Chapter 14
Acids And Bases

Arrhenius Definition

- Acids produce hydrogen ions in aqueous solution.
- Bases produce hydroxide ions when dissolved in water.
- Limits to aqueous solutions.
- Only one kind of base.
- NH_3 ammonia could not be an Arrhenius base.

Bronsted-Lowry Definitions

- And acid is an proton (H^+) donor and a base is a proton acceptor.
- Acids and bases always come in pairs.
- HCl is an acid.
- When it dissolves in water it gives its proton to water.
- $HCl(g) + H_2O(l) \rightleftharpoons H_3O^+ + Cl^-$
- Water is a base -makes hydronium ion

Pairs

- General equation
- $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$
- Acid + Base $\rightleftharpoons$ Conjugate acid + Conjugate base
- This is an equilibrium.
- Competition for H^+ between H_2O and A^-
- The stronger base controls direction.
- If H_2O is a stronger base it takes the H^+
- Equilibrium moves to right.

Acid dissociation constant K_a

- The equilibrium constant for the general equation.
- $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$
- $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$
- H_3O^+ is often written H^+ ignoring the water in equation (it is implied).

Acid dissociation constant K_a

- $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$
- $K_a = \dfrac{[H^+][A^-]}{[HA]}$
- We can write the expression for any acid.
- Strong acids dissociate completely.
- Equilibrium far to right.
- Conjugate base must be weak.

Back to Pairs

■ Strong acids	■ Weak acids
■ K_a is large	■ K_a is small
■ $[H^+]$ is equal to $[HA]$	■ $[H^+] <<< [HA]$
■ A^- is a weaker base than water	■ A^- is a stronger base than water

Types of Acids

- Polyprotic Acids- more than 1 acidic hydrogen (diprotic, triprotic).
- Oxyacids - Proton is attached to the oxygen of an ion.
- Organic acids contain the Carboxyl group -COOH with the H attached to O
- Generally very weak.

Amphoteric

- Behave as both an acid and a base.
- Water autoionizes
- $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
- $K_W = [H_3O^+][OH^-] = [H^+][OH^-]$
- At 25^oC $K_W = 1.0 \times 10^{-14}$
- In EVERY aqueous solution.
- Neutral solution $[H^+] = [OH^-] = 1.0 \times 10^{-7}$
- Acidic solution $[H^+] > [OH^-]$
- Basic solution $[H^+] < [OH^-]$

pH

- $pH = -\log[H^+]$
- Used because $[H^+]$ is usually very small
- As pH decreases, $[H^+]$ increases exponentially
- Sig figs only the digits after the decimal place of a pH are significant
- $[H^+] = 1.0 \times 10^{-8}$ pH= 8.00   2 sig figs
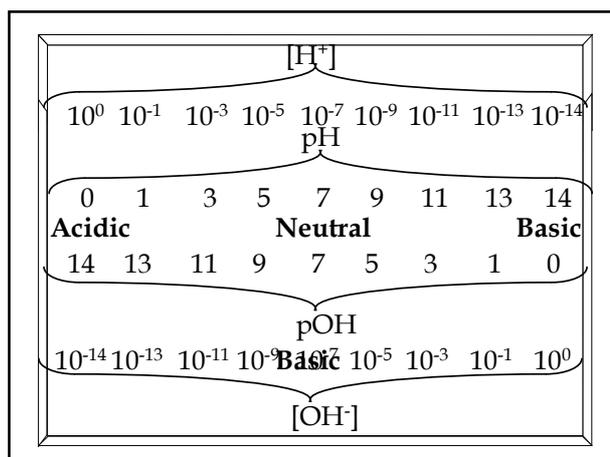- $pOH = -\log[OH^-]$
- $pKa = -\log K$

Relationships

- $K_W = [H^+][OH^-]$
- $-\log K_W = -\log([H^+][OH^-])$
- $-\log K_W = -\log[H^+] + -\log[OH^-]$
- $pK_W = pH + pOH$
- $K_W = 1.0 \times 10^{-14}$
- $14.00 = pH + pOH$
- $[H^+],[OH^-],pH$ and pOH
  Given any one of these we can find the other three.

Problems

- If a solution has a $[H^+]$ of .0035M what is the pH?

- $[OH^-]$?

- pOH?

Problems

- If a solution has a pOH of 9.28 what is the $[H^+]$?

- If a solution has a pH of 9.28 what is the $[OH^-]$?

$[H^+]$

10^0	10^{-1}	10^{-3}	10^{-5}	10^{-7}	10^{-9}	10^{-11}	10^{-13}	10^{-14}

pH

0	1	3	5	7	9	11	13	14
Acidic				**Neutral**				**Basic**
14	13	11	9	7	5	3	1	0

pOH

10^{-14}	10^{-13}	10^{-11}	10^{-9}	**Basic** 10^{-7}	10^{-5}	10^{-3}	10^{-1}	10^0

$[OH^-]$

Calculating pH of Solutions

- Always write down the major ions in solution.
- Remember these are equilibria.
- Remember the chemistry.
- Don't try to memorize there is no one way to do this.

