4. Acids and Bases

- Ionization of Water
  - Protons and hydroxide ions associate readily to give H_2O
- pH
  - A logarithmic scale for proton concentration
- Acid - base chemistry
  - Buffer properties are governed by Kd and pK

Water ionizes very weakly to give small concentrations of H^+ and OH^-

- Water ionizes with difficulty
- Ionization is enhanced by interactions with other water molecules
- *2* H_2O <==> H_3O^+ + OH^-
- In reality H^+ is a very rare species
- Most positive charge is carried in association with water molecules and clusters
- Transport of charge through water is fast
  - Addition to one end of the network and dissociation from the other

Association and dissociation constants

- Biochemists usually use dissociation constants
  - Reaction written with more products than reactants
- H_2O <==> $H^+ + OH^-$
  - Equilibrium dissociation constants have units of Molar
  - Kd = $[H^+]$ M$[OH^-]$M /$[H_2O]$M = M^2/M= Molar
  - The lower the Kd the tighter the association
- Physical chemists use association constants
- $H^+ + OH^-$ <==> H_2O association reaction
  - Products over reactants always, Units are M^{-1}
  - The higher the K the tighter the association

The dissociation constant of H_2O is 10^{-14}M

- Kw= K [H2O]= $[H^+][OH^-] = 10^{-14}\ M^2$
- When H^+ predominates ($[H^+] > 10^{-7}$)
  - the solution is acidic
- When $[H^+] = [OH^-] = 10^{-7}$
  - the solution is neutral
- When OH^- predominates ($[OH^-] > 10^{-7}$)
  - the solution is basic

pH is the negative log of the proton concentration

- $pH = -\log[H^+]$
- Since $[H^+]$ and $[OH^-]$ are tiny and can vary over many orders of magnitude it is convenient to monitor their concentrations in powers of 10
- Also remember the chemical potential is proportional varies with the log of the concentration

$$\mu = \mu^\circ + RT\ln C$$

Exponents and Logarithms

- Any number can be described as 10 to an exponent
  - $100 = 10^2$ $0.01 = 10^{-2}$ $32=10^{1.505}$
- The base 10 ($\log_{10}$ or log) of a number is the exponent required on 10 to give that number
  - Log100=2 log 0.01=-2 log 32=1.505
- The natural log (ln) is the exponent required on e (2.718)
  - ln100=4.605 log 0.01=? log 32=3.466
- A logarithmic scale is compressed
  - allows one to plot an exponential function as linear.

Acid base equilibria

- HA <=> $H^+ + A^-$
- HA is the acid

  (eg. sulfuric acid, acetic acid, phosphoric acid)
- A^- is the conjugate base

  (suffix -ate, eg sulfate, acetate, phosphate)
- Acid Dissociation constant $K = [H^+][A^-]/[HA]$
- $pK = -\log K$
- The larger the dissociation constant the w

The Henderson Hasselbalch equation relates pH, pK and $[A^-]/[HA]$

- $[H^+] = K [HA] / [A^-]$

  $\log [H^+] = \log (K [HA] / [A^-]) = \log Ka + \log([HA] / [A^-])$

  $- \log [H^+] = -\log K - \log([HA] / [A^-]) = -\log Ka + \log([A^-] /[HA])$

- $pH = pK + \log([A^-] /[HA])$
- When $[A^-] = [HA]$ the acid is half dissociated

  $[A^-] / [HA] = 1$;

  $\log ([A^-] / [HA]) = 0$;

  $pH = pK$

Strong acids and weak acids.

- Strong acids essentially ionize completely in water
  - pKs are very low
  - Mineral acids Hydrochloric, Sulfuric, Nitric etc.
- Weak acids have moderate dissociation constants
  - Substantial concentrations of the un-dissociated acid (HA) remain near the pK
  - At very low pH (High $[H^+]$) mostly HA
  - At very high pH (High $[OH^-]$) mostly A^-
  - When pH = pK $[HA] = [A^-]$

Buffers are weak acids or bases that minimize changes in pH near their pKs

- H^+ and OH^- exist at minute concentrations
  - only a small amount of a strong acid or base can cause a large pH change.
- Biological molecules have many ionizable groups,
  - large pH shifts change local charges
- Buffers in sufficient concentration can absorb added protons or hydroxide ions
  - Effective pH range for a buffer is ~ pK ± 1 pH unit

Polyprotic acids

- Phosphate Buffers have multiple ionization states
- Phosphoric Acid - H_3PO_4

  $pK_1 = 2.15$
- Dihydrogen Phosphate - $H_2PO_4^-$

  $pK_2 = 6.82$
- Hydrogen Phosphate HPO_4^{2-}

  $pK_3 = 12.38$
- Phosphate PO_4^{3-}