

# Chapter 6 Aqueous Thermodynamics

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## Overview

Understanding aqueous thermodynamics can be a daunting task. In this chapter we will describe some of the essential topics in aqueous thermodynamics and present them in a logical, relatively easy to understand manner. We will be using the AQ thermodynamic framework for these examples.

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## The Equilibrium Constant

The evaluation of the following equation is central to the OLI Software:

$$\Delta_R \bar{G}^o = -RT \ln K$$

Where  $\Delta_R \bar{G}^o$  is the partial molal, standard-state Gibbs Free Energy of Reaction, R is the Gas Constant (8.314 J/mole/K), T is the temperature (Kelvin) and K is the equilibrium constant. The subscript **R** refers not to the gas constant but to an equilibrium reaction.

We define  $\Delta_R \bar{G}$  as:

$$\Delta_R \bar{G} = \sum_i v_i \Delta_f \bar{G}_i (\text{PRODUCTS}) - \sum_i v_i \Delta_f \bar{G}_i (\text{REACTANTS})$$

Where  $v_i$  is the Stoichiometric coefficient and  $\Delta_f \bar{G}_i$  is the Gibbs Free Energy of Formation for a species.

### Question:

Consider the equilibrium:



## What is the Gibbs Free Energy of Reaction? What is the equilibrium constant at 25 °C (298.15K)<sup>10</sup>?

The reference state thermodynamic values are readily available:<sup>11</sup>

$$\Delta_f \bar{G}^R (Na_2SO_4) = -1270100 J / mole^{12}$$

$$\Delta_f \bar{G}^R (Na^+) = -261800 J / mole$$

$$\Delta_f \bar{G}^R (SO_4^{2-}) = -744460 J / mole$$

For the Gibbs Free Energy of reaction:

$$\Delta_R \bar{G}^R = \left( 2\Delta_f \bar{G}^R (Na^+) + \Delta_f \bar{G}^R (SO_4^{2-}) \right) - \Delta_f \bar{G}^R (Na_2SO_4)$$

$$\Delta_R \bar{G}^R = \left( 2(-261800) + (-744460) \right) - (-1270100) = 2640 J / mole$$

By rearranging our equilibrium equation we get:

$$\ln K^R = -\frac{\Delta_R \bar{G}^R}{RT}$$

By now substituting the appropriate numbers we get:

$$\ln K^R = -(2640 J/mole) / ((8.314 J/mole/K)(298.15K)) = -1.07$$

$$K^R = 0.34$$

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## Principal Thermodynamic Properties

Each thermodynamic property is composed of two parts. The first is the standard state part which is only a function of temperature and pressure (denoted by the superscript <sup>o</sup>).

The second is the excess part which is a function of temperature and pressure as well as concentration (denoted by the superscript <sup>E</sup>).

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<sup>10</sup> 25°C (298.15K) is also known as the reference temperature.

<sup>11</sup> NBS Tables of Chemical Thermodynamic Properties - Selected Values for Inorganic and C1-C2 Organic Substances in SI Units, Wagman, D.D., et al, 1982

<sup>12</sup> The subscript **f** refers the energy of formation from the elements. The superscript **R** refers to the reference state. This is a special case of the standard state normally denoted with a superscript **o**.

**Partial Molal Gibbs Free Energy**

$$\bar{G}_i = \bar{G}_i^o + \bar{G}_i^E$$

**Partial Molal Enthalpy**

$$\bar{H}_i = \bar{H}_i^o + \bar{H}_i^E$$

**Partial Molal Entropy**

$$\bar{S}_i = \bar{S}_i^o + \bar{S}_i^E$$

**Partial Molal Heat Capacity**

$$\bar{C}p_i = \bar{C}p_i^o + \bar{C}p_i^E$$

**Partial Molal Volume**

$$\bar{V}_i = \bar{V}_i^o + \bar{V}_i^E$$

**Note:** Superscript <sup>o</sup> = Standard State Property  
Superscript <sup>E</sup> = Excess Property

## HKF (Helgeson-Kirkham-Flowers) Equation of State<sup>13,14</sup>

Working since 1968, Helgeson, et. al., have found that the standard-state thermodynamic property of any species in water can be represented by a function with seven terms which have specific values for each species.

These seven terms ( $a_{1-4}$ ,  $c_{1-2}$ , and  $\omega$ ) are integration constants for volume (a), heat capacity (c) and temperature and pressure properties of water ( $\omega$ ). They are independent of the data system used to obtain them.

$$\bar{H}_i^o = \bar{H}_i^R + f_{Hi}(a_1, \dots, a_4, c_1, c_2, \omega)$$

$$\bar{G}_i^o = \bar{G}_i^R - \bar{S}_i^R(T - T^R) + f_{Gi}(a_1, \dots, a_4, c_1, c_2, \omega)$$

$$\bar{S}_i^o = \bar{S}_i^R + f_{Si}(a_1, \dots, a_4, c_1, c_2, \omega)$$

$$\bar{C}p_i^o = \bar{C}p_i^R + f_{Cpi}(a_1, \dots, a_4, c_1, c_2, \omega)$$

<sup>13</sup> H.C.Helgeson, D.H.Kirkham, G.C.Flowers. Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures - Parts I through IV. American Journal of Science 1974, 1976, 1981.

