

# Fundamentals of Analytical Chemistry

## Chapter 10 Effect of Electrolytes on Chemical Equilibria

## Homework

- 7, 8, 10-12, 14
- Test 1 will be given when we finish Chapter 10!

## Equilibrium

- For the reaction  $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$
- What is the effect when adding
  - $\text{AgNO}_3$
  - $\text{NaCl}$
  - $\text{NaNO}_3$

## Concentration Equilibrium Constant

- It can be shown that the equilibrium constant (as we know it) is a limiting value
  - Minimum value for the system
  - Value will increase as the number and/or charge of ions in solution increases
  - Up to about 0.1M effect is independent of the type of ion
    - Above this value we get ion-specific variations
- Define  $K' = [\text{Ag}^+][\text{Cl}^-]$ 
  - Note that  $K'$  changes with the ionic strength of the solution

## Ionic Strength

- Solution parameter
- Accounts for both concentration and charge of ions in solution
  - $$\mu = \frac{1}{2} \sum C_i Z_i^2$$
- Allows us to predict the effect on individual ions IF  $\mu$  is less than about 0.1

## Ionic Strength

- Note that for a solution consisting of only singly-charged ions, the ionic strength will equal the concentration of the salt(s)
  - For solutions with higher charged ions, the ionic strength will always be greater than the concentration of the salts!
- The ionic strength has no effect on uncharged species

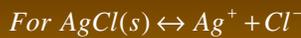
## Activity Coefficient

- Effective concentration of ions
  - Applies to individual ions in solution
  - Maximum value will be the equilibrium concentration of the ion
  - Decrease from there as a function of
    - It's charge
    - It's 'hydrated radius'
    - The ionic strength of the solution
- Activity
  - $a_x = [X]\gamma_x$ 
    - $\gamma_x$  = activity coefficient

## Activity Coefficient

- Maximum value = 1
  - Only when  $\mu = 0$ 
    - Essentially = 1 when  $\mu < 10^{-5}$
- Redefine K
  - For dissociation of AgCl,  $K = a_{Ag}a_{Cl}$ 
    - Substitute activities for concentrations
    - Thermodynamic equilibrium constant
      - Tabulated values are K, not K'
      - NOT a function of ionic strength
    - K' = concentration equilibrium constant

## Relationship of K and K'



$$K = a_{Ag^+} a_{Cl^-}$$

$$K = [Ag^+]\gamma_{Ag^+} \cdot [Cl^-]\gamma_{Cl^-}$$

$$\frac{K}{\gamma_{Ag^+} \gamma_{Cl^-}} = [Ag^+][Cl^-]$$

But  $[Ag^+][Cl^-] = K'$

$$\therefore K' = \frac{K}{\gamma_{Ag^+} \gamma_{Cl^-}}$$

## Calculating $\gamma$

- Debye-Huckel equation

$$\log \gamma_x = -\frac{0.51 Z_x^2 \sqrt{\mu}}{1 + 3.3 \alpha_x \sqrt{\mu}}$$

- $\gamma_x$  = activity coefficient of X
- $Z_x$  = charge on X
- $\mu$  = ionic strength of the solution
- $\alpha_x$  = diameter of hydrated ion in nm
- 0.51, 3.3 function of water at 25°C

## Table 10-2

- Hydrated radii of ions
- Also contains calculated values for the activity coefficient for many ions at the indicated ionic strengths
  - If  $\mu$  is equal to or close to one of the tabulated values, then you can look up  $\gamma$  rather than calculate it!!!

## Problems

- We are interested in the concentration of species, not the activity
- Equilibrium data provided is for activities, not concentrations
- MUST be able to relate the two