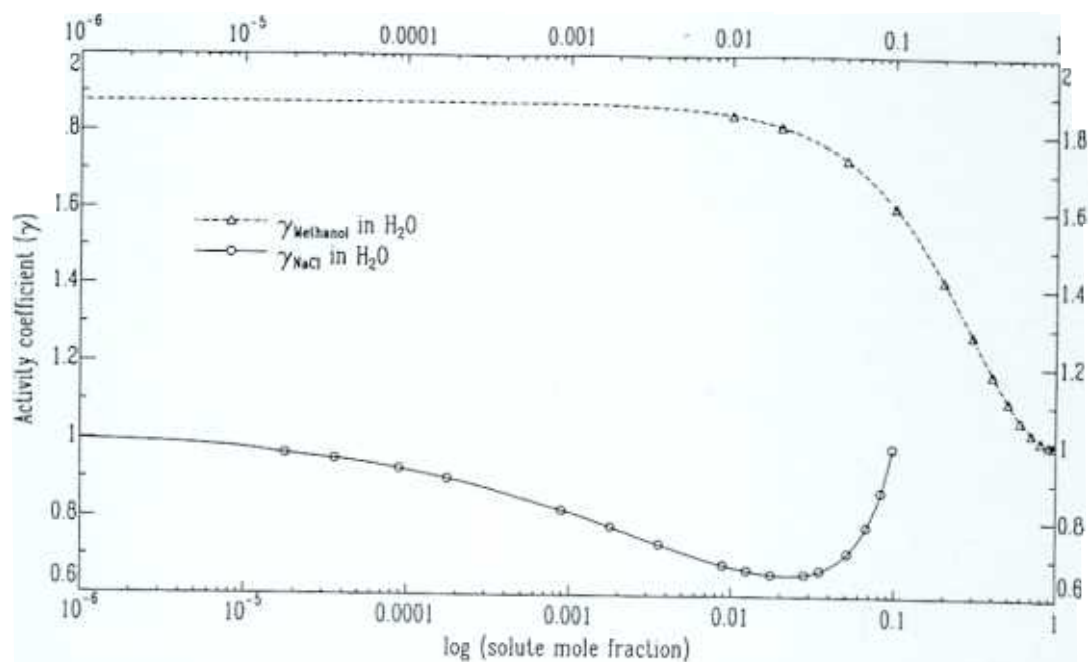


Figure 1 Comparison of the asymmetric versus the symmetric activity coefficient conventions.

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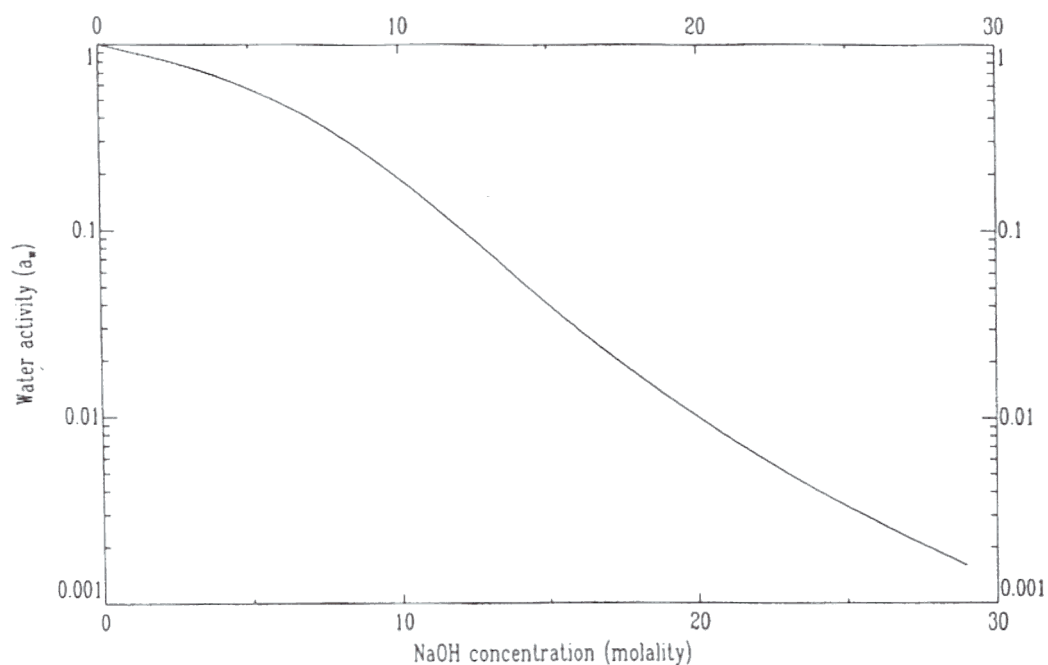
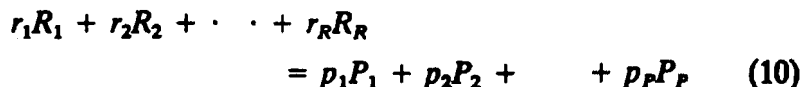


Figure 2 Water activity (a_w) in the NaOH-H₂O system at 25°C. (From Stokes, 1945).

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species and P different aqueous-phase product species:



Consider next the fact that thermodynamics tells us that, for any equilibrium reaction, the sum of the chemical potential (partial molal Gibbs free energy of all reactants) equals the sum of the same quantities over all products, or

$$\sum_{i=1}^r r_i \bar{G}_i = \sum_{i=1}^p p_i \bar{G}_i \quad r_1 \bar{G}_1 + r_2 \bar{G}_2 + \cdots + r_R \bar{G}_R = p_1 \bar{G}_1 + p_2 \bar{G}_2 + \cdots + p_P \bar{G}_P \quad (11)$$

where r_i is the stoichiometric coefficient of reactant i and p_i is the stoichiometric coefficient of product i .

Using Eq. (9), the reaction shown in Eq. (10), and Eq. (11), we get the following after collecting and reorganizing terms:

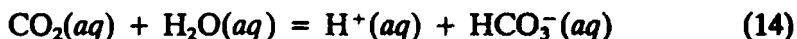
$$K = \frac{(\gamma_{P_1} m_{P_1})^{p_1} (\gamma_{P_2} m_{P_2})^{p_2} \cdots (\gamma_{P_P} m_{P_P})^{p_P}}{(\gamma_{R_1} m_{R_1})^{r_1} (\gamma_{R_2} m_{R_2})^{r_2} \cdots (\gamma_{R_R} m_{R_R})^{r_R}} \quad (12)$$

where K is the equilibrium constant, which is equal to

$$K = \exp \left[\frac{-(p_1 \bar{G}_{P_1}^0 + p_2 \bar{G}_{P_2}^0 + \cdots + p_P \bar{G}_{P_P}^0) - (r_1 \bar{G}_{R_1}^0 + r_2 \bar{G}_{R_2}^0 + \cdots + r_R \bar{G}_{R_R}^0)}{RT} \right] \quad (13)$$

Equation (12) is the classical form of the thermodynamic equilibrium relationship. This equation plays an important role in our later work in building a deterministic mathematical model of aqueous systems. The equilibrium constant, K , is a function of both temperature and pressure but not of composition (concentration).

To illustrate this, consider the equilibrium



The application of Eq. (11) leads to the following equations corresponding to Eqs. (12) and (13):

$$K = \frac{(\gamma_{\text{H}^+} m_{\text{H}^+})(\gamma_{\text{HCO}_3^-} m_{\text{HCO}_3^-})}{(\gamma_{\text{CO}_2(aq)} m_{\text{CO}_2(aq)})(a_{\text{H}_2\text{O}})} \quad (15)$$

$$K = \exp \left[\frac{-(\bar{G}_{\text{H}^+}^0 + \bar{G}_{\text{HCO}_3^-}^0) - (\bar{G}_{\text{CO}_2(aq)}^0 - \bar{G}_{\text{H}_2\text{O}(aq)}^0)}{RT} \right] \quad (16)$$

III. WRITING THE BASIC AQUEOUS-PHASE MATHEMATICAL MODEL

We are now prepared to consider the basic aqueous modeling problem. All mathematical models containing an aqueous phase will contain this basic model, and the solution to the larger problem will usually rest heavily on this aqueous model. Stated simply, the basic problem is:

Given: The temperature, pressure and the relative amounts of the chemicals which are fully dissolved in water not necessarily at saturation.

Calculate: The moles of undissociated water and the molality of each true species in the water.

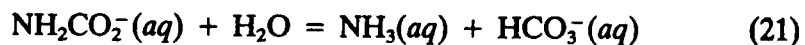
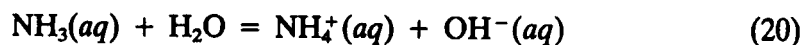
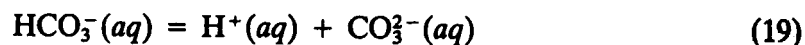
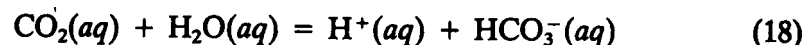
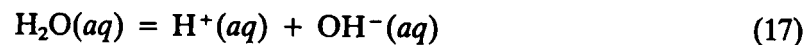
For the practical purposes of this section, we will take an actual problem and work it through. The problem is as follows.

Given: Temperature represented as T , pressure represented as P , and water, carbon dioxide, and ammonia, the relative amounts of which are represented by $F_{\text{H}_2\text{O}}$, F_{CO_2} , and F_{NH_3} , respectively.

Calculate: The amount of water (H_2O) and the molalities of hydrogen ion (m_{H^+}), hydroxide ion (m_{OH^-}), molecular carbon dioxide (m_{CO_2}), molecular ammonia (m_{NH_3}), bicarbonate ion ($m_{\text{HCO}_3^-}$), carbonate ion ($m_{\text{CO}_3^{2-}}$), ammonium ion ($m_{\text{NH}_4^+}$), and carbamate ion ($m_{\text{NH}_2\text{CO}_2^-}$) in solution.

Thus, we have a problem involving the calculation of nine unknowns. Writing a proper deterministic model will involve providing nine mathematical equations to describe this system. The following procedure is an ordered recipe for preparing these equations.

Step 1: Write a chemical equation of the form of Eq. (10) for all the independent aqueous intraphase equilibrium reactions. We will not at this time discuss how to determine a valid set of equilibrium equations; rather, we will provide the equilibria for this example. The equilibria we have considered for this example are



Utilizing Eq. (12) and the notation suggested for representing the species in the *Calculate* description above, we obtain the following five equations:

$$K_{\text{H}_2\text{O}(aq)} = \frac{(\gamma_{\text{H}^+} m_{\text{H}^+})(\gamma_{\text{OH}^-} m_{\text{OH}^-})}{a_{\text{H}_2\text{O}}} \quad (22)$$

$$K_{\text{CO}_2(aq)} = \frac{(\gamma_{\text{H}^+} m_{\text{H}^+})(\gamma_{\text{HCO}_3^-} m_{\text{HCO}_3^-})}{(\gamma_{\text{CO}_2} m_{\text{CO}_2}) a_{\text{H}_2\text{O}}} \quad (23)$$

$$K_{\text{HCO}_3^-(aq)} = \frac{(\gamma_{\text{H}^+} m_{\text{H}^+})(\gamma_{\text{CO}_3^{2-}} m_{\text{CO}_3^{2-}})}{(\gamma_{\text{HCO}_3^-} m_{\text{HCO}_3^-})} \quad (24)$$

$$K_{\text{NH}_3(aq)} = \frac{(\gamma_{\text{NH}_4^+} m_{\text{NH}_4^+})(\gamma_{\text{OH}^-} m_{\text{OH}^-})}{(\gamma_{\text{NH}_3} m_{\text{NH}_3}) a_{\text{H}_2\text{O}}} \quad (25)$$

$$K_{\text{NH}_2\text{CO}_2^-(aq)} = \frac{(\gamma_{\text{NH}_4^+} m_{\text{NH}_4^+})(\gamma_{\text{HCO}_3^-} m_{\text{HCO}_3^-})}{(\gamma_{\text{NH}_2\text{CO}_2^-} m_{\text{NH}_2\text{CO}_2^-}) a_{\text{H}_2\text{O}}} \quad (26)$$

This then provides the first five of the nine required equations.

It is important to note that each equilibrium constant, noted as K , is generally a function of temperature and pressure, and that each activity coefficient is generally a function of temperature, pressure, and composition.

Step 2: Write an electroneutrality equation. The electroneutrality equation is really just a charge balance. This equation will be part of every basic aqueous model. For the example under discussion, this equation becomes

$$m_{\text{H}^+} + m_{\text{NH}_4^+} = m_{\text{NH}_2\text{CO}_2^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{HCO}_3^-} + m_{\text{OH}^-} \quad (27)$$

Note that the sum of the cation concentrations on the left-hand side of this equation equals the sum of the anion concentrations on the right-hand side. The concentration of each ion is multiplied by the absolute value of its respective charge.

This then provides the sixth of the required nine equations.

Step 3: Write a sufficient number of material balances to complete the model. Writing material balances in aqueous systems can be difficult. Remembering the following rules can be helpful.

- 1 You should write only one of the following three balances: a hydrogen balance, an oxygen balance, or an overall atom balance. For simplicity we will always write a hydrogen balance in this chapter. The overall balance is eliminated because it is redundant to write such a balance while also writing all elemental balances. The oxygen balance is eliminated because the writing of the electroneutrality balance makes the writing of both a hydrogen balance and an oxygen balance redundant.
- 2 A separate balance should be written for each oxidation state of a particular element. For example, sulfur (S) may be present in the form of sulfide ($\text{S}[2-]$), sulfite ($\text{S}[4+]$), sulfate ($\text{S}[6+]$), etc. The only time that separate balances would not be written would be in a case where there was redox equilibrium. Such cases are beyond the scope of this present treatment.

- 3 Nonelectrolytes should have their own balances in which the amount of the inflowing material is simply equated to the amount present in the aqueous phase. This is done regardless of the oxidation state of the individual atoms comprising the nonelectrolyte molecule.

