

CHE2615
BASIC PHYSICAL CHEMISTRY
PART 3
CHEMICAL EQUILIBRUM

Outline

1. Standard reference states, Activities of solutions and Activity Coefficients
2. Activity of strong and weak electrolytes
3. Ionic strength and the Debye-Huckel limiting law
4. Equilibrium Expression from the Fundamental thermodynamic equation
5. Chemical equilibrium, Acid-base equilibrium and pH
6. Electrochemistry
7. Electrical Conductance of electrolytes
8. Galvanic and Electrolytic cells
9. Activity, mean activity coefficients, thermodynamic functions

Standard reference states

- All thermodynamic measurements are of differences between states
- There is no absolute value for any property (exception: entropy does have an absolute measure from theory, but it's the only one).
- In order to quantify thermodynamics, we choose by convention a reference state.
- Most common choice is the "Standard Ambient Temperature and Pressure (SATP)".

Temp: 298K (25 ° C)

Press: 1 bar (10^5 Pa)

Conc: 1 molal (mol of solute/kg of solvent)

- Atmosphere is a widely used unit of pressure.
- 1 atm = 1.0134 bar

Reference State for Pressure is usually 1 atm

- Molality is better than molarity
- Solvent density is T dependent
- Volume changes with T

But...

Reference states are indicated by superscript $^{\circ}$
 C° or P°

- Volume is easier to measure than mass
- Density of water (the most common solvent) is close to 1
- **The most commonly used reference state is that of 1.0 M (mol/liter)**

Activity

- Measure of a species' **effective** concentration as determined by colligative properties.
- How **active** is this substance in this reaction compared to how it would behave if it were present in its standard state?
- Activity scales with concentration or partial pressure.

$$a \propto C/C^\circ \quad \text{OR} \quad a \propto P/P^\circ$$

BUT...

- Intermolecular interactions
- Deviations from a direct correspondence with pressure or concentration

Activity coefficients

- Definition of activity

$$a = \gamma \frac{C}{C^\circ}$$

$$a = \gamma \frac{P}{P^\circ}$$

- Activity coefficients is close to 1 for dilute solutions and low partial pressures.
- It changes with concentration, temperature, other species, etc. Can be very complex.
- Generally, we ignore activity coefficients for educational simplicity, but careful work requires its consideration.

Approximate Activity

- Activity is unit less
- Activity coefficient is complex over wide ranges of conditions
- Since
 - ✓ activity coefficients are close to 1 for dilute solutions
 - ✓ reference states for partial pressure and concentration have numerical value of 1
- Therefore, we often approximate activity by concentration (M) or partial pressure (atm).

Solids, solvents and liquids

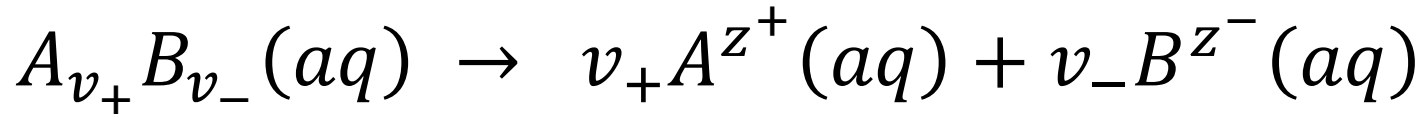
- SOLID: reference is itself
- PURE LIQUID: reference is itself
- SOLVENT: reference is itself

$a = 1$ for all of these materials

- Increase amount of these: reaction goes longer, but not faster.

