Chapter 6 Activity Scales and Activity Corrections

(10/11/04)   **James W. Murray**
                                                        Univ. Washington

6.1 Total Activity Coefficient: Electrostatic Interactions and Ion Complexing

The goal of this chapter is to learn how to convert total concentrations into activities. These corrections include calculating the percent of the total concentration that is the species of interest (f_i) and then correcting for an ionic strength effect using free ion activity coefficients (γ_i). In the process we will learn how to do speciation calculations with emphasis on the speciation of the major ions in seawater.

6.1.A Activity

Ions in solution interact with each other as well as with water molecules. At low concentrations (C_i) and low background salt concentrations these interactions can possibly be ignored, but at higher concentrations ions behave chemically like they are less concentrated than they really are. Equilibrium constants calculated from the standard free energy of reaction (e.g. $\Delta G_r°$) are expressed in terms of this effective concentration, which is formally called the activity, which is the concentration available for reaction. Thus we define activity as:

$$\text{Activity } (a_i) = \text{Effective concentration}$$

In infinitely dilute solutions where ionic interactions can be ignored: $a_i = C_i$. These are called **ideal solutions**. In concentrated solutions like seawater: $a_i < C_i$. These are **non-ideal solutions**.

There are two main reasons for these differences:

6.1.B Electrostatic Interactions

The background ions in solution shield the charge and interactions between ions. Example: Say we have a solution of calcium (Ca^{2+}) and sulfate (SO_4^{2-}) in water.
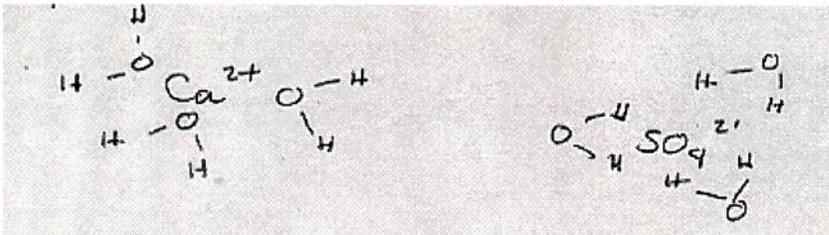
The tendency of Ca^{2+} and SO_4^{2-} ions to hydrate induces shielding which affects the ability of Ca^{2+} and SO_4^{2-} to meet and react (and precipitate as a solid in this case). If we add other ions like Na^+ and Cl^- to solution, they are attracted to the ions of opposite charge
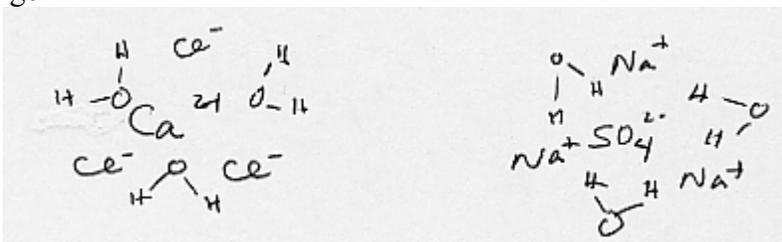
and we effectively increase the amount of electrostatic shielding. The other ions decrease the ability of Ca^{2+} and SO_4^{2-} to interact. Therefore, gypsum or $CaSO_4 \cdot 2H_2O$, will appear more soluble in seawater than in freshwater. These interactions result in **non-ideal solutions**. Ions with higher charge are more effective than ions with lower charge at this shielding effect.

6.1.C Ion Complexing or specific interaction

In some cases there are specific interactions between ions - solutes come close enough that they make direct contact and are considered a new species! These new species are called ion pairs (when ions are separated by H_2O molecules but share their first hydration shell) or complexes (when ions are in contact and share electrons).

Example:

$$Ca^{2+} + SO_4^{2-} == CaSO_4°$$
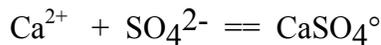
Let's say we have a solution containing some of the major ions:

$$Ca^{2+}, K^+, F^- \text{ and } SO_4^{2-}$$
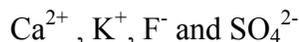
The negatively charged species like F^- and SO_4^{2-} are known as **ligands**. Because of the interaction between ions, not only do we have the free ions present (e.g. Ca^{2+}, F^-) but also complexes such as:

$$CaF^+, CaSO_4°, KF°, \text{ and } KSO_4^-$$

Like shielded or hydrated ions these complexes are less able to react so their formation lowers the effective concentration. In some cases complexes are so dominant that the free ion population is only a small fraction of the total. We will see this later for some trace metals. For example, the speciation of iron and copper in seawater is dominated by complexes with organic compounds and the free, uncomplexed Fe^{3+} and Cu^{2+} ions have very low concentrations..

We can ignore higher order complexes involving more than one cation and one anion such as:

$$CaF_2°, Ca(SO_4)_2^{2-}, \text{ etc}$$

These may form but their concentrations are very small and they can be ignored.

