Ch 7

Systematic Treatment of Equilibrium and Activity

Systematic Treatment of Equilibrium

- Complicated systems have several unknown variables – species of unknown concentration

- Generally, you need to come up with as many independent equations as unknown variables

- Strategy (ie. PbI_2 problem)
  - Write down all pertinent equilibrium expressions
  - Write mass balance equations
  - Write down charge balance equations
  - Substitution to reduce problem to one equation with one variable

Mass Balance

Let's look at a triprotic system, such as H_3PO_4, as an example

There are four different species within this system

- H_3PO_4
- $H_2PO_4^-$
- HPO_4^{2-}
- PO_4^{3-}

0.050 M NaH_2PO_4

$0.050 = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$

Charge Balance

- All solutions must be electrically neutral!!!!!!!! Which means they carry a no net charge.

  mole positive charges = moles negative charges

- ex. A dilute solution of acetic acid, HA

  What species exist in solution?

  HA, A^-, OH^-, H_3O^+

From HA $\leftrightarrow$ H^+ + A^- and $2H_2O \leftrightarrow H_3O^+ + OH^-$

- A mole of A^- carries a mole of negative charge. A mole of OH^- carries a mole of negative charge. A mole of HA carries no charge. A mole of H_3O^+ carries a mole of positive charge. Therefore, the charge balance equation is

$$[H_3O^+] = [A^-] + [OH^-]$$

Charge Balance for the 0.050 M NaH$_2$PO$_4$ solution

- 1 mole of H$_3$PO$_4$ carries no moles of charge
- 1 mole of H$_2$PO$_4^-$ carries 1 mole of (-) charge
- 1 mole of HPO$_4^{2-}$ carries 2 moles of (-) charge
- 1 mole of PO$_4^{3-}$ carries 3 moles of (-) charge

Therefore,

$$[Na^+] + [H_3O^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$$

Why is this useful?

- In many instances when we are dealing with very complex equilibria, it is useful to use mass balance and charge balance in efforts to reduce an expression to one variable.

- Stay tuned. We will utilize mass and charge balance in the next couple of chapters

Write a mass balance and charge balance equation for a 0.010 M solution of H_2SO_4 (HSO_4^- is a very strong weak acid)

Mass Balance

- $0.010\ M = [H_2SO_4] + [HSO_4^-] + [SO_4^{2-}]$

Charge Balance

- $[H_3O^+] = [HSO_4^-] + 2[SO_4^{2-}] + OH^-$

Chapter 8
Activity

CH 313 Experiment
Solubility of $CaSO_4$

solution	$[Ca^{2+}]$
Sat. $CaSO_4$ in H_2O	1.5E-03 M
Sat. $CaSO_4$ in Na_2SO_4	8.8 E-04 M
Sat. $CaSO_4$ in KNO_3	2.3E-03 M

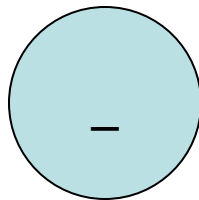# The "true" nature of ionic species in solution