In our example, every species is an electrolyte. Thus, there would be material balances for H[1+], C[4+], and N[3-]. They would be written as follows:

$$3F_{\text{NH}_3} + 2F_{\text{H}_2\text{O}} = 2\text{H}_2\text{O} + \text{Wk}(m_{\text{H}^+} + m_{\text{OH}^-} + 3m_{\text{NH}_3} + 4m_{\text{NH}_4^+} + m_{\text{HCO}_3^-} + 2m_{\text{NH}_2\text{CO}_2^-}) \quad (28)$$

$$F_{\text{CO}_2} = \text{Wk}(m_{\text{CO}_2} + m_{\text{HCO}_3^-} + m_{\text{NH}_2\text{CO}_2^-} + m_{\text{CO}_3^{2-}}) \quad (29)$$

$$F_{\text{NH}_3} = \text{Wk}(m_{\text{NH}_3} + m_{\text{NH}_4^+} + m_{\text{NH}_2\text{CO}_2^-}) \quad (30)$$

where Wk is the constant representing the ratio of the number of moles of water in this system to the number of moles of water in 1 kg. Thus Wk is approximately equal to $\text{H}_2\text{O}/55.508$, which converts all molalities to moles. It is assumed that $F_{\text{H}_2\text{O}}$, F_{NH_3} , F_{CO_2} are on a molar basis. In writing the model in this way, H_2O will be computed on a molar basis as well. It is worth emphasizing that due to the electrolyte reactions, the amount of molecular water, H_2O , after dissolving the solutes, NH_3 and CO_2 , will not be equal to the inflow amount of water, $F_{\text{H}_2\text{O}}$. These three equations complete the set of nine equations required.

This completes the recipe for a basic aqueous-phase speciation-only model. One question worth asking is where are the variables T and P which were part of the *Given* portion of the problem statement. The answer is that these variables are embedded in the thermodynamic equilibrium constants, $K(T, P)$ and the activity coefficients, $\gamma(T, P, m)$. Representing these thermodynamic variables, as well as the thermodynamic properties of interest, is the subject of the next section of this chapter.

It is important to observe that mathematical models of the type developed above are generally highly nonlinear and require the use of a computer to effect reasonable numerical solutions. In

Fig. 3, we see the results of using such a computer code (Pro-Chem) to solve various cases involving the ternary system $\text{H}_2\text{O}-\text{CO}_2-\text{NH}_3$. A comparison of these predictions versus the experimental data is also shown.

IV. REPRESENTING THE THERMODYNAMIC PROPERTIES

In Section II, we introduced a number of aqueous partial molal thermodynamic properties (Gibbs free energy, enthalpy, entropy, heat capacity, and volume). Each of these properties was then expressed as the sum of a standard state and an excess term. The concept of a standard state and a reference state was then discussed. Finally, the concept of an equilibrium reaction, equilibrium constants, and thermodynamic activities and activity coefficients were also discussed. In this section we will discuss three important subtopics:

- 1 A unified representation (thermodynamically consistent) of the thermodynamic properties
2. Sources of data for the thermodynamic properties
3. Specific mathematical representations of the thermodynamic properties

Each of these will be discussed in the following separate subsections

A. Unified Representation of Thermodynamic Properties

We have identified five partial molal thermodynamic properties of interest: Gibbs free energy, enthalpy, entropy, heat capacity, and volume. We have also identified that the state of an aqueous system is characterized by the temperature (T), pressure (P), and composition (m_1, m_2, \dots). The following relationships emphasize some important facts about these properties and their interrelationships.

All five partial molal thermodynamic properties are extensive in nature. Thus, using \bar{P}_i and \bar{P}_T to represent any of these prop-

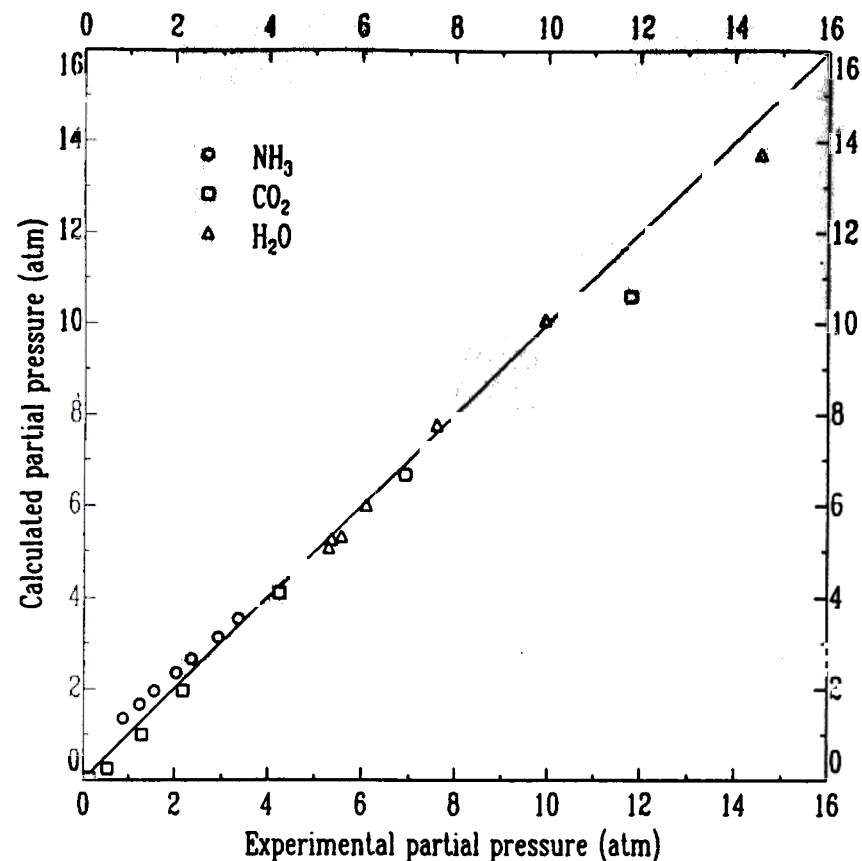


Figure 3 Comparison of predicted versus experimental partial pressures for the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ ternary system at 120°C .

erties for a single species and the overall solution, respectively,

$$P_T = \sum_{i=1}^n \bar{P}_i N_i \quad (31)$$

where N_i is the number of moles of species i and n is the number of distinct species present.

All five thermodynamic properties are interrelated. This helps give rise to the term “*thermodynamic consistency*.” In other words, any equation of state representation of these properties should obey the interrelationship equations noted below. The word “state” in equation of state means simply that we express the properties in terms of the state T , P , m_1 , m_2 , The interrelationship equations are

$$\bar{S}_i = - \left(\frac{\partial \bar{G}_i}{\partial T} \right)_{P,m} \quad (32)$$

$$\bar{H}_i = \bar{G}_i + T\bar{S}_i \quad (33)$$

$$\bar{C}_{p_i} = \left(\frac{\partial \bar{H}_i}{\partial T} \right)_{P,m} \quad (34)$$

$$\bar{V} = - \left(\frac{\partial \bar{G}_i}{\partial P} \right)_{T,m} \quad (35)$$

It should further be remembered that once we substitute the definition of the total Gibbs free energy in terms of the standard-state and excess terms and then substitute the activity-coefficient form of the excess term, the equations above then explicitly contain the activity coefficient as well as its partial derivatives with respect to temperature and pressure.

B. Sources of Data

When performing calculations described in this chapter, it is helpful to have a list of references from which data can be obtained. The following provides important references organized with respect to several categories of data.

1. *Compilations of Gibbs Free Energy, Enthalpy, Entropy, and Heat Capacity*

Chase et al. (1985) provide reference-state information for solids, liquids, and gases and at elevated temperature.

Cox et al. (1989) provide reference-state information for solids, liquids, gases, and aqueous species.

Daubert and Danner (1989) provide reference-state information as well as temperature-dependent data for gaseous compounds. There is a heavy emphasis on organic compounds.

Glushko et al. (1965–1981) provide reference state information for aqueous species. This compilation is usually referred to as the Russian Handbook and is analogous to the NBS Handbook.

Kelly (1960) provides enthalpy, heat capacity, and entropy information at the reference state for solids.

Robie et al. (1978) provide similar information as Chase et al. (1985), with an emphasis on geologically important compounds.

Shock, Helgeson, and Sverjensky (Shock and Helgeson, 1988, 1990; Shock et al., 1989) provide reference-state information for aqueous species.

Stull et al. (1987) provide reference-state thermodynamic values for organic compounds for solid, liquids, and gases.

Wagman et al. (1982) provide reference-state thermodynamic values of inorganic and some organic compounds. This is commonly referred to as the NBS Handbook.

2. *Compilations of Equilibrium Constants*

With rare exceptions, most of these compilations are for 25°C only.

Baes and Mesmer (1976) have compiled and critically reviewed the hydrolysis equilibria for many metal cations.

Smith and Martell (1975–1989) have critically reviewed complexation equilibria for many classes of anions, including organic anions.

3. *Compilations of Activity Coefficient Data*

Goldberg (1981) compiled and reviewed data for 36 univalent and bivalent electrolytes (e.g., Na_2CO_3).

Goldberg and Nutall (1978) compiled and reviewed data for alkaline earth metals (e.g., CaCl_2).

Hamer and Wu (1972) reviewed univalent electrolytes (e.g., NaCl).

Lobo (1989) has compiled (although not reviewed) activity coefficient data for many electrolytes. In addition, this reference contains viscosity, transport, density, and osmotic coefficient data.

4. *Compilations of Solubility Data*

Horvath (1982) has compiled and reviewed solubility data for halogenated hydrocarbons.

Linke and Seidell (1958, 1965) have the most comprehensive compilation of solubility data of inorganic compounds. Most of this data is unreviewed.

Stephen and Stephen (1963) have compiled solubility data for many organic compounds. All of this data is unreviewed.

C. *Specific Formulations*

Bearing in mind that the partial molal thermodynamic properties of interest are the sum of a standard-state term and an excess term, the objective of this subsection is to provide guidance as to alternative ways to represent mathematically both the standard state and excess partial molal Gibbs free energy in terms of the system state (T, P, m_1, m_2, \dots). As we have seen earlier [Eqs. (31)–(35)], once this is done, the mathematical representation of the other thermodynamic properties can be derived. Our purpose here is to present the working equations and to direct the reader to other published works for details.

The material below is separated into standard-state and excess properties, respectively.

1. *Standard State Properties* [$\bar{G}_i^0(T, P)$, $\bar{H}_i^0(T, P)$, $\bar{S}_i^0(T, P)$, $\bar{C}_p^0(T, P)$, $\bar{V}_i^0(T, P)$]

The key to representing the standard-state partial molal thermodynamic properties of species in an aqueous solution is in representation of the heat capacity. The choices are assuming a

constant value of zero (in the absence of data), an estimated constant value, a constant value equal to the reference-state value, a value which is a function of temperature, or a value which is a function of temperature and pressure. The accuracy of the thermodynamic standard-state property predictions will very much depend on the choice made. The two methods described below exemplify the range of choices and are both practical to use.

Method 1: Representing the Equilibrium Constant. In this first method we are seeking only to calculate the thermodynamic equilibrium constant. The equilibrium constant is, as was shown earlier, a standard-state property based on the sum and difference of the partial molal Gibbs free energy of the individual species participating in a chemical equilibrium reaction. In this first method, we are simply seeking to develop a representation of the equilibrium constant rather than a complete description of the five standard-state thermodynamic properties. We have seen in Eq. (13) that

$$\ln K = -\frac{\Delta \bar{G}_R^0}{RT} \quad (36)$$

where $\Delta \bar{G}_R^0$ is a shorthand notation for the change in the standard-state Gibbs free energy across the reaction. This shorthand will apply to enthalpy and heat capacity, as well.

Differentiating with respect to T , we get

$$R \frac{d \ln K}{dT} = -\frac{d(\Delta \bar{G}_R^0/T)}{dT} \quad (37)$$

Using the interrelationships among the properties presented in Eqs. (31)–(35), we eventually integrate to obtain

$$\ln K = \left(\frac{\Delta \bar{G}_R^R}{RT^R} - \frac{\Delta \bar{H}_R^R}{R} \left(\frac{1}{T} - \frac{1}{T^R} \right) - \int_{T^R}^T \Delta \bar{C}_p^0 dT \right) \quad (38)$$

where T^R is the reference-state temperature of 298.15 K. At this point, we either provide a function for heat capacity in terms of temperature or assume a constant value. If we assume a constant value, then we get the closed form shown below:

$$\ln K = -\left(\frac{\Delta \bar{G}_R^R}{RT^R} \right) - \frac{\Delta \bar{H}_R^R}{R} \left(\frac{1}{T} - \frac{1}{T^R} \right) - \frac{\Delta \bar{C}_p^R}{R} \left(\ln \frac{T}{T^R} - \frac{T^R}{T} + 1 \right) \quad (39)$$

The detailed derivations of Eq. (38) and Eq. (39) can be found in the *Handbook of Aqueous Electrolyte Thermodynamics* (Zemaitis et al., 1986).

If we choose a particular temperature function for heat capacity, we can also readily develop a more accurate, albeit complicated, closed-form expression for the equilibrium constant.

The use of this method is dependent on being able to obtain data on the reference-state partial molal Gibbs free energy, enthalpy, and heat capacity of each of the participants in an aqueous equilibrium reaction. The sources of these data have been discussed in the previous section.

A typical plot of K versus T is provided in Fig. 4, where the experimental data for the dissociation constant of water is compared to predicted values based on Eq. (39). Since there are times when only $\Delta \bar{G}_R^R$ or only $\Delta \bar{G}_R^R$ and $\Delta \bar{H}_R^R$ may be available, it is particularly instructive to observe the improvement in the predictions when all reference-state properties are available. These predictions would be even better if the heat capacity as a function of temperature were known and applied, as in Eq. (38).

