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

Reference states are indicated by superscript °

C° or P°

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

But…

- 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

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

- 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 $A_{v_+}B_{v_-}$.
- The dissociation equation is thus given as:

$$A_{v_+}B_{v_-}(aq) \rightarrow v_+A^{z^+}(aq) + v_-B^{z^-}(aq)$$

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

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

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

$$a_{A_{v_+}B_{v_-}\,(aq)} \underset{-}{=} (v_+ a_{A^{z+}})^{v_+} (v_- a_{B^{z-}})^{v}$$

$$= (v_+ c\, \gamma_+)^{v_+} (v_- c\, \gamma_-)^{v_-}$$

$$= v_+^{v_+} v_-^{v_-} c^{v_+} c^{v_-} \gamma_+^{v_+}\ \gamma_-^{v_-}$$

$$= v_\pm^{v_\pm} c^{v_\pm} \gamma_\pm^{v_\pm}$$

where

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

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

$$\gamma_\pm = mean\ ionic\ activity\ coefficient$$

In general

$$A_{v_+}B_{v_-}(aq) \quad \rightarrow \quad v_+A^{z^+}(aq) \quad + \quad v_-B^{z^-}(aq)$$

$$c \qquad\qquad\qquad v_+c \qquad\qquad\qquad v_-c$$

$$a_{A_{v_+}B_{v_-}(aq)} \quad = \quad (v_+c\,\gamma_+)^{v_+} \qquad (v_-c\,\gamma_-)^{v_-}$$

$$v_+ = \text{no. of cations}$$
$$v_- = \text{no. of anions}$$

Example

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

$$HCl\,(aq) \quad \rightarrow \quad H^{+}(aq) \quad + \quad Cl^{-}(aq)(v$$

$$c \qquad\qquad (v_{+}c\,\gamma_{+})^{v_{+}} \qquad {}_{-}c\,\gamma_{-})^{v_{-}}$$

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

- For HCl v_{+} = 1 and v_{-}= 1

$$a_{HCl\,(aq)} = 1^{1}1^{1}c^{1+1}\gamma_{\pm}^{1+1}$$

$$= c^{2}\gamma_{\pm}^{2}$$

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

$$\begin{array}{ccccc} H_2SO_4(aq) & \rightarrow & 2H^+(aq) & + & SO_4^{2-}(aq) \\ c & & (v_+c\,\gamma_+)^{v+} & & (v_-c\,\gamma_-)^{v-} \end{array}$$

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

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

$$a_{HCl\,(aq)} = 2^2 1^1 c^{2+1} \gamma_\pm^{2+1}$$

$$= 4c^3\gamma_\pm^3$$

Ionic strength

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

$$A_{v_+}B_{v_-}(aq) \rightarrow v_+A^{z^+}(aq) + v_-B^{z^-}(aq)$$

$$c \qquad\qquad\qquad v_+c \qquad\qquad\qquad v_-c$$

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

$$I = \frac{1}{2}[v_{1+}cz_{1+}^2 + v_{1-}cz_{1-}^2 \ldots v_{n+}cz_{n+}^2 + v_{n-}cz_{n-}^2]$$

$$z_+ = charge\ on\ cations\text{:}\ \ z_- = charge\ on\ anions$$

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

For a 1:1 electrolyte

- Refer both to coefficients and charges

Example:

calculate the ionic strength of a 0.1M HCl.

$$HCl\ (aq) \rightarrow\ H^{+}(aq) +\ Cl^{-}(aq)$$

$$0.1M \qquad\qquad 0.1M \qquad\qquad 0.1M$$

$$c = 0.1\ M$$

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

$$i.e., \qquad I = \mathrm{c}$$

For a 2:1 or 1:2 electrolyte

Example:

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

$$\begin{array}{ccccc} CuCl_2\,(aq) & \rightarrow & Cu^{2+}(aq) & + & 2Cl^-(aq) \\ 0.1M & & 0.1M & & 2(0.1M) \end{array}$$

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

$$i.e., \qquad I = 3\mathrm{c}$$

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

Example:

calculate the ionic strength of a 0.1M $\mathrm{MgSO_4}$ or $\mathrm{CuSO_4}$.

$$CuSO_4\ (aq) \rightarrow\ Cu^{2+}(aq) + SO_4{}^{2+}(aq)$$

$$0.1M \qquad\qquad 0.1M \qquad\qquad (0.1M)$$

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

$$i.e., \qquad I = 4\mathrm{c}$$

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,

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

- 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)

- 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

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

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

$$\text{at } 298.15\mathrm{K}$$

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

Extended Debye-Hückel Law

- Applicable for concentrations >0.01M

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