CHAPTER 14

ACIDS AND BASES

Topics

- **Definition of acids and bases**
- **Bronsted-Lowry Concept**
- **Dissociation constant of weak acids**
- **Acid strength**
- **Calculating pH for strong and weak acids and bases**
- **Polyprotic acids**
- **Acid-base properties of salts**
- **effect of structure on acid base properties**
- **Acid-Base Properties of Oxides**
- **Lewis Acids and Base**

14.1 The nature of acids and base
1. Arrhenius Definition

- **Acids produce hydrogen ions in aqueous solution.**

- **Bases produce hydroxide ions when dissolved in water.**

- **The definition is limited to aqueous solutions.**

- **Only one kind of bases is identified.**

- **Ammonia, NH_3 could not be an Arrhenius base.**

Bronsted-Lowry Definitions

- **Acid is a proton (H^+) donor and a base is a proton acceptor.**

- **Acids and bases always <u>come in pairs.</u> HCl is an acid.**

- **When acid dissolves in water it gives its proton to water.**

- **$HCl(g) + H_2O(l) \rightleftharpoons H_3O^+ + Cl^-$**

- **H_2O acts as a base by making hydronium ion, H_3O^+**

Conjugate Acid/Base Pairs

- $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$
-     conj   conj   conj   conj
    acid 1   base 2   acid 2   base 1

- **conjugate base**: everything that remains of the acid molecule after a proton is lost.

- **conjugate acid**: formed when the proton is transferred to the base.

Comments on Bronsted lawry concept for acids and bases

- NH_3 is a base:

  $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
- CO_3^{2-} is a base

  $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$
- HCO_3^- is ampheprotic:

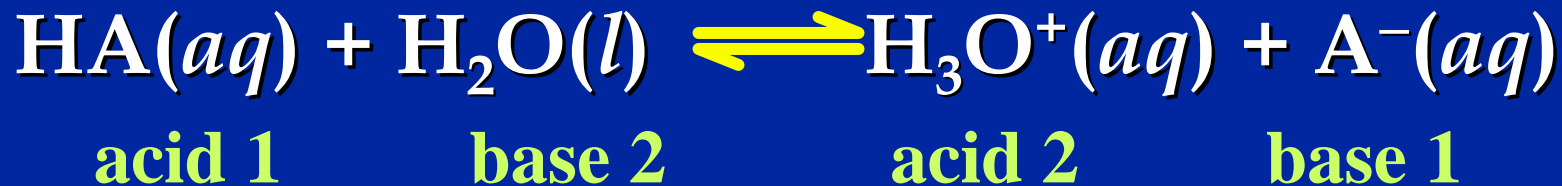 $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$

  $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

- Ions could be acids or bases
- Solvent could be an acid or a base
- Some ions could behave as acids or bases (ampheprotic)
- Acids and bases are not limited to aqueous solutions

$$NH_3(g) \ + \ HCl(g) \ \rightleftharpoons \ NH_4Cl(s)$$

Strength of conjugate pairs

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

acid 1   base 2   acid 2   base 1

- The two bases: H_2O and A^- will compete for H^+

- The stronger base controls the 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.**
- **$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$**

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- **H_3O^+ is often written as H^+ ignoring water in the equation**
- We can write this expression for any week acid as follows:
- **$HA(aq) \rightleftharpoons H^+ + A^-$**

14.2 Acid Strength

- **Strong acids dissociate completely; Ka = ∞, Why?**
- $HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$

$$Ka = \frac{[H_3O][Cl^-]}{[HCl]?}$$

$$[HCl] = ?$$

$$[HCl] = 0$$

$$Ka = \infty$$

- **For strong acids, equilibrium lies far to right.**
- **For weak acids, equilibrium lies far to left.**

Strong acids VS weak acids

$$HCl(aq) \longrightarrow H^+ + Cl^-$$

$$HA(aq) \rightleftharpoons H^+ + A^-$$

- **Strong acids**
- K_a is large
- $[H^+]$ is equal to $[A^-]$
- A^- is a weaker base than water
- It yields a weak conjugate base

