

# Physical Chemistry

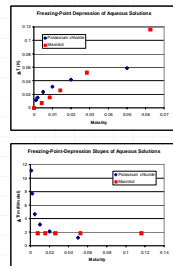
## Lecture 36 Ionic Solutions

### Ionic versus nonionic solutions

- ◆ Ionic materials dissociate (at least partially) in solution
- ◆ Ionic solutions conduct electricity relatively well
- ◆ Colligative properties of ionic solutions differ greatly from predictions based on the molality
- ◆ Strong electric interactions between solvent and solutes
- ◆ Nonionic materials remain molecular in solution
- ◆ Nonionic solutions do not conduct electricity very well
- ◆ Colligative properties (more or less) follow predictions based on molality
- ◆ Relatively weak interactions between solvent and solute

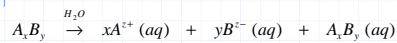
### Colligative properties

- ◆ Behaviors of ionic and nonionic solutions are different
- ◆ Example: Freezing-point depression of aqueous solutions
  - Slope should be close to the same for all molalities by the simple theory
  - Almost true for mannitol
  - Not true for KCl
- ◆ Similar examples for other materials



### Van't Hoff factors

- ◆ van't Hoff indicated that the important factor is the total number of particles in solution, whether molecular or the result of dissociation
- ◆ "Molality" from colligative properties should be based on number of particles
- ◆ Works for some solutions, but not others

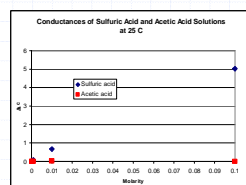


$$\text{Effective molality} = m(1-\alpha) + \nu m\alpha = (1+(\nu-1)\alpha)m = im$$

$$\Delta_f T = i K_f m$$

### Electrolytes and conduction

- ◆ Materials that dissociate in solution
- ◆ Two types
  - Strong electrolytes always totally dissociated in solution
  - Weak electrolytes only partially dissociated in solution
- ◆ Reflected in conductances of solutions



### Activities of strong electrolytes

- ◆ Totally ionized in solution
- ◆ Ionic free energies have contributions from strong electrical interactions
  - Makes activities very different from concentrations
- ◆ Activity reflects free energy

$$\mu_i = \mu_i^\theta(T) + RT \ln a_i$$

- ◆ Solution free energy is a sum over all species
- $$\begin{aligned} \mu &= \nu_+ \mu_+^\theta(T) + \nu_- \mu_-^\theta + RT(\nu_+ \ln a_+ + \nu_- \ln a_-) \\ &= \mu^\theta(T) + RT \ln a_+^\nu a_-^\nu = \mu^\theta(T) + RT \ln a \end{aligned}$$

## Activities in ionic solutions

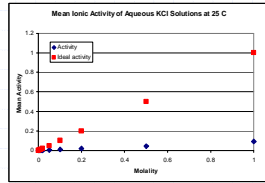
- Cannot measure activities of anions and cations independently

- Total activity  

$$a = a_+^{\nu_+} a_-^{\nu_-} = a_{\pm}^{\nu}$$

- Determine the mean activity,  $a_{\pm}$ , per ion from the total activity

$$a_{\pm} = \sqrt[\nu]{a}$$



## Example of ionic-activity calculation for CdCl<sub>2</sub>

- A solution of the strong electrolyte CdCl<sub>2</sub> at  $m$
- Molality of each species

$$\text{Cd}^{2+} : m_+ = m$$

$$\text{Cl}^- : m_- = 2m$$

- Activity in terms of the mean activity coefficient,  $\gamma_{\pm}$

$$a = a_{\text{Cd}} a_{\text{Cl}}^2 = (\gamma_{\pm} m_{\pm})^3 = 4\gamma_{\pm}^3 m^3$$

$$a = a_{\pm}^3$$

$$a_{\pm} = \sqrt[3]{4}\gamma_{\pm} m$$

- Note the effect on the chemical potential

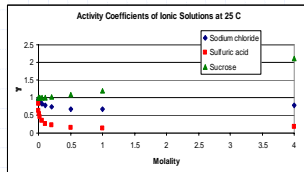
$$\mu = \mu^{\circ}(T) + RT \ln a = \mu^{\circ}(T) + RT \ln a_{\pm}^3$$

$$= \mu^{\circ}(T) + RT \ln 4m^3 + 3RT \ln \gamma_{\pm}$$

$$= \mu_{\text{ideal}}(T) + 3RT \ln \gamma_{\pm}$$

## Activity coefficients of ionic species

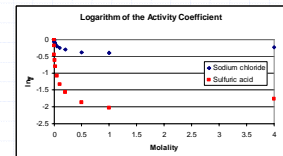
- Ionic activity coefficients may be far from 1, even at low concentrations
  - Nonideal behavior
- Reflects substantial extra free energy of solution compared to an ideal solution



## Activity coefficients and practical osmotic coefficients

- Activity coefficients and practical osmotic coefficients express the same solution quality in different ways
- Often see plots of logarithm of the activity coefficient

$$\ln \gamma_{\pm} = \phi(m) - 1 + \int_0^m \frac{\phi(m')}{m'} dm'$$

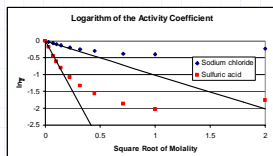


## Debye-Hueckel theory of activity coefficients

- Electrostatic theory
- Point-charge ions
- Coulombic interactions
- Solvent continuous dielectric material
- Ions approach only to a certain distance,  $a_0$
- DHG limiting law:  $Ba_0 \approx 1$
- Ionic strength,  $I$
- $\alpha = 1.177$  for aqueous solutions at 25 C
  - Slight temperature dependence

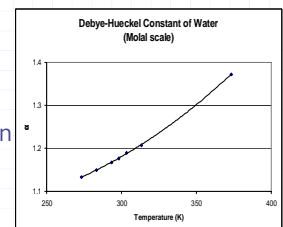
$$\ln \gamma_{\pm} = - \alpha |z_+ z_-| \frac{\sqrt{I}}{1 + Ba_0 \sqrt{I}}$$

$$I = \frac{1}{2} \sum_i m_i z_i^2$$



## Temperature dependence of Debye-Hueckel constant

- $\alpha$  is a function of
  - Temperature
  - Dielectric constant
  - Density
- Can be calculated, in principle
- Will be different for different solvents



## Summary

- ◆ Ionic solutions very different from molecular solutions
  - Strong electrolytes decompose totally upon dissolution
  - Weak electrolytes only decompose partially
- ◆ Activities dominated by strong interactions in solution
- ◆ "Correction" for nonideality often large
- ◆ Activity coefficients not near 1, except for extremely dilute solutions
- ◆ Can characterize the solution process in terms of activity coefficients or practical osmotic coefficients or chemical potentials
- ◆ Debye-Hueckel theory explains behavior at low concentrations