Earlier we studied common ion effect on decreasing the solubility

\[ \text{CaCO}_3 \rightleftharpoons \text{Ca}^{+2} + \text{CO}_3^{-2} \]

• Add Ca\(^{+2}\) or CO\(_3^{-2}\) and decrease solubility

• Add other electrolyte and CaCO\(_3\) solubility increases due to interaction of other electrolytes and H\(_2\)O and a shielding effect

• The Ca\(^{++}\) might form a Cl\(^-\) complex and become shielded from reaction with CO\(_3^{-2}\)

• Overall concentration of electrolytic solutions is very important in describing reactions that take place.
ACTIVITY & ACTIVITY COEFFICIENTS-1

- Instead of simple molality, the ionic strength is used and is described as:
  \[ I = \frac{1}{2} \sum (m_i z_i^2) \]
- Where \( m_i \) is the concentration of the ion, \( i \)
- \( z_i \) is the charge of ion \( i \)
- Examples:
  - 1m NaCl: \( I = \frac{1}{2} (1*1^2 + 1*1^2) = 1 \)
  - 1m CaCl₂: \( I = \frac{1}{2} (1*2^2 + 2*1^2) = \frac{1}{2} (1*4 + 2*1) = 3 \)
- \( I \), in comparison to \( \sum \) of molal conc’s, emphasizes the effect of higher charges of multivalent ions
- \( I \) gives a good measure of the effect of electrolytes on solubility

ACTIVITY & ACTIVITY COEFFICIENTS-2

- Activity, \( a \)
  - the effective concentration of a solute
  - the extrapolated solubility at zero ionic strength; about equivalent to the solubility in D.I. H₂O
- At infinite dilution, \( a = m \)
- As the conc. increases, \( m \) becomes greater than \( a \), where
  \[ a = \gamma m \quad \gamma = \text{activity coefficient} \]
- For CaCO₃:
  \[ a_{\text{CaCO}_3} = \gamma_{\text{CaCO}_3} m_{\text{CaCO}_3} \]
  \[ a_{\text{Ca}^{++}} = \gamma_{\text{Ca}^{++}} m_{\text{Ca}^{++}} \quad a_{\text{CO}_3^{-2}} = \gamma_{\text{CO}_3^{-2}} m_{\text{CO}_3^{-2}} \]
- In dilute (\( I < 0.001 m \)) solutions, \( \gamma \approx 1 \) and \( a \approx c \)
ACTIVITY & ACTIVITY COEFFICIENTS-3

Mean ion-activity coefficients

\[ K_{2\text{SO}_4(c)} = 2\text{K}^+ + \text{SO}_4^{2-} \]

- For which we obtain

\[ K_{sp} = (\gamma_{\text{K}^2})(\gamma_{\text{SO}_4})(m\text{K}^+)^2 (m\text{SO}_4^{-2}) \]

- Cannot measure individual ion activities, just total effect on \( K_{sp} \)

\[ \gamma_{\pm \text{K}_2\text{SO}_4} = [(\gamma_{\text{K}^2})(\gamma_{\text{SO}_4})]^{1/3} \]

\[ K_{sp} = \gamma_{\pm \text{K}_2\text{SO}_4}^3 (m\text{K}^+)^2 (m\text{SO}_4^{-2}) \]

- So, mean ion-activity coefficient:

\[ \gamma_{\pm} = [(\gamma_{+}^n)(\gamma_{-}^n)]^{1/n} \]

ACTIVITY & ACTIVITY COEFFICIENTS-4

- For more precise calculations, the Debye-Hückel theory yields the expression:

\[ \log \gamma_i = \frac{-A \ z_i^2 \ \sqrt{I}}{1 + B \ a_i \ \sqrt{I}} \]

- Where

  - \( A \) is a constant depending on \( T \), density & the dielectric constant of the solvent (H\(_2\)O), \( \approx 0.51 \) in H\(_2\)O at 25 \( ^\circ \)C
  - \( B \) is a constant related to the \( T \) & density of H\(_2\)O
  - \( a \) is the effective diameter of the ion (Å)
  - see text for explanation of these terms
ACTIVITY & ACTIVITY COEFFICIENTS-5