Method 2: Helgeson Equation of State. A particularly useful equation of state has been developed by Helgeson and co-workers (Helgeson and Kirkham, 1974a, 1974b, 1976; Helgeson et al., 1981; Tanger, 1986). The equations for the five thermodynamic properties of interest as developed by Helgeson et al. are presented in Table 1. For each species in an aqueous solution, it is simply required that there be available values for the reference-state properties (free energy, enthalpy, and entropy) as well as

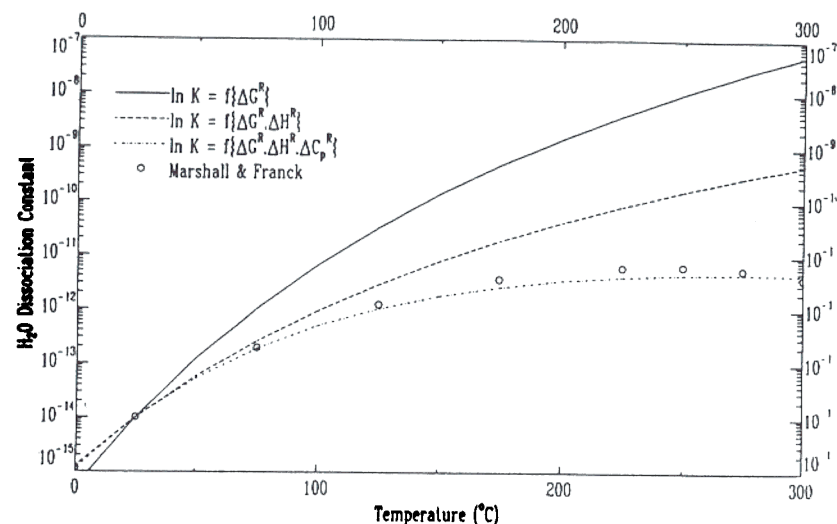


Figure 4 Dissociation constant for H_2O versus temperature calculated using Eq. (39) and showing improvement in fit with additional reference-state property terms. (From Marshall and Frank, 1981.)

the seven Helgeson equation of state coefficients (ω , c_1 , c_2 , a_1 , a_2 , a_3 , a_4). If pressure effects are not important (pressures under 200 bar), then only the set ω , c_1 , c_2 is required. Helgeson and co-workers (Shock and Helgeson, 1988, 1990; Shock et al., 1989) have published values for large numbers of inorganic ions, neutrals, and complexes, as well as organic nonelectrolytes. Correlations have also been developed to allow for estimation of the equation of state coefficients. All other variables in the equations presented in Table 1 are either calculable properties of pure water (ϵ , the dielectric constant of pure water and its derivatives) or equation of state constants as noted.

Table 2 provides a summary of the information required to utilize the Helgeson equation of state for a sampling of 10 species in water.

Of the two methods provided to calculate the standard-state thermodynamic properties, the Helgeson equation of state is strongly recommended because it covers more properties over a wider range

Table 1 Standard State Thermodynamic Values Using the Helgeson Equation of State

$$\begin{aligned} \bar{V}^0 &= a_1 + a_2 \left(\frac{1}{\psi + P} \right) + \left[a_3 + a_4 \left(\frac{1}{\psi + P} \right) \right] \left(\frac{1}{T - \theta} \right) \\ &\quad - \omega Q + \left(\frac{1}{\epsilon} - 1 \right) \left(\frac{\partial \omega}{\partial P} \right)_T \\ \bar{C}_P^0 &= c_1 + c_2 \left(\frac{1}{T - \theta} \right)^2 - \left(\frac{2T}{T - \theta} \right)^3 \\ &\quad \times \left[a_3 (P - P_r) + a_4 \ln \left(\frac{\psi + P}{\psi + P_r} \right) \right] + \omega T X \\ &\quad + 2TY \left(\frac{\partial \omega}{\partial T} \right)_P - T \left(\frac{1}{\epsilon} - 1 \right) \left(\frac{\partial^2 \omega}{\partial T^2} \right)_P \\ \bar{S}^0 &= \bar{S}_{Pr,Tr}^0 + c_1 \ln \left(\frac{T}{T_r} \right) - \frac{c_2}{\theta} \left\{ \left(\frac{1}{T - \theta} \right) - \left(\frac{1}{T_r - \theta} \right) \right. \\ &\quad \left. + \frac{1}{\theta} \ln \left[\frac{T_r (T - \theta)}{T (T_r - \theta)} \right] \right\} \\ &\quad + \left(\frac{1}{T - \theta} \right)^2 \left[a_3 (P - P_r) + a_4 \ln \left(\frac{\psi + P}{\psi + P_r} \right) \right] \\ &\quad + \omega Y - \left(\frac{1}{\epsilon} - 1 \right) \left(\frac{\partial \omega}{\partial T} \right)_P - \omega_{Pr,Tr} Y_{Pr,Tr} \end{aligned}$$

where

ϵ = dielectric constant of the solvent (for our studies the solvent is water)

ψ = a constant term in pressure (= 2600 bar)

θ = a constant term in temperature (= 228 K)

ω = Born term in temperature and pressure (Tanger, 1986)

$$Y = \frac{1}{\epsilon^2} \left(\frac{\partial \epsilon}{\partial T} \right)_P$$

where P is the pressure (in bar) and T is the temperature (in kelvins)

$$X = \left(\frac{\partial Y}{\partial T} \right)_P$$

$$Q = \frac{1}{\epsilon^2} \left(\frac{\partial \epsilon}{\partial P} \right)_T$$

of temperatures and pressures and is supported by more estimation methods for the seven equation of state coefficients.

2. Excess Properties

The key to predicting the excess (nonideal) contribution to the partial molal thermodynamic properties of species in aqueous solution are the activity coefficients of these individual species.

Models for Electrolyte Solutions

Values for Chok and Helgeson

The two types of species which appear in aqueous solution are charged and uncharged.

For charged species, there has been, historically, a large body of work leading to the development of a number of modern mathematical representations of the asymmetric-form activity coefficients for aqueous solution. Before discussing these various alternative representations, it is useful to present the unifying concept of ionic strength. Ionic strength in an aqueous solution is defined as

$$I = \frac{1}{2} \sum_{i=1}^{nI} z_i^2 m_i \quad (40)$$

where I is the ionic strength, z_i is the charge on an individual species i , and nI is the number of charged species in solution.

While each of the different methods has a somewhat different specific mathematical representation, the following elements are common to nearly all of these methods:

- 1 The log of the activity coefficient is comprised of a long-range term and a short-range term.
- 2 The long-range term describes what happens in dilute solutions, where the constituent solute species are relatively far apart and the activity coefficient is mostly influenced by the general charged environment. This term was originally described by Debye and Hückel 1923a, 1923b, 1924, and nearly all formulations contain a Debye-Hückel term or, alternatively, a modified Debye-Hückel term. Activity coefficient models involving only a long-range term (e.g., Debye-Hückel) are adequate only to very low ionic strengths. These activity coefficients are then said to approach the Debye-Hückel limiting law.
- 3 The short-range term describes what happens in concentrated solutions where the constituent solute species get relatively close. Generally this term is the sum of individual ion-ion and ion-molecule pair interaction terms. The general form of the individual terms is, for species i ,

$$b_{ij}(T, I) \quad m_j$$

where b_{ij} , a function of temperature and ionic strength and ion charge, is termed an interaction coefficient. In most practical treatments of aqueous solutions, the principal interactions considered are cation-anion interactions. In fact, as a first approximation we can usually consider only interactions involving species at least one of which has significant concentration. The b_{ij} values can generally be developed based on binary vapor pressure/water activity data. The values thus fitted are then used in predicting the behavior of multicomponent systems.

One problem which arises is that for slightly soluble substances (e.g., CaSO_4), the binary data will allow a fit for the interaction only up to a low ionic strength. Usage in multicomponent systems may involve considerably higher ionic strengths. This then requires an extrapolation technique for the b_{ij} to allow stable predictions of activity coefficients including this b_{ij} . A method for estimation and/or extrapolation of activity coefficients is presented in the next section.

The mathematical representations of a number of these activity coefficient models is given in Table 3, which provides details for a single salt in water. The term γ_{\pm} , used in the tables, refers to the mean activity coefficient. The mean activity coefficient for the salt C_xA_y is defined as

$$\gamma_{\pm} = (\gamma_+^x \gamma_-^y)^{1/(x+y)} \quad (41)$$

where x and y are the stoichiometric coefficients on the cation C and the anion A , and γ_+ and γ_- are the activity coefficients of the cation and anion raised to the respective stoichiometric coefficients.

The following comments should provide some perspective:

- 1 *Debye-Hückel*—Presented for historical perspective and because it is a common element of all of the others (Debye and Hückel, 1923a, 1923b, 1924).

Table 3 Activity Coefficient Formulations

Debye-Hückel: $\log \gamma_{\pm} = \frac{-A|Z_+Z_-|^{1/2}}{(1 + a_0 B I^{1/2})}$

Bromley: $\log \gamma_{\pm} = \frac{-A|Z_+Z_-|^{1/2}}{1 + I^{1/2}} + \frac{(0.06 + 0.6B)|Z_+Z_-|I}{[1 + \frac{1.5}{1Z + Z - 1}I]^2} + BI$

Pitzer: $\ln \gamma_{\pm} = |Z_+Z_-|f^{\gamma} + m \left(\frac{2\nu_+ \nu_-}{\nu} \right) B_{\pm}^{\gamma}$
 $+ m^2 \left[\frac{2(\nu_+ \nu_-)^{1.5}}{\nu} \right] C_{\pm}^{\gamma}$

Helgeson: $\log \bar{\gamma}_{\pm} = \frac{-A_{\gamma}|Z_i Z_j|^{1/2}}{(1 + a_0 B_{\gamma} I^{1/2})} + \Gamma_{\gamma}$
 $+ \left(\frac{\omega_k}{\nu_k} \sum_k b_k Y_k I + \frac{\nu_{i,k}}{\nu_k} \sum_l \frac{b_{il} \bar{Y}_l I^{1/2}}{\psi_l} \right.$
 $\left. + \frac{\nu_{i,k}}{\nu_k} \sum_l \frac{b_{il} \bar{Y}_l I}{\psi_l} \right)$

2. *Bromley*—A very useful method in that there are a significant number of interaction values available, new values are relatively easy to develop based on data, and in the absence of such data, the interaction coefficients can be estimated based on correlations. The author does suggest an extended mathematical form to cover higher ionic strengths (Bromley, 1972, 1973).
3. *Pitzer*—A very popular method in that there have been extensive publications of Pitzer coefficients based on experimental data. The availability of higher-order terms allows for extraordinarily good fits to experimental data. There do not appear to be any reasonable correlations for the Pitzer coefficients to extend the fits outside the range of the experimental data set (Pitzer, 1973, 1975; Pitzer and

Kim, 1974; Pitzer and Mayorga, 1973; Pitzer and Silvester, 1977, 1978).

4. *Helgeson*—A major attempt to develop an equation of state approach to the excess properties quite analogous to the standard-state treatment of Helgeson. The more limited success with these excess properties seems to stem from the fact that there are only a limited amount of data available, particularly at temperatures other than the reference state. As a result, the work is largely applicable to naturally occurring minerals in an aqueous solution of sodium chloride over the range 0–6 molal in ionic strength (Helgeson et al., 1981).
5. *Chen*—A method patterned after the NRTL (nonrandom two-liquid) method. This leads to an ability to accommodate multisolute electrolyte models, but the model is highly dependent on regression of available experimental data (Chen et al., 1982).
6. *Meissner*—A highly predictive and extrapolative method which is of limited accuracy and is best used in conjunction with other methods, in the absence of experimental data, as a means of extrapolating to high concentrations and temperatures (Meissner, 1978).

Figures 5 and 6 show a comparison of these six methods versus experimental data over a limited concentration range (0–6 m) and then over a more extensive concentration range (0–16 m). The coefficients for each of the six methods were obtained from the *Handbook of Aqueous Electrolyte Thermodynamics* (Zemaitis et al., 1986).

While Table 2 and Figs. 5 and 6 all depict binary systems of a single salt in water, all of these methods have straightforward extensions for multicomponent systems which involve a sum of the underlying binary interactions. Higher-order interactions are generally unnecessary.

For uncharged species there is a much smaller body of work. Table 4 provides a mathematical description of two formulations which can be used for the activity coefficients of molecules in

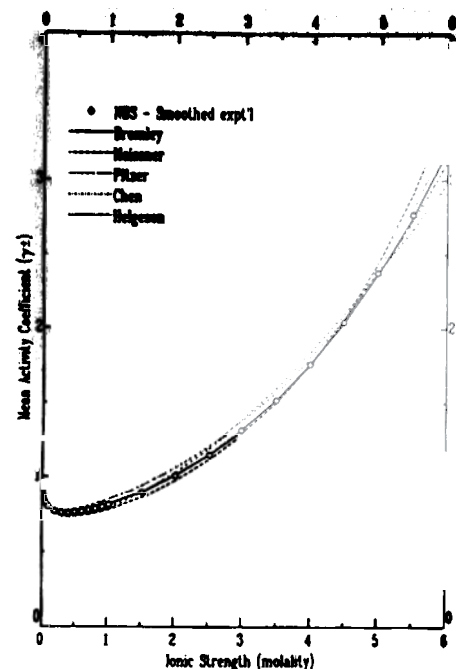


Figure 5 Mean activity coefficient versus ionic strength for HCl at 25°C using various methods (limited concentration range). (From Zemaitis et al., 1986.)

aqueous solutions. As with charged-species activity coefficients, the two methods available both rely on the short-range interactions between the molecular species and the individual ions in solutions. The second method also provides for the interaction of molecules with other molecules. The methods are as follows.

