

Basic Chemistry Concepts I

Today's lecture

- Chemistry – basics of the basics
- Chemical reactions
- Equilibrium chemistry
- Reaction kinetics
- Concentration units in water
- Carbonate system

Mole & molarity

- Mole = Avogadro's number (6.02×10^{23}) of molecules
- Molarity (M) = number of moles per liter of solution (mole/L)
cf) molality (m) = number of moles per kg of solvent

Activity

- Related to chemical potential of a substance or a component in a mixture
 - * chemical potential determines the tendency for a reaction to occur
- Represented by $\{ \}$ (cf. molarity by $[]$)

Activity

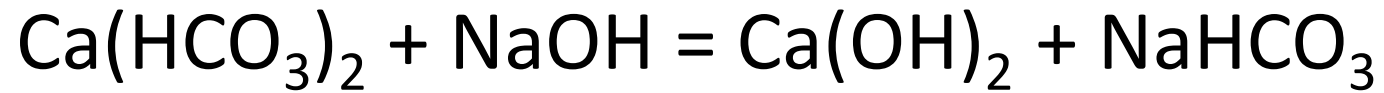
- In dilute aqueous solutions, the ions do not significantly interact with one another:

$$\{i\} \approx [i]$$

- As concentration increases, the ion-ion interaction becomes more significant:

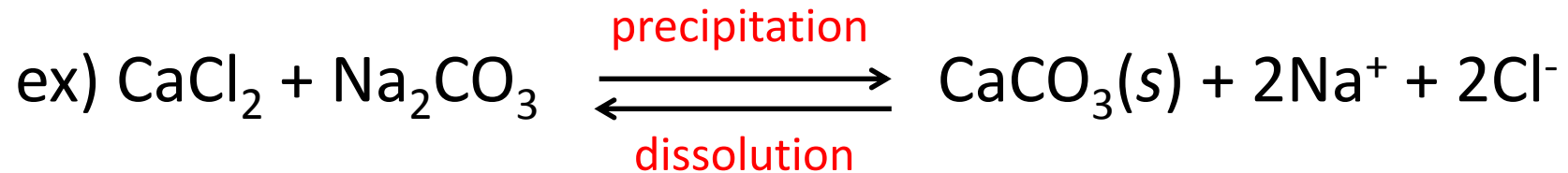
$$\{i\} = \gamma_i \cdot [i] \quad \text{where } \gamma_i = \text{activity coefficient}$$

Balancing chemical reactions



Types of chemical reactions

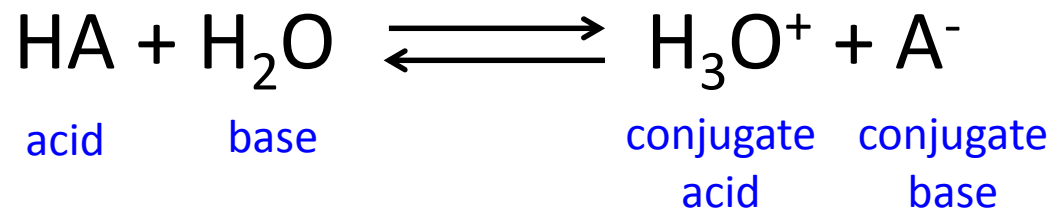
- Precipitation-dissolution reactions



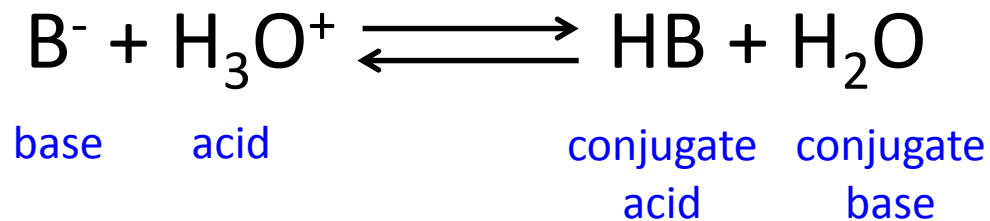
Usage: softening, phosphorous removal, heavy metal removal

Acid-base reactions

- Brønsted-Lowry acid: any substance that can donate a proton (i.e., proton donor)

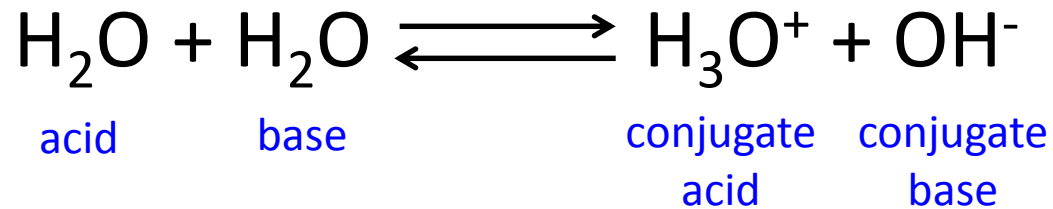


- Brønsted-Lowry base: any substance that can accept a proton (i.e., proton acceptor)



Acid-base reactions

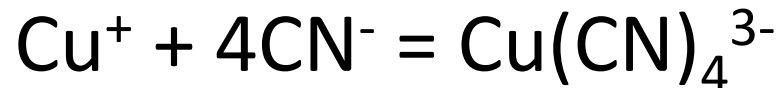
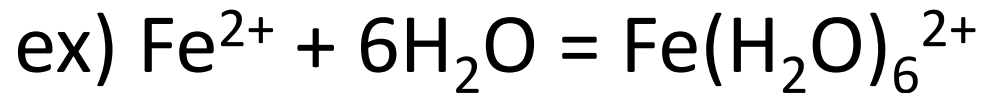
- Water is amphoteric – can be either an acid or a base