<sup>14</sup> J.C.Tanger, IV Doctorial Thesis. "Calculation of the Standard Partial Molal Thermodynamic Properties of Aqueous Ions and Electrolytes at High Pressures and Temperatures" University of California at Berkley, 1986 H.C.Helgeson Advisor.

$$\overline{V}_i^o = \overline{V}_i^R + f_{Vi}(a_1, \dots, a_4, c_1, c_2, \omega)$$

Superscript <sup>R</sup>	– Reference State Property (25°C, 1 bar)
Superscript <sup>o</sup>	– Standard State Property
$a_1, \dots, a_4$	– Pressure Effects
$c_1, c_2$	– Temperature Effects
$\omega$	– Pressure, Temperature Effects

The Helgeson Equation of State Parameters are used to predict equilibrium constants.

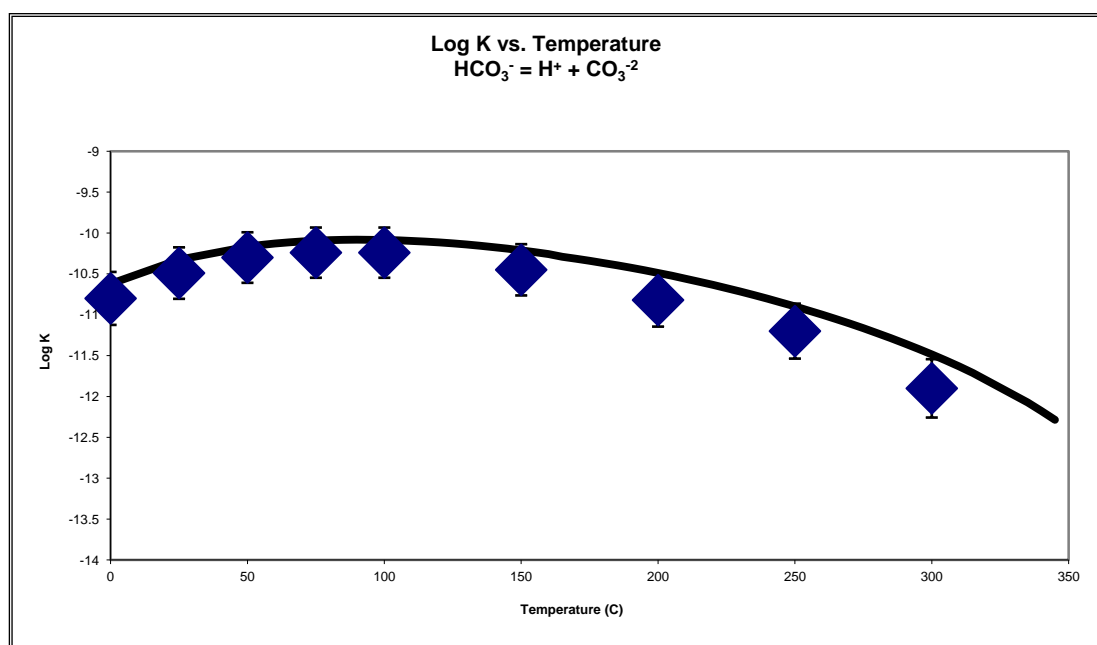


Figure 6-1 The logarithm of the equilibrium constant (LOG K) for the dissociation of the bicarbonate ion as a function of temperature at saturation pressure. The symbols represent the data taken from the references listed in the footnotes<sup>15,16,17,18,19</sup> but the line was generated from the equation of state.

<sup>15</sup> H.S.Harned and S.R.Scholes. The Ionization Constant of  $\text{HCO}_3^-$  – from 0 to 50°. *J.Am.Chem.Soc.* **63**,1706 (1941)

<sup>16</sup> R.Nasanen. Zur Einwirkung der Saure und Basenzusatze auf die Fallungskurvevon Bariumcarbonate. *Soumen Kemistilehti* **90**,24 (1946)

<sup>17</sup> F. Cuta and F.Strafelda. The second dissociation constant of carbonic acid between 60 and 90°C. *Chem. Listy* **48**,1308 (1954)

<sup>18</sup> B.N.Ryzhenko. *Geochemistry International* **1**,8 (1963)

<sup>19</sup> C.S.Patterson, G.H.Slocum, R.H.Busey and R.E.Mesmer. Carbonate equilibrium in hydrothermal systems: First ionization of carbonic acid in NaCl media to 300°C. *Geoch.Cosmoh.Acta* **46**,1653 (1982)

## The Helgeson Equation of State

### Enthalpy

$$\begin{aligned}\overline{\Delta H_{p,T}^o} &= \overline{\Delta H_f^o} + c_1(T - T_r) - c_2 \left[ \left( \frac{1}{T - \Theta} \right) - \left( \frac{1}{T_r - \Theta} \right) \right] + a_1(P - P_r) + a_2 \ln \left( \frac{\Psi + P}{\Psi + P_r} \right) \\ &+ \left( a_3(P - P_r) + a_4 \ln \left[ \frac{\Psi + P}{\Psi + P_r} \right] \right) \left[ \frac{2T - \Theta}{(T - \Theta)^2} \right] + \omega \left( \frac{1}{\varepsilon} - 1 \right) + \omega TY - T \left( \frac{1}{\varepsilon} - 1 \right) \left( \frac{\partial \omega}{\partial T} \right)_p \\ &\quad - \omega_{Pr,T_r} \left( \frac{1}{\varepsilon_{Pr,T_r}} - 1 \right) - \omega_{Pr,T_r} T_r Y_r\end{aligned}$$