Setschenow—This formulation is based on the observation that the ratio of the solubility of a nonelectrolyte molecule in aqueous solution involving a single salt versus the solubility in aqueous solutions not containing the salt are proportional to the salt concentration (Setschenow, 1889). This observation is true largely for strong-electrolyte salts at fairly low concentrations. Based on a growing body of data,

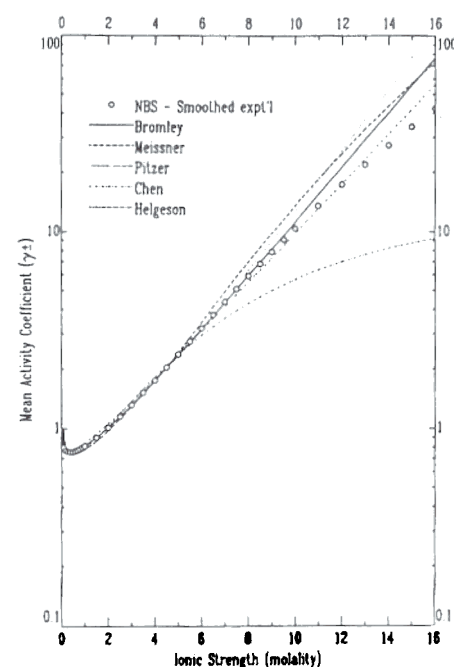


Figure 6 Mean activity coefficient versus ionic strength for HCl at 25°C using various methods (extrapolated concentration range). (From Zemaitis et al., 1986.)

Table 4 Activity Formulations for Neutral Species

$$\text{Setschenow: } \ln \gamma_{aq} = \frac{S_0}{S_s} = km_s$$

where S_0 is the solubility of the gas in pure water, S_s is the solubility of the gas in a salt solution, k is the Setschenow coefficient, and m_s is the concentration of the salt

$$\text{Pitzer: } \ln \gamma_{aq} = 2\beta_{\alpha(m-m)}m_m + 2\beta_{\alpha(m-s)}m_s$$

where $\beta_{\alpha(m-m)}$ is the Pitzer molecule-molecule or ion-molecule interaction for the neutral, and m_m is the concentration of the neutral species

it appears that at higher concentrations the relationship is not linear. However, the relationship in Table 4 is simple and is a relatively easy form with which to regress available data. The principal problems are that a good correlation is lacking and, in many cases, the data are not available. Much of the data that exist in this area has been compiled by McDevit and Long, 1952).

Pitzer—This method, discussed earlier in the context of charged species, again provides an excellent interpolative framework for molecular activity coefficients (Pitzer, 1979). The problem is that this method relies on the availability of data and is applicable only over the range of the regressed data. This is a limiting factor if one seeks to extend the interaction to systems containing chemicals not present in the original experimental system.

V. ESTIMATION OF THERMODYNAMIC PROPERTIES

Much work has been done on the estimation of the thermodynamic properties of species in the gaseous and organic liquid phases. Such material has been discussed elsewhere in this text. The subject of this section is the estimation of the thermodynamic properties of species in the aqueous phase. We will, however, discuss the estimation of solid-phase free energies, since the thermodynamic properties of solids enter in the calculation of solid-liquid equilibrium constants.

With respect to the aqueous phase there is, as has been discussed previously, a fairly substantial body of experimental data available with respect to thermodynamic properties. There is, however, a great deal of chemistry of potential interest which is not covered by experimental data. In general, the following can be said on this subject.

Reference state—Much of the available data has been measured at the reference state of 25°C and 1 bar. The principal gaps in the available data tend to be with respect to the

thermodynamic properties of complexes, both charged and neutral. The body of available data is sufficient to support efforts to find estimation methods for determining many of the properties not supported by available data.

Standard state—There is considerable data available on the standard-state heat capacities and volumes of species in aqueous solution. The body of available data is sufficient to support efforts to find estimation methods for determining many of the properties not supported by available data.

Excess—There is only a very limited amount of data available on the excess properties of species in aqueous solution. As a result, the estimation methods tend to be rather primitive and more inaccurate than those for the reference and standard-state properties.

With respect to the solid phase, which will be discussed in Section VI, we need be concerned only with the reference-state properties.

In the material which follows, we will separately discuss estimation methods in each of these areas.

A. Aqueous Reference-State Properties

Traditionally, estimation of reference-state properties for aqueous species, both ionic and neutral, has been difficult. Since 1987, work has been going on at several institutions to develop estimation techniques for reference-state thermodynamics.

The two major efforts are directed in the area of determining equilibrium constants for aqueous dissociation (Brown and Sylva, 1987a, b) and in the area of determining entropy, heat capacity, and volume reference-state properties (Sverjensky, 1987). Each effort now will be discussed in somewhat more detail.

1. Estimation of \bar{G}^R (Gibbs Free Energy of Reaction)

In the examples in Section III we can see that the ultimate thermodynamic quantity that we must have is the equilibrium constant. We know from Eq. (36) (at the reference state) that the equilibrium constant is related to the Gibbs free energy of re-

action. We also know that the free energy of reaction is the difference between the sum of the free energies of formation for the products of a reaction and the sum of the free energies of formation for the reactants of the reaction. We desire a method to estimate the free energy of reaction (and thus the equilibrium constant) when this free energy of formation data is lacking.

Brown and Sylva (1987a, 1987b) believe that there is a correlation between the equilibrium constant for the equilibrium of the type found in Eq. (42) and the fundamental construction of the metal cation and the structure of the ligand.



where M is a metal cation and L is a ligand (for simplicity, the charges have been left out).

The fundamental construction of the metal cation can be thought of as how the electrons are arranged around the nucleus of the metal cation. How many *d* electrons are there? How many *p* and *s* electrons are there? Also affecting this correlation is the structure of the ligand. Is the ligand an oxyanion? Is the anion capable of accepting more than one hydrogen (in the Brønsted sense of acids and bases)?

These two factors help determine the "electronicity" of the cation and the anion. This term, developed by Brown and Sylva, is plotted against the log of the equilibrium constant for many known dissociations. Thus, a slope and intercept can be determined for any ligand for a given metal cation. This correlation allows us to predict the equilibrium constant for an equilibrium of the type in Eq. (42) just by knowing the structure and electronicity of the component ions.

In practice, the correlations are difficult to obtain. Electronicity values are obtained from a series of equilibrium constants which either have a constant ligand (for ligand electronicities) or a constant cation (for cation electronicities). The equilibrium constants must be at infinite dilution for accurate electronicities and in practice are difficult to obtain.

Once a reliable equilibrium constant has been obtained, use of Eq. (13) can determine the Gibbs free energy of reaction. Then the free energy of formation (at the reference state) for the complex can be determined assuming that the free energy of formation of the products of Eq. (42) are known.

2. Estimation of Reference-State Thermodynamic Properties Other Than \bar{G}^R

Once the equilibrium constant (and hence the free energy of reaction) is known or estimated, it is desirable to estimate the remaining thermodynamic properties, heat capacity, entropy, volume, and enthalpy. Sverjensky and co-workers have developed a method to estimate reference-state entropy (as well as heat capacity and volume) for reaction of Eq. (42). Using the known equilibrium constant (which relates to the free energy of reaction) and Eq. (43), one can calculate the enthalpy of reaction (and thus the enthalpy of formation of the products and reactions).

$$\Delta_r \bar{G} = \Delta_r \bar{H} - T \Delta_r \bar{S} \quad (43)$$

where *G* is the Gibbs free energy of reaction, *H* is the enthalpy of reaction, and *S* is the entropy of reaction. *T* is the absolute temperature in kelvin.

Sverjensky and co-workers have developed a method of correlating the entropy (and heat capacity and volume) of reaction for equilibria like Eq. (42) versus the absolute entropy of the metal cation [*M* in Eq. (42)]. The entropy (and heat capacity and volume) of many types of equilibria were plotted versus the absolute entropy of the metal cation and several families of lines appeared. These lines were of similar slope but differed in the intercept value. These intercept values were, in turn, correlated against the charge of the metal cation.

This correlation has worked very well for all conceivable metal cations and all ligands with a charge of -1 . Metal-ligand complexes up to the type ML_4 have been correlated for all univalent anions with the exception of hydroxide ion (OH^-). Hydroxide ion will correlate well only up to the first complex, ML , and no

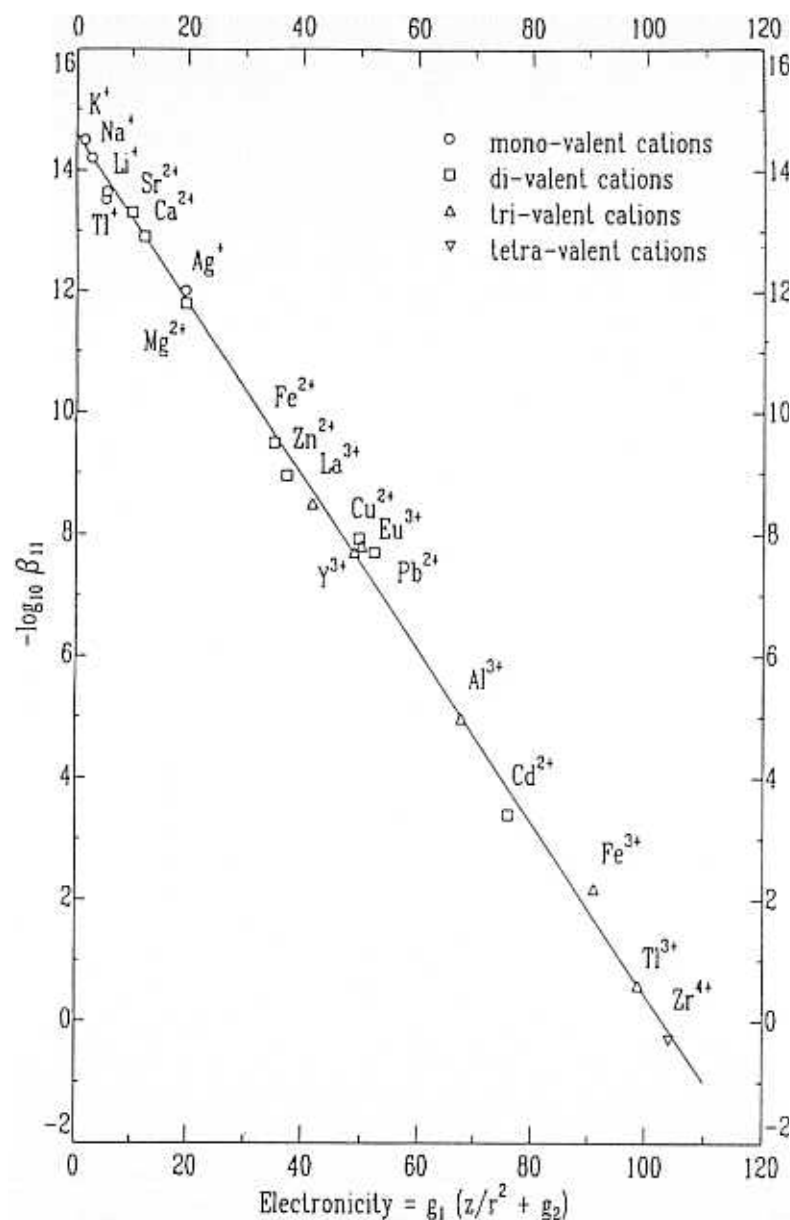


Figure 7 $-\log(\beta_{11})$ versus temperature for metal hydroxide complexes where $L = \text{OH}$ and $q = 1$ in Eq. (42). (From Brown and Sylva, 1987b.)

further. This may be due to the fact that the solvent, water, also contains hydroxide ion.

A tentative (and as of August 1991, unpublished) correlation for divalent ligands has been found. A reasonable correlation for sulfates and carbonates has been found for entropy. The same correlations for heat capacity are not as good, and for volume they are almost nonexistent. This is probably due to the lack of experimental data on dissociation constants near the reference temperature.

The limitations of this technique are that it is limited to univalent ligands up to the tetra-coordinated complex, up to the mono-coordinated complex for hydroxides, and limited to the divalent anions SO_4^{2-} and CO_3^{2-} up to a mono-coordinated complex.

B. Aqueous Standard State Properties

In Section IV.C we discussed two methods for dealing with the standard-state properties. In this section we will discuss estimation methods which are useful when applied to each of these methods.

Method 1: Representing the Heat Capacities

In the first method, it was shown that the equilibrium constants, a standard-state property of an aqueous reaction, can be predicted based exclusively on reference-state partial molal Gibbs free energies, enthalpies, and heat capacities. However, there are two reasons for wanting to estimate the heat capacity at temperatures other than the reference state. Specifically:

1. Such an estimate would allow the equilibrium constant to be refined by integrating the heat capacity function over temperature rather than using the reference-state value as an estimate over the whole range.
2. Accurate calculations of the enthalpy of a solution requires that the heat capacity of the individual species, most notably the charged species, be known or estimated as a function of temperature.

A correlation for the heat capacity of ions has been provided by Criss and Cobble (Criss and Cobble, 1964). Their general

approach has been to correlate the heat capacity of various types of ions with the reference-state entropies of the ions. The Criss and Cobble equations are summarized in Table 5.

Method 2: Helgeson Equation of State

The second method involves the Helgeson equation of state for the standard-state properties of species in aqueous solution. In this method, we require the reference-state properties (estimation methods have been discussed above) as well as the seven (or three if pressures are below 200 bar) equation of state parameter values per species. In the work of Shock and Helgeson, estimation methods are presented for most species in solution except for complexes (Shock and Helgeson, 1988). The estimation for many classes of complexes is being provided by Sverjensky (Sverjensky, 1987).

Of these two methods, the Helgeson equation of state is recommended because it applies to all thermodynamic properties of interest and it can be applied to more species with broader ranges of temperature and pressure.

In Fig. 8 we see a comparison of heat capacity predictions for various species using the two methods.