- **Weak acids**
- K_a is small
- $[H^+] <<< [HA]$
- A^- is a stronger base than water
- The weaker the acid the stronger its conjugate base

Types of Acids

- **Polyprotic Acids- more than 1 acidic hydrogen (diprotic, triprotic).**
- H_2SO_4 **(?) diprotic** H_3PO_4 **(?) triprotic**
- **Oxyacids - Proton is attached to the oxygen of an ion (H-OCl)**
- **Organic acids contain the Carboxyl**

group -COOH with the H attached to O
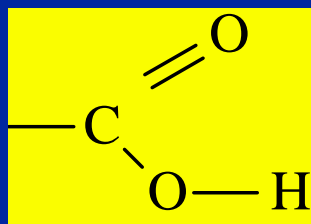
- Organic acids are generally very weak.

Water as an Acid and a Base

■ **Water is amphoteric (it can behave either as an acid or a base).**

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+ (aq) + OH^- (aq)$$

acid 1   base 2   acid 2 (conj)   base 1 (conj)
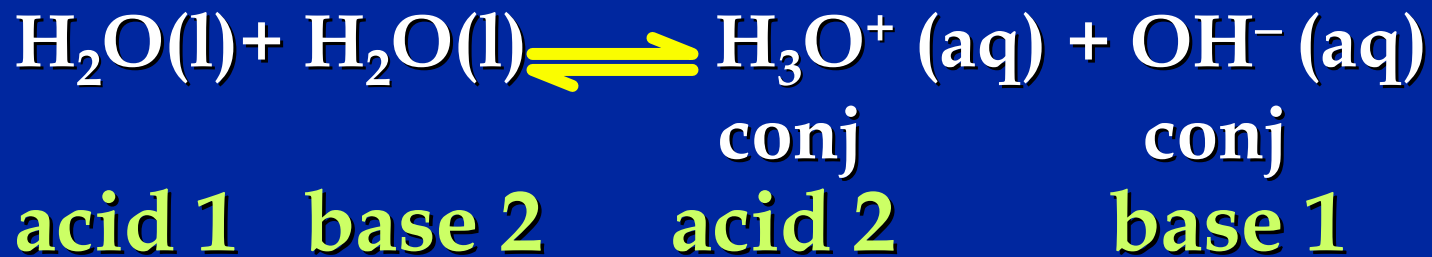
■ $K = [H^+][OH^-] = K_w = 1 \times 10^{-14}$ **at 25°C**
 In *EVERY* aqueous solution

■   **K = ion-product constant (dissociation constant of water)**

- Thus, water behaves as both an acid and a base.
- Water **autoionizes**
- Water is **amphoteric or ampheorotic** substance
- **Neutral** solution $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M
- **Acidic** solution $[H^+] > [OH^-] = > 1.0 \times 10^{-7}$ M
- **Basic** solution $[H^+] < [OH^-] = < 1.0 \times 10^{-7}$ M

14.3 The pH Scale

- $pX = -\log X$; $pH = -\log[H^+]$
- $[H^+] = 10^{-pH}$
- pH is used because $[H^+]$ is usually very small
- As pH decreases, $[H^+]$ increases exponentially
- **# of decimal places** in the log is equal to the number of significant figures in the original number
- $[H^+] = \underline{1.0} \times 10^{-8}$ $pH = 8.\underline{00}$ 2 sig figs
- $pOH = -\log[OH^-]$
- $pKa = -\log Ka$

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.

