

# GEOL 414/514

## ACTIVITY COEFFICIENTS OF DISSOLVED SPECIES

### Chapter 4

## LANGMUIR

### ACTIVITY & ACTIVITY COEFFICIENTS

- Earlier we studied common ion effect on decreasing the solubility  
$$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{+2} + \text{CO}_3^{-2}$$
- Add  $\text{Ca}^{+2}$  or  $\text{CO}_3^{-2}$  and decrease solubility
- Add other electrolyte and  $\text{CaCO}_3$  solubility increases due to interaction of other electrolytes and  $\text{H}_2\text{O}$  and a shielding effect
- The  $\text{Ca}^{++}$  might form a  $\text{Cl}^-$  complex and become shielded from reaction with  $\text{CO}_3^{-2}$
- 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:

$$1\text{m NaCl: } I = \frac{1}{2}(1 \cdot 1^2 + 1 \cdot 1^2) = 1$$

$$1\text{m CaCl}_2: I = \frac{1}{2}(1 \cdot 2^2 + 2 \cdot 1^2) = \frac{1}{2}(1 \cdot 4 + 2 \cdot 1) = 3$$

- $I$ , 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

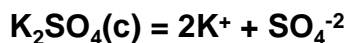
## ACTIVITY & ACTIVITY COEFFICIENTS-2

- Activity,  $a$ 
  - the effective concentration of a solute
  - the extrapolated solubility at zero ionic strength; about equivalent to the solubility in D.I. H<sub>2</sub>O
- At infinite dilution,  $a = m$
- As the conc. increases,  $m$  becomes greater than  $a$ , where
 
$$a = \gamma m \quad \gamma = \text{activity coefficient}$$
- For CaCO<sub>3</sub>:  $a_{\text{CaCO}_3} = \gamma_{\text{CaCO}_3} \cdot m_{\text{CaCO}_3}$ 

$$a_{\text{Ca}^{++}} = \gamma_{\text{Ca}^{++}} \cdot m_{\text{Ca}^{++}} \quad a_{\text{CO}_3^{2-}} = \gamma_{\text{CO}_3^{2-}} \cdot m_{\text{CO}_3^{2-}}$$
- In dilute ( $I < 0.001\text{m}$ ) solutions,  $\gamma \approx 1$  and  $a \approx c$

## ACTIVITY & ACTIVITY COEFFICIENTS-3

Mean ion-activity coefficients



- For which we obtain

$$K_{\text{sp}} = (\gamma_{\text{K}^+})^2 (\gamma_{\text{SO}_4^{-2}}) (m_{\text{K}^+})^2 (m_{\text{SO}_4^{-2}})$$

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

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

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

- 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 ( $\text{H}_2\text{O}$ ),  $\approx 0.51$  in  $\text{H}_2\text{O}$  at 25 °C
- B is a constant related to the T & density of  $\text{H}_2\text{O}$
- 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  $I$ :

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

- Extension of the Debye-Hückel by Davis gives:

$$\log \gamma = -Az^2 \left[ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right]$$

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

## ACTIVITY & ACTIVITY COEFFICIENTS-6

CaCO<sub>3</sub> example in text:

- For CaCO<sub>3</sub> in 0.001 *m* NaCl, the K<sub>sp</sub> is increased by a factor of 1.15 over K<sub>sp</sub> at infinite dilution
- Solubility of CaCO<sub>3</sub> in 0.5 *m* NaCl is increased >4X that in a dilute solution & the K<sub>sp</sub> – 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<sub>2</sub>O in dilute solutions  $\approx 1$
- Unionized solutes (H<sub>4</sub>SiO<sub>4</sub>, SiO<sub>2(aq)</sub>) have  $\gamma \approx 1$
- Estimates of  $\gamma$  place major emphasis on *l*

## ACTIVITY CORRECTIONS APPLIED TO SOLUBILITY CALCULATIONS

- If  $m_A$  = total molality for the CO<sub>2</sub>-H<sub>2</sub>O system,

$$m_{A(\text{CO}_2)} = m_{\text{CO}_2(\text{aq})} + m_{\text{H}_2\text{CO}_3} + m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}}$$

$$m_{A(\text{CO}_2)} = \frac{a_{\text{CO}_2(\text{aq})}}{\gamma_{\text{CO}_2(\text{aq})}} + \frac{a_{\text{H}_2\text{CO}_3}}{\gamma_{\text{H}_2\text{CO}_3}} + \frac{a_{\text{HCO}_3^-}}{\gamma_{\text{HCO}_3^-}} + \frac{a_{\text{CO}_3^{2-}}}{\gamma_{\text{CO}_3^{2-}}}$$

- Sphalerite example:
- ZnS in a NaCl-ZnCl<sub>2</sub>(aq)-H<sub>2</sub>S-H<sub>2</sub>O sol'n at 250 °C & 50 bar
- Possible species: Zn<sup>+2</sup>, ZnOH<sup>+</sup>, ZnCl<sup>+</sup>, ZnCl<sub>2</sub>(aq), ZnCl<sub>3</sub><sup>-</sup>, ZnCl<sub>4</sub><sup>-2</sup>, H<sub>2</sub>S, HS<sup>-</sup>, S<sup>-2</sup>, NaCl(aq), NaOH(aq), Na<sup>+</sup>, Cl<sup>-</sup>, H<sup>+</sup>, OH<sup>-</sup> & HCl(aq)
- 15 chem species, 31 independent equations

## ACTIVITY CORRECTIONS APPLIED TO SOLUBILITY CALCULATIONS

- At  $I > 2-3.5$  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<sub>2</sub>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<sub>3</sub><sup>-</sup> 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  $I$