- A simplified version is sometimes useful at small values of $I$:

$$\log \gamma = -A z^2 I^{1/2}$$

- Extension of the Debye-Hückel by Davis gives:

$$\log \gamma = -A z^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$$

- Note $\gamma$ as a function of $I$ & $z$ in Fig 4.2, page 128 in text

ACTIVITY & ACTIVITY COEFFICIENTS-6

**CaCO$_3$ example in text:**

- For CaCO$_3$ in 0.001$m$ NaCl, the $K_{sp}$ is increased by a factor of 1.15 over $K_{sp}$ at infinite dilution

- Solubility of CaCO$_3$ in 0.5$m$ NaCl is increased >4X that in a dilute solution & the $K_{sp}$ – concentration product – is about 200X the activity product

- This example emphasizes the importance of $I$ on solid phase solubilities
### CONVENTIONS REGARDING SOLUBILITIES

- Activities are formally defined as dimensionless numbers.
- Equilibrium constants expressed in terms of activities are true constants (are independent of composition).
- In dilute solutions, $a \approx m$, but in concentrated solutions differences may be > 1 order of magnitude.
- Activities of pure solids & pure liquids = 1, by definition.
- Activity of $H_2O$ in dilute solutions $\approx 1$.
- Unionized solutes ($H_4SiO_4$, $SiO_2(aq)$) have $\gamma \approx 1$.
- Estimates of $\gamma$ place major emphasis on $I$.

### ACTIVITY CORRECTIONS APPLIED TO SOLUBILITY CALCULATIONS

- If $m_A$ = total molality for the $CO_2$-$H_2O$ system,
  
  $$m_{A(CO2)} = m_{CO2(aq)} + m_{H2CO3} + m_{HCO3-} + m_{CO3-2}$$

  $$m_{A(CO2)} = \frac{a_{CO2(aq)}}{\gamma_{CO2(aq)}} + \frac{a_{H2CO3}}{\gamma_{H2CO3}} + \frac{a_{HCO3-}}{\gamma_{HCO3-}} + \frac{a_{CO3-2}}{\gamma_{CO3-2}}$$

- Sphalerite example:
  - $ZnS$ in a NaCl-ZnCl$_2(aq)$-$H_2S$-$H_2O$ sol’n at 250 °C & 50 bar
  - Possible species: $Zn^{2+}$, $ZnOH^+$, $ZnCl^+$, $ZnCl_2(aq)$, $ZnCl_3^-$, $ZnCl_4^{2-}$, $H_2S$, $HS^-$, $S^{2-}$, $NaCl(aq)$, $NaOH(aq)$, $Na^+$, $Cl^-$, $H^+$, $OH^-$ & $HCl(aq)$
  - 15 chem species, 31 independent equations
ACTIVITY CORRECTIONS APPLIED TO SOLUBILITY CALCULATIONS

- At $I > 2.3$ mol/kg, high sol'n density may lead to binary & ternary interactions; need different model

- High ionic strengths & Pitzer Model
  - includes “interaction parameters” involving aqueous species & major species in H$_2$O
  - few data yet available for trace species
  - useful over widest range of ionic strengths

- Note the overview and summary comparison (Fig 4.5) of different activity coefficient models as a function of $I$

- Example 4.5 shows applicability of Pitzer Model to computation of HCO$_3$- activity in sea water

OVERVIEW OF ACTIVITY COEFFICIENT MODELS FOR IONS

- Algorithms that describe the change in $\gamma_i$ with $I$ all relate the log of $\gamma_i$ to a function of $I^{1/2}$, with or without additional functions (See Fig 4.5)

- At $I \leq 0.02$ mol/kg, the Debye-Hückel limiting law applies

- From 0.02 - 0.7 mol/kg, the Davies equation works well

- From 0.02 - 2 mol/kg, the TJ equation is reliable

- From 0.02 - 3.5 mol/kg, the SIT model works well

- From 0.02 - 6 mol/kg, the Pitzer model is applicable, is best for high $I$