6.2 The Activity Coefficient

We generally only know the total concentration of an element (m_T). This is usually what can be most easily measured analytically. First we need to convert the total concentration (m_T) to the concentration of the ion or species (m_i) that we are interested in. In order to calculate m_i from m_T we need to do an equilibrium calculation of the percent free which we express as f_i. Thus:

$$m_i = m_T \times f_i$$

For the case where we have Ca_T but we want Ca^{2+} we need to calculate the ratio:

$$f_{Ca2+} = [Ca^{2+}]/\ Ca_T = [Ca^{2+}]\ /\ ([Ca^{2+}]+ [CaSO_4°]+ [CaCO_3°])$$

Once we have the concentration of the free ion (m_i) we need to convert it to the activity of the free ion (a_i). To do that we use the free ion activity coefficient (γ_i) that corrects for electrostatic shielding by other ions. This correction is written as:

$$a_i = \gamma_i \times m_i$$

molal concentration of a free ion
free ion activity coefficient for that species

The total expression with both correction factors is then written as:

$$a_i = \gamma_i \times f_i \times m_T$$

m_T is the total ion concentration
% of the total concentration, m_T, that is free

Sometimes γ_i and f_i are combined together and called the total activity coefficient, γ_T. Then,

$$a_i = \gamma_T\ m_T$$

Where, the total activity coefficient $= \gamma_T = \gamma_i\ f_i$

example: a solution with Ca^{2+}, SO_4^{2-} and CO_3^{2-} forms the complexes $CaSO_4°$ and $CaCO_3°$

$$\gamma_{T,Ca} = \quad f_i \quad \times \quad \cdot \gamma_{Ca2+}$$
$$= ([Ca2+]/\ Ca_T) \times \cdot \gamma_{Ca2+}$$
$$= ([Ca^{2+}]/\ ([Ca^{2+}]+ [CaSO_4°] + [CaCO_3°])) \times \gamma_{Ca2+}$$

How do we obtain values for γ_i and f_i.

1. γ_i --- Free Ion Activity Coefficient

The free ion activity coefficient describes the relation between the activity and concentration of a free ion species. We use either some form of the Debye-Huckel type equations or the mean salt method

2. f_i --- % free ==== We obtain this from a chemical speciation calculation done by hand or using a computer program like MINTEQA2 or HYDRAQL.

6.3 Ionic Strength

First you need to know the ionic strength (I) of the solution because the electrostatic interactions depend on the concentration of charge. The value of I is calculated as follows:

$$I = 1/2 \ \Sigma \ m_i \cdot Z_i^2$$

concentration of i th ion, charge of i th ion

Note that the ionic strength places greater emphasis on ions with higher charge. A 2+ charged ion contributes 4 times more to the ionic strength than a 1+ ion For a monovalent ion, its contribution to the ionic strength is the same as its concentration. The ionic strength has concentration units.

Example: Compare the ionic strength of freshwater and seawater.

	Molality	
	Seawater (SW)	Lake Water (LW)
Na^+	0.49	0.2×10^{-3}
Mg^{2+}	0.053	0.14×10^{-3}
Ca^{2+}	0.010	0.22×10^{-3}
K^+	0.010	0.03×10^{-3}
Cl^-	0.57	0.09×10^{-3}
SO_4^{2-}	0.028	0.102×10^{-3}
HCO_3^-	0.002	0.816×10^{-3}

$$I_{SW} = 1/2 \ (m_{Na} \times 1^2 + m_{Mg} \times 2^2 + m_{Ca} \times 2^2 + m_K \times 1^2 + m_{Cl} \times 1^2 + m_{SO4} \times 2^2 + m_{HCO3} \times 1^2)$$

$$= 0.72 \ mol \ kg^{-1}$$

$$I_{LW} = 0.0015 = 1.5 \times 10^{-3} \ mol \ kg^{-1}$$

So the ionic strength of seawater is about 500 times larger than that of fresh water.

6.4 Activity Scales

The free energy change for an infinitely small change in concentration is called the partial molal free energy or chemical potential. The chemical potential (μ) for gaseous, aqueous and solid solutions is written as:

$$\mu_i = \mu_i°(T,P) + RT \ln a_i$$

or

$$\mu_i = \mu_i°(T,P) + RT \ln c_i + RT \ln \gamma_i$$

where $\mu_i°(T,P)$ is the standard partial molal free energy and a_i is the activity and c_i is the concentration. The value of μ_i depends on how $\mu_i°$ and γ_i are defined.

The **standard state** determines the value of $\mu_i°$. It is the hypothetical situation chosen so that μ_i at infinite dilution is not $-\infty$. For aqueous solutions it is the unobtainable hypothetical situation where both the concentration (C_i) and activity coefficient (γ), and thus the activity (a), are equal to one (e.g., $C_i = \gamma_i = a_i = 1$), and thus the log terms are equal to zero. Then $\mu_i = \mu_i°(T,P)$.

The **reference state** is the solution limit where $C_i = a_i$ and thus $\gamma_i = 1$. The choice of reference states determined the value of the activity coefficient, γ_i.

The differences in the activity scales show up as changes in $\mu°$. This is because $\mu_i = \mu_i°$ when $\gamma_i = 1$.

The value of $\mu°$ also includes identification of a concentration scale because $\mu_i = \mu_i°$ at $C_i = 1$. The choices include molarity (m in mol l^{-1}), molality (M in mol $kg_{solvent}^{-1}$) or mole fraction (X_i in %). Oceanographers use a slightly different form of molality as M in mol kg_{sw}^{-1}. The concentrations of m and M are related by the density (ρ) of the solution (m = M/ρ)

There are two main activity scales that lead in turn to different equilibrium constants.

6.4.A Infinite Dilution Scale

Remember that $\gamma_A = (A) / [A]$

On the infinite dilution scale $\gamma_A \to 1$ as the concentration of all salts approaches zero or: $(C_A + \Sigma C_i) \to 0$

The reference state is chosed to be an infinitely dilute aqueous solution.

The standard state is a hypothetical solution with $C_A = 1M$ and properties of infinite dilution. In other words a 1M solution with ideal behaviour (e.g., $\gamma_A = 1$).

For solutes, $\gamma_A = 1.0$ at infinite dilution and decreases as concentration (or ionic strength) increases.

The value of the partial molal free energy of formation (or chemical potential) $\mu°$ represents the work necessary to produce an infinitesimal amount of species or compound, A, from the elements in their standard states. Values of $\mu°$ on this scale are tabulated because the scale is commonly used.