- Ions are charged molecules
- As a result, they tend to attract polar solvent molecules (like water, for instance) and other ions
  - Hydrated radius
  - Ionic atmosphere
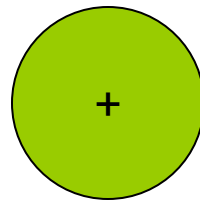- The thickness of the ionic atmosphere is a function of the ionic strength of the solution "the concentration of charge"
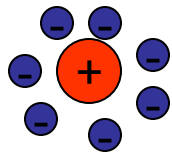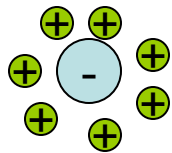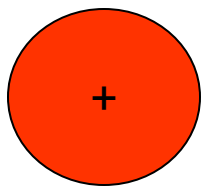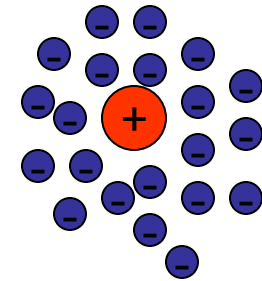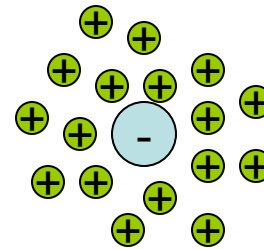
Hydrated radius
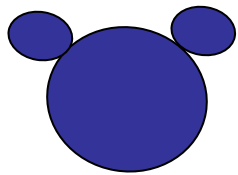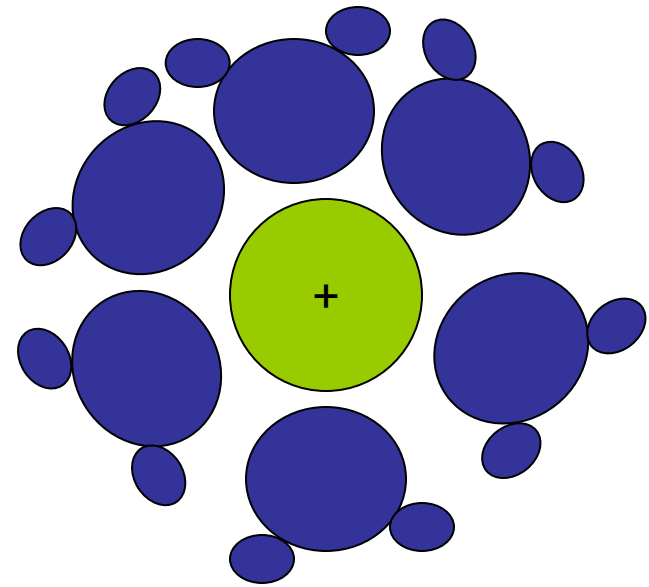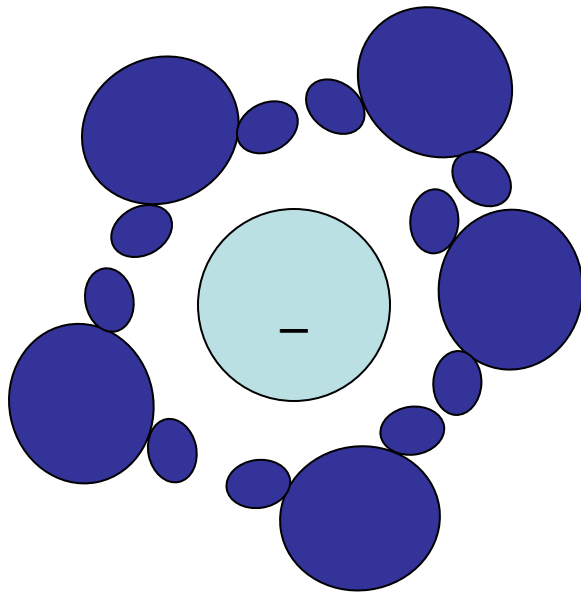
water   Chloride   Sodium ion
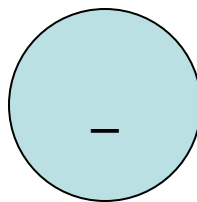
Ionic Atmosphere and Shielding
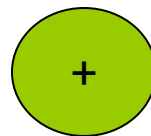
Low ionic strength

High ionic strength

Calcium ion

Sulfate ion

Sodium ion
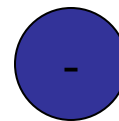
Chloride ion

Activity

- All ionic species in any equilibrium expression are more accurately expressed as activities.

$\mathscr{A}_{Ca2+} = [Ca^{2+}]\gamma_{Ca2+}$

or

$A + H_2O \leftrightarrow A^- + H_3O^+$
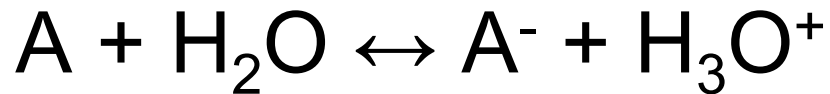
$Ka = \mathscr{A}_{A-}\,\mathscr{A}_{H3O+} / [A] = [A^-]\gamma_{A-}[H_3O^+]\gamma_{H3O+} / [A]$

where γ is the activity coefficient and is a function of the ionic radius of the ion and the ionic strength of the solution.

Activity - continued

- The higher the ionic strength of the solution, the larger the smaller the activity coefficient.

- Rationalization: At higher ionic strengths the ion cloud around any ion is thicker, which weakens the attractive forces between the ion and its counterpart, inhibiting recombination.

