Basic Chemistry Concepts I

Basic chemistry concepts

- Chemistry – basics of the basics
- Chemical reactions
- Equilibrium chemistry

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

- Determines the tendency for a reaction to occur
- Represented by { } (cf. molarity by [ ])
- 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:

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

Balancing chemical reactions

$Ca(HCO_3)_2 + NaOH = Ca(OH)_2 + NaHCO_3$

Types of chemical reactions

- Precipitation-dissolution reactions

ex) $CaCl_2 + Na_2CO_3 \underset{\text{dissolution}}{\overset{\text{precipitation}}{\rightleftharpoons}} CaCO_3(s) + 2Na^+ + 2Cl^-$

Usage: softening, phosphorous removal, heavy metal removal

Acid-base reactions

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

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

acid base conjugate acid conjugate base

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

$$B^- + H_3O^+ \rightleftharpoons HB + H_2O$$

base acid conjugate acid conjugate base

cf) Lewis definition
Lewis acid: electron pair acceptor
Lewis base: electron pair donor

Water as both acid & base

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

$$H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$$

H_2O	H_2O	OH^-	H_3O^+
acid	base	conjugate base	conjugate acid

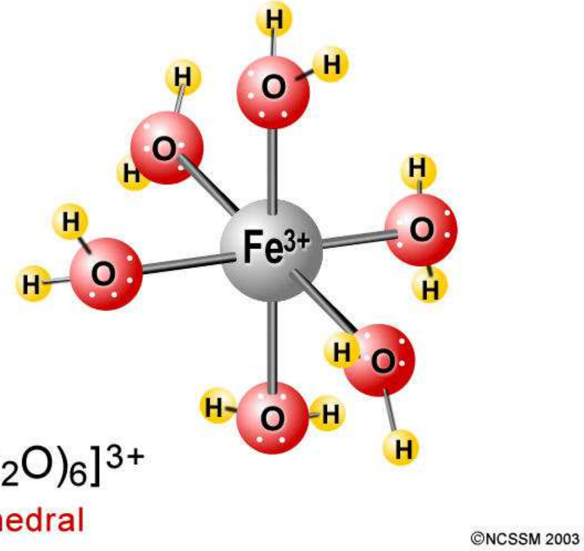
- pH = -log{H^+}   (“p” denotes “-log”)

Complexation reactions

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

ex) $Fe^{3+} + 6H_2O = Fe(H_2O)_6{}^{3+}$

$Cu^{+} + 4CN^{-} = Cu(CN)_4{}^{3-}$



$[Fe(H_2O)_6]^{3+}$

Octahedral

- Complex ion = a metal ion (Lewis acid) coordinated with ligands (Lewis bases)

Complexation reactions - implications

- Many metal ions exist as complex ions in water (metal aquo complex)

  ex) $[Cr(H_2O)_6]^{2+}$, $[Cr(H_2O)_6]^{3+}$, $[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[Co(H_2O)_6]^{2+}$, $[Cu(H_2O)_6]^{2+}$

- 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!

respiration using glucose:

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ ΔG_r^0=-2880 kJ/mol $C_6H_{12}O_6$

photosynthesis of glucose:

$6CO_2 + 6H_2O + \text{sunlight} \rightarrow C_6H_{12}O_6 + 6O_2$

ΔG_r^0=+2880 kJ/mol $C_6H_{12}O_6$

Balancing redox reactions

- Have to consider <u>electron balance</u> in addition to atom balance!

ex) $SO_2 + O_2 + H_2O \rightarrow H_2SO_4$

Chemical equilibrium

- For a reversible reaction

  aA + bB $\rightleftharpoons$ cC + dD

  at chemical equilibrium,

  rate(forward rxn) = rate(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

$A_aB_b(s) \rightleftharpoons aA^{x+} + bB^{y-}$

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

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

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

Ionic strength

- In most cases we want to know [ ] at equilibrium, not { }
- Recall {i} = γ_i[i]:

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

- γ_i<1 in concentrated solutions because of ion-ion interactions
- 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):

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

A ≈ 0.5 for water at 25˚C

z_i = charge of the ion

There are many approximations available, verified at different ranges of ionic strength. Let's use Davies equation for this class.