6.4.B <u>Ionic Medium Scale</u>
Examples of a constant ionic medium are 1M KCl or seawater. This is the situation where there is a swamping electrolyte that has a much higher concentration than the solutes of interest, and this background electrolyte is constant. For this case we define that the activity coefficient goes to 1 in this ionic medium.
Thus:

$\gamma_A \rightarrow 1$ as $C_A \rightarrow 0$ in a solution where the total concentration of other electrolytes remains constant at Σc_i

The reference state is the ionic medium (Σc_i)

Standard states are chosen so that $\gamma_A = (A)/[A] \rightarrow 1$ when $[A] \rightarrow 0$ in the ionic medium.

6.5 <u>Mean Ion Activity Coefficients</u>
Mean ion activity coefficients are determined experimentally and represent the average effects of all ions in the solution. The symbol for the mean ion activity coefficient is $\gamma_\pm$. Because chemical potential is defined using log terms for the concentrations and activity coefficients the average contribution is a geometric mean as follows.

Example: $\gamma_\pm NaCl$

The chemical potential (see section 6.4) for Na^+ and Cl^- are written as follows.

$\mu_{Na+} = \mu°_{Na+} + RT \ln C_{Na} + RT \ln \gamma_{Na+}$

$\mu_{Cl-} = \mu°_{Cl-} + RT \ln C_{Cl} + RT \ln \gamma_{Cl-}$

The totel free energy is written as the sum, thus:

$G_T = \mu_{Na+} + \mu_{Cl-} = \mu°_{Na+} + \mu°_{Cl-} + RT \ln C_{Na}C_{Cl} + RT \ln \gamma_{Na}\gamma_{Cl}$

For the average contribution we divide by two:

$(\mu_{Na+} + \mu_{Cl-}) \div 2 = (\mu°_{Na+} + \mu°_{Cl-}) \div 2 + RT \ln (C_{Na}C_{Cl})^{1/2} + RT \ln (\gamma_{Na}\gamma_{Cl})^{1/2}$

or

$$\mu\pm \ = \ \mu\pm° \ + \ RT \ln C\pm \ + \ RT \ln \gamma\pm$$

Values of measured $\gamma\pm$ versus ionic strength (I) are plotted in Fig 6-2 (from Garrels and Christ, 1965). These show the expected pattern in that they approach one at low ionic strength and decrease as ionic strength increases. The values for divalent salts are lower than for monovalent salts.

6.6 Free Ion Activity Coefficients

There are several theoretically-based expressions that can be used to estimate single ion activity coefficients (Table 6-1) (e.g. Table 5.2 of Libes). However each is only good for a limited range of ionic strength and none are really valid to apply directly to seawater.

6.6.A Debye-Huckel Equations:

6.6.A.1 Limiting Law $\log \boldsymbol{\gamma_i} = -A \, z_i^2 \, I^{1/2}$ applicable for $I < 10^{-2}$

This equation is the only one of these Debye-Huckel type equations that can be derived from first principles. There is an especially thorough derivation given in Bockris and Reddy (1970). The key assumption is that the central ion is a point charge and that the other ions are spread around the central ion with a Gaussian distribution. Its range is limited to $I < 0.01$ which means it is not useful for seawater. This range does include many freshwater environments. The constant A has a constant value of 0.51 at 25°C.

This equation predicts that the log of the activity coefficient decreases linearly with the square root of the ionic strength. All ions of the same charge will have the same value.

6.6.A.2 Extended D-H $\log \boldsymbol{\gamma_i} = -A \, z_i^2 \, I^{1/2} / (1 + a_i \cdot B \cdot I^{1/2})$ for $I < 10^{-1}$

For water at 25°C the constants are:
  A = 0.51
  B = 0.33 x 10^8

Because the Debye-Huckel limiting law has a limited range of application chemists added a term to take into account that the central ion has a finite radius. Thus the extended D-H equation has a term called the ion size parameter (a). This term is supposed to take into account the fact that ions have a finite radius and are not point charges. Values are given in Table 6-2. The values in this table are given in angstroms but need to be in cm for the extended D-H equation (e.g. for Ca^{2+} = 6 angstroms = 6 x 10^{-8} cm)

The ion size parameter has no clear physical meaning. It is too large to correspond to the ionic radii of the ions. It therefore must include some aspect of the hydrated radii. In

reality it is merely an adjustable parameter that has been used by modellers to empirically extend the fit of the equation to higher ionic strength.

Values of γ_i for different ions (H^+, Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-} and Ca^{2+}), calculated using the extended Debye Huckel equation, are plotted versus ionic strength in Fig 6-1. They are in good agreement with values calculated by the mean salt method up to $I = 0.1$.

Table 6-1 Summary table of Debye-Huckel type equations. The f in these equations is the same as what we are calling γ.

TABLE 3.3   INDIVIDUAL ION ACTIVITY COEFFICIENTS

Approximation	Equation[a]		Approximate Applicability [ionic strength (M)]
Debye–Hückel	$\log f = -Az^2\sqrt{I}$	(1)	$<10^{-2.3}$
Extended Debye–Hückel	$= -Az^2 \dfrac{\sqrt{I}}{1 + Ba\sqrt{I}}$	(2)	$<10^{-1}$
Güntelberg	$= -Az^2 \dfrac{\sqrt{I}}{1 + \sqrt{I}}$	(3)	$<10^{-1}$ useful in solutions of several electrolytes
Davies	$= -Az^2 \left(\dfrac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$	(4)[b]	<0.5

[a] I (ionic strength) $= \frac{1}{2}\sum C_i z_i^2$; $A = 1.82 \times 10^6 (\varepsilon T)^{-3/2}$ (where $\varepsilon = $ dielectric constant); $A \approx 0.5$ for water at 25°C; $z = $ charge of ion; $B = 50.3(\varepsilon T)^{-1/2}$; $B \approx 0.33$ in water at 25°C; $a = $ adjustable parameter (angstroms) corresponding to the size of the ion. (See Table 3.4.)