Ionic strength

- A measure of the concentration of ions in solution

$$\mu = \frac{1}{2} \sum c_i z_i^2$$

0.010 M $Ca(NO_3)_2$

$$\mu = \frac{1}{2} ([NO_3^-](-1)^2 + [Ca^{2+}](2+)^2) =$$
$$\frac{1}{2} \{(0.02)(-1)^2 + (0.01)(2)^2 \} = 0.03 \text{ M}$$

$\gamma_{Ca2+}@\mu=0.03$ = ?

Use extended Debye-Huckle eq or Table 8.1 and extrapolation

Take home message

- At high ionic strengths, solubility increases slightly (by a factor of 2-10).

- pH is influenced by ionic strength

- Weak acid and base dissociation is influenced a little by ionic strength

- Significant figures?

Example 8-12

- Solubility of Hg_2Br_2
  - in pure water
  - in 0.00100 M KNO_3
  - in 0.0100 M KNO_3
  - in 0.100 M KNO_3

In pure water

$Hg_2Br_2 \leftrightarrow Hg_2^{2+} + 2Br^-$

$Ksp = [Hg_2^{2+}]_{\gamma Hg22+} [Br^-]^2 \gamma_{Br-}^2$

$2[Hg_2^{2+}] = [Br^-]$ and let $[Hg_2^{2+}] = x$

Ionic strength is very low.

$\gamma Hg22+$ and γ_{Br-} are close to 1.00

so,

$$Ksp = 4 [x]^3 = 5.6 \cdot 10^{23}$$

$$x = 2.4 \cdot 10^{-8} M$$

Activity coefficient as a function of ionic strength Table 8 -1

	$\mu = 0.001$	$\mu = 0.01$	$\mu = 0.1$
Hg_2^{2+}	0.867	0.660	0.335
Br^-	0.964	0.898	0.75