$[H^+]$

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} 10^{-7} 10^{-5} 10^{-3} 10^{-1} 10^0

$[OH^-]$

14.4 Calculating the pH of strong acid solutions

➢ **write down the major species (ions) in solutions**

➢ **Choose species that can produce H^+ and write reactions.**

➢ **List initial concentrations in dominant equilibrium.**

➢ **pH value can be +ve, -ve, or 0**

Strong Acids

- HBr, HI, HCl, HNO_3, H_2SO_4, $HClO_4$
- They all are completely dissociated
- $[H^+] = [HA]$; $[H^+] = [HCl]$
- $[OH^-]$ is going to be small because of equilibrium

   $10^{-14} = [H^+][OH^-]$

- If $[HA] \leq 10^{-7}$ water contributes H^+

Calculating pH

- Calculate pH for a solution of 0.10 M HCl

$$[H]_{(HCl)} >>> [H^+] (H_2O)$$

$$[H^+] = ?$$

- Calculate pH for a solution of 1.0 M HNO_3

$$[H^+]_{(HNO3)} >>> [H^+] (H_2O)$$

$$[H^+] = ?$$

- Calculate pH for a solution of 1×10^{-10} M HCl

$$[H^+]_{(HCl)} <<< [H^+] (H_2O)$$

$$[H^+] = ?$$

17.5 Calculating the pH of weak Acid solutions

- Choose species that can produce H$^+$ and write reactions. (e.g., HF and H$_2$O)

- Based on Ka values, decide on dominant equilibrium. (e.g., HF >> H$_2$O)

- Kw (H$_2$O) = 1X10^{-14}; Ka (HF) = 7.2X10^{-4}

- Write equilibrium expression for dominant equilibrium. (For HF)

- List initial concentrations in dominant equilibrium.

- Continue using the equilibrium const concept

Solving Weak Acid Equilibrium Problems

➢ Define change at equilibrium (as "x").

➢ Write equilibrium concentrations in terms of x.

➢ Substitute equilibrium concentrations into equilibrium expression.

➢ Solve for x the "easy way."

➢ Verify assumptions using 5% rule.

➢ Calculate [H^+] and pH.

Solving Weak Acid Equilibrium Problems (continued)

- $HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$
- Change   -X   +X   +X

$$Ka = \frac{[H^+][C_2H_3O_2^-]}{[HA]_0 - [C_2H_3O_2^-]}$$

$$\text{Assumining} [HA]_0 \gg [C_2H_3O_2^-]$$

$$X^2 \approx ka[HA]_0$$

$$X = \sqrt{ka[HA]_0}$$

Example

- Calculate the pH of 2.0 M acetic acid $HC_2H_3O_2$ with a Ka 1.8 $x10^{-5}$. Calculate pOH, $[OH^-]$, $[H^+]$

- $Ka (HC_2H_3O_2) >>> Ka (H_2O)$

- $$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

- Initial   2.00 M   0   0

- Change   -x   + x   +x

- Equilib   2.00-x   x   x

- $$Ka = \frac{(x)(x)}{2.00-x} = \frac{x^2}{2.00-x} = 1.8 \times 10^{-5} = \approx \frac{x^2}{2.00}$$

- $X = 2.55 \times 10^{-5} \Rightarrow pH -\log 2.55 \times 10^{-5} = 4.59 \Rightarrow pOH = 14-4.59 = 9.41$

- $[H^+] = X = 2.55 \times 10^{-5} M \Rightarrow$

- $[OH^-] = 1.00 \times 10^{-14} / 2.55 \times 10^{-5} = 3.92 \times 10^{-10} M$

How to check the validity of approximation

$$[HC_2H_3O_2] - X = 2.00 - 2.55 \times 10^{-5} \approx 2.00 M$$

To check the validity of the assumption find

- $$\frac{X}{[HA]_0} X100 = \frac{X}{[HC_2H_3O_2]} X100$$

- $$\frac{2.55 \times 10^{-5}}{2.00} X100 = 0.0013\%$$

- If this percentage is less than 5%, the approximation is correct

Aspirin, $(HC_9H_7O_4)$, Solution is prepared by dissolving 3.60 g per liter. The pH of this solution is found to be 2.60. Calculate k_a.

$$[HC_9H_7O_4]_0 = \frac{3.60g}{1L} \times \frac{1mol}{180.15g} = 2.00 \times 10^{-2} M$$