### Gibbs Free Energy

$$\begin{aligned}\overline{\Delta G_{p,T}^o} &= \overline{\Delta G_f^o} - \overline{S_{Pr,T_r}^o} (T - T_r) - c_1 \left[ T \ln \left( \frac{T}{T_r} \right) - T + T_r \right] + a_1(P - P_r) + a_2 \ln \left( \frac{\Psi + P}{\Psi + P_r} \right) \left( \frac{\Psi + P}{\Psi + P_r} \right) \\ &+ \left[ a_3(P - P_r) + a_4 \ln \left( \frac{\Psi + P}{\Psi + P_r} \right) \right] \left( \frac{1}{T - \Theta} \right) - c_2 \left[ \left( \left( \frac{1}{T - \Theta} \right) - \left( \frac{1}{T_r - \Theta} \right) \right) \left( \frac{\Theta - T}{\Theta} \right) - \frac{T}{\Theta^2} \ln \left( \frac{T_r(T - \Theta)}{T(T_r - \Theta)} \right) \right] \\ &\quad + \omega \left( \frac{1}{\varepsilon} - 1 \right) - \omega_{Pr,T_r} \left( \frac{1}{\varepsilon_{Pr,T_r}} - 1 \right) + \omega_{Pr,T_r} Y_{Pr,T_r} (T - T_r)\end{aligned}$$

### Volume

$$\overline{V^o} = a_1 + a_2 \left( \frac{1}{\Psi + P} \right) + \left[ a_3 + a_4 \left( \frac{1}{\Psi + P} \right) \right] \left( \frac{1}{T - \Theta} \right) - \omega Q + \left( \frac{1}{\varepsilon} - 1 \right) \left( \frac{\partial \omega}{\partial P} \right)_T$$

### Heat Capacity at Constant Pressure

$$\overline{Cp^o} = c_1 + c_2 \left( \frac{1}{T - \Theta} \right)^2 - \left( \frac{2T}{(T - \Theta)^3} \right) \left[ a_3(P - P_r) + a_4 \ln \left( \frac{\Psi + P}{\Psi + P_r} \right) \right] + \omega TX + 2TY \left( \frac{\partial \omega}{\partial T} \right)_p - T \left( \frac{1}{\varepsilon} - 1 \right) \left( \frac{\partial^2 \omega}{\partial T^2} \right)_p$$

### Entropy

$$\begin{aligned}\overline{S^o} &= \overline{S_{Pr,T_r}^o} + c_1 \ln \frac{T}{T_r} - \frac{c_2}{\Theta} \left\{ \left( \frac{1}{T - \Theta} \right) - \left( \frac{1}{T_r - \Theta} \right) + \frac{1}{\Theta} \ln \left( \frac{T_r(T - \Theta)}{T(T_r - \Theta)} \right) \right\} + \left( \frac{1}{T - \Theta} \right)^2 \left[ a_3(P - P_r) + a_4 \ln \left( \frac{\Psi + P}{\Psi + P_r} \right) \right] \\ &\quad + \omega Y - \left( \frac{1}{\varepsilon} - 1 \right) \left( \frac{\partial \omega}{\partial T} \right)_p - \omega_{Pr,T_r} Y_{Pr,T_r}\end{aligned}$$

**Where,**

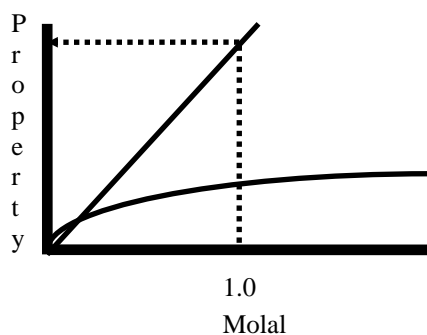
H	=	Enthalpy
G	=	Gibbs Free Energy
V	=	Volume
C <sub>p</sub>	=	Heat Capacity at constant Pressure
S	=	Entropy
T	=	Temperature
P	=	Pressure
Θ	=	228 K
Ψ	=	2600 Bar
ω	=	Temperature and Pressure dependent term for electrostatic nature of the electrolytes
Q	=	Pressure functions of the dielectric constant
ε	=	Dielectric constant of water
a <sub>1</sub> ...a <sub>4</sub>	=	Pressure dependent terms
c <sub>1</sub> , c <sub>2</sub>	=	Temperature dependent terms

## What is the standard State?

The standard state refers to a thermodynamic value at a defined state (temperature, pressure and concentration)<sup>20</sup>.

### Aqueous:

The hypothetical 1.0 molal solution extrapolated from infinite dilution.



### Vapor:

The Ideal Gas Pure Component (mole fraction = 1.0)

### Organic Liquid:

The Ideal Gas Pure Component (mole fraction = 1.0)

### Solid:

The pure component solid.

<sup>20</sup> M. Rafal, J.W. Berthold, N.C. Scrivner and S.L. Grise."Chapter 7:Models for Electrolyte Solutions", Models for Thermodynamic and Phase Equilibria Calculations. Stanley I Sandler, ed. Marcel-Dekker, Inc. New York: 1994. pp. 686.

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## Excess Properties

Excess properties are a function of temperature, pressure and composition. It is with the excess properties that we begin to introduce the concept of activities and activity coefficients.

The excess property that we are most concerned with is the excess Gibbs Free Energy.