[b] Davies has proposed 0.3 (instead of 0.2) as a coefficient for the last term in parentheses.

Table 6-1 Ion size parameters (*a*) for the extended Debye-Huckel equation.

TABLE 3.4   PARAMETER *a* AND INDIVIDUAL ION ACTIVITY COEFFICIENTS

Ion Size Parameter, *a* (Å)[a]	Ion	Activity Coefficients Calculated with (2) of Table 3.3 for Ionic Strength				
		10^{-4}	10^{-3}	10^{-2}	0.05	10^{-1}
9	H^+	0.99	0.97	0.91	0.86	0.83
	$Al^{3+}, Fe^{3+}, La^{3+}, Ce^{3+}$	0.90	0.74	0.44	0.24	0.18
8	Mg^{2+}, Be^{2+}	0.96	0.87	0.69	0.52	0.45
6	$Ca^{2+}, Zn^{2+}, Cu^{2+}, Sn^{2+}, Mn^{2+}$ Fe^{2+}	0.96	0.87	0.68	0.48	0.40
5	$Ba^{2+}, Sr^{2+}, Pb^{2+}, CO_3^{2-}$	0.96	0.87	0.67	0.46	0.39
4	$Na^+, HCO_3^-, H_2PO_4^-, CH_3COO^-$	0.99	0.96	0.90	0.81	0.77
	SO_4^{2-}, HPO_4^{2-}	0.96	0.87	0.66	0.44	0.36
	PO_4^{3-}	0.90	0.72	0.40	0.16	0.10
3	$K^+, Ag^+, NH_4^+, OH^-, Cl^-$ $ClO_4^-, NO_3^-, I^-, HS^-$	0.99	0.96	0.90	0.80	0.76

[a] After J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937). Reproduced with permission from American Chemical Society.

6.6.A.3 Davies Equation

$$\log \gamma_i = -A\, z_i^2 \{ I^{1/2} / (1 + I^{1/2}) - 0.2\, I \} \quad ; \text{ for } I < 0.5 \text{ (almost seawater)}$$

In this version of the D-H equation a simple term, linear in I, was added at the end of the equation. This term improves the empirical fit to higher I but it has no theoretical justification. So this equation is purely empirical. Because of its simplicity it is used in many of the chemical equilibrium computer programs.

In this equation all ions of the same charge have the same value of γ_i because there is no ion size parameter. For example: If we use the Davies equation to calculate γ_i for seawater ionic strength (I = 0.72) we get the following values:

monovalent ions = γ_i = 0.69

divalent ions   = γ_i = 0.23

trivalent ions   = γ_i = 0.04

These are realistic values even though seawater ionic strength is outside the valid range of this equation.

Fig 6-1 Comparison of free ion activity coefficients determined using the Extended Debye-Huckel equation (symbols) and the mean salt method (lines) as a function of ionic strength. The Extended Debye-Huckel equation is only valid to I = 0.1.
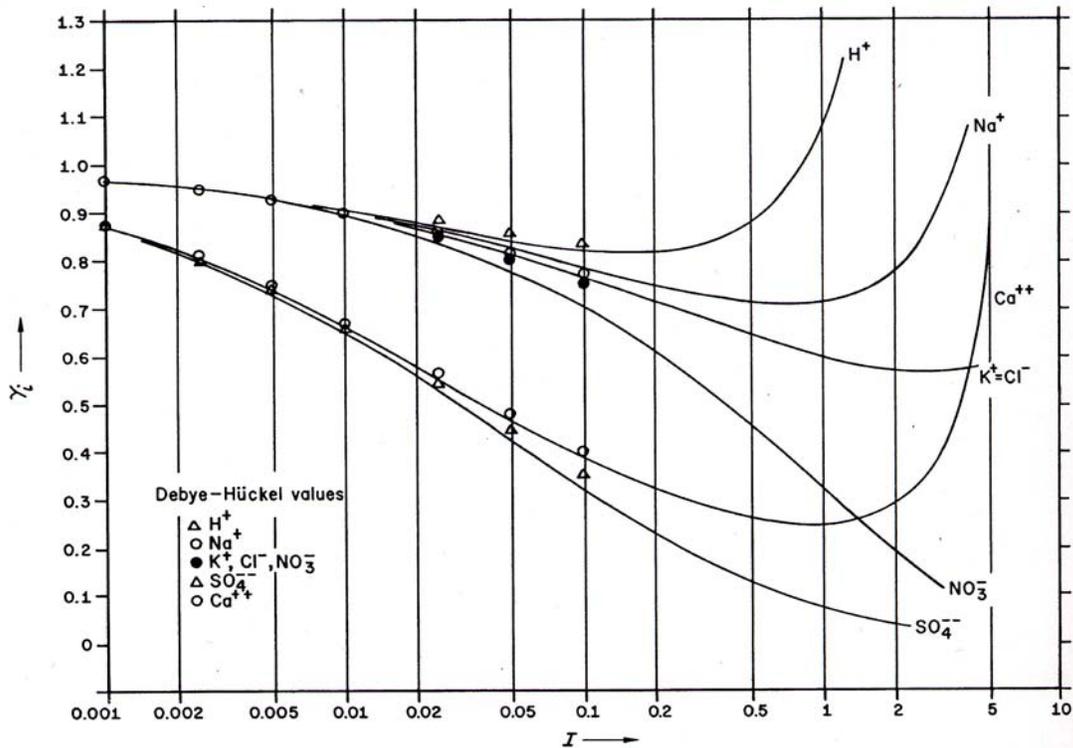

FIG. 2.15. Single ion activity coefficients vs. ionic strength for some common ions. Solid lines represent the values calculated by the mean salt method. Debye-Hückel values were calculated using equation (2.76), with $10^8/\mathring{a}_i = 9$ for H^+; 4 for Na^+; 3 for K^+, Cl^-, NO_3^-; 6 for Ca^{++}; and 4 for SO_4^{--}. The Debye-Hückel Y_i values for the monovalent ions converge, within experimental error, for $I < 0.01$.