Activity of strong electrolytes

- Consider a strong electrolyte $A_{\nu_+}B_{\nu_-}$.
- The dissociation equation is thus given as:



- The activity of the electrolyte $A_{\nu_+}B_{\nu_-}$ is given by

$$a_{A_{\nu_+}B_{\nu_-}(aq)} = (\nu_+ a_{A^{z^+}})^{\nu_+} (\nu_- a_{B^{z^-}})^{\nu_-}$$

$$a_i = \gamma_i \frac{c_i}{c^0} : \quad \text{but, } c^0 = 1 \frac{\text{mol}}{L} : \quad \text{hence, } a_i = \gamma_i c_i$$

$$\begin{aligned}
a_{A\nu_+ B\nu_- (aq)} &= (\nu_+ a_{A^{z+}})^{\nu_+} (\nu_- a_{B^{z-}})^{\nu_-} \\
&= (\nu_+ c \gamma_+)^{\nu_+} (\nu_- c \gamma_-)^{\nu_-} \\
&= \nu_+^{\nu_+} \nu_-^{\nu_-} c^{\nu_+} c^{\nu_-} \gamma_+^{\nu_+} \gamma_-^{\nu_-} \\
&= \nu_{\pm}^{\nu_{\pm}} c^{\nu_{\pm}} \gamma_{\pm}^{\nu_{\pm}}
\end{aligned}$$

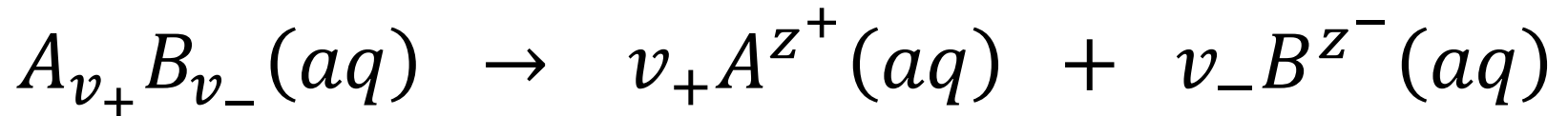
where

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

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

γ_{\pm} = mean ionic activity coefficient

In general



c

$\nu_+ c$

$\nu_- c$

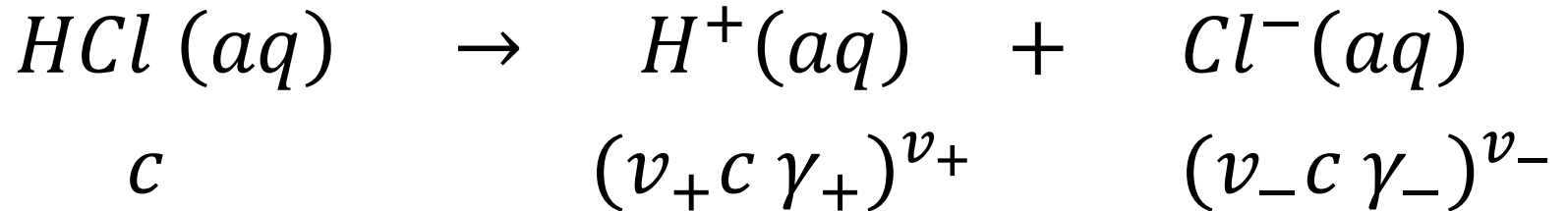
$$a_{A_{\nu_+} B_{\nu_-} (aq)} = (\nu_+ c \gamma_+)^{\nu_+} (\nu_- c \gamma_-)^{\nu_-}$$

ν_+ = no. of cations

ν_- = no. of anions

Example

- For a 1:1 electrolyte (e.g. HCl)