But pH = 2.60

$$\therefore [H^+] = 10^{-2.60} = 2.5 \times 10^{-3} M$$

$$H C_9 H_7 O_4 \text{ (aq)} \rightleftharpoons H^+ \text{(aq)} + C_9 H_7 O_4^- \text{(aq)}$$
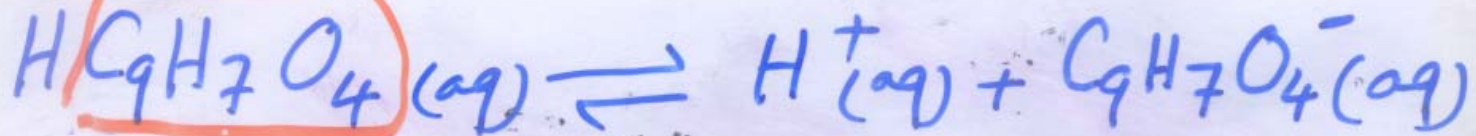
$[\ ]_0$	$0.0200\ M$	0.00	0.00
	$-x$	$+x$	$+x$
$\Delta[\ ]$	$-2.5 \times 10^{-3}\ M$	$+2.5 \times 10^{-3}$	$+2.5 \times 10^{-3}$
$[\ ]_{eq}$	$0.0175\ M$	$0.0025\ M$	$0.0025\ M$

$$K_a = \frac{[H^+][C_9 H_7 O^-]}{[H C_9 H_7 O_4]} = \frac{(2.5 \times 10^{-3})^2}{0.0175} = 3.6 \times 10^{-4}$$

$$\% \text{ dissociation} = \frac{2.5 \times 10^{-3}}{2.0 \times 10^{-2}} \times 100 = 12\ \%$$

Example

- A solution of nicotinic acid (ka $=1.4 \times 10^{-5}$) is prepared by dissolving 0.100 mol of Hnic in a liter of solution. Determine $[H^+]$ in the solution.

$$HNic \rightleftharpoons H^+ + Nic^-$$

Initial   0.100 M   0   0

$$HNic \rightleftharpoons H^+ + Nic^-$$

	HNic	H^+	Nic^-
Initial	0.100 M	0	0
Change	$-x$	$+x$	$+x$
Equilib	$0.100-x$	x	x
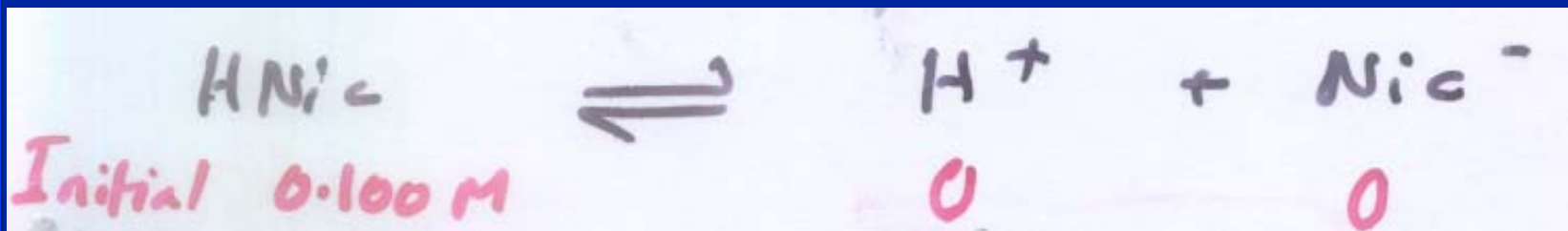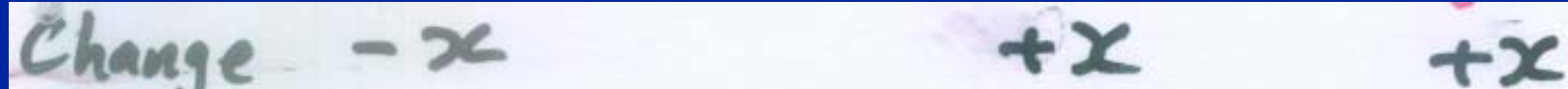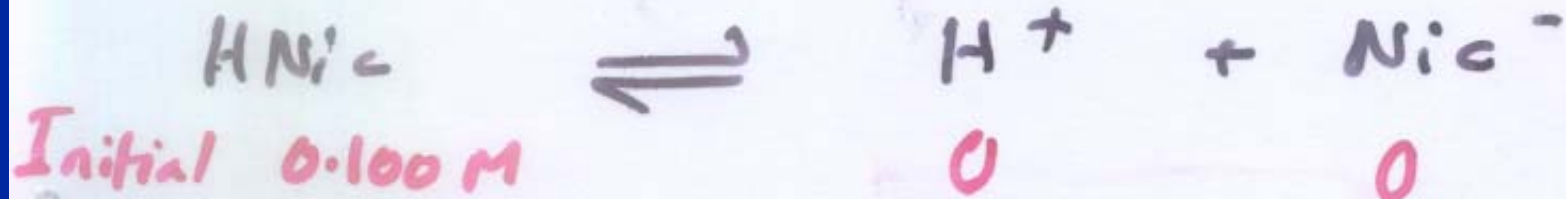
$$K_a = \frac{[H^+][Nic^-]}{[HNic]} = \frac{(x)(x)}{0.1-x} = 1.4 \times 10^{-5}$$