6.6.B Mean Salt Method

This is an empirical method that uses the experimental determinations of activity coefficients ($\gamma\pm$). Usually such data are obtained by measuring the deviation from ideality of the colligative properties of solutions (e.g. osmotic pressure, vapor pressure of water). Activity coefficients are always measured on salt solutions which contain both cations and anions. The mean value is reported which is expressed as the geometric mean ($\gamma_\pm$) as given below for a generic salt MCl. Tabulations of such experimental data are available in Harned and Owen (1958). The Mean Activity Coefficients for typical salts are plotted against Ionic Strength in Fig 6-2. This approach can be used for any ionic strength for which experimental data are available so it can be applied to seawater and higher ionic strengths.

In order to calculate the free energy change for a specific set of conditions (ΔG_r), we need the values of the individual ion activity coefficients (e.g. γ_{M+}). Using the MacInnes Assumption, which states that $\gamma_{\pm KCl} = \gamma_{K+} = \gamma_{Cl-}$, we replace the activity coefficient for Cl⁻ (e.g. γ_{Cl-}) with the mean activity coefficient for KCl (e.g. $\gamma_{\pm KCl}$).

$$\text{e.g. } \gamma_{\pm MCl} = [\gamma_{M+} \cdot \gamma_{Cl-}]^{1/2} \quad \text{where M}^+ \text{ is any singly charged cation}$$
$$= [\gamma_{M+} \cdot \gamma_{\pm KCl}]^{1/2}$$

Thus:
$$\gamma_{M+} = (\gamma_{\pm MCl})^2 / \gamma_{\pm KCl}$$

For a divalent cation the procedure is similar:

$$\gamma_{\pm MCl2} = [\gamma_{M2+} \cdot \gamma_{Cl-}^2]^{1/3} = [\gamma_{M2+} \cdot \gamma_{\pm KCl}^2]^{1/3}$$
$$\gamma_{M2+} = (\gamma_{\pm MCl})^3 / \gamma_{\pm KCl}^2$$

The single ion activity coefficients by the mean salt method are compared with values calculated from the extended Debye-Huckel equation in Fig. 6-1. Note the good agreement to I = 0.1. Also note that at high I ($I \geq 1M$) the activity coefficients increase with ionic strength. This is called the salting out effect. Its origin is probably due to the fact that at high salt concentrations the hydration spheres of the ions tie up a significant amount of the water molecules so that the concentration of water for ions to be soluble in decreases. Thus, the effective concentrations (activities) appear larger than the real concentrations.

Fig 6-2 Mean ion activity coefficients as a function of ionic strength. From Garrels and Christ (1965).
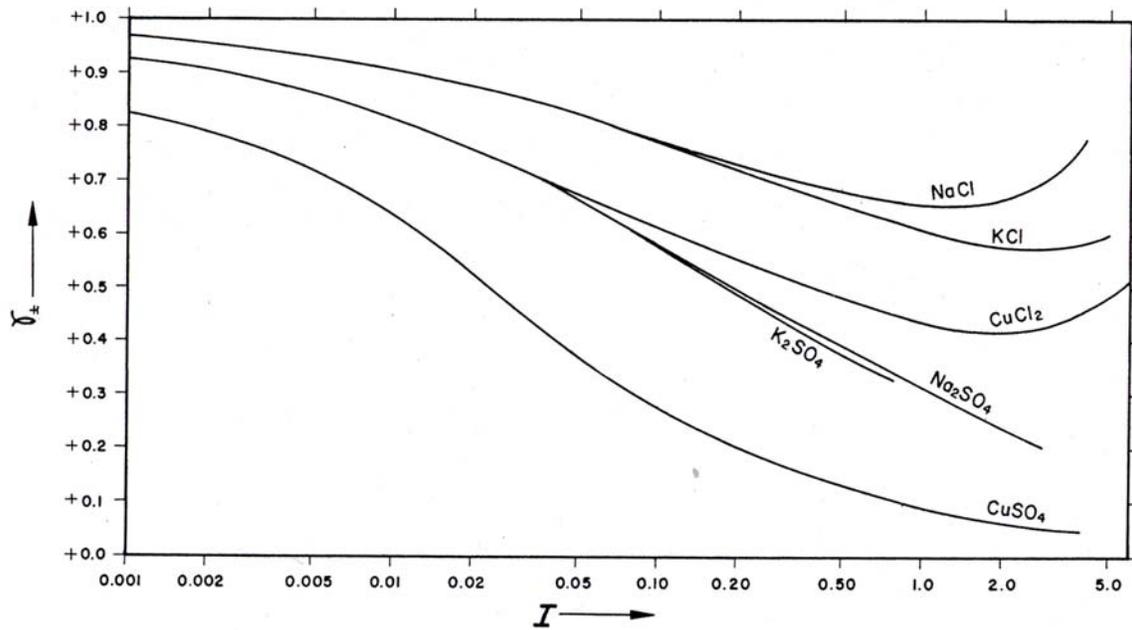

FIG. 2.14. Mean activity coefficients of typical salts plotted against the ionic strength (log scale). Note the similarity of the behavior of salts of the same valence type at ionic strengths below 0.1. [Data from W. M. Latimer, *op. cit.*, p. 354.]