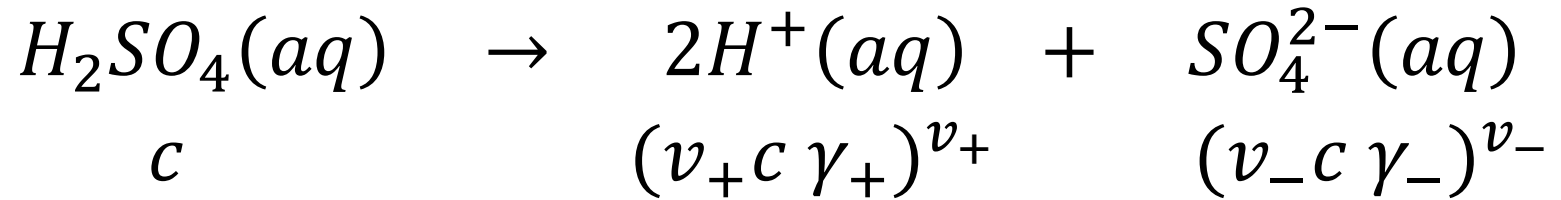


$$a_{HCl(aq)} = v_+^{v_+} v_-^{v_-} c^{v_+ + v_-} \gamma_{\pm}^{v_+ + v_-}$$

- For HCl $v_+ = 1$ and $v_- = 1$

$$\begin{aligned} a_{HCl(aq)} &= 1^1 1^1 c^{1+1} \gamma_{\pm}^{1+1} \\ &= c^2 \gamma_{\pm}^2 \end{aligned}$$

- For a 2:1 or 1:2 electrolyte (e.g. H_2SO_4 or $CuCl_2$)



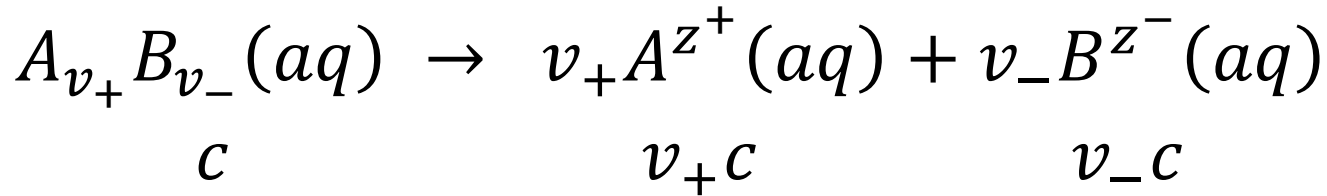
$$a_{H_2SO_4}(aq) = v_+^{v_+} v_-^{v_-} c^{v_{\pm}} \gamma_{\pm}^{v_{\pm}}$$

- For H_2SO_4 $v_+ = 2$ and $v_- = 1$

$$\begin{aligned}
 a_{HCl}(aq) &= 2^2 1^1 c^{2+1} \gamma_{\pm}^{2+1} \\
 &= 4c^3 \gamma_{\pm}^3
 \end{aligned}$$

Ionic strength

- G.N. Lewis defined ionic strength (I) of electrolytes in a solution as



$$I = \frac{1}{2} \sum_{i=1}^n v_i c_i z_i^2$$

$$I = \frac{1}{2} [v_{1+} c z_{1+}^2 + v_{1-} c z_{1-}^2 \dots v_{n+} c z_{n+}^2 + v_{n-} c z_{n-}^2]$$

z_+ = charge on cations: z_- = charge on anions

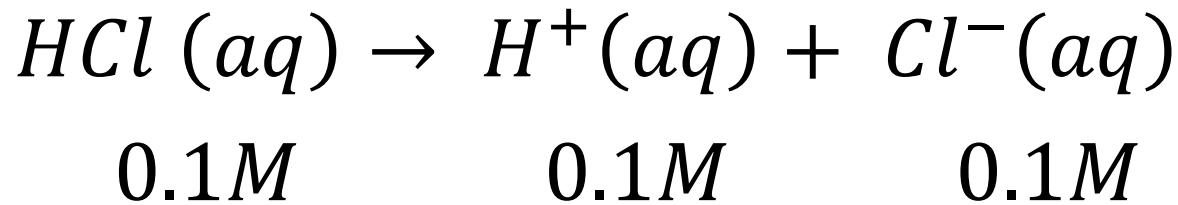
$$\text{units of } I = \frac{\text{mol}}{L}$$

For a 1:1 electrolyte

- Refer both to coefficients and charges

Example:

calculate the ionic strength of a 0.1M HCl.