- $\text{pH} = -\log\{\text{H}^+\}$ (“p” denotes “-log”)

Complexation reactions

- Coordination of two or more atoms, molecules, or ions resulting in the formation of a more stable product



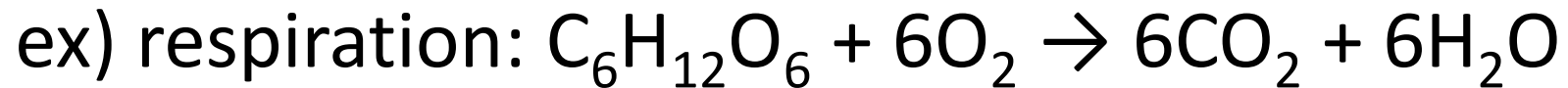
- Complex ion = a metal ion with Lewis bases (electron pair donor)
- Ligand = Lewis bases attached to a metal ion

Complexation reactions

- Many metal ions exist as complex ions in water (metal aquo complex)
ex) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$,
 $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
- Environmental significance: complexation of metals affects the uptake, biodegradability, toxicity, and mobility of the metal

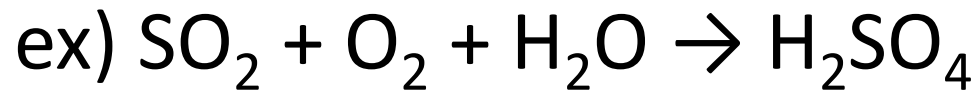
Oxidation-reduction (redox) reactions

- Involves changes in the oxidation state
- Essential for life: photosynthesis and respiration are redox reactions!



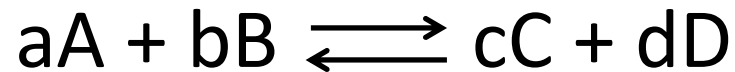
Oxidation-reduction (redox) reactions

- Balancing redox reactions
 - 1) list all elements
 - 2) identify number of e⁻ transferred
 - 3) balance electrons
 - 4) check atom balance



Chemical equilibrium

- For a reversible reaction



at chemical equilibrium,

$$\text{rate}(\text{forward rxn}) = \text{rate}(\text{reverse rxn})$$

- Equilibrium constant, K

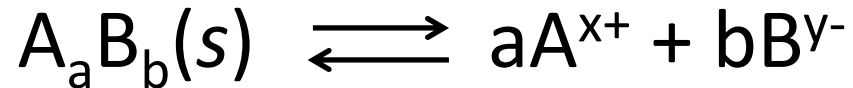
$$K = \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b}$$

For pure solid, activity = 1

For gases, activity = partial pressure

Chemical equilibrium: solubility

- For a precipitation-dissolution reaction



$$K = \frac{\{A^{x+}\}^a \cdot \{B^{y-}\}^b}{\{A_a B_b\}}$$

as $\{A_a B_b\} = 1$ (pure solid), $K = \{A^{x+}\}^a \{B^{y-}\}^b$

- Solubility product, $K_s = \{A^{x+}\}^a \{B^{y-}\}^b$

Ionic strength

- Recall that $\{i\} = \gamma[i]$:

$$K_s = \{A^{x+}\}^a \{B^{y-}\}^b = (\gamma_A [A^{x+}])^a \cdot (\gamma_B [B^{y-}])^b$$

- Ionic strength, I : measure of interaction among ions in a solution

$$I = \frac{1}{2} \sum C_i z_i^2$$

C_i = molarity of the i^{th} ion

z_i = charge of the i^{th} ion

Calculating activity coefficients

- Davies equation (for $I < 0.5$ M):

$$\log \gamma = -Az^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$$

$A \approx 0.5$ for water at 25°C

z = charge of the ion

Selected solubility products (@ 25°C)

Substance	Equilibrium Reaction	pK _s	Application
Aluminum hydroxide	$\text{Al(OH)}_3 (s) \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^-$	32.9	Coagulation
Aluminum phosphate	$\text{AlPO}_4 (s) \rightleftharpoons \text{Al}^{3+} + \text{PO}_4^{3-}$	22.0	Phosphate removal
Calcium carbonate (aragonite)	$\text{CaCO}_3 (s) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	8.34	Softening, corrosion control
Ferric hydroxide	$\text{Fe(OH)}_3 (s) \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^-$	38.57	Coagulation, iron removal
Ferric phosphate	$\text{FePO}_4 (s) \rightleftharpoons \text{Fe}^{3+} + \text{PO}_4^{3-}$	21.9	Phosphate removal
Magnesium hydroxide	$\text{Mg(OH)}_2 (s) \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$	11.25	Removal of calcium and magnesium
Dolomite (CaMg(CO ₃) ₂) (ordered)	$\text{CaMg(CO}_3)_2 \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$	17.09	Weathering of dolomitic minerals
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ \rightleftharpoons 2\text{Al}^{3+} + 2\text{Si(OH)}_4 + \text{H}_2\text{O}$	7.44	Weathering of kaolinite clays
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	4.58	Weathering of gypsum minerals

Selected solubility products (@ 25°C)

- Q: Added 30g of CaCO_3 in water of make 1.00 L solution containing 0.01 M NaCl. Assuming Ca^{2+} in solution is at equilibrium with $\text{CaCO}_3(s)$, what would be the Ca^{2+} concentration?
($T = 25^\circ\text{C}$, $\text{p}K_s$ for $\text{CaCO}_3 = 8.48$)

Caveat!

- The equilibrium/solubility product constants do not tell anything about the reaction rate!
- Differentiate equilibrium and kinetics

Reading assignment

- Textbook Ch2 p. 32-51