The activity of a species in solution can be defined as:

$$a_i = \gamma_i m_i$$
$$\overline{G}_i = \overline{G}^o + RT \ln a_i$$
$$\overline{G}_i = \overline{G}^o + RT \ln m_i + RT \ln \gamma_i$$
$$\overline{G}_i^E = RT \ln \gamma_i$$

**Note:** Other excess properties involve various partial derivatives of  $\gamma_i$  with respect to temperature and/or pressure.

$$\overline{H}_i^E = RT^2 \left. \frac{\delta \ln \gamma_i}{\delta T} \right]_P$$

## Ionic Strength

Ionic Strength is defined by the following equation:

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

where,

$nI$  = number of charged species

For Example, a 1.0 molal solution of NaCl has 1.0 moles of  $\text{Na}^{+1}$  ion and 1.0 moles of  $\text{Cl}^{-1}$  ion per Kg  $\text{H}_2\text{O}$ .

$$I = \frac{1}{2} \left( (Z_{\text{Na}^{+1}})^2 (m_{\text{Na}^{+1}}) + (Z_{\text{Cl}^{-1}})^2 (m_{\text{Cl}^{-1}}) \right) = \frac{1}{2} \left( (1)^2 (1) + (-1)^2 (1) \right) = 1$$

Therefore the ionic strength is 1.0 molal.

For Example, a 1.0 molal solution of  $\text{CaCl}_2$  has 1.0 moles of  $\text{Ca}^{+2}$  ion and 2.0 moles of  $\text{Cl}^{-1}$  ion per Kg of  $\text{H}_2\text{O}$ .

$$I = \frac{1}{2} \left( (Z_{Ca^{+2}})^2 (m_{Ca^{+2}}) + (Z_{Cl^{-1}})^2 (m_{Cl^{-1}}) \right) = \frac{1}{2} \left( (2)^2 (1) + (-1)^2 (2) \right) = 3$$

There for the ionic strength is 3.0 molal, or we can say that a 1.0 Molal solution of CaCl<sub>2</sub> behaves similar to a 3.0 molal Solution of NaCl

## Definition of Aqueous Activity Coefficients

$$\log \gamma_i = \text{long range} + \text{short range}$$

**Long Range:** Highly dilute solutions (e.g., 0.01 m NaCl). The ions are separated sufficiently such that the only interactions are between the ions and the solvent.

**Short Range:** Increased concentrations. The ions are now beginning to interact with themselves (oppositely charged species attract, like charged species repel) in addition to the interactions with the solvent.

### Long Range Terms

$$\ln \gamma_i = \frac{-z^2 A(T) \sqrt{I}}{1 + \overset{\circ}{A} B(T) \sqrt{I}}$$

**Where,**

$\overset{\circ}{A}$  ion size parameter

A(T), B(T) Debye-Huckel parameters related to dielectric constant of water.

At 25 °C and 1 Atmosphere<sup>21</sup>:

$$A(T) = 0.5092 \text{ kg}^{1/2}/\text{mole}^{1/2}$$

$$B(T) = 0.3283 \text{ kg}^{1/2}/\text{mole}^{1/2}\text{-cm} \times 10^{-8}$$

<sup>21</sup> H.C.Helgeson and D.H.Kirkham. American Journal of Science Vol. 274, 1199 (1974)



## Short Range Terms

$$\sum_{j=1}^{n^{\circ}} (b_{ij}(T,I)m_j)$$

Where,

$n^{\circ}$  = Number of oppositely charged species.

For example, consider H<sub>2</sub>O/CO<sub>2</sub>/NH<sub>3</sub>

Cations: H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>

Anions: OH<sup>-</sup>, HCO<sub>3</sub><sup>-1</sup>, CO<sub>3</sub><sup>-2</sup>, NH<sub>2</sub>CO<sub>2</sub><sup>-</sup>

### Short Range Term for NH<sub>4</sub><sup>+</sup>:

$$b_{11}(T,I) * m_{\text{HCO}_3} + b_{12}(T,I) * m_{\text{CO}_3} + b_{13}(T,I) * m_{\text{OH}} + b_{14}(T,I) * m_{\text{NH}_2\text{CO}_2}$$

11 = NH<sub>4</sub>:HCO<sub>3</sub>

12 = NH<sub>4</sub>:CO<sub>3</sub>

13 = NH<sub>4</sub>:OH

14 = NH<sub>4</sub>:NH<sub>2</sub>CO<sub>2</sub>

## Modern Formulations

### 1. Bromley - Meissner : Semi-Correlative<sup>22,23</sup>

Can predict and extrapolate excess properties when data is limited or unavailable.

### 2. Pitzer: Highly Interpolative<sup>24</sup>

Somewhat model dependent. Considerable caution is required when using the large amount of published data to verify the standard state model employed.

### 3. Helgeson: Limited in Scope<sup>25</sup>

<sup>22</sup> L.A.Bromley. J.Chem.Thermo.,**4**,669 (1972)

<sup>23</sup> H.P.Meissner. AIChE Symp.Ser.No. 173,74,124 (1978)

<sup>24</sup> K.S.Pitzer,et.al. J.Soln.Chem,**4**,249(1975); J.Phys.Chem.,**81**,1872(1977); J.Soln.Chem. **7**,327(1978); J.Am.Chem.Soc.**96**,5701(1974)

<sup>25</sup> H.C.Helgeson, D.H.Kirkham and G.C.Flowers. Am.J.Sci. **281**,1249(1981)