General Rules for Free Ion activity Coefficients

1. $\gamma_i \rightarrow 1$ as $I \rightarrow 0$ i.e. activity = concentration at infinite dilution

2. $\gamma_i \downarrow$ as $I \uparrow$ i.e., the free ion activity coefficient decreases with ionic strength

3. $\gamma_{2+} < \gamma_+$ i.e., the activity corrections increase with charge

4. $\gamma_i \uparrow$ at high I i.e., in very concentrated salt solutions the free ion activity coefficients become greater than 1. This is called the salting out effect. Why do you think this occurs??

5. There is good agreement between mean salt method and extended Debye-Huckel equation to $I = 0.1$ (see Fig 5-1).

6. **Rules of Thumb** for free ion activity coefficients in seawater. When stuck for an answer use the following values.

ion charge	range	
±1	0.6 to 0.8	avg = 0.7
±2	0.1 to 0.3	avg = 0.2
±3	0.01	
±4	< 0.01	

6.7 Solution Speciation - % Free

When ion pairs are formed we distinguish between:

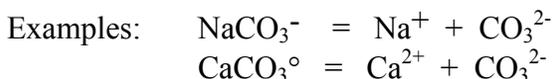Free ion activity coefficients (γ_i)

Total activity coefficients (γ_T)

The link between these is the percent free. The link is:

$$\gamma_T = \%free \cdot \gamma_i$$

We now focus on how to obtain values for the % Free and discuss the speciation of seawater.

Specific interactions between ions lead to formation of new species called ion pairs and complexes. Complexes, where two ions are in direct contact, are considered to be more stable than ion pairs, where waters of hydration separate the ions. The distinction is hard to make so these terms are frequently used interchangeably.

Examples: $NaCO_3^- = Na^+ + CO_3^{2-}$
$CaCO_3^\circ = Ca^{2+} + CO_3^{2-}$

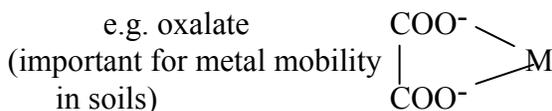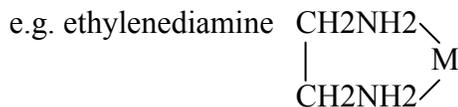Ion Pairs have all the properties of dissolved species:
    1. Their dissociation reactions have equilibrium constants
    2. Ion pairs have their own individual ion activity coefficients (γ_i)

Calculations of speciation can be done by hand or by computer.

Here are some general rules:
    1. higher the charge on an ion $\Rightarrow$ the greater the complexing
    2. higher the concentration of complexing ions $\Rightarrow$ the greater the complexing
    3. ignore higher order complexes $\Rightarrow$ these are species formed from 3 or more
        ions, e.g. $Ca(HCO_3)_2°$
    4. Cl^- ion pairs are very weak and can be ignored.
    5. +3 and higher ions (e.g. Fe^{3+}) form strong hydroxyl (OH^-) complexes. The
        reactions of the metal with water that form these species are called hydrolysis
        reactions (e.g. $Fe^{3+} + H_2O = FeOH^{2+} + H^+$) .
    6. organic compounds with reactive functional groups tend to form strong
        complexes with many transition metals (e.g. Ni^{2+}, Cu^{2+}, Zn^{2+}).
    When a single organic compound has more than one functional group this can
be called "chelation" from Greek for "claw". Below are examples of bedentate complexes
of metal with ethylenediamine and oxalate.

e.g. ethylenediamine   CH2NH2
                          | M
                       CH2NH2

e.g. oxalate   COO⁻
(important for metal mobility | M
    in soils)   COO⁻

Example: Speciation of a Ca^{2+}, CO_3^{2-}, HCO_3^-, SO_4^{2-} solution

Imagine a solution with one cation and three anions: Ca^{2+}, CO_3^{2-}, HCO_3^- and SO_4^{2-}
Ca^{2+} can form complexes with all three anions and we can write their dissociation reactions as:

$$CaCO_3° \leftrightarrow Ca^{2+} + CO_3^{2-}$$
$$CaHCO_3^+ \leftrightarrow Ca^{2+} + HCO_3^-$$
$$CaSO_4° \leftrightarrow Ca^{2+} + SO_4^{2-}$$
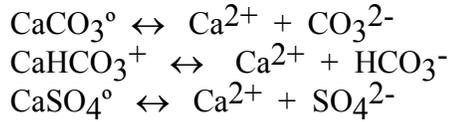
Such reactions can be written as either dissociation or formation reactions. Garrels and Thompson (1962) and Libes (Chpt 5) write them as dissociation reactions as shown here. We need to obtain the concentrations of 4 chemical species: one free ion and three complexes, so we have 4 unknowns. This assumes we know the concentrations of CO_3^{2-}, HCO_3^- and SO_4^{2-}.

To solve for 4 unknown concentrations we need 4 equations:

        1) One equation is the mass balance or sum of the concentrations of the
           four species:

$$Ca_T == [Ca^{2+}] + [CaCO_3°] + [CaHCO_3^-] + [CaSO_4°]$$

        2) Three equations are the equilibrium constants for formation of the
           complexes. (remember ( ) = activity and [ ] = concentration)

    e.g. $K_{CaCO3°} = (Ca^{2+})(CO_3^{2-}) / (CaCO_3°)$

                $= [Ca^{2+}] \gamma_{Ca2+} [CO_3^{2-}] \gamma_{CO3} / [CaCO_3°] \gamma_{CaCO3°}$

These γ are all free ion activity coefficients.

    We can solve this equation for the concentration of [CaCO3°].