Selected solubility products (@ 25ºC)

Substance	Equilibrium Reaction	pK_s	Application
Aluminum hydroxide	$Al(OH)_3\,(s) \rightleftharpoons Al^{3+} + 3OH^-$	32.9	Coagulation
Aluminum phosphate	$AlPO_4\,(s) \rightleftharpoons Al^{3+} + PO_4^{3-}$	22.0	Phosphate removal
Calcium carbonate (aragonite)	$CaCO_3\,(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$	8.34	Softening, corrosion control
Ferric hydroxide	$Fe(OH)_3\,(s) \rightleftharpoons Fe^{3+} + 3OH^-$	38.57	Coagulation, iron removal
Ferric phosphate	$FePO_4\,(s) \rightleftharpoons Fe^{3+} + PO_4^{3-}$	21.9	Phosphate removal
Magnesium hydroxide	$Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+} + 2OH^-$	11.25	Removal of calcium and magnesium
Dolomite ($CaMg(CO_3)_2$) (ordered)	$CaMg(CO_3)_2 \rightleftharpoons Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	17.09	Weathering of dolomitic minerals
Kaolinite	$Al_2Si_2O_5(OH)_4 + 6H^+ \rightleftharpoons 2Al^{3+} + 2Si(OH)_4 + H_2O$	7.44	Weathering of kaolinite clays
Gypsum	$CaSO_4 \cdot 2H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O$	4.58	Weathering of gypsum minerals

Chemical equilibrium: solubility

Q: You added 30 g 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 $CaCO_3(s)$, what would be the Ca^{2+} concentration?

(T =25^{o}C, pK_s for $CaCO_3$ = 8.48)

Reading assignment

- Textbook Ch2 p. 32-51

Balancing chemical reactions

Slide#5 solution)

Basic rule: conservation of matter (atoms)

$aCa(HCO_3)_2 + bNaOH = cCa(OH)_2 + dNaHCO_3$

$Ca: a = c \quad (1)$

$Na: b = d \quad (2)$

$H: 2a + b = 2c + d \quad (3)$

$C: 2a = d \quad (4)$

$O: 6a + b = 2c + 3d \quad (5)$

Four unknowns → three equations needed (obtain the ratio of each)

e.g., use (1), (2) & (4): 2a = 2c = b = d (satisfies (3) & (5) as well)

→ $\mathbf{Ca(HCO_3)_2 + 2NaOH = Ca(OH)_2 + 2NaHCO_3}$

Balancing redox reactions

Slide#12 solution)

Basic rule: conservation of matter ***(atoms + electrons)***

$aSO_2 + bO_2 + cH_2O \rightarrow dH_2SO_4$

$S: a = d \quad (1)$

$O: 2a + 2b + c = 4d \quad (2)$

$H: 2c = 2d \quad (3)$

$e^-: (O_2\,[0] + 4e^- \rightarrow 2O^{2-}) \times b; \quad (S^{4+} \rightarrow S^{6+} + 2e^-) \times a$

$4b = 2a \quad (4)$

e.g., use (1), (2) & (4): $a = 2b = c = d$ *(satisfies (2) as well)*

$\rightarrow$ $\mathbf{2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4}$

Chemical equilibrium: solubility

Slide#18 solution)

i) Assume ionic strength is negligible (activity = molarity)

$[Ca^{2+}] = [CO_3^{2-}]$

$K_s = 10^{-8.48} = [Ca^{2+}][CO_3^{2-}] = [Ca^{2+}]^2$

$[Ca^{2+}] = 5.75 \times 10^{-5}$ M

ii) Without the assumption

Let's assume NaCl is a sole contributor of ionic strength

$$I = \frac{1}{2}[(0.01\ M)\cdot(1^2) + (0.01\ M)\cdot(1^2)] = 0.01\ M$$

$$log\gamma_{Ca} = log\gamma_{CO_3} = -0.5 \cdot 2^2 \left(\frac{\sqrt{0.01\ M}}{1+\sqrt{0.01\ M}} - 0.2 \cdot 0.01\ M\right) = -0.175$$

$$\gamma_{Ca} = \gamma_{CO_3} = 10^{-0.175} = 0.664$$

$$\gamma_{Ca}[Ca^{2+}] = 5.75 \times 10^{-5}\ M$$

$[Ca^{2+}] = 8.66 \times 10^{-5}$ M *(valid if within 5% error is accepted)*