Strong Acids

- HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_4$
- Completely dissociated
- $[H^+] = [HA]$
- $[OH^-]$ is going to be small because of equilibrium
- $10^{-14} = [H^+][OH^-]$
- If $[HA] < 10^{-7}$ water contributes H^+

Weak Acids

- Ka will be small.
- It will be an equilibrium problem from the start.
- Determine whether most of the H^+ will come from the acid or the water.

- Compare K_a or K_w
- Rest is just like last chapter.

Example

- Calculate the pH of 1.6 M HCl(aq)
- Calculate the pH of 1.6×10^{-10} M HCl(aq)
- Calculate the pH of 2.0 M acetic acid $HC_2H_3O_2$ with a Ka = 1.8×10^{-5}
- Calculate pOH, $[OH^-]$, $[H^+]$

A mixture of Weak Acids

- The process is the same.
- Determine the major species.
- The stronger acid will predominate.
- Bigger Ka if concentrations are comparable
- Calculate the pH of a mixture 1.20 M HF ($Ka = 7.2 \times 10^{-4}$) and 3.4 M HOC_6H_5 ($Ka = 1.6 \times 10^{-10}$)

Percent dissociation

- = $\dfrac{\text{amount dissociated}}{\text{initial concentration}}$ x 100
- For a weak acid percent dissociation increases as acid becomes more dilute.
- Calculate the % dissociation of 1.00 M and .00100 M Acetic acid ($Ka = 1.8 \times 10^{-5}$)
- As $[HA]_0$ decreases $[H^+]$ decreases but % dissociation increases.
- Le Châtelier

The other way

- What is the Ka of a weak acid that is 8.1 % dissociated as 0.100 M solution?

Bases

- The OH^- is a strong base.
- Hydroxides of the alkali metals are strong bases because they dissociate completely when dissolved.
- The hydroxides of alkaline earths $Ca(OH)_2$ etc. are strong dibasic bases, but they don't dissolve well in water.
- Used as antacids because $[OH^-]$ can't build up.

Bases without OH^-

- Bases are proton acceptors.
- $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
- It is the lone pair on nitrogen that accepts the proton.
- Many weak bases contain N
- $B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$
- $K_b = \dfrac{[BH^+][OH^-]}{[B]}$

Strength of Bases

- Hydroxides are strong.
- Others are weak.
- Smaller K_b weaker base.
- Calculate the pH of a solution of 4.0 M pyridine ($K_b = 1.7 \times 10^{-9}$)

Polyprotic acids

- Always dissociate stepwise.
- The first H^+ comes of much easier than the second.
- Ka for the first step is much bigger than Ka for the second.
- Denoted Ka_1, Ka_2, Ka_3

Polyprotic acid

- $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
  $$Ka_1 = 4.3 \times 10^{-7}$$
- $HCO_3^- \rightleftharpoons H^+ + CO_3^{-2}$
  $$Ka_2 = 4.3 \times 10^{-10}$$
- Base in first step is acid in second.
- In calculations we can normally ignore the second dissociation.

Calculate the Concentration

- Of all the ions in a solution of 1.00 M Arsenic acid H_3AsO_4
  - $Ka_1 = 5.0 \times 10^{-3}$
    - $Ka_2 = 8.0 \times 10^{-8}$
      - $Ka_3 = 6.0 \times 10^{-10}$

Sulfuric acid is special

- In first step it is a strong acid.
- $Ka_2 = 1.2 \times 10^{-2}$
- Calculate the concentrations in a 2.0 M solution of H_2SO_4
- Calculate the concentrations in a 2.0×10^{-3} M solution of H_2SO_4

Salts as acids and bases

- Salts are ionic compounds.
- Salts of the cation of strong bases and the anion of strong acids are neutral.
- for example NaCl, KNO_3
- There is no equilibrium for strong acids and bases.
- We ignore the reverse reaction.

Basic Salts

- If the anion of a salt is the conjugate base of a weak acid – solution is basic.
- In an aqueous solution of NaF
- The major species are Na^+, F^-, and H_2O
- $F^- + H_2O \rightleftharpoons HF + OH^-$
- $K_b = \dfrac{[HF][OH^-]}{[F^-]}$
- For HF- the acid form- $Ka = \dfrac{[H^+][F^-]}{[HF]}$

Basic Salts

- $K_a \times K_b = \dfrac{[HF][OH^-]}{[F^-]} \times \dfrac{[H^+][F^-]}{[HF]}$

Basic Salts

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- $K_a \times K_b = \dfrac{[\cancel{HF}][OH^-]}{\cancel{[F^-]}} \times \dfrac{[H^+][\cancel{F^-}]}{[\cancel{HF}]}$
- $K_a \times K_b = [OH^-][H^+]$