    $[CaCO_3°] = [Ca^{2+}] \gamma_{Ca2+} [CO_3^{2-}] \gamma_{CO3} / K_{CaCO3°} \gamma_{CaCO3°}$

When we substitute the K's for the three complexes in the mass balance we obtain one equation to solve:

$$Ca_T == [Ca^{2+}] + [Ca^{2+}] \gamma_{Ca2+} [CO_3^{2-}] \gamma_{CO3} / K_{CaCO3°} \gamma_{CaCO3°}$$
$$+ [Ca^{2+}] \gamma_{Ca2+} [HCO_3^-] \gamma_{HCO3} / K_{CaHCO3} \gamma_{CaHCO3}$$
$$+ [Ca^{2+}] \gamma_{Ca2+} [SO_4^{2-}] \gamma_{SO4} / K_{CaSO4°} \gamma_{CaSO4°}$$

What information do we need?

    1) the values for the three equilibrium constants, K
    2) The free ion activity coefficients for the free ions e.g. γ_{Ca2+}, γ_{CO3}, γ_{CO3}
    3) The free ion activity coefficients for the complexes e.g. γ_{CaCO3}, γ_{CaHCO3^-}

Then:

% Free $= [Ca^{2+}] / Ca_T = 1 / \{1 + \gamma_{Ca2+} [CO3] \gamma_{CO3} / K_{CaCO3°} \gamma_{CaCO3°}$

            $+ \gamma_{Ca2+} [HCO3^-] \gamma_{HCO3} / K_{CaHCO3} \gamma_{CaHCO3+}$

            $+ \gamma_{Ca2+} [SO4] \gamma_{SO4}° / K_{CaSO4°} \gamma_{CaSO4°} \}$

Example: Speciation of Major Ion seawater

Garrels and Thompson (1962) first calculated the speciation of major ion seawater that in their case consisted of 4 cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and 4 anions (Cl^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}). The entire problem needs to be solved simultaneously because of the interaction of all the ions with each other.

This system has 24 species that need concentrations (unknowns). This includes:
  8 free ions
  16 ion pairs (G & T allowed only 1:1 complexes , e.g. $MgSO_4^o$)

To solve for 24 unknowns we need 24 equations

8 mass balance equations
  (e.g. $Ca_T = [Ca^{2+}] + [CaCl^+] + [CaCO_3^o] + [CaHCO_3^+] + [CaSO_4^o]$)
16 equilibrium constants, K

In 1962 computers did not exist so G&T solved this problem by hand. They used a brute force sequential substitution method. In order to make it easier they made some simplifying assumptions using their chemical intuition.

1. They assumed Cl- forms no complexes - this eliminates 5 unknowns by eliminating, the 4 Cl^- ion pairs and making the Cl mass balance the trivial balance of ($Cl_T = Cl^-$)
2. They assumed K forms no CO_3^{2-} or HCO_3^- complexes - this eliminates 2 more unknowns. The problem has now been simplified to 17 unknowns.
3. They assumed that all single charged ions (both + and -) have the same free ion activity coefficient as HCO_3^- thus, $\gamma_{HCO3} = 0.68$ (see attached table 6-3)
4. They assumed that all neutral complexes had the value of $\gamma_{H2CO3} = 1.13$
5. For the first iteration they assumed that all the cations were 100% free. Turns out to not be a good assumption because Cl^- balances most of the cations and Cl^- does not form complexes.

See Table 6-3, Fig 6-3 and pages 66-68 in Libes for more discussion and results.

The Abstract of the Garrels and Thompson (1962) paper summarizes the results and is attached here (Fig. 6-3).

Q. How would the solution composition change the solubility of gypsum ($CaSO_4 \cdot 2H_2O$)?

Q. Using the same approach predict the major ion speciation of Lake Washington. The composition was given in Lecture 5.

Q Speculate about the speciation in hydrothermal vents. Do you know in what ways end-member hydrothermal vent chemistry differs from normal seawater? How would its speciation be different?

Table 6-3 Free Ion Activity Coefficients used by Garrels and Thompson (1962)

Ionic Activity Coefficients for the Major Ions and Their Ion Pairs at 35‰, 25°C, and 1 atm

Dissolved Species	Activity Coefficient
$NaHCO_3^0$	1.13
$MgCO_3^0$	1.13
$CaCO_3^0$	1.13
$MgSO_4^0$	1.13
$CaSO_4^0$	1.13
Na^+	0.76
HCO_3^-	0.68
$NaCO_3^-$	0.68
$NaSO_4^-$	0.68
KSO_4^-	0.68
$MgHCO_3^+$	0.68
$CaHCO_3^+$	0.68
K^+	0.64
Mg^{2+}	0.36
Ca^{2+}	0.28
SO_4^{2-}	0.12
CO_3^{2-}	0.20

Fig 6-3 Abstract and summary of results for the Garrels and Thompson model for the speciation of the major ions of seawater. Missing from this Table is that the Molality of Total Cl⁻ = 0.5543. This can be calculated from the charge balance of the other ions.

A CHEMICAL MODEL FOR SEA WATER AT 25°C AND ONE ATMOSPHERE TOTAL PRESSURE*

R. M. GARRELS and M. E. THOMPSON

Department of Geological Sciences, Harvard University,
Cambridge, Massachusetts

ABSTRACT. Dissociation constants involving Ca^{++}, Mg^{++}, Na^+, K^+, SO_4^{--}, HCO_3^-, and CO_3^{--} ions, and individual ion activity coefficients have been used to calculate the distribution of dissolved species in sea water at 25°C and one atmosphere total pressure. The distribution obtained for sea water of chlorinity 19‰ and pH 8.1 are:

Ion	Molality (Total)	% Free Ion	% Me-SO_4 pair	% Me-HCO_3 pair	% Me-CO_3 pair
Ca^{++}	0.0104	91	8	1	0.2
Mg^{++}	0.0540	87	11	1	0.3
Na^+	0.4752	99	1.2	0.01	—
K^+	0.0100	99	1	—	—