#### 4. Mixed Solvent Electrolyte: OLI's New Framework

##### **Bromley**

$$\text{Log } \gamma_{\pm} = \frac{-A |Z_+ Z_-| \sqrt{I}}{1 + \sqrt{I}} + \frac{(0.06 + 0.6B) |Z_+ Z_-| I}{\left(1 + \frac{1.5I}{|Z_+ Z_-|}\right)^2} + BI$$

##### **Where,**

- A = Debye-Huckel Constant
- I = Ionic Strength
- B = Bromley parameter
- $\gamma$  = Mean activity coefficient
- Z+ = Charge of the cation
- Z- = Charge of the anion

##### **Meissner**

$$\Gamma = \gamma_{\pm}^{1/Z_+ Z_-}$$

$$\Gamma^o = \left(1.0 + B(1.0 + 0.1I)^q - B\right) \Gamma^*$$

$$B = 0.75 - 0.065q$$

$$\text{Log } \Gamma^* = \frac{-0.5107\sqrt{I}}{1 + C\sqrt{I}}$$

$$C = 1.0 + 0.055q \exp(-0.02312I^3)$$

Where  $\Gamma$  is the reduced activity coefficient, q is the Meissner q value, I is the ionic strength.

The family of q values are:

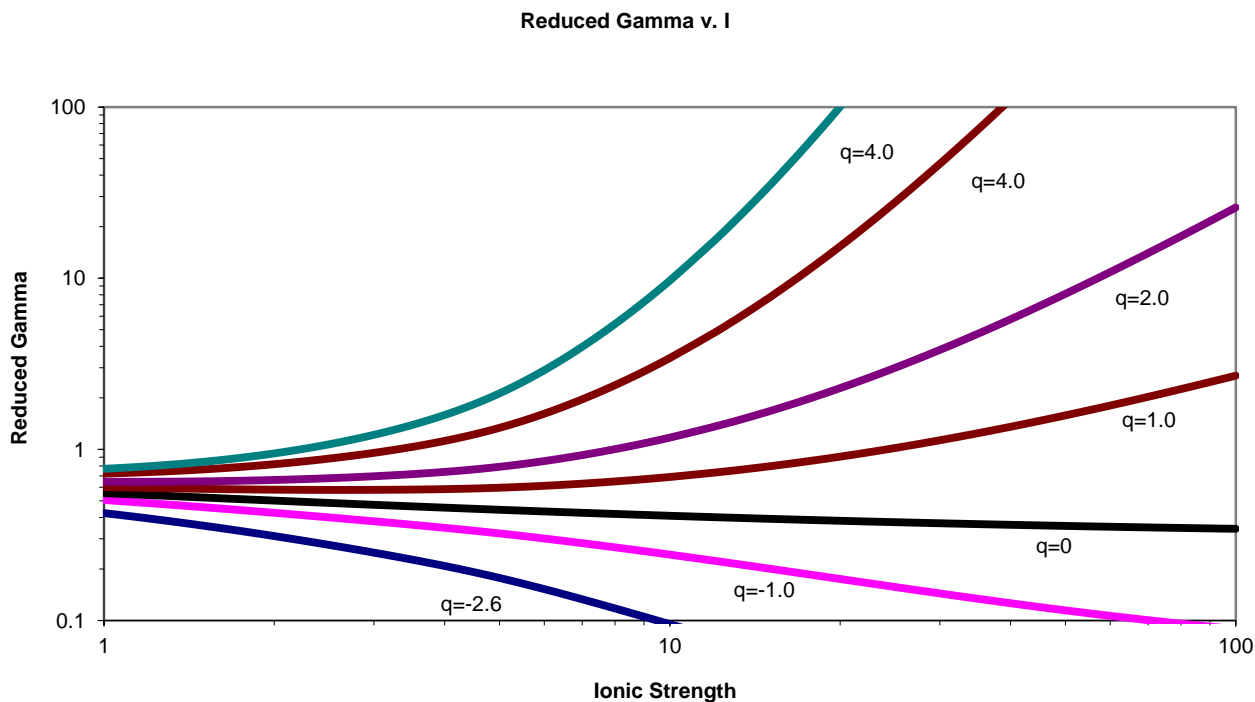


Figure 6-2 The Meissner q lines

### Bromley-Zematis

Joseph Zematis, of OLI Systems, Inc., now deceased, extended the work of Bromley in that he added two new terms<sup>26</sup>. The Bromley-Zematis activity model is:

$$\text{Log } \gamma_{\pm} = \frac{-A |Z_+ Z_-| \sqrt{I}}{1 + \sqrt{I}} + \frac{(0.06 + 0.6B) |Z_+ Z_-| I}{\left(1 + \frac{1.5}{|Z_+ Z_-| I}\right)^2} + BI + CI^2 + DI^3$$

Where C and D are new terms. Each of the B, C, and D terms have the following temperature functionality.

$$B = B_1 + B_2 T + B_3 T^2 \quad (\text{Where } T \text{ is temperature in centigrade})$$

The other coefficients have the same form:

$$C = C_1 + C_2 T + C_3 T^2$$

$$D = D_1 + D_2 T + D_3 T^2$$

<sup>26</sup> Zemaitis, J.F., Jr, Clark, D.M., Rafal, M. and Scrivner, N.C., *Handbook of Aqueous Electrolyte Thermodynamics*, American Institute of Chemical Engineers, New York, 1986.

