CHEMICAL CONCEPTS

CE 370 – Lecture 3

Inorganic Chemistry

- Definitions
- Concentration Units
- Chemical Equilibria
- pH and Alkalinity

DEFINITIONS

- Atomic Weight: is the weight of an element when compared to Carbon (Carbon atomic weight is 12)
  - Atomic weight of Calcium (Ca) is equal to 40 g or (g/mole)
- Molecular weight of a compound (MW): is the sum of the atomic weights of the combined elements
  - For Calcium Carbonate ($CaCO_3$), MW = 40+12+3(16)=100 g/mole
- Valence: is the combining power of the element when compared to Hydrogen (Hydrogen has a combining power of 1)
  - For example Calcium (Ca^{+2}) has a valence of +2, Na^{+} has a valence of +1
- Equivalent Weight of an element = Atomic Weight / Valence
  - Equivalent weight of Ca^{+2} = 40 (g/mole) / 2 (eq/mole) = 20 (g/eq)

    or, Ca^{+2} = 40 g / 2 = 20 g

DEFINITIONS

- Equivalent weight of a compound: is that weight of the compound which contains 1 gram atom of available hydrogen or its chemical equivalent.
  - Equivalent weight = Molecular weight / Z,

    where Z is an number whose value depends on the chemical context (reaction). Usually, it is the number of available protons (H^+) or (OH^-).
  - For Acids: Z is equal to the moles of H^+ obtained from 1 mole of acid.

    for example Z=2 for H_2SO_4 (because this acid contains 2 moles of H^+)

    Its equivalent weight = (2×1 + 32 + 4×16) / 2 = 49 g or (g/eq)
  - For base: Z is equal to the number of moles of H^+ with which 1 mole of base will react. For $Ca(OH)_2$, Z = 2
  - For salts: Z is the oxidation or valence state of the ion.

    for $Al_2(SO_4)_3$, Z=6 because $2Al^{+3}$ is equivalent to 6 moles of H^+.

Concentration Units

- milligram per liter (mg/l)
  - Weight of solute per volume of solution
- part per million (ppm)
  - When the specific gravity is unity, 1 mg/l is equal to ppm.
- kilograms per million liters
  - Chemical doses are usually expressed in kilograms per million liters or pounds per million gallons.
- milliequivalents per liter (meq/l) = [(mg/l) / eq weight]
  - Example: the concentration $CaCO_3$ in a water sample is 76 mg/l. Express the concentration in meq/l.
  - Solution: eq. wt. of $CaCO_3$ = MW/Z = 100/2 = 50 eq
    conc. in (meq/l) = 76/50 = 1.52 meq/l

Concentration Units

- Expressing Hardness, Alkalinity, and others
  - Hardness and Alk are due to different ions, therefore, they are expressed in unit weights of $CaCO_3$ in order to facilitate for computations.
  - The following equation can be used to express concentration as $CaCO_3$:

$$\text{mg/l as CaCO}_3 = [\text{mg/l of substance}] \times \left[\frac{\text{eq. wt. CaCO}_3}{\text{eq. wt of substance}}\right]$$

  - Example: The concentration of $Ca(HCO_3)_2$ was found to be 60 mg/l. Express the concentration in unites as $CaCO_3$.
    Solution: eq. wt. of $Ca(HCO_3)_2$ = MW/Z = 162/2 = 81g.
    conc. as $CaCO_3$ = 60mg/l (50/81) = 37.0 mg/l as $CaCO_3$.

Hydrogen Ion Concentration

When pure water dissociates:

- $H_2O \Leftrightarrow H^+ + OH^-$
- concentration of H^+ ion is 10^{-7} mole per liter
- concentration of OH^- ion is 10^{-7} mole per liter
- Since H^+ concentration = OH^- concentration , the pure water is neutral

Acidic or Basic?