C. Aqueous Excess Properties

As was noted above, there is only a modest amount of experimental data available on which to base the excess properties. Fortunately, there is enough to provide at least some rudimentary estimation methods. Since the excess properties are really deter-

Table 5 Criss and Cobble Correlations for Heat Capacity

$\overline{Cp}^0(T_2) - \overline{Cp}^0(T_{25}) = \frac{a_{T_2} - \overline{S}_{25}^0(1 - b_{T_2})}{\ln(T_2/298.15)}$	
where	T_2 = the temperature at the second temperature (K)
	T_{25} = the temperature at the reference state (K)
	a_{T_2} and b_{T_2} = correlation coefficients based on the ion type
	Cp = heat capacity

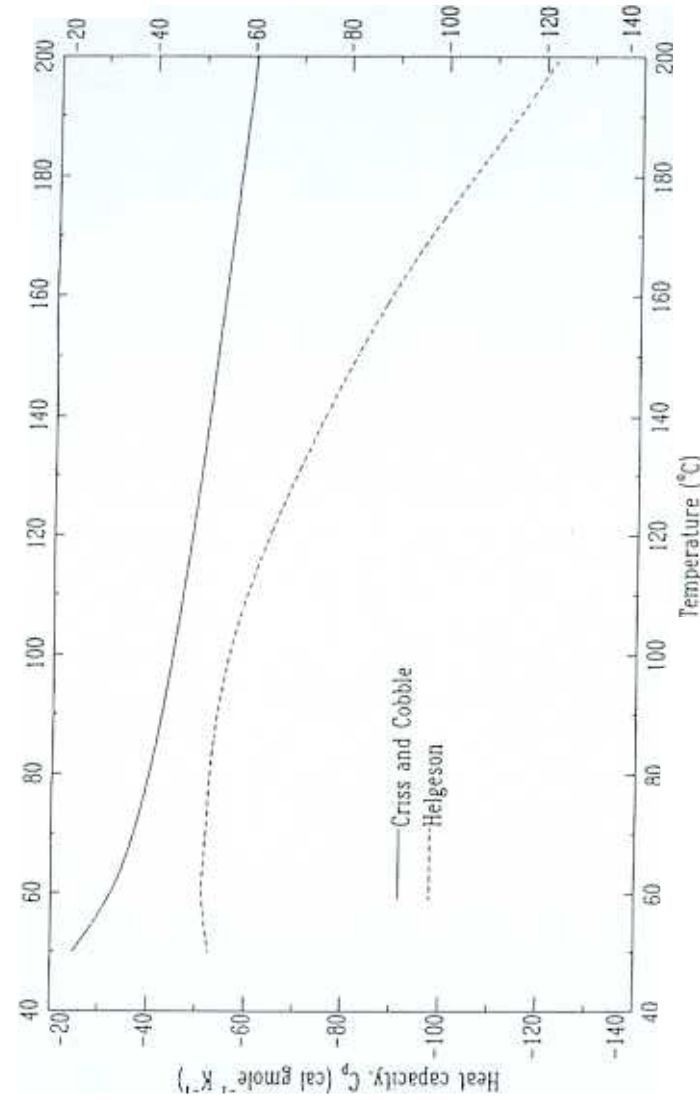


Figure 8 Comparison of heat capacity predictions versus temperature for SO_4^{2-} ion by two different methods.

mined by the activity coefficients, the methods described below apply to the activity coefficients.

Method 1: Bromley's Method

Bromley developed, based on available data, b_{ij} values at 25°C for a substantial number of individual cation anion interactions (Bromley, 1972). Bromley then used these data to develop linear correlations with respect to ionic entropy for several broad classes of ions (Bromley, 1973). A summary of these linear equations is given in Table 6. These interaction correlations are often quite coarse and, in particular, do not adequately cover interactions involving most complexes.

Method 2: Model Substance

In the model substance approach, all interactions involving cations and anions of charge +1 and -1, respectively, are assumed to be equal to that of the model substance, usually taken as NaCl [$\text{Na}^+(aq)$ interacting with $\text{Cl}^-(aq)$ is used]. Since this substance has been studied over very broad ranges of temperature, pressure, as well as the complete soluble concentration range, the b_{ij} as a function of temperature and ionic strength is well established by experimental measurements. For 2:1 salts, the well-studied model substance is CaCl_2 [$\text{Ca}^{+2}(aq)$ interacting with $\text{Cl}^-(aq)$]. For 1:2,

2:2, and other interaction categories, the model substance is less clear. These model substances can be chosen either on the basis of availability of experimental data or, if practical, on the basis of a substance common to most of the systems of interest in one's own work.

Method 3: Meissner's Method

One of the most interesting and useful methods has been provided by Meissner (Meissner, 1978). In this method, a great deal of available data on activity coefficients versus ionic strength for binary salt-water systems has been correlated based on what Meissner calls the reduced activity coefficient:

$$\Gamma = \gamma_{\pm}^{1/z_+ + z_-} \quad (44)$$

where Γ is the reduced activity coefficient, γ_{\pm} is the mean activity coefficient, and Z_+ and Z_- are the charges on the cation and anion, respectively.

When plotted on this basis, the reduced activity coefficient versus ionic strength yields a family of curves. This family of curves can be generated based on equations containing a single, "Meissner q ," parameter. Given this family of curves, if one has even a single experimental data point on activity coefficient and ionic strength (e.g., at the solubility limit), that value can be plotted and the Meissner q determined. Once the Meissner q is determined, in principle all other points along the curve can be determined.

The Meissner q value is used in the following equations to generate mean activity coefficients:

$$\Gamma^0 = (1.0 + B(1.0 + 0.1I)^q - B)\Gamma \quad (45)$$

$$B = 0.75 - 0.065q \quad (46)$$

$$\log \Gamma^* = \frac{-0.5107\sqrt{I}}{1 + C\sqrt{I}} \quad (47)$$

$$C = 1.0 + 0.055q \exp(-0.0231I^3) \quad (48)$$

Table 6 Bromley's Estimation of Mean Activity Coefficients

In Bromley's representation of the mean activity coefficient discussed previously, the B term can be represented by

$$B = B_+ + B_- + \delta_+ \delta_-$$

where B_+ and δ_+ are constants for a specific cation and B_- and δ_- are constants for a specific anion.

Bromley found that the B term could be correlated with entropy:

$$B_i = a_i \bar{S}_i^0 + b_i$$

where B_i is either B_+ or B_- , a_i and b_i are coefficients specific for the ion class under consideration and \bar{S}_i^0 is the reference-state entropy of the ion. When the use of this correlation is required, the δ_+ and δ_- terms are ignored.

where I^0 is the reduced activity coefficient at 25°C and I is the ionic strength of the solution in mol/kg H_2O .

There are a number of ways in which the Meissner method is of use and benefit. The obvious one has been discussed above. In addition, certain salts are of limited solubility in water. For this reason, their interaction parameters can be fitted only to a limited ionic strength. $CaSO_4$ is an example of such a salt. Nonetheless, such salts can exist in solutions of much higher ionic strength. An example is $CaSO_4$ in a 5 m NaCl solution. Unless the b_{ij} interaction is extrapolated to 5 m (and greater), the inclusion of this interaction in a multicomponent model will likely result in bizarre predication of certain activity coefficients containing the $Ca^{2+}(aq)$, $SO_4^{2-}(aq)$ interaction. In this way, the Meissner extrapolations allow one to create a set of interactions which are "tamed" in terms of their use in multicomponent systems.

Another extended application of Meissner is to use a Bromley estimation of a b_{ij} , generally applicable up to ionic strengths of about 6, and then use the Meissner curves to extrapolate beyond 6, and finally to refit the extended curve to a higher-order (three-parameter) Bromley model.

The Meissner family of curves is shown in Fig. 9. In this figure we have plotted a single point corresponding to NaCl at its solubility limit.

At 25°C the reported solubility for NaCl is 6.1 m. Based upon the reported equilibrium constant of 38.2179 for

$$K_{NaCl} = \gamma_{Na^+} + m_{Na^+} + \gamma_{Cl^-} - m_{Cl^-} = \gamma_{\pm}^2 m_{NaCl}^2 \quad (49)$$

for $\gamma_{\pm, NaCl} = 0.987$. Since for a 1:1 salt like NaCl the mean activity and the reduced activity coefficient (Γ) are equal, we have a point on the Meissner chart. All other points can then be estimated.

we can solve the equation

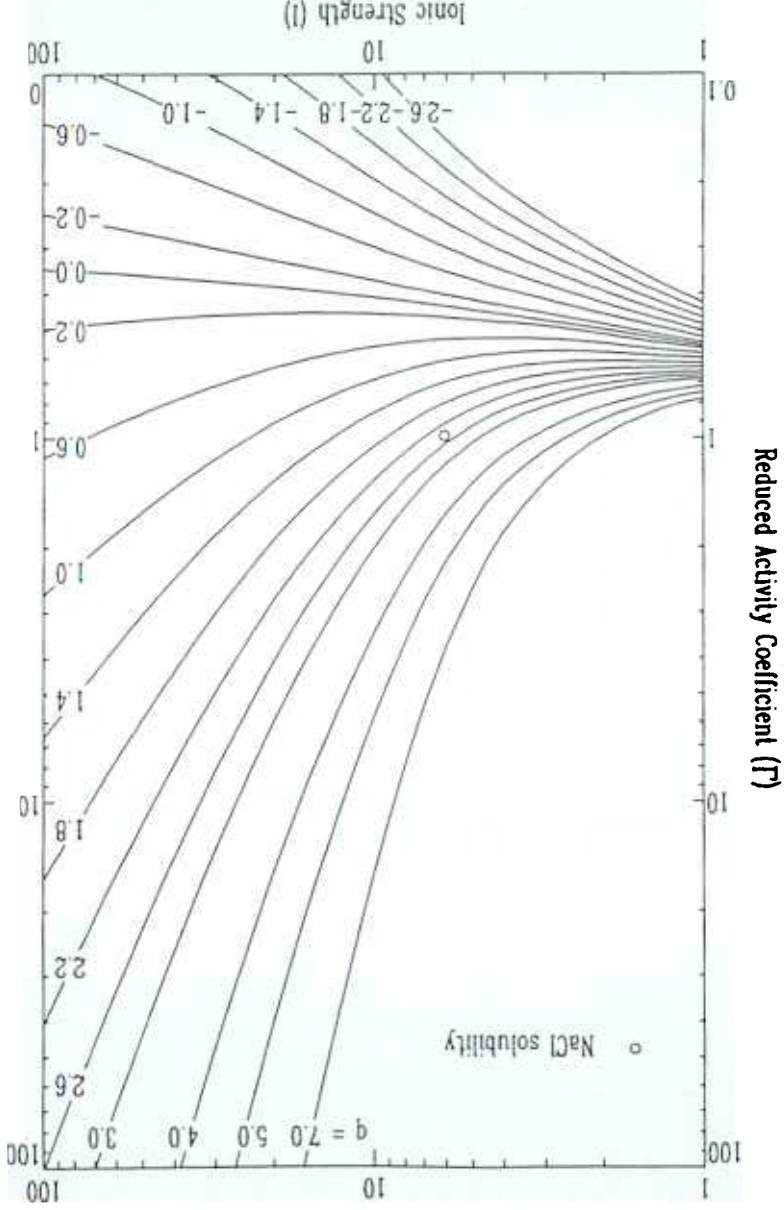


Figure 9 Isothermal Meissner q lines of reduced activity coefficient versus total ionic strength. Single point given for NaCl solubility.

D. Solid Reference State Properties

This section explains the formalism for developing aqueous electrolyte equilibrium models. A major limitation of applying the models to process and environmental problems involving solids are the gaps in thermodynamic databases for Gibbs free energies of both solids and aqueous ions. Previous methods for predicting the Gibbs free energies of solids have errors of ± 5 to 10 kcal/mol or larger.

This means that the error in calculating the Gibbs free energy of reaction can be larger than ± 5 to 10 kcal/mol because several Gibbs free energies are summed in the calculation. The Gibbs free energy of reaction is used to calculate the reactions equilibrium constant (K_{eq}) as shown in Eq. (13). Note that the Gibbs free energy of reaction is in the argument of the exponent function, so the error in K_{eq} increases very rapidly with the error in Gibbs free energy of reaction. The ratio of "error" K_{eq} to "true" K_{eq} is shown in Fig. 10 for a ± 2 -kcal/mol error range in Gibbs free energy of reaction (the heavy solid line). For example, the ratio is 30 if the error in the Gibbs free energy of reaction is -2 kcal/mol and is 0.02 kcal/mol if the error is $+1$ kcal/mol.

To carry this example further, consider how this error in K_{eq} propagates into error in the calculated solubility of a solid that generates 1 mol of cations and 1 mol of anions upon solution, such as



The ratio of "error" solubility to "true" solubility is also shown in Fig. 10 (light solid line). The ratio is 5.4 for -2 kcal/mol error in Gibbs free energy of reaction and 0.43 for $+1$ kcal/mol error.

A new correlation was recently published (Sverjensky and Molling, 1992) that allows prediction of the Gibbs free energy of crystalline solids with an accuracy of ± 1 kcal/mol. A three-parameter correlation equation was developed for each isostructural mineral family. The correlation can then be used to estimate values of Gibbs free energies for other members of the same crystal structure family.