in 0.00100 M KNO3

$$\mu = \tfrac{1}{2} ((.001)(+1)^2 + (0.001)(-1)^2 = 0.001 \text{ M}$$

$$\gamma_{Hg_2^{2+} @ \mu = 0.001} = 0.867$$

$$\gamma_{Br^-}^2{}_{@ \mu = 0.001} = 0.964$$

$$Ksp = 4 \, \gamma_{Hg_2^{2+}} \gamma_{Br^-}^2 [x]^3 = 5.6 \cdot 10^{-23}$$

$$x = 2.6 \cdot 10^{-8} \text{ M}$$

in 0.0100 M KNO3

$\mu = \frac{1}{2} ((.01)(+1)^2 + (0.01)(-1)^2 = 0.01$ M

$\gamma_{Hg_2^{2+} \, @ \, \mu = 0.001} = 0.660$

$\gamma_{Br^-}^2 {}_{@ \, \mu = 0.001} = 0.898$

$Ksp = 4 \, \gamma_{Hg_2^{2+}} \, \gamma_{Br^-}^2 \, [x]^3 = 5.6E\text{-}23$

$x = 3.0 \cdot 10^{-8}$ M

in 0.100 M KNO3
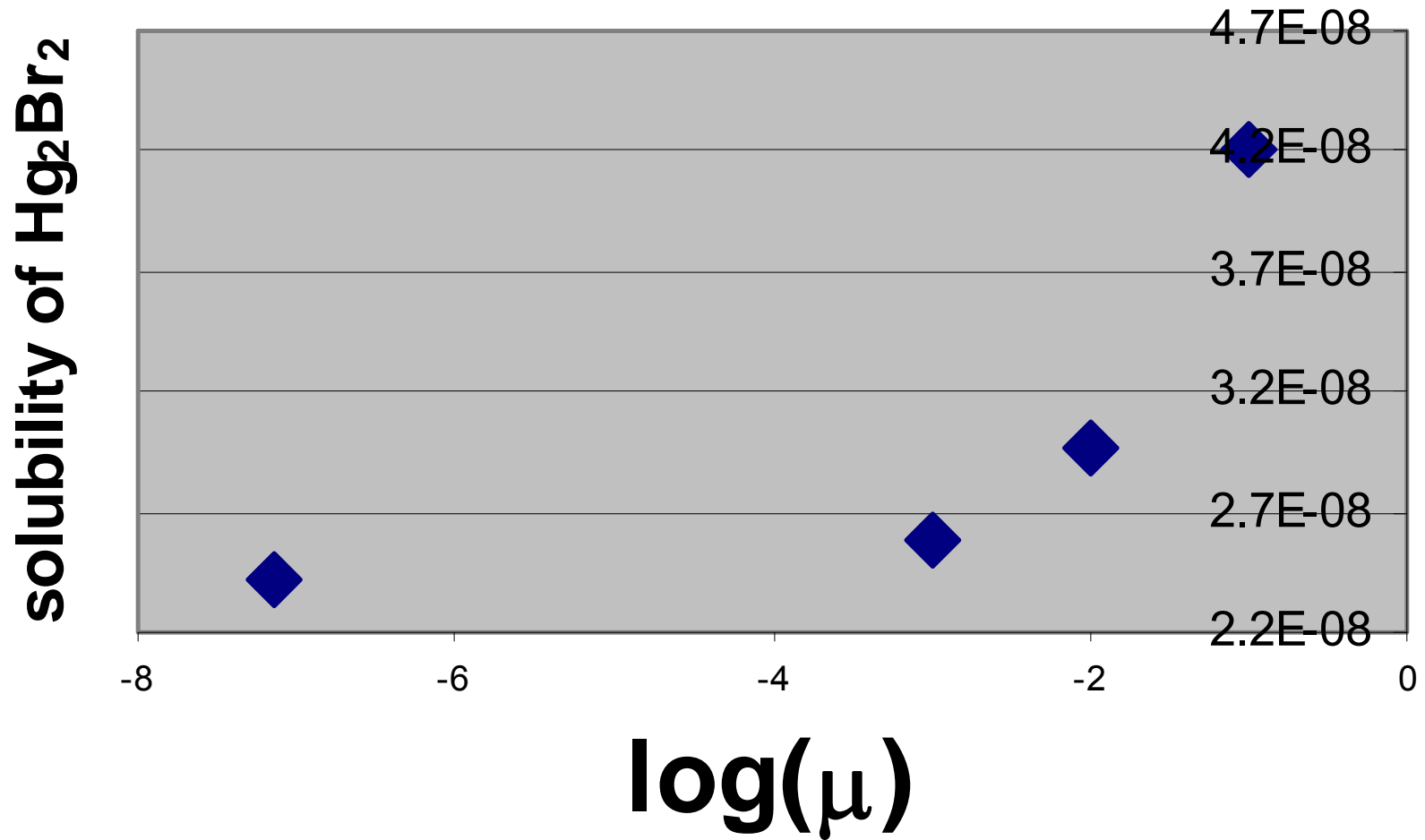
$\mu = \frac{1}{2}((0.1)(+1)^2 + (0.1)(-1)^2 = 0.1$ M

γ_{Hg22+} @ $\mu = 0.001$ = 0.335

γ_{Br-}^2 @ $\mu = 0.001$ = 0.75

$Ksp = 4\,\gamma_{Hg22+}\,\gamma_{Br-}^2\,[x]^3 = 5.6E\text{-}23$

$x = 4.2 \cdot 10^{-8}$ M

pH and ionic strength

- True definition of pH

$$pH = -\log \mathscr{A}_{H+} = -\log \{[H^+]\gamma_{H+}\}$$

- pH of a 0.00100 M HCl solution
  - Ionic strength, μ, = 0.001; γ_{H+} = 0.967
  - pH = -log(.001*.967) = 3.01

- pH of a 0.100 M HCl solution
  - Ionic strength, μ, = 0.1; γ_{H+} = 0.83
  - pH = -log(0.1*0.83) = 1.08

- pH of a 0.00100 M HCl/0.100 M NaCl solution
  - Ionic strength, μ, = 0.1; γ_{H+} = 0.83
  - pH = -log(0.001*0.83) = 3.08

What is the concentration H^+ and OH^- in a 0.100 M NaCl solution?

$Kw = [OH^-]\gamma_{OH-}[H^+]\gamma_{H+} = 1.01 \cdot 10^{-14}$

At $\mu = 0.100$, $\gamma_{OH-} = 0.76$ and $\gamma_{H+} = 0.83$

H_2O is the only source of H^+ and OH^- so let x = $[H^+] = [OH^-]$

$Kw = (0.76)(0.83)\, x^2$

$x = 1.2_7 \cdot 10^{-7}$ M