

# Ions in Solution

## CHEM 361A: Introduction to Physical Chemistry

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### Lecture 12

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Learning Objective: Quantify the activity coefficient for ionic solutions and apply it to sparingly soluble salts.

References:

- Atkins and de Paula Focus 5G and 5H
- Chang §8.4 and §8.5

# $\mu$ for an Electrolyte in Solution

Electrolyte solutions (molecules that break down into charged ions in solution) deviate from ideal conditions at low concentrations.

- Coulombic forces between ions cause long range interactions

For real solutions we write activities as

$$a_J = \gamma_J \frac{m_J}{m^\ominus}$$

where

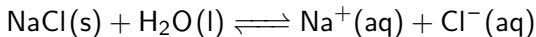
- $m^\ominus$  is  $1 \text{ mol kg}^{-1}$  (molality is temperature independent)
- $\gamma_J$  is the **activity coefficient**. It quantifies the degree to which the solute is non-ideal.
  - As  $m_J \rightarrow 0$  then  $\gamma_J \rightarrow 1$

Having defined the activity of the solute, we can write

$$\mu_J = \mu_J^\ominus + RT \ln a_J$$

# Determining the Activity Coefficient $\gamma_J$

Consider the dissociation of table salt in water



The activities for this process are

$$a_{\text{Na}^+} = \gamma_+ \frac{m_{\text{Na}^+}}{m^\ominus}$$
$$a_{\text{Cl}^-} = \gamma_- \frac{m_{\text{Cl}^-}}{m^\ominus}$$

However, no procedure currently exists to measure  $\gamma_J$  since separating the effect of the cation from the anion is not possible.

- They both occur simultaneously and are not easily separated

# Determining the Average Activity Coefficient $\gamma_{\pm}$

Consider a salt  $M_{\nu_+}X_{\nu_-}$ , where M forms the positive ion and X forms the negative ion. The Gibbs Free Energy for the salt is

$$G = n_+\mu_+ + n_-\mu_-$$

Using the definition of the chemical potential for non-ideal dilute solutions

$$\mu_J = \mu_J^{\ominus} + RT \ln a_J; \quad a_J = \gamma_J \frac{m_J}{m^{\ominus}}$$

It can be shown that an **average activity coefficient**,  $\gamma_{\pm}$ , can be defined as:

$$\gamma_{\pm}^{\nu_+ + \nu_-} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$$

such that

$$G = n_+ \left( \mu_+^{\ominus} + RT \ln \left( \gamma_{\pm} \frac{m_+}{m^{\ominus}} \right) \right) + n_- \left( \mu_-^{\ominus} + RT \ln \left( \gamma_{\pm} \frac{m_-}{m^{\ominus}} \right) \right)$$

# Average Activity Coefficient Example

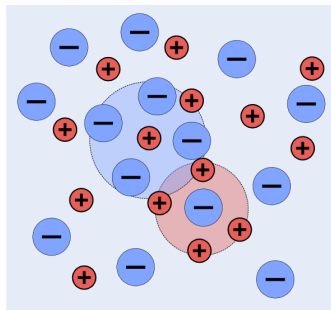
Suppose we were able to measure the activity coefficients for  $\text{Na}^+$  (0.98) and  $\text{SO}_4^{2-}$  (0.84) when  $\text{Na}_2\text{SO}_4$  is dissolved in water to form a  $0.01 \text{ mol kg}^{-1}$  solution. Determine

- 1 the average activity coefficient,  $\gamma_{\pm}$
- 2 the activities of each ion,  $a_{\text{Na}^+}$  and  $a_{\text{SO}_4^{2-}}$ , using  $\gamma_{\pm}$

# Debye-Hückel Limiting Law

Peter Debye and Erich Hückel developed a theory to determine the average activity coefficient

- Assumed that each charge was surrounded by a cloud of opposite charge
- This lowers the potential energy of the system
- Quantified as  $\gamma_{\pm} < 1$
- Law becomes more valid as the concentration of the ions approaches zero
- When the concentration of ions in solution are large, then empirical modifications should be employed



# Debye-Hückel Limiting Law (cont.)

The Debye-Hückel Limiting Law is

$$\log \gamma_{\pm} = -A |z_+ z_-| I^{\frac{1}{2}}$$

where

- A is a constant (for water at 25°C, A = 0.509)
- $z_{\pm}$  is the charge of the positive/negative ion
- I is the ionic strength of the solution and is defined in terms of the molalities of *all ions* in the solution

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



# Using the Debye-Hückel Limiting Law

Estimate the mean activity coefficient for the ions of a  $0.0010 \text{ mol kg}^{-1}$  solution of  $\text{Na}_2\text{SO}_4(\text{aq})$  at  $25^\circ\text{C}$ .

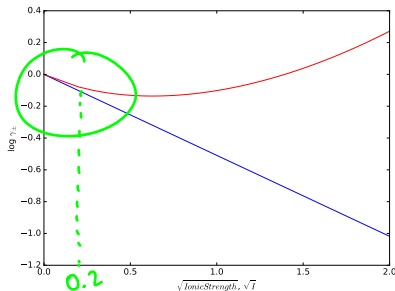
# Extended Debye-Hückel Law

- The **Debye-Hückel Limiting Law** is only for dilute solutions (low  $I$ ).

$$\log \gamma_{\pm} = -A |z_+ z_-| I^{\frac{1}{2}}$$

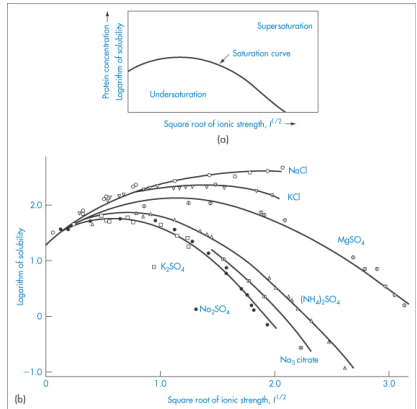
- The **Davies Equation** is an empirical correction to fit the data better at high  $I$

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| \left( \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.3I \right)$$



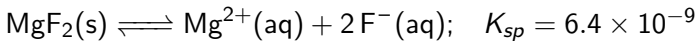
# Varying the Solubility of an Ionic Solution

The ionic strength of a solution can directly affect the solubility of a substance. This is called salting-in and salting-out.



# Springly Soluble Compounds Example

A sparingly soluble compound is something that dissolves only slightly in water. Take for example:



- 1 If enough  $\text{MgF}_2(\text{s})$  is used to saturate a solution of 1 kg of water determine the equilibrium concentration of the ions.
- 2 At equilibrium, 0.01 M  $\text{KNO}_3$  (a very soluble salt) is added to the  $\text{MgF}_2$  solution. What is the new concentration of the dissolved  $\text{MgF}_2$ ?
- 3 At equilibrium, 2.0 M  $\text{KNO}_3$  (a very soluble salt) is instead added to the  $\text{MgF}_2$  solution. What is the new concentration of the dissolved  $\text{MgF}_2$ ?

# Summary

- Ions in solution deviate properties of mixtures from ideal conditions
- The deviation is quantified in the average activity coefficient which can be calculated using
  - The Debye-Hückel Limiting Law (low ionic strength)

$$\log \gamma_{\pm} = -A |z_+ z_-| I^{\frac{1}{2}}$$

- The Davies Equation (high ionic strength -  $\sqrt{I} > 0.2$ )

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| \left( \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.3I \right)$$