Basic Salts

- $K_a \times K_b = \dfrac{[\cancel{HF}][OH^-]}{\cancel{[F^-]}} \times \dfrac{[H^+][\cancel{F^-}]}{[\cancel{HF}]}$
- $K_a \times K_b = [OH^-][H^+]$
- $K_a \times K_b = K_W$

K_a tells us K_b

- The anion of a weak acid is a weak base.
- Calculate the pH of a solution of 1.00 M NaF. Ka of HF is 7.2×10^{-4}
- $H^+ + F^- \rightleftharpoons HF$
- The F^- ion competes with OH^- for the H^+

Acidic salts

- A salt with the cation of a weak base and the anion of a strong acid will be acidic.
- The same development as bases leads to
- $K_a \times K_b = K_W$
- Calculate the pH of a solution of 0.40 M NH_4Cl (the K_b of NH_3 1.8 x 10^{-5}).
- Other acidic salts are those of highly charged metal ions.
- More on this later.

Anion of weak acid, cation of weak base

- $K_a > K_b$ acidic
- $K_a < K_b$ basic
- $K_a = K_b$ Neutral
- NH_4CN
  - Ka for HCN is 6.2 x 10^{-10}
  - K_b for NH_3 is 1.8 x 10^{-5}

Structure and Acid base Properties

- Any molecule with an H in it is a potential acid.
- The stronger the X-H bond the less acidic (compare bond dissociation energies).
- The more polar the X-H bond the stronger the acid (use electronegativities).
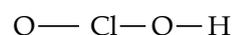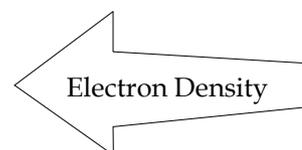- The more polar H-O-X bond -stronger acid.

Strength of oxyacids

- The more oxygen hooked to the central atom, the more acidic the hydrogen.
- $HClO_4 > HClO_3 > HClO_2 > HClO$
- Remember that the H is attached to an oxygen atom.
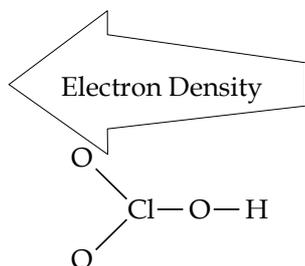- The oxygens are electronegative
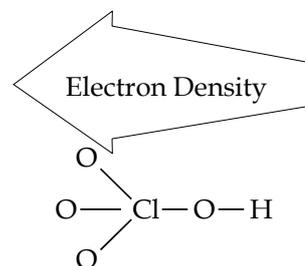- Pull electrons away from hydrogen

Strength of oxyacids

Electron Density

Cl—O—H

Strength of oxyacids

Electron Density

O— Cl—O—H

Strength of oxyacids

Electron Density
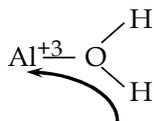
O
Cl—O—H
O

Strength of oxyacids

Electron Density

O
O—Cl—O—H
O
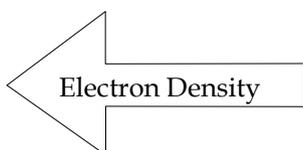
Hydrated metals

- Highly charged metal ions pull the electrons of surrounding water molecules toward them.
- Make it easier for H^+ to come off.
- Make solution acidic

Al^{+3} O
H
H

Acid-Base Properties of Oxides

- Non-metal oxides dissolved in water can make acids.
- $SO_3 (g) + H_2O(l) \longrightarrow H_2SO_4(aq)$
- Ionic oxides dissolve in water to produce bases. (metal oxides)
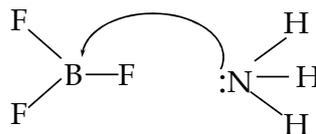- $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$
- Hydroxides

Lewis Acids and Bases

- Most general definition.
- Acids are electron pair acceptors.
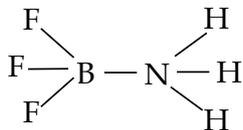- Bases are electron pair donors.
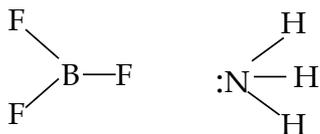
F
B—F
F

H
:N—H
H

Lewis Acids and Bases

- Boron triflouride wants more electrons.

F
B—F
F

H
:N—H
H

Lewis Acids and Bases

- Boron triflouride wants more electrons.
- BF_3 is Lewis base NH_3 is a Lewis Acid.

$$F-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{B}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}}-H$$

Lewis Acids and Bases

$$Al^{+3} + 6 \left(\overset{H}{\underset{H}{\ddot{O}}} \right)$$

$$\left[Al-\left(\overset{H}{\underset{H}{\ddot{O}}} \right)_6 \right]^{+3}$$