$$K_a = \frac{[H^+][Nic^-]}{[HNic]} = \frac{(x)(x)}{0.1-x} = 1.4 \times 10^{-5}$$

$$x^2 + 1.4 \times 10^{-5} x - 1.4 \times 10^{-6} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-1.4 \times 10^{-5} \pm \sqrt{(1.4 \times 10^{-5})^2 + 4 \times 1.4 \times 10^{-6}}}{2}$$

APPROXIMATION $\quad x = [H^+] = 1.169 \times 10^{-3} M \leftarrow * \quad \approx 1.2 \times 10^{-3} M \checkmark$

If $[HNic] \gg x$; $\Rightarrow$ $\therefore$ $0.1 - x \approx 0.100$

$\therefore$ $K_a = 1.4 \times 10^{-5} = \dfrac{x^2}{0.1}$

$x = [H^+] = \sqrt{1.4 \times 10^{-6}} = \boxed{1.183 \times 10^{-3} M} \leftarrow * \quad \boxed{\approx 1.2 \times 10^{-3} M}$

% dissociation $= \dfrac{[H^+] = x}{\text{orig. conc. HNic}} \times 100 = \dfrac{1.2 \times 10^{-3}}{0.100} \times 100 = 1.2\%$

% dissociation $= \dfrac{[H^+] = x}{\text{Orig. Conc. HNic}} \times 100 = \dfrac{1.2 \times 10^{-3}}{0.100} \times 100 = 1.2\%$

Orig. Conc. HNic

✴ In general, the approximation is valid when % dissociation is < 5%.

pH for a mixture of Weak Acids

- Determine the major species in solution
- The stronger will predominate
- Bigger Ka if concentrations are comparable
- Calculate the pH of a mixture 1.20 M HF (Ka = 7.2×10^{-4}) and 3.4 M HOC_6H_5 (Ka = 1.6×10^{-10})

- The weak acid that has the highest Ka will decide the pH of the final solution.
- Write the dissociation equilibria for HF, HOC_6H_5 and H_2O. ← **1.0X10^{-7}** **7.2X10^{-4}** **1.6X10^{-10}**
- Which one is the highest?
- Solve as before
- If you are asked to find $[OC_6H_5^-]$ for the acid HOC_6H_5
- Use its Ka and solve an equilibrium problem but assuming that the $[H^+]$ is the same as that calculated from the dissociation of HF.