$$c = 0.1 M$$

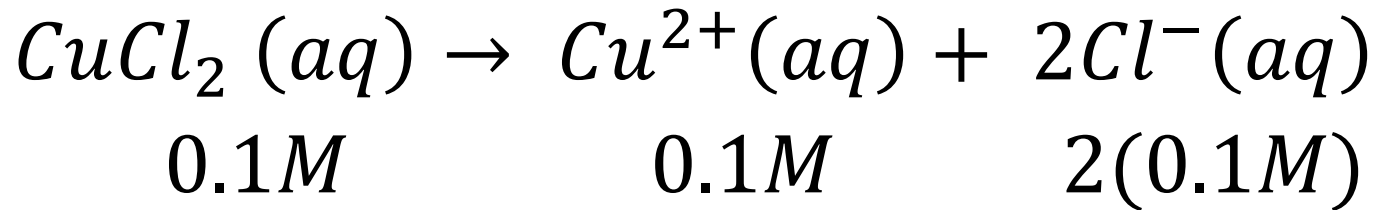
$$I = \frac{1}{2} [0.1(1)^2 + 0.1(-1)^2] = 0.1 M$$

$$i. e., \quad I = c$$

For a 2:1 or 1:2 electrolyte

Example:

calculate the ionic strength of a 0.1M H_2SO_4 or $CuCl_2$.



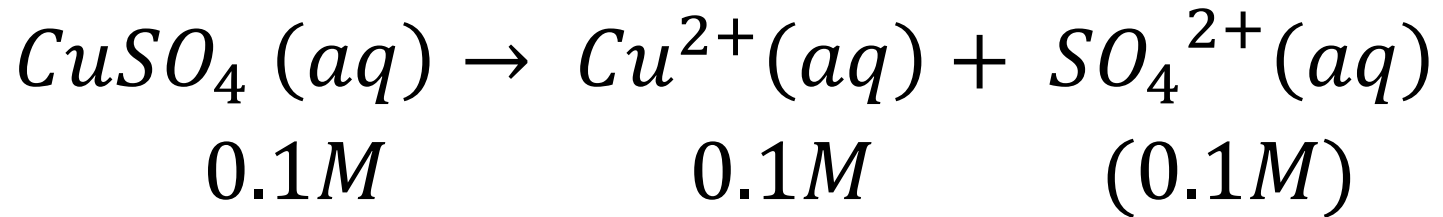
$$I = \frac{1}{2} [0.1(2)^2 + 0.2(-1)^2] = 0.3 M$$

$$i. e., \quad I = 3c$$

For a 1:1 but a 2:2 in charge electrolyte

Example:

calculate the ionic strength of a 0.1M
MgSO₄ or CuSO₄.



$$I = \frac{1}{2} [0.1(2)^2 + 0.1(-2)^2] = 0.4 M$$

$$i.e., \quad I = 4c$$

Debye-Hückel limiting law(D-HLL)

- This law determines the mean activity coefficient by considering the Coulombic electrostatic and repulsion interaction of the ions in solution
- This is a theory for the activity coefficients of dilute electrolyte solutes.
- Ions exert large forces on each other, and these forces are called **long-range forces** because they act over large distances compared with other intermolecular forces.
- Oppositely charged ions attract one another.

- The electrostatic force on a charge Q_1 due to a charge Q_2 is given by Coulomb's law,
- r_{12} is the distance between the charges
- ϵ is the permittivity of the medium between the charges
- As a result, anions are more likely to be found near cations in solution, and vice versa
- Overall, the solution is electrically neutral, but near any given ion there is an excess of counter ions (ions of opposite charge)

$$\mathbf{F}_{12} = \mathbf{e}_r \frac{Q_1 Q_2}{4\pi\epsilon r_{12}^2}$$

- The model leads to the result that at very low concentrations the activity coefficient can be calculated from the Debye–Hückel limiting law
- D-HLL is valid at low concentration less than 0.01 M

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

$$A = 0.509 (\text{L mol}^{-1})^{1/2}$$

at 298.15 K

$$\log \gamma_{\pm} = - 0.509 |z_+ z_-| \sqrt{I}$$

Extended Debye-Hückel Law

- Applicable for concentrations $>0.01\text{M}$

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