## Pitzer

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

Where,

$f^{\gamma}$	=	The “Debye-Huckel” term. <sup>27</sup>
$v_+$	=	Stoichiometric coefficient for the cation
$v_-$	=	Stoichiometric coefficient for the anion
$\nu$	=	$v_+ + v_-$
$m$	=	Concentration in molal
$B_{\pm}^{\gamma}$	=	Pitzer B term, containing the adjustable parameters
$C_{\pm}^{\gamma}$	=	Pitzer C term, containing adjustable parameters

## Helgeson

$$\text{Log } \bar{\gamma}_{\pm} = \frac{-A_{\gamma} |Z_i Z_l| \sqrt{\bar{I}}}{1 + a_0 B_{\gamma} \sqrt{\bar{I}}} + \Gamma_{\gamma} + \left( \frac{\omega_k}{\nu_k} \sum_k b_k Y_k \bar{I} + \frac{\nu_{i,k}}{\nu_k} \sum_l \frac{b_{il} \bar{Y}_l \sqrt{\bar{I}}}{\Psi_l} + \frac{\nu_{l,k}}{\nu_k} \sum_i \frac{b_{il} \bar{Y}_i \sqrt{\bar{I}}}{\Psi_i} \right)$$

Where,

$A_{\gamma}$	=	Debye-Huckel constant according to Helgeson
$Z_i$	=	Charge on the cation
$Z_l$	=	Charge on the anion
$a_0$	=	ion size parameter
$B_{\gamma}$	=	Extended Debye-Huckel term according to Helgeson
$\bar{I}$	=	True ionic strength which includes the effects of complexation
$\Gamma_{\gamma}$	=	Conversion of molal activity to mole fraction activity
$\omega_k$	=	Electrostatic effects on the solvent due to the species k
$\nu_k$	=	moles of electrolyte (summation)
$\nu_{i,k}$	=	moles of cation per mole of electrolyte
$\nu_{l,k}$	=	moles of anion per mole of electrolyte
$b_{i,l}$	=	adjustable parameter for the ion-ion interaction.
$\bar{Y}_i$	=	fraction of ionic strength on a true basis attributed to the cation
$\bar{Y}_l$	=	fraction of ionic strength on a true basis attributed to the anion
$\Psi_i$	=	½ the cation charge
$\Psi_l$	=	½ the anion charge
$Z_i$	=	the cation charge
$Z_l$	=	the anion charge

<sup>27</sup> IBID, Page 74

## Neutral Species

Neutral molecules in water are affected by other species in solution. The salting in and out of a gas is a typical example. When Oxygen is dissolved into pure water, it has a typical solubility. When salt is added, the solubility decreases. This is most-likely due to an interaction between the sodium ions and the neutral oxygen molecule and the interaction between the chloride ions and the neutral oxygen molecule.

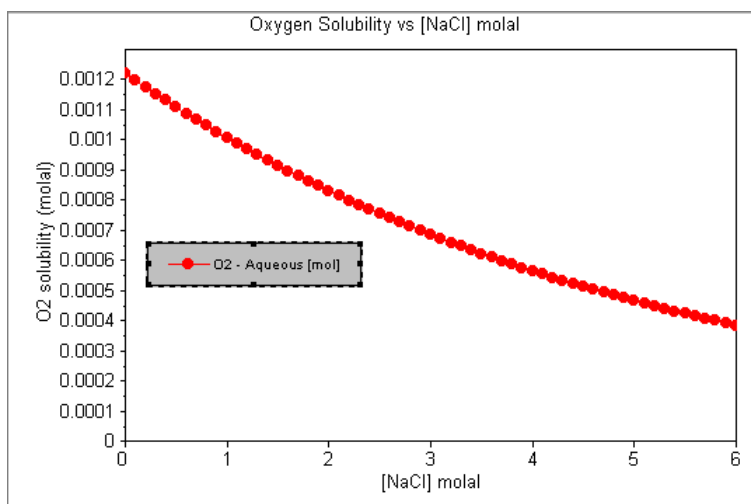


Figure 6-3 The solubility of oxygen in NaCl solutions at 25 C, 1 Atmosphere

### 1. Setschenow<sup>28</sup>

This characterizes a phenomena known as salting in/out. The formulation is in terms of the ratio of solubilities in pure water to an aqueous salt solution at a constant temperature.

$$\ln \gamma_{aq} = \frac{S_0}{S_S} = km_S$$

Where,

- $S_0$  = Solubility of the gas in pure water
- $S_S$  = Solubility of the gas in a salt solution
- $K$  = Setschenow coefficient
- $m_s$  = Concentration of the salt.

In this case, the  $K$  is approximately equal to -0.0002.

Unfortunately, this approach is limited to a single temperature.

<sup>28</sup> J.Setchenow., Z.Physik.Chem., **4**,117 (1889)

## 2. Pitzer<sup>29</sup>

A more rigorous approach than Setschenow. Effects of temperature and composition can be modeled.

$$\ln \gamma_{aq} = 2\beta_{0(m-m)}m_m + 2\beta_{0(m-s)}m_s$$

Where,

$\beta_{0(m-m)}$  = The adjustable parameter for molecule – molecule interactions.  
(a function of temperature)

$\beta_{0(m-s)}$  = The adjustable parameter for molecule – ion interactions.  
(A function of temperature)

$m_s$  = The concentration of the neutral species.