Percent dissociation

$$\text{Percent dissociation} = \frac{\text{Amount dissociated (M)}}{\text{Initial concetration (M)}} \, X100$$

- **For a weak acid percent dissociation increases as acid becomes more dilute.**

- **Calculate the % dissociation of 1.00 M and 0.00100 M Acetic acid (Ka = 1.8 x 10^{-5})**

- **As [HA]$_0$ decreases [H$^+$] decreases but % dissociation increases.**

%Dissociation increases with dilution

$$Ka = \frac{x^2}{C_{HA}}$$

$$x = \sqrt{KaXC_{HA}}$$

$$x(1.0M) = 4.25X10^{-3}M$$

$$\% Dissociation(1.0M) = \frac{4.25X10^{-3}M}{1.00M} X100 = 0.425\%$$

$$x(0.001M) = 1.34X10^{-4}M$$

$$\% Dissociation(0.00100M) = \frac{4.25X10^{-3}M}{0.00100M} X100 = 13.0\%$$

Calculating of Ka from % dissociation

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

- $HA \rightleftharpoons H^+ + A^-$

- $-X \qquad\qquad +X \quad +X$

$$\frac{X}{[HA]_0} X100 = \frac{X}{0.100} X100 = 8.1$$

X = 8.1X10^{-3} M

$$Ka = \frac{X^2}{0.100 - X} = \frac{(8.1X10^{-3})^2}{(0.100 - 8.1X10^{-3})} = 7.1X10^{-5}$$

14.6 Bases

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

- **Slaked lime is used in scrubbing stack gases to remove SO_2 from the exhaust of power plants and factories**
- $SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3 (aq)$
- $Ca(OH)_2 (aq) + H_2SO_3(aq) \rightleftharpoons CaSO_3(s) + 2H_2O(l)$
- **Lime-soda process is also used in water treatment plants**
- $CaO (s) + H_2O(l) \rightleftharpoons Ca(OH)_2 (aq)$
- $Ca(OH)_2 (aq) + Ca^{2+}(aq) + 2HCO_3^-(aq) \longleftarrow$ **Soda ash**

  $\rightleftharpoons 2CaCO_3(s) + 2H_2O$
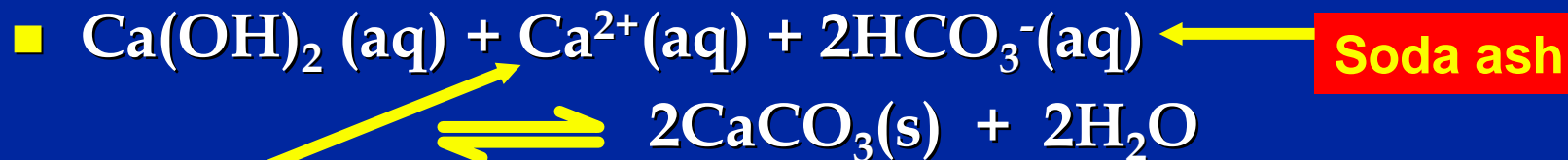
Hard water

The pH of strong bases

- **The major species in the solution of NaOH is Na^+, OH^- and H_2O**

- **NaOH is a strong base thus the dissociation of H_2O is negligible**

- **$[OH^-] >>> [H^+]$**

- **In a $5.0 \times 10^{-2} M$ NaOH;**

- **$[OH^-] = 5.0 \times 10^{-2} M \Rightarrow pOH = \log 5.0 \times 10^{-2} = 1.30$**