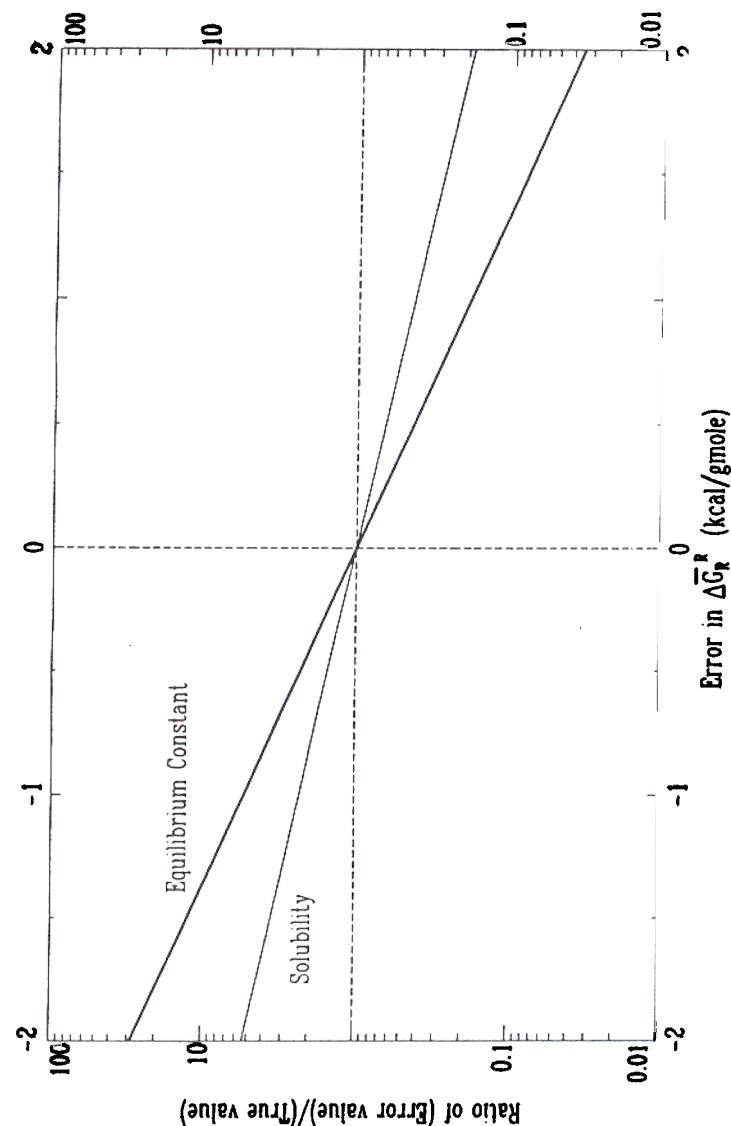


Figure 10 Ratio of error value to true value versus error in ΔG_R^R (kcal/mol).

As an example, consider the 18 possible divalent metal carbonates. Calcite and aragonite (CaCO_3) are the two dominant crystal structures. There is sufficiently accurate thermodynamic data to develop a correlation line for each crystal structure. Six cations (Ca^{2+} , Mg^{2+} , Mn^{2+} , Cd^{2+} , Zn^{2+} , and Fe^{2+}) form the calcite carbonate structure. Four cations (Ba^{2+} , Sr^{2+} , Ca^{2+} , and Pb^{2+}) form the aragonite carbonate structure. From these two correlations, it is possible to estimate the Gibbs free energy of formation for all 18 divalent cation carbonates in both the aragonite and calcite crystal forms.

CaCO_3 occurs in both the calcite and aragonite forms, but most of the other cations do not form both structures. The estimation procedure allows one to estimate Gibbs free energies for some hypothetical compounds. These values can be used to predict the stable crystal structure for compounds that present experimental problems. Such a compound is RaCO_3 . The estimated Gibbs free energy of the calcite form is -266.9 kcal/mol, while that of the more stable aragonite form is -272.0 kcal/mol. These hypothetical values are also used in predicting the distribution of cations between the aqueous phase and the coprecipitating solids solution phase (Scrivner and Rafal, 1992). This estimation method is referred to as the linear free energy method. Currently this linear free energy method is used only at 25°C , but it can be extended to higher temperatures. The method should be useful in predicting accurate values for aqueous ions (at 25°C and at higher temperatures) when the thermodynamic properties of the solids are accurately known.

VI. WRITING THE GENERAL MULTIPHASE MATHEMATICAL MODEL

In Section III we discussed preparation of the basic aqueous-phase model. This model can now be coupled with the thermodynamic equilibrium equations describing the equilibrium of additional phases with the aqueous phase. In this section we will describe how to couple one or more solid phases, a vapor phase, and a nonaqueous liquid phase. Of particular interest will be the ther-

modynamically consistent modeling of the multiphase behavior in which different standard states are used for the aqueous and nonaqueous phases.

A. Incorporation of One or More Solid Phases

In this section we consider the addition of one or more pure solid phases. A solid phase is said to be pure when it is independent of all other solid phases. The activity of a solid in such a phase is always unity. Thus, for each pure solid, we augment our aqueous-phase speciation model with precisely one new independent equation. This equation is the solid-aqueous physical equilibrium reaction. The starting point in writing this equation is to write a general equilibrium reaction for such an equilibrium:

$$S_i = p_1 P_1 + p_2 P_2 + \cdots + p_p P_p \quad (50)$$

It is necessary that we show multiple species on the right-hand side of this equation, because in the aqueous phase most solids dissociate into one or more species.

If we apply the thermodynamic relationship (10), which provides for the equality of chemical potential across phases in physical equilibrium, we then get

$$G_{S_i} = \sum_{i=0}^p \overline{G}_{P_i} \quad (51)$$

Expanding, based on earlier relationships, we get the equation

$$K_{S_i} = \frac{(\gamma_{P_1} m_{P_1})^{p_1} (\gamma_{P_2} m_{P_2})^{p_2} \cdots (\gamma_{P_p} m_{P_p})^{p_p}}{a_s} \quad (52)$$

where a_s is the activity of the solid. Since the solid phase is assumed to be ideal, $a_s = 1.0$ and the equation is further simplified.

This equation is the required addition to our aqueous-phase model which couples in the solid.

With respect to the term G_{Si} , the following thermodynamic formulation should suffice:

$$G_{Si} = G_{Si}^R - S_{Si}^R(T - T^R) + \int_{T^R}^T C_p dT + \int_{P^R}^P V dP \quad (53)$$

Using the Maier-Kelly representation of the heat capacity with respect to temperature (Kelly, 1960):

$$C_p = a_1 + a_2T - \frac{a_3}{T^2} \quad (54)$$

and using the assumption that $V = V^R$ we get the closed form,

$$G_{Si} = G_{Si}^R - S_{Si}^R(T - T^R) + a_1 \left[T - T^R - T \ln \left(\frac{T}{T^R} \right) \right] + \frac{a_3 - a_2T(T^R)^2(T - T^R)^2}{2T(T^R)^2 + V^R(P - P^R)} \quad (55)$$

In addition to this equation, one must be quite careful to augment the material balances, described in section III, with the inclusion of terms reflecting the amount of excess solid present in the solution.

There is one very significant problem which arises with the above formulation. Specifically, this equation holds only when a particular solid has saturated the solution. In other words, if an amount less than the saturation amount is present in the solution, the above equation does not hold and should not be included in the model. One way to handle this problem is to start a calculation without any solid–aqueous equilibrium, and then, based on the resulting speciation and aqueous-phase activity coefficients, to compute the value of the equilibrium constant. If this value is greater than the thermodynamic equilibrium constant, this solid–aqueous equation should be included and the system recalculated. Of course, when multiple solids compete for the same ion(s), the

situation can become quite calculated and a number of iterative solutions may be required to figure out just which solids occur.

With respect to the basic aqueous model, there is one important consideration. Specifically, the material balances must be augmented for the presence of any solids which, due to saturation of the solution, actually come out of solution. In other words, one or more pure solids streams may emerge from the system after equilibrium.

A simple illustration of solid–aqueous equilibrium is provided by the salt $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum). Applying Eq. (52), we obtain

$$K_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}} = (\gamma_{\text{Ca}^{2+}} m_{\text{Ca}^{2+}})(\gamma_{\text{SO}_4^{2-}}^2 m_{\text{SO}_4^{2-}}^2)(a_{\text{H}_2\text{O}})^2 \quad (56)$$

B. Mixed Equation of State Model

There is a considerable body of work which has been done on nonaqueous systems thermodynamics. Much of this work, concerning molecular species in a vapor and/or nonaqueous liquid phase, has been cast in the form of equations of state. The SRK (Soave-Redlich-Kwong) methods are typical of these equations of state (Soave, 1972). One of the significant benefits of using such a method is that the equation of state parameters for individual species have been correlated so that they can be estimated for species for which experimental measurements have not been made. This can be particularly useful for the many nonelectrolyte organic chemicals of environmental concern in wastewaters. Thus, the objective of most aqueous modelers has been to use the extensive body of work on the nonaqueous systems when dealing with multiphase systems containing an aqueous phase.

There is a significant problem which arises at this point. Specifically, nearly all of the nonaqueous thermodynamic formulations are based on a different standard state than the one described earlier for aqueous systems. Activity coefficients are also usually based on different conventions. For review purposes, these differences are highlighted below.

Aqueous standard state—A hypothetical 1 molal solution of the solvent at unit activity extrapolated to infinite dilution.

- 2 *Nonaqueous standard state*—The pure ideal gas.
- 3 *Aqueous activity coefficients*—Based on the asymmetric convention in which the activity coefficient approaches unity when the species molality approaches zero.
- 4 *Nonaqueous activity coefficients*—Based on the symmetric convention in which the activity coefficient approaches unity when the species mole fraction approaches unity.

There are now two approaches which can be taken. In one approach, there is some attempt to reconcile these differences. In these so-called local composition methods, a symmetric convention is imposed on the aqueous-phase activity coefficients. This approach has the virtue of allowing for multisolvent interpolative models to be built, but now the b_{ij} interaction terms must be developed for each cation–anion pair with respect to each solvent present, including, of course, water. This leads to a very large number of regression coefficients and the concurrent need for considerable experimental data.

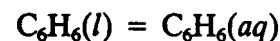
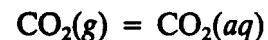
A more predictive approach is to couple the phases via a mixed equation of state model. In this approach, we accept the differences noted in 1–4 above and we reconcile the differences in the standard state by an equilibrium constant. Once this is done, the excess, or activity coefficient-based, terms can be computed based on the separate conventions noted above. With this approach the best equations of state for both aqueous and nonaqueous phases and their associated correlations can be used to describe the phases which they were designed to describe. The equilibrium constant is thus the quantity which reconciles the differences in a thermodynamically consistent way.

At this point, we can write the following equation to describe the equilibrium between a molecule in aqueous solution and a molecule in either a vapor or nonaqueous liquid phase:

$$M_{i\text{nonaqueous}} = M_{i\text{aqueous}} \quad (57)$$

We are assuming in this treatment that whenever there is equilibrium involving a molecule in a nonaqueous phase, there is a

corresponding molecular species in the aqueous phase. The species may, in fact, be a weak electrolyte, partially dissociated in the aqueous phase, but the assumption is that there will always be at least some presence of the molecular species in the aqueous phase. Two examples of such physical equilibria are



As noted previously, the governing thermodynamic equation which describes the physical equilibrium for Eq. (57) is Eq. (11), which in this case reduces to

$$\overline{G}_{Naqi} = \overline{G}_{aqi} \quad (58)$$

Note that the equilibrium constant is introduced because of the difference in the standard states. In other words, G for the aqueous phase and the nonaqueous phases is different. It is also interesting to note that although liquid–liquid equilibrium is usually represented in the literature by the equation

$$a_{Naqi} = a_{aqi} \quad (59)$$

in our treatment the correct equation is

$$K_D = \frac{a_{aqi}}{a_{Naqi}} \quad (60)$$

where K_D is the equilibrium constant (also termed the distribution constant) between the nonaqueous and aqueous phases. This is the essence of the mixed equation of state approach.

The straightforward application of Eq. (60) for $\text{CO}_2(g)$ and $\text{C}_6\text{H}_6(l)$ provides:

$$K_{\text{CO}_2(g)} = \frac{a_{\text{CO}_2(aq)}}{a_{\text{CO}_2(g)}} \quad (61)$$

$$K_{\text{C}_6\text{H}_6(l)} = \frac{a_{\text{C}_6\text{H}_6(aq)}}{a_{\text{C}_6\text{H}_6(l)}} \quad (62)$$

In the following sections we discuss a more detailed representation for both the vapor and nonaqueous liquid phases, respectively.

1. Incorporation of a Vapor Phase

In this section we consider the addition of a vapor phase to augment the basic aqueous-phase speciation model. Unlike the situation when we added the solid phases, we will consider only a single vapor phase. In addition, this phase, in equilibrium with the aqueous phase, will be multicomponent and thus have its own speciation to be determined. The vapor phase is incorporated by the following sequence of steps.

Step 1: Write an equation, based on Eq. (58), to describe the physical vapor aqueous phase equilibrium for each molecular species which can form in the vapor phase. Using the equilibrium constant form which we have utilized earlier, these equations are of the form

$$K_{iD} = \frac{\gamma_{i_{aq}} m_{i_{aq}}}{f_{i_v} y_{i_v} P} \quad (63)$$

where f_{i_v} are the fugacity coefficients (analogous to the activity coefficients in the aqueous phase), which represent the nonideal (excess) free-energy effects in the vapor phase. The y_i terms are the vapor-phase mole fractions for each species in the vapor phase.

Step 2: Write a single equation describing the fact that the sum of the y_i mole fractions is equal to unity. This equation has the form

$$\sum_{i=1}^{nM} y_i = 1 \quad (64)$$

Step 3: Add the appropriate terms to the material balances. For a given individual species, these terms will be of the form

$$c_i y_i V$$

where c_i are the appropriate coefficients describing the number of times the particular balancing element or group appears in the molecule and V is the total vapor rate.

What we have done is to add a total of $nM + 1$ equations to our system to cover the $nM + 1$ new variables ($y_i, i = 1, 2, \dots, nM$, and V).

As with the solids, there is the problem of phase existence. The recommendation is that where a vapor phase may occur, the appropriate equations should be included and solved for. If the solution to the nonlinear equation set is persistently trying to drive the vapor rate, V , negative, then the equations describing the vapor phase should be eliminated and the y_i variables and V should be set to zero and the diminished equation set solved for.

Using the binary system H_2O and CO_2 as an example, Eq. (63) can be applied as follows:

$$K_{CO_2,D} = \frac{\gamma_{CO_2(aq)} m_{CO_2(aq)}}{f_{CO_2(g)} y_{CO_2(g)} P} \quad (65)$$

$$K_{H_2O,D} = \frac{a_{H_2O}}{f_{H_2O(g)} y_{H_2O(g)} P} \quad (66)$$

Equation (64) becomes

$$y_{CO_2} + y_{H_2O} = 1 \quad (67)$$

The elemental hydrogen and carbon balances would contain the terms of the form $2y_{H_2O}V$ and $y_{CO_2}V$, respectively.