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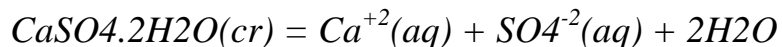
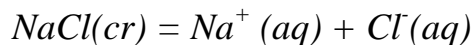
## Multiphase Model

### Solid-Aqueous Equilibrium

**General Equilibrium Form:**

$$S_i = p_1 P_1 + p_2 P_2 + \dots p_p P_p$$

**Examples:**



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<sup>29</sup> K.S.Pitzer,et.al. J.Soln.Chem,**4**,249(1975); J.Phys.Chem.,**81**,1872(1977); J.Soln.Chem. **7**,327(1978); J.Am.Chem.Soc.**96**,5701(1974)

## Solid Phase Thermodynamic Properties

$$\bar{G}_{Si} = \bar{G}_{Si}^R + \bar{S}_{Si}^R (T - T^R) + \int_{T^R}^T C_p dT + \int_{P^R}^P V dP$$

Under the typical simulation conditions, the compressibility of the solid remains constant.

$$C_p = a_1 + a_2 T + a_3 T^{-2}$$

$$V = b_1$$

$$\text{Log}_{10} K_{sp}(T, P) = A + B/T_K + CT_K + DT_K^2 + E + FP + GP^2$$

## Mixed EOS Model

**General Thermodynamic Equation:**

**Vapor-Aqueous**

$$\bar{G}_{V_i} = \bar{G}_{Aqi}$$

$$\bar{G}_{V_i}^o + RT \ln(\phi_{V_i} y_i P) = \bar{G}_{Aqi}^o + RT \ln(\gamma_i m_i)$$

$$a_{Aqi} = \gamma_i m_i$$

$$f_{V_i} = \phi_{V_i} y_i P$$

The reference state for the vapor is the ideal gas.

$$\bar{G}_{V_i}^o + RT \ln(f_{V_i}) = \bar{G}_{Aqi}^o + RT \ln(a_{Aqi})$$

$$K = \text{EXP}\left[\frac{\bar{G}_{Aqi}^o - \bar{G}_{V_i}^o}{RT}\right] = \frac{a_{Aqi}}{f_{V_i}}$$

## Non-Aqueous Liquid-Aqueous

$$\overline{G}_{Li} = \overline{G}_{Aqi}$$

Notice that the reference state for the non-aqueous liquid is the ideal gas vapor.

$$\overline{G}_{Vi}^o + RT \ln(\phi_{Li} x_i P) = \overline{G}_{Aqi}^o + RT \ln(\gamma_i m_i)$$

$$f_{Li} = \phi_{Li} X_i P$$

$$\overline{G}_{Vi}^o + RT \ln(f_{Li}) = \overline{G}_{Aqi}^o + RT \ln(a_{Aqi})$$

$$K = \text{EXP}\left[\frac{\overline{G}_{Aqi}^o - \overline{G}_{Li}^o}{RT}\right] = \frac{a_{Aqi}}{f_{Li}}$$

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## Limitations of the Current OLI Thermodynamic Model<sup>30</sup>

### Aqueous Phase

$$X_{H_2O} > 0.65$$

$$-50^\circ\text{C} < T < 300^\circ\text{C}$$

$$0 \text{ Atm} < P < 1500 \text{ Atm}$$

$$0 < I < 30$$

### Non-aqueous Liquid

Currently no separate activity coefficient Model (i.e., no NRTL, Unifaq/Uniqac)

Non-aqueous and vapor fugacity coefficients are determined from the Enhanced SRK<sup>31</sup> Equation of State.

Vapor critical parameters ( $T_c$ ,  $P_c$ ,  $V_c$ , and  $\omega$ <sup>32</sup>) are correlated to find a Fugacity coefficient.

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<sup>30</sup> This refers only to the traditional OLI Aqueous Model and not the MSE model.

<sup>31</sup> G. Soave. Chem. Eng. Sci. **27**, 1197 (1972)

<sup>32</sup> This is the acentric factor which is not the same as Helgeson's  $\Omega$  term)



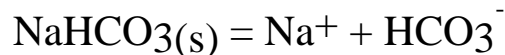
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# Scaling Tendencies

## What is a scaling tendency?

It is the ratio of the real-solution solubility product to the thermodynamic limit based on the thermodynamic equilibrium constant.

**For Example, Consider this dissolution:**



The Ion Activity Product (IAP) is defined as the product of specific ions (in this case the ions resulting from the dissociation of a particular solid).

**Let's consider a 1.0 molal NaHCO<sub>3</sub> solution:**

$$\text{IAP} = \gamma_{\text{Na}} m_{\text{Na}} \gamma_{\text{HCO}_3} m_{\text{HCO}_3}$$

Assuming Ideal Solution Activities:

$$\gamma_{\text{Na}} = 1.0 \qquad \gamma_{\text{HCO}_3} = 1.0$$

$$m_{\text{Na}} = 1.0 \qquad m_{\text{HCO}_3} = 1.0$$

$$\text{IAP} = (1.0)(1.0)(1.0)(1.0)$$

$$\text{IAP} = 1.0$$

The Solubility Product ( $K_{\text{SP}}$ ) is the thermodynamic limit of ion availability:

$$K_{\text{SP}} = 0.265038^{33}$$

The Scaling Tendency is then the ratio of available ions to the thermodynamic limit.