- $pH = \log (1/[H^+])$
  - [ ] means molar concentration (mole/l)
- When $[H^+]$ concentration is 10^{-7}, then pH =7, which represents the neutral state.
- If pH > 7, then it is basic
- If pH < 7, then it is acidic
- Water ionization is represented by:
  - $[H^+][OH^-] = K_w = 10^{-14}$ (K_w is the ionization constant)

    Example: If the concentration of H^+ in water is 10^{-2} mole/l, what is the concentration of OH^- and the pH of the water.

    Solution: $[OH^-] = K_w / [H^+] = 10^{-14} / 10^{-2} = 10^{-12}$

    $pH = \log (1/ 10^{-2}) = 2$

Chemical Equilibria

- $aA + bB \Leftrightarrow cC + dD$
  - A and B are the reactants
  - C and D are the products
  - Most reactions are reversible, an increase of A or B shift the reaction to the right and vice versa. The relationship may be expressed by the mass action equation:

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

  - [ ] = molar concentration and K=equilibrium constant

Chemical Equilibria

- In Water Chemistry, the carbonic acid-bicarbonate-carbonate system is very important.
  - The carbonic acid dissociate as the following:
    - $H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$

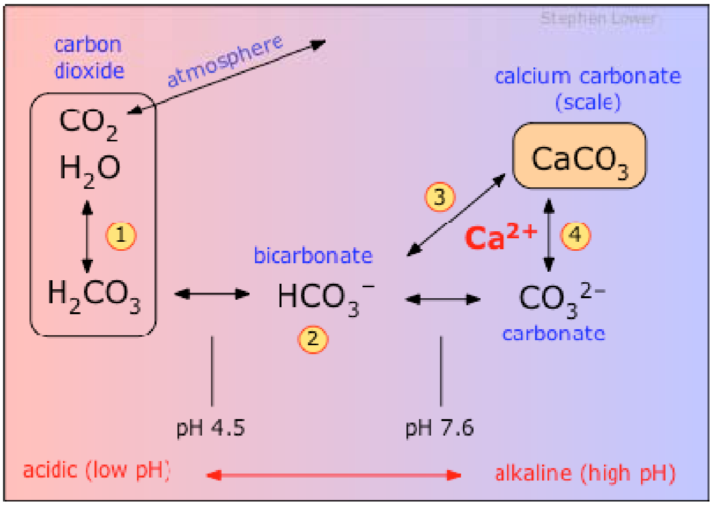
$$\frac{[H^+][HCO_3]}{[H_2CO_3]} = K_1 = 4.45 \times 10^{-7}\ at\ 25^o C$$

  - The bicarbonate dissociate as the following:
    - $HCO_3^- \Leftrightarrow H^+ + CO_3^{-2}$

$$\frac{[H^+][CO_3^{-2}]}{[HCO_3]} = K_2 = 4.69 \times 10^{-11}\ at\ 25^o C$$

    - These reactions are called Homogenous Chemical Equilibria, because reactants and products occur in the same physical state.

Carbonic acid-bicarbonate-carbonate System



- Heterogeneous equilibria, reactants and products occur in different physical states. Important reaction is the following:
  - $CaCO_3 \Leftrightarrow Ca^{+2} + CO_3^{-}$

$$\frac{[Ca^{+2}][CO_3^{-2}]}{[CaCO_3]} = K$$

  - Since $CaCO_3$ is solid, it can be treated as constant, K_s, then
  - $[Ca^{+2}][CO_3^{-}] = KK_s = K_{sp} = 5 \times 10^{-9}$ @ 25° C
  - K_{sp} = solubility products constant
  - If $[Ca^{+2}][CO_3^{-}] < K_{sp}$, the solution is undersaturated
  - If $[Ca^{+2}][CO_3^{-}] > K_{sp}$, the solution is supersaturated, precipitation will occur.