2. Incorporation of a Nonaqueous Liquid Phase

In this section we consider the addition of a nonaqueous liquid phase to augment the basic aqueous-phase speciation model. Like the situation when we added the vapor phase, we will consider only a single nonaqueous liquid phase. As with the vapor phase, the nonaqueous liquid phase in equilibrium with the aqueous phase will be multicomponent and thus will have its own speciation to be determined. The nonaqueous liquid phase is incorporated by the following sequence of steps.

Step 1: Write an equation, based on Eq. (58), to describe the physical nonaqueous phase–aqueous phase equilibrium for each species which can occur in the nonaqueous liquid phase. Using

the equilibrium constant form which we have utilized earlier, these equations are of the form

$$K_{ID} = \frac{\gamma_i(aq)m_i(aq)}{f_{ii}x_iP} \quad (68)$$

where f_{ii} are the fugacity coefficients (analogous to the activity coefficients in the aqueous phase) which represent the nonideal (excess) free-energy effects in the second liquid phase. The x_i terms are the second-liquid-phase mole fractions for each species in the second liquid phase.

Step 2: Write a single equation describing the fact that the sum of the x_i mole fractions is equal to unity. This equation has the form

$$\sum_{i=1}^{nM} x_i = 1 \quad (69)$$

Step 3: Add the appropriate terms to the material balances. For a given individual species, these terms will be of the form

$$c_i x_i L$$

where c_i are the appropriate coefficients describing the number of times the particular balancing element or group appears in the molecule and L is the total vapor rate.

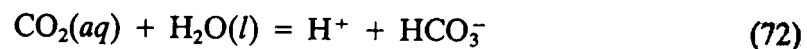
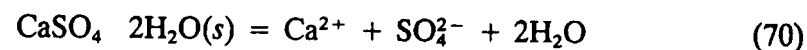
What we have done is to add a total of $nM + 1$ equations to our system to cover the $nM + 1$ new variables (x_i , $i = 1, 2, \dots, nM$, and L).

As with the solids, there is the problem of phase existence. The recommendation is that where a nonaqueous liquid phase may occur, the appropriate equations should be included and solved for. If the solution to the nonlinear equation set is persistently trying to drive the nonaqueous liquid rate, L , negative, then the equations describing the nonaqueous liquid phase should be eliminated and the x_i variables and L should be set to zero and the diminished equation set solved for.

VII. AN ILLUSTRATIVE EXAMPLE

It is now useful to pull together the above material and to write a complete mathematical model for the three-phase equilibrium involving H_2O , CO_2 , $NaCl$, and $CaSO_4$. In this model we will consider the vapor, aqueous, and the single independent solid phase, $CaSO_4 \cdot 2H_2O$.

Let us consider the following equilibria. We will not consider how to arrive at a valid set of equilibria to represent the chemistry, rather on how to write a valid set of nonlinear equations which represents the chosen equilibria.



Now write the equilibrium constant equations for Eqs. (70)–(80)

$$K_{CaSO_4 \cdot 2H_2O} = \gamma_{Ca^{2+}} m_{Ca^{2+}} \gamma_{SO_4^{2-}} m_{SO_4^{2-}} a_{H_2O}^2 \quad (81)$$

$$K_{CaSO_4(aq)} = \frac{\gamma_{Ca^{2+}} m_{Ca^{2+}} \gamma_{SO_4^{2-}} m_{SO_4^{2-}}}{\gamma_{CaSO_4(aq)} m_{CaSO_4(aq)}} \quad (82)$$

$$K_{\text{CO}_2(aq)} = \frac{\gamma_H + m_H + \gamma_{\text{HCO}_3^-} m_{\text{HCO}_3^-}}{\gamma_{\text{CO}_2(aq)} m_{\text{CO}_2(aq)} a_{\text{H}_2\text{O}}} \quad (83)$$

$$K_{\text{CO}_2(g)} = \frac{\gamma_{\text{CO}_2(aq)} m_{\text{CO}_2(aq)}}{f_{\text{CO}_2(g)} \gamma_{\text{CO}_2(g)} P} \quad (84)$$

$$K_{\text{H}_2\text{O}(aq)} = \frac{\gamma_H + m_H + \gamma_{\text{OH}^-} m_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} \quad (85)$$

$$K_{\text{H}_2\text{O}(g)} = \frac{a_{\text{H}_2\text{O}}}{f_{\text{H}_2\text{O}(g)} \gamma_{\text{H}_2\text{O}(g)} P} \quad (86)$$

$$K_{\text{HCl}(aq)} = \frac{\gamma_H + m_H + \gamma_{\text{Cl}^-} m_{\text{Cl}^-}}{\gamma_{\text{HCl}(aq)} m_{\text{HCl}(aq)}} \quad (87)$$

$$K_{\text{HCl}(g)} = \frac{\gamma_{\text{HCl}(aq)} m_{\text{HCl}(aq)}}{f_{\text{HCl}(g)} \gamma_{\text{HCl}(g)} P} \quad (88)$$

$$K_{\text{HCO}_3^-} = \frac{\gamma_H + m_H + \gamma_{\text{CO}_3^{2-}} m_{\text{CO}_3^{2-}}}{\gamma_{\text{HCO}_3^-} m_{\text{HCO}_3^-}} \quad (89)$$

$$K_{\text{HSO}_4^-} = \frac{\gamma_H + m_H + \gamma_{\text{SO}_4^{2-}} m_{\text{SO}_4^{2-}}}{\gamma_{\text{HSO}_4^-} m_{\text{HSO}_4^-}} \quad (90)$$

$$K_{\text{NaSO}_4^-} = \frac{\gamma_{\text{Na}^+} m_{\text{Na}^+} + \gamma_{\text{SO}_4^{2-}} m_{\text{SO}_4^{2-}}}{\gamma_{\text{NaSO}_4^-} m_{\text{NaSO}_4^-}} \quad (91)$$

Based on these equations, we have the following unknowns to solve for:

$$n_{\text{CaCO}_4 \cdot 2\text{H}_2\text{O}}, n_{\text{H}_2\text{O}}, \gamma_{\text{H}_2\text{O}}, \gamma_{\text{HCl}}, \gamma_{\text{CO}_2}, m_{\text{Ca}^{2+}}, m_{\text{SO}_4^{2-}},$$

$$m_{\text{CaSO}_4(aq)}, m_{\text{CO}_2(aq)}, m_{\text{OH}^-}, m_{\text{HCl}(aq)}, m_{\text{CO}_3^{2-}}, m_{\text{HSO}_4^-},$$

$$m_{\text{NaSO}_4^-}, m_{\text{Na}^+}, m_{\text{Cl}^-}, m_{\text{H}^+}, m_{\text{HCO}_3^-}, V$$

for a total 19 unknowns. Counting the equilibrium constant equations above Eqs. (81)–(91), we have 11 equations and need to develop eight more.

Now we can write a charge balance

$$2m_{\text{Ca}^{2+}} + m_{\text{H}^+} + m_{\text{Na}^+} = 2m_{\text{SO}_4^{2-}} + m_{\text{HCO}_3^-} + m_{\text{OH}^-} + m_{\text{Cl}^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{HSO}_4^-} + m_{\text{NaSO}_4^-} \quad (92)$$

We now have 12 equations and require seven more. We know that the mole fractions of all the vapor species must add up to unity (this is the definition of mole fractions), so we can write Eq. (93):

$$(93)$$

We now have 13 equations and require six more.

We can write material balance equations for the total amounts of carbon, chloride, calcium, sulfate, sodium, and hydrogen. These balances look like the following (please note that we are continuing to use the conventions used earlier):

$$\text{Carbon} \quad (m_{\text{CO}_2(aq)} + m_{\text{CO}_3^{2-}} + m_{\text{HCO}_3^-}) * Wk + \gamma_{\text{CO}_2} \cdot V = F_{\text{CO}_2(aq)} \quad (94)$$

$$\text{Chloride:} \quad (m_{\text{HCl}(aq)} + m_{\text{Cl}^-}) * Wk + \gamma_{\text{HCl}} \cdot V = F_{\text{HCl}} + F_{\text{NaCl}} \quad (95)$$

$$\text{Calcium:} \quad (m_{\text{CaSO}_4(aq)} + m_{\text{Ca}^{2+}}) * Wk + n_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}} = F_{\text{CaSO}_4} \quad (96)$$

$$\text{Sulfate:} \quad (m_{\text{CaSO}_4(aq)} + m_{\text{SO}_4^{2-}} + m_{\text{HSO}_4^-} + m_{\text{NaSO}_4^-}) * Wk + n_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}} = \quad (97)$$

$$\text{Sodium:} \quad (98)$$

$$\begin{aligned} \text{Hydrogen} \quad & (m_{\text{H}^+} + m_{\text{HCl}(aq)} + m_{\text{HSO}_4^-} \\ & + m_{\text{HCO}_3^-} + m_{\text{OH}^-}) * Wk \\ & + V(2\gamma_{\text{H}_2\text{O}} + \gamma_{\text{HCl}}) \\ & + 4n_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}} = 2F_{\text{H}_2\text{O}} \end{aligned} \quad (99)$$

Remember that W_k is equal to $n_{\text{H}_2\text{O}}/55.50868$ and that n_i is the total number of moles of species i .

These six material balance equations complete the set necessary to model the chemistry mathematically. We now have

$$\begin{aligned} &11 \text{ equilibrium equations} + 1 \text{ charge balance} \\ &+ 1 \text{ vapor balance} + 6 \text{ material balances} = 19 \text{ unknowns} \end{aligned}$$

If you were to change the chemistry, let's say by adding a new chemical species such as CaOH^+ , you would be adding one new unknown (for new total of 20), then adding one new equilibrium expression (for a new total of 12), but you would not be adding any new material balances, just augmenting the charge, calcium and hydrogen balances, so the new relationship is

$$\begin{aligned} &12 \text{ equilibrium equations} + 1 \text{ charge balance} \\ &+ 1 \text{ vapor balance} + 6 \text{ material balances} = 20 \text{ unknowns} \end{aligned}$$

This is the requirement for developing a set of nonlinear equations to solve.

VIII. SOLVING THE MATHEMATICAL MODEL

Previous sections have dealt with developing an equation set to describe the speciation of an aqueous solution, and how to find (or estimate) the thermodynamic data necessary to satisfy the deterministic model. This section will tie these together so that a quantitative model can be developed and solved. The resulting rigorous thermodynamic model can be used to provide understanding of an aqueous system.

A. Using General Equation-Solving Software

General equation-solving software can be used to solve mathematical equations for an aqueous model. They do not, of course, provide the underlying thermodynamic coefficients for the chemistry involved; the user must have these available.

The equations to be solved are nonlinear and difficult to solve. Many programming options exist, ranging from programming the

entire model and numerical solutions algorithm to solving a greatly simplified model using a computer spreadsheet program such as Lotus 1-2-3. The most practical and accurate methods fall between those extremes. Packaged subroutines and programs to solve sets of nonlinear equations are numerous, including IMSL libraries and Mathematica for mainframe applications and PC-based programs such as TK Solver and Eureka. Most of these are based on Newton-Raphson type algorithms.

TK Solver Plus, by UTS (Universal Technical Systems, Inc., Rockford, Illinois), is probably the most straightforward of all the programs to use. No programming (in the traditional sense) is necessary. TK Solver Plus uses a declarative language; that is, equations can be entered into the system "as is" and do not have to be explicit in any particular variable. A simple binary TK Solver Plus model describing the equilibrium for HCl in H_2O is shown in Fig. 11. The reader should not be concerned with the data used in this example model, but rather should study the structure of the model.

One particularly useful feature of TK Solver Plus is the ability to "switch variables." This should be a feature one looks for in any equation-solving software. The model developed should involve a square ($m \times m$) solutions matrix—that is, the number of unknowns equals the number of independent equations. It does not matter which m variables are unknown, so long as the known values and the solution values are within a range that provides real answers. The ability to fix variables which are usually considered unknowns, such as pH or partial pressure, allows one to calculate bubble-point pressures, saturation concentrations, feed component rates necessary to attain a desired pH, and many other important "input" variables. This feature was used in the HCl/ H_2O example presented in Fig. 11. The total amount of vapor was fixed ($V = 0.0001$), and the pressure was unknown. The result is the bubble-point pressure of a 3 m HCl solution at 25°C.