- **pH $= 14.0 - 1.30 = 12.7$**

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

- $B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$
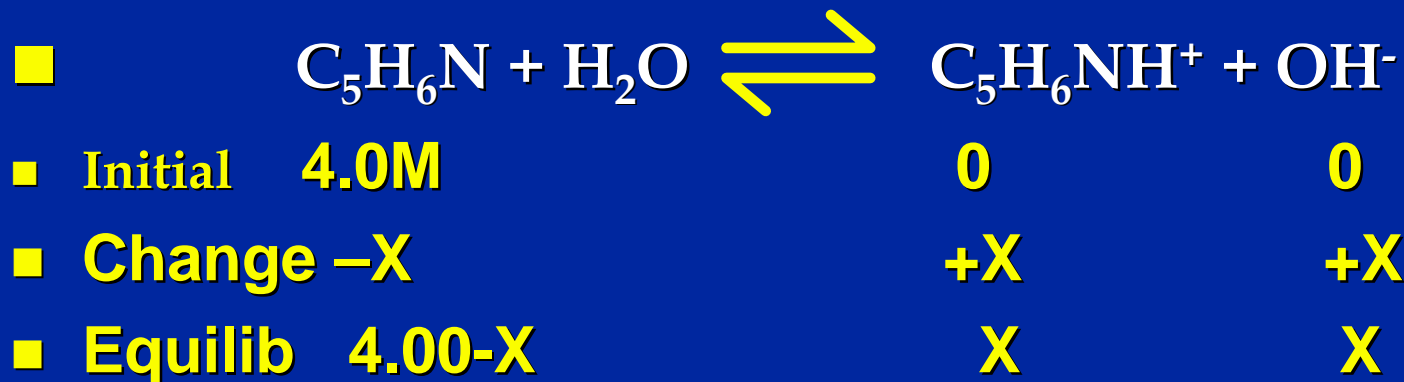
$$Kb = \frac{[BH^+][OH^-]}{[B]}$$

- Kb refers always to the reaction of a base with water to form conjugate acid and the hydroxide ion

Strength of Bases

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

N:

The pH of weak bases

$C_5H_6N + H_2O \rightleftharpoons C_5H_6NH^+ + OH^-$

Initial   **4.0M**   **0**   **0**

Change –X   +X   +X

Equilib   4.00-X   X   X
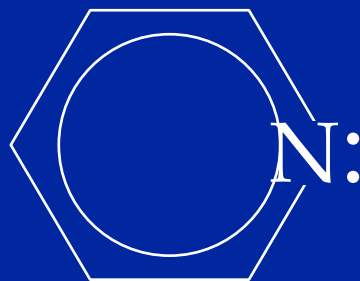
$$kb = \frac{[C_5H_6NH^+][OH^-]}{[C_5H_6N]} = 1.7 \text{ x } 10^{-9}$$

$$kb = \frac{(X)(X)}{4.0 - X} = 1.7 \text{ x } 10^{-9} = \frac{X^2}{4.0 - X} \approx \frac{X^2}{4.0}$$

X = 1.65×10^{-4} M = [OH$^-$] $\Rightarrow$ pOH =-log [OH$^-$]= 3.78
pH = **10.22**

Checking the approximation

$$\frac{X}{[B]_0} X 100$$

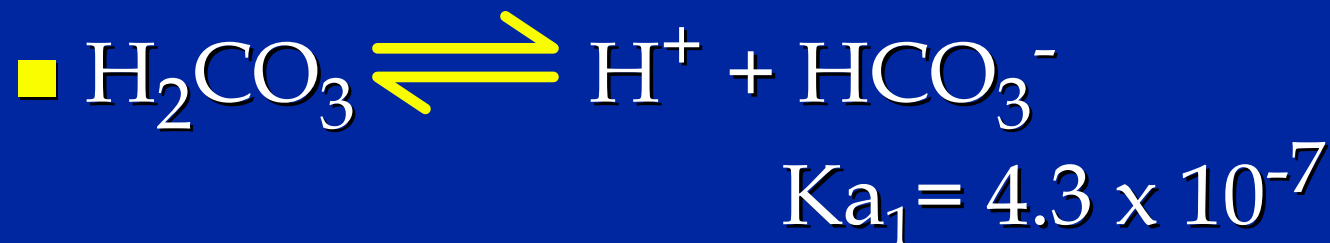$$\frac{X}{[B]_0} X 100 = \frac{1.65 X 10^{-4}}{4.00} X 100 = 0.0041\%$$

Thus, approximation is valid

14.7 Polyprotic acids

- Acids that furnish more than one proton in solution
- They are weak acids containing more than one ionizble hydrogen atom
- 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 