Shift of Equilibria

- How to shift equilibria
  - Produce insoluble products
  - Produce gaseous products
  - Produce weakly ionized products
  - Produce oxidation-reduction reaction
- Examples of Equilibria Shift
  - Adding lime ($Ca(OH)_2$) to remove Ca^{+2}
    - $Ca^{+2} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2CO_2$
  - Adding Chlorine (Cl_2) to remove Ammonia (NH_3)
    - $3Cl_2 + 2NH_3 \rightarrow N_2 \uparrow + 6H^+ + 6Cl^-$
  - Adding acid or base to produce poorly ionized product
    - $2H^+ + SO_4^{-2} + 2Na^+ + 2OH^- \rightarrow 2H_2O + 2Na^+ + SO_4^{-2}$
  - Adding Chlorine (Cl_2) to Cyanide ion to complete the reaction
    - $5Cl_2 + 2CN^- + 8OH^- \rightarrow 10Cl^- + 2CO_2 + N_2 \uparrow + 4H_2O$

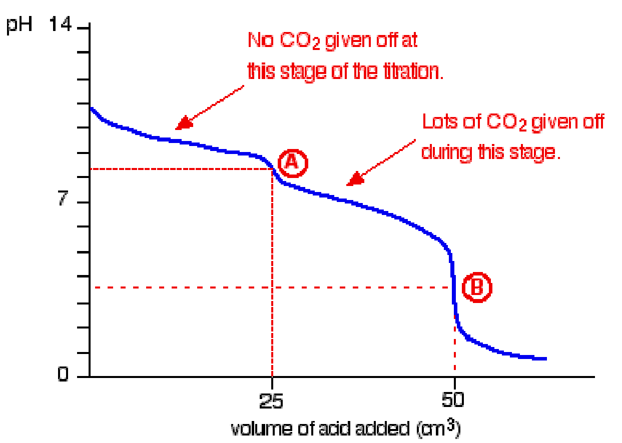
Alkalinity

- What is alkalinity?
  - Is the capacity of the water to neutralize acids without significant change in the pH value
- How is alkalinity determined?
  - Titrating the water with standardized sulfuric acid solution (known normality, usually 0.02N)
- What causes alkalinity?
  - Bicarbonate (HCO_3^-)
  - Carbonate (CO_3^{-2})
  - Hydroxyl ions (OH^-)
- Importance of alkalinity?
  - Important in treatment of waster: coagulation, softening, evaluating buffering capacity of water. Example:
    - Adding lime ($Ca(OH)_2$) to remove Ca^{+2}
    - $Ca^{+2} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2CO_2$

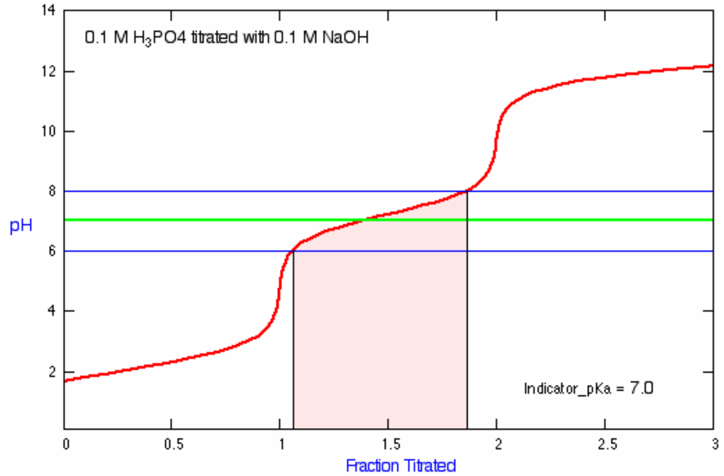
Buffers

- Buffers are substances that offer resistance to a pH change
- The main buffering system in water and wastewater is the bicarbonate-carbonate system

Buffers



Buffers


0.1 M H_3PO4 titrated with 0.1 M NaOH
Indicator_pKa = 7.0
pH
Fraction Titrated
14
12
10
8
6
4
2
0
0.5
1
1.5
2
2.5
3