Ion	Molality (Total)	% Free Ion	% Ca-anion pair	% Mg-anion pair	% Na-anion pair	% K-anion pair
SO_4^{--}	0.0284	54	3	21.5	21	0.5
HCO_3^-	0.00238	69	4	19	8	—
CO_3^{--}	0.000269	9	7	67	17	—
Cl^-	0.5543	100	—	—	—	—

The activities calculated for free ions are $a_{Ca^{++}} = 0.00264$, $a_{Mg^{++}} = 0.0169$, $a_{Na^+} = 0.356$, $a_{K^+} = 0.0063$, $a_{CO_3^{--}} = 4.7(10^{-6})$, $a_{HCO_3^-} = 9.75 (10^{-4})$, $a_{SO_4^{--}} = 1.79(10^{-3})$.

6.8 Total Activity Coefficients

Remember that the total activity coefficient is the product of the % Free times the free ion activity coefficient

$$\gamma_T = \% \text{ Free} \ \ x \ \ \gamma_i$$

These values are calculated below for the Garrels and Thompson model for major ion speciation.

Ion	γ_i	% Free	γ_T
Ca^{2+}	0.28	0.91	0.25
Mg^{2+}	0.36	0.87	0.31
Na^+	0.76	0.99	0.75
K^+	0.64	0.99	0.63
SO_4^{2-}	0.12	0.54	0.065
HCO_3^-	0.68	0.69	0.42
CO_3^{2-}	0.20	0.09	0.018
Cl^-	0.63	1.00	0.63

6.9 Specific Interaction Models (text here is incomplete)

The specific interaction models give an estimate of γ_T.

Bronsted-Guggenheim Model (Whitfield, 1973)

$$\log \gamma\pm_{MX} = \log \gamma_{EL} + \underline{v} \ B_{MX} \ [MX]$$

where $\gamma\pm_{MX}$ is the mean activity coefficient for the salt MX. γ_{EL} represents the long range electrostatic interactions.

$$\gamma_{EL} = - A \ (Z_m Z_X)(I^{1/2} / 1 + B \ a \ I^{1/2})$$

and

B_{MX} is the short range interaction coefficient between M and X.

Pitzer Model (Whitfield, 1975; Millero, 1983)

$$\text{Log } \gamma\pm_{MX} = \log EL + B_{MX} \ [MX] + C_{MX} \ [MX]^2$$

6.10 Equilibrium Constants on Different Scales

Earlier we defined the infinite dilution and ionic medium activity scales. Equilibrium constants are defined differently on these two scales. There are both advantages and disadvantages of the infinite dilution and ionic medium approaches.

Consider the generic acidity reaction:

$$HA = H^+ + A^-$$

We define the equilibrium constants as follows.

A. On the **infinite dilution scale** the equilibrium constant (K) is defined in terms of activities.

$$K = (H^+)(A^-) / (HA)$$

On this scale K can be calculated from $\Delta G_f°$ or measured directly in very dilute solutions.

B. On the **ionic medium scale** the equilibrium constant (K') is defined in terms of concentrations in the ionic medium of interest.

$$K' = [H^+] [A^-] / [HA]$$

The only way you can obtain K' is to measure it in the ionic medium of interest (e.g. seawater) for a given set ot temperature, pressure and salinity. When the measurements are done with care the ionic medium approach can be more accurate than the infinite dilution approach. Fortunately this has been done for many of the important reactions in seawater, like the carbonate system reactions.

When pH is measured as the activity of H^+, as it is commonly done, the mixed constant is defined in terms of (H^+).

$$K' = (H^+) [A^-] / [HA]$$

The difference between K and K' is the ratio of the total activity coefficients.

$$K = K' \, \gamma_H \, \gamma_A / \gamma_{HA}$$

Example: Determine the state of solubility of $CaCO_3(s)$ in surface seawater using the infinite dilution and ionic medium approaches.

Problems:

1. Using the Davies equation, calculate the effect of ionic strength alone on the solubility of gypsum as you go from a very dilute, ideal solution to a NaCl solution with $I = 0.5$. Here we can express the solubility as the product of the concentrations of total calcium times sulfate or $[Ca^{2+}][SO_4^{2-}]$. Assume no ion pair species form. Remember that for:

$$CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$$
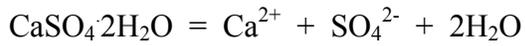
$$K = 2.40 \times 10^{-5}$$

The Davies Equation is

$$\log \gamma_i = -Az_i^2 \{ I^{1/2} / (1 + I^{1/2}) - 0.2I \}$$

where $A = 0.51$

References:

Bockris J. O'M. and A.K.N. Reddy (1973) Modern Electrochemistry, Volume 1. Plenum Press, New York, 622pp.

Garrels R.M. and C.L. Christ (1965) Solutions, Minerals and Equilibria. Freeman, Cooper & Company, San Francisco, 450pp.

Garrels R.M. and M.E. Thompson (1962) A chemical model for sea water at 25°C and one atmosphere total pressure. Aner. J. Sci. 260, 57-66.

Harned H.S. and B.B. Owen (1958) The Physical Chemistry of Electrolyte Solutions. Reinhold Book Corp., New York, 803pp.

Millero (1983) Geochim. Cosmochim. Acta, 47, 2121.

Pitzer (1973) J. Phys. Chem., 77, 268.

Pitzer and Kim (1974) J. Amer. Chem. Soc., 96, 5701.

Robinson R.A. and R.H. Stokes (1959) Electrolyte Solutions, 2nd Ed. Butterworths, London, 571pp.

Whitfield (1973) Marine Chemistry, 1, 251.

Whitfield (1975) Marine Chemistry, 3, 197.