$$\text{ST} = \text{IAP}/K_{\text{SP}}$$

$$\text{ST} = 1.0/0.265038$$

$$\text{ST} = 3.77$$

**Was assuming ideal conditions valid??**

The actual species concentration and activity coefficients are:

$$\gamma_{\text{Na}} = 0.566 \qquad \gamma_{\text{HCO}_3} = 0.566$$

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<sup>33</sup> Based on the OLI PUBLIC databank version 9.2.6

$$m_{\text{Na}} = 0.764 \quad m_{\text{HCO}_3} = 0.739$$

This results in a different IAP:

$$\text{IAP} = (0.566)(0.764)(0.566)(0.739)$$

$$\text{IAP} = 0.181$$

The new Scaling Tendency is therefore:

$$\text{ST} = \text{IAP}/K_{\text{sp}}$$

$$\text{ST} = 0.181/0.265038$$

$$\text{ST} = 0.682$$

Why the concentrations were not equal to 1.0? Speciation and chemical equilibria tend to form complexes which provide a “Sink” for carbonate species. In this example:

$$\begin{aligned} \text{CO}_2^0 &= 0.014 \text{ molal} \\ \text{NaHCO}_3^0 &= 0.233 \text{ molal} \\ \text{CO}_3^{2-} &= 0.011 \text{ molal} \\ \text{NaCO}_3^- &= 0.003 \text{ molal} \end{aligned}$$

### ***What does the Scaling Tendency Mean?***

If  $\text{ST} < 1$ , then the solid is under-saturated  
 If  $\text{ST} > 1$ , then the solid is super-saturated  
 If  $\text{ST} = 1$ , then the solid is at saturation

$$\text{Scaling Index} = \text{Log (ST)}$$

### ***What is the TRANGE?***

TRANGE is a nomenclature for solids that have been fit to a polynomial form rather than pure thermodynamics.

The polynomial has this functional form:

$$\text{Log K} = A + B/T + CT + DT^2$$

It is known that polynomials may not extrapolate well. Incorrect predictions of Scaling Tendency may result. Therefore the applicable range is generally limited to data set.

## Consider Na<sub>2</sub>CO<sub>3</sub>/H<sub>2</sub>O

There are 4 solids of interest in this system. They are:

Table 6-1 Sodium Carbonate hydrate transition ranges

Solid	Temperature Range (C)
Na <sub>2</sub> CO <sub>3</sub> •10H <sub>2</sub> O	0-35
Na <sub>2</sub> CO <sub>3</sub> •7H <sub>2</sub> O	35-37
Na <sub>2</sub> CO <sub>3</sub> •1H <sub>2</sub> O	37-109
Na <sub>2</sub> CO <sub>3</sub>	109-350

This table implies that these solids change their form as the temperature increases. Each solid was fit to the above polynomial. There may be problems if the extrapolated values from higher number hydrates extend to the regions where the lower number hydrates are stable.

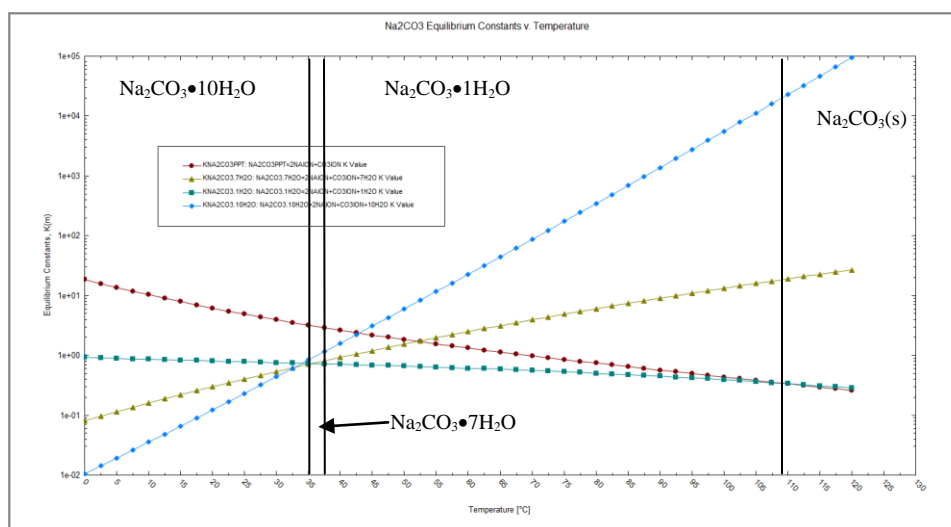


Figure 6-4 Plot of  $K$  vs. Temperature. The  $K$ 's have been extrapolated.

In this plot, the concentration of Na<sup>+</sup> ion and CO<sub>3</sub><sup>2-</sup> ion is held constant. This means that the more stable solid (higher scaling tendency) will be the solid with the smaller  $K$  value.

It can be seen that the mono-hydrate species does not extrapolate well to lower temperatures. In the range 35 to 37 °C, that the mono-hydrate equilibrium constant is smaller than the hepta-hydrate. If we concern ourselves with 36°C, we can see that if the mono-hydrate solid was allowed to be in the model, the equilibrium based solver will attempt include it over the actual solid which is the hepta-hydrate.

Since the mono-hydrate species is outside its temperature range in this region, it will be mathematically eliminated from the equations.

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## Calculating Osmotic Pressures

OLI is asked frequently how the osmotic pressure calculated in the software. We use a very traditional method of calculating the osmotic pressure.

$$\pi = -RT \ln a_{H_2O} V_{H_2O}$$

Where

$\Pi$  is the osmotic pressure

$R$  is the gas constant

$T$  is the temperature

$a_{H_2O}$  is the activity of water at temperature  $T$

$V_{H_2O}$  is the partial molal volume of water at temperature  $T$

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## Summary

We have seen that the evaluation of the equilibrium constant is an important factor in simulating aqueous systems. A rigorous thermodynamic framework has been developed to support the simulation.