Once the equation set has been developed, the two most significant problems encountered while programming and solving electrolyte models are (1) the nonlinearity of the equations, and (2) the dynamic range of the variables. The example in Fig. 11

VARIABLE SHEET				
St Input	Name	Output	Unit	Comment
3	F_HCl		gmol	HCl feed
55.51	F_H2O		gmol	H2O feed
298.16	TK		Kelvins	Temperature
	P	.02791993	atm	Pressure
1389800	K_HCl			Equil const: $\text{HCl(aq)} = \text{H}(+) + \text{Cl}(-)$
1.46	K_HClva			Equil const: $\text{HCl(vap)} = \text{HCl(aq)}$
1.01E-14	K_H2O			Equil const: $\text{H2O} = \text{H}(+) + \text{OH}(-)$
31.78	K_H2Ova			Equil const: $\text{H2O(vap)} = \text{H2O}$
	m_H	3.0832024	molal	H(+) ion concentration
	m_OH	-3.604E-9	molal	OH(-) ion concentration
	m_Cl	3.0832024	molal	Cl(-) ion concentration
	m_HCl	9.8158E-6	molal	HCl(aq) concentration
	H2O	54.009905	gmol	Moles of water
.887	aw			Water activity
	I	3.0832024	molal	Ionic strength
	pH	-.6377377		Solution pH
1	phi			Gas phase fugacity coefficient
.0001	V		gmol	Moles of gas
	y_H2O	.99966714		Vapor mole fraction H2O
	y_HCl	.00033286		Vapor mole fraction HCl
	g_H	1.4084312		H(+) ion activity coefficient
	g_OH	1.4084312		OH(-) ion activity coefficient
	g_Cl	1.4084312		Cl(-) ion activity coefficient
	g_HCl	1.3822827		HCl(aq) activity coefficient
.5091	gamma	1.4084312		Helgeson Mean Activity Coefficient
1	A_gam			>
-1	Z1			>
	LAMBDA	3.8189071		>
	GAMMA	-.0457491		> Helgeson parameters
.139	b_gam			>
	mstar	6.1664048		>
4.89E-8	ao			>
32830000	B_gam			>
	GAM_G	-62.41999		>
.105	k_HCl		1/molal	Setchenow coeff for HCl(aq)
1.987	R		cal/gmolK	gas constant

(a)

Figure 11 TK! Solver model for HCl/H₂O

clearly shows the dynamic range problem; the model must consider numerical values ranging from $1.4\text{E} + 6$ (K_{HCl}) to $1.0\text{E} - 14$ ($K_{\text{H}_2\text{O}}$). The combination of these two problems makes the solution of electrolyte speciation models by traditional techniques extremely difficult. One technique that can be used to minimize the impact of these problems is to linearize the model equations by transforming them into logarithms. This transformation converts exponents into coefficients and shrinks the dynamic range by many orders of magnitude. A useful exercise for the reader would be to program the example in Fig. 11 both as shown and

RULE SHEET	
S Rule	
"	Step 1: Write equilibrium constant equation for each of the independent chemical reactions and/or vapor-liquid equilibrium relations.
"	
"	$K_{\text{H}_2\text{O}} = g_{\text{H}} \cdot m_{\text{H}} \cdot g_{\text{OH}} \cdot m_{\text{OH}} / a_{\text{w}}$
"	$K_{\text{HCl}} = g_{\text{H}} \cdot m_{\text{H}} \cdot g_{\text{Cl}} \cdot m_{\text{Cl}} / g_{\text{HCl}} \cdot m_{\text{HCl}}$
"	$K_{\text{H}_2\text{Ovap}} = a_{\text{w}} / \phi / P / y_{\text{H}_2\text{O}}$
"	$K_{\text{HClvap}} = g_{\text{HCl}} \cdot m_{\text{HCl}} / \phi / P / y_{\text{HCl}}$
"	
"	Step 2: Write an electroneutrality equation.
"	$m_{\text{H}} = m_{\text{OH}} + m_{\text{Cl}}$
"	
"	Step 3: Write a sufficient number of material balances to "complete the model".
"	
"	$F_{\text{HCl}} = (m_{\text{Cl}} + m_{\text{HCl}}) \cdot \text{H}_2\text{O} / 55.508 + V \cdot y_{\text{HCl}}$
"	$2 \cdot F_{\text{H}_2\text{O}} = 2 \cdot \text{H}_2\text{O} + (m_{\text{H}} + m_{\text{OH}}) \cdot \text{H}_2\text{O} / 55.508 + 2 \cdot V \cdot y_{\text{H}_2\text{O}} + V \cdot y_{\text{HCl}}$
"	
"	Step 4: Write equation describing the sum of the vapor phase mole fractions is equal to unity.
"	
"	$y_{\text{HCl}} + y_{\text{H}_2\text{O}} = 1.0$
"	
"	Step 5: Complete the model by including additional equations to describe remaining unknowns (such as ionic strength, pH, and activity coefficients).
"	
"	"...for ionic strength
"	$I = 0.5 \cdot (m_{\text{H}} + m_{\text{OH}} + m_{\text{Cl}})$
"	"...for pH
"	$\text{pH} = -\log(g_{\text{H}} \cdot m_{\text{H}})$
"	"...for activity coefficients
"	$\ln(g_{\text{HCl}}) = k_{\text{HCl}} \cdot m_{\text{Cl}}$
"	Helgeson equations used for this model
"	$\log(\text{gamma}) = -A_{\text{gam}} \cdot \text{abs}(Z1 \cdot Z1) \cdot \sqrt{\text{abs}(I)} / \text{LAMBDA} + \text{GAMMA} + b_{\text{gam}} \cdot I$
"	$\text{GAMMA} = \text{GAM}_G / 2.303 \cdot R / \text{TK}$
"	$\text{GAM}_G = -2.303 \cdot R \cdot \text{TK} \cdot \log(1.0 + 0.0180153 \cdot mstar)$
"	$mstar = 2.0 \cdot I$
"	$\text{LAMBDA} = 1 + ao \cdot B_{\text{gam}} \cdot \sqrt{\text{abs}(I)}$
"	$\text{gamma} = g_{\text{H}}$
"	$\text{gamma} = g_{\text{OH}}$
"	$\text{gamma} = g_{\text{Cl}}$

Note: The use of the term 'sqrt(abs(I))' in the above equations is to facilitate convergence. With some initial guesses, 'I' becomes negative during the convergence causing a fatal math error. The use of the 'abs' operator allows variable I to venture into negative space prior to convergence.

(b)

then in linearized form. The difference in "ease of convergence" will quickly become obvious.

The model in Fig. 11 shows the equations and data necessary to build a simple HCl-H₂O model. The generalized methods discussed throughout this chapter become very complex when considering multicomponent systems, particularly with regard to activity coefficients. In Fig. 11, the individual ion activity coefficients are set equal to the mean activity coefficient. This sim-

plification can be made only for binary systems. An excellent discussion of multicomponent activity coefficients is provided elsewhere (Zemaitis et al., 1986). For multicomponent problems, a commercial software package should be seriously considered.

B. Using Aqueous Simulation Programs

Aqueous simulation programs provide for both the solution of the aqueous model and for the insertion of the appropriate thermodynamic coefficients. Of course, each program is limited by the scope of the chemistry in the database made available to the user.

At least 20 different commercial programs available from various university and private sources are designed specifically to solve aqueous-phase speciation models. Some of these programs include ProChem/ESP, Aspen Plus, ECHEM, EQUILIB, EQ3/EQ6, MINTEQ, PHREEQE, WATEQ4F, SOILCHEM, COMICS, ECCLES, HALTAFALL, MINEQL, MINQUAD, SCOGS, SOLMNQ, GEOCHEM, ESTA, CHEMEQUIL-2, EQUIL, and IONPAIR. This list is in no way intended to be complete, and the authors apologize for any programs that may have been omitted. Some attempts have been made to compare these programs (Mangold and Tsang, 1991; Duffield et al., 1991; Nordstrom et al., 1979). All reviews agree that to compare all commercial aqueous simulation codes would be a very difficult task.

There are at least four very important considerations in choosing a commercial aqueous simulation program. First, and without question most important, is the database. Even the best solution algorithm will generate incorrect and misleading answers if the database contains incorrect thermodynamic data. Some of the questions to ask of a commercial database include:

- How extensive is the database?
- Where did the data come from?
- Are the data references available?
- Are there estimation techniques programmed?
- Has the database been validated?
- Can proprietary databases be developed?

- Are there regression capabilities for developing thermodynamic parameters from proprietary data?
- Is the database internally consistent?

The second consideration has to do with structure of the program, whether it is a chemical speciation analysis or a reaction path analysis. Each structure has advantages, depending on the desired results. In general, a chemical speciation analysis is most useful for traditional equilibrium problems and a reaction path analysis is most useful when kinetics become important or are the controlling phenomena. Ideally, the program should be able to consider both.

A third consideration is the question, "Does the model equation set include a charge balance"? Some of the available programs do not.

Yet another consideration is the "front end" of the program. The previous sections of this chapter have shown the complexity of aqueous electrolyte equilibrium models. Does the commercial software help a user define the chemistry and all the constituent ions? Does the commercial software write the equations and compile them? Does the commercial software search the database and organize the thermodynamic data for solution of the problem? Is the program "user-friendly" or "user-hostile"?

Commercial electrolyte modeling programs usually pay for themselves quickly, allowing an engineer to bypass the writing and debugging of a program and proceed directly to what he or she has been asked to do—solve the problem!

IX. NOMENCLATURE

- $a_{\text{H}_2\text{O}}$ = activity of water
- a_i = activity of species i
- a_{T_2} = Criss and Cobble coefficient at T_2
- a_1 = Helgeson equation of state parameter (cal/mol/bar)
- a_1 = Maier-Kelly heat capacity coefficients J/mol/K

- a_2 = Helgeson equation of state parameter (cal/mol)
 a_2 = Maier-Kelly heat capacity coefficient (J/mol/K²)
 a_3 = Helgeson equation of state parameter (cal-K/mol/bar)
 a_3 = Maier-Kelly heat capacity coefficient J-K/mol
 a_4 = Helgeson equation of state parameter (cal-K/mol)
 a_0 = Debye-Hückel radius term (Å)
 A = Debye-Hückel constant
 aq = aqueous-phase designator
 b_{ij} = Generic ion-ion interaction term
 b_k = Helgeson ion-ion interaction term
 b_{T_2} = Criss and Cobble coefficient at T_2
 B = Bromley B ion-ion interaction term
 B_{iL} = Helgeson ion-molecule interaction term
 B_+ , B_- = Bromley cation and anion terms
 B_{\pm} = Pitzer ion-ion interaction term
 c_1 = Helgeson equation of state parameter (cal/mol/K)
 c_2 = Helgeson equation of state parameter (cal-K/mol)
 cr = crystal-phase designator (also referred to as solid phase)
 C^{\pm} = Pitzer ion-ion interaction term
 \overline{Cp}_i , \overline{Cp}_i^0 , \overline{Cp}_i^E = partial molal heat capacity at constant pressure for the sum, standard state, and excess for species i (J/mol/K)
 $\Delta\overline{Cp}_R^R$ = standard-state heat capacity of reaction at the reference state (298.15 K, 1 atm; J/mol/K)
 $f_{i,phase}$ = Fugacity of species i in the designated phase
 f^γ = Pitzer fugacity coefficient
 F_i = amount of inflowing material i (mol)

- g = gas-phase designator (also referred to as vapor phase)
 \overline{G}_i , \overline{G}_i^0 , \overline{G}_i^E = partial molal Gibbs free energy for sum, standard state, and excess for species i (J/mol)
 \overline{G}_i^E = excess partial molal Gibbs free energy at the reference state (298.15 K, 1 atm; J/mol)
 $\Delta\overline{G}_R^R$ = standard-state partial molal Gibbs free energy of reaction at the reference state (298.15 K, 1 atm; J/mol)
 $\Delta\overline{G}_R^0$ = standard-state partial molal Gibbs free energy of reaction (J/mol)
 \overline{H}_i , \overline{H}_i^0 , \overline{H}_i^E = partial molal enthalpy for sum, standard state, and excess for species i (J/mol)
 $\Delta\overline{H}_R^0$ = standard partial molal enthalpy of reaction at the reference state (298.15 K, 1 atm; J/mol)
 I = ionic strength (molality)
 \bar{I} = true ionic strength (corrected for ion complexation, molality)
 k = Setchenow coefficient, obtained by plotting S_0/S , versus molality of the salt solution
 K = symbol designating the equilibrium constant (see Section II)
 K_D = vapor/aqueous or nonaqueous/aqueous distribution coefficient [see Eq. (60)]
 l = liquid-phase designator
 L = refers to an anion (ligand)
 L = total nonaqueous liquid (mol)
 m_i = molality of species i (mol/kg water)
 M = refers to a metal cation
 p_i = stoichiometric coefficient of product i
 P = pressure (bar or atm)
 \overline{P}_i = generic term for product i
 \overline{P}_i = partial molal property of species i
 \overline{P}_i^E = excess partial molal property of species i

\overline{P}_R' = standard-state partial molal property of species i at the reference state (298.15 K, 1 atm)
 \overline{P}_0' = standard-state partial molal property of species i
 P_i' = pressure at the reference state (1 bar)
 P_T = the sum of the partial molal property for all species in solution
 q = Meissner q value
 Q = derivative of the dielectric constant of water with respect to pressure
 r_i = stoichiometric coefficient of reactant i
 R = the gas constant (8.135 J/mol/K)
 R_i = generic term for reactant i
 s = solid-phase designator (also referred to as crystal phase)
 $\underline{S}, \underline{S}_0', \underline{S}_1', \underline{S}_T'$ = partial molal entropy for the sum, standard state, and excess for species i (J/mol/K)
 S_i = solubility of a neutral molecule in a salt solution (molality)
 S_0 = solubility of a neutral molecule in pure water (molality)
 \underline{S}_{25}^0 = standard-state partial molal entropy at 25°C (298.15 K)
 T = temperature (K)
 T_R = reference-state temperature = 298.15 K
 T_i = temperature at the reference state (298.15 K)
 T_2 = temperature at other than 298.15 K
 V = total vapor (mol)
 $\underline{V}, \underline{V}_0', \underline{V}_1', \underline{V}_T'$ = molar volume for the sum, standard state, and excess for species i (m³/mol)
 X = second derivative of the dielectric constant of water with respect to temperature (see Table 1)
 $X_{i,\text{phase}}$ = mole fraction of species i in the designated phase

Y = first derivative of the dielectric constant of water with respect to temperature (see Table 1)
 $Y_{i,\text{phase}}$ = mole fraction of species i in the designated phase
 Y_i = Helgeson ion-ion interaction term
 $Y_{P,T}$ = first derivative of the dielectric constant of water with respect to temperature at the reference state (298.15 K, 1 bar)
 Z_i = charge on species i ; i may be represented as + or -
 β_0 = Pitzer ion-molecule or molecule-molecule interaction term
 γ_{aq} = activity coefficient of an aqueous molecule
 γ_i = activity coefficient of species i
 γ_{\pm} = mean activity coefficient [see Eq. (40)]
 Γ = Meissner's reduced activity coefficient [see Eq. (44)]
 Γ_y = Helgeson ion-ion interaction term
 Γ_y^0 = Meissner's reduced activity coefficient at 298.15 K
 δ^+, δ^- = Bromley cation and anion terms
 ϵ = dielectric constant of water
 θ = temperature constant used in the Helgeson equation of state (228 K)
 v = sum of the stoichiometric coefficients
 $v_{i,k}$ = stoichiometric coefficients of species i in electrolyte k
 ν_k = sum of ions in electrolyte k
 ν_+, ν_- = stoichiometric coefficient of the cation and anion
 ψ = pressure constant used in the Helgeson equation of state (2600 bar)
 ω = Born coefficient used in the Helgeson equation of state (cal/mol)
 $\omega_{P,T}$ = Born coefficient at the reference state (298.15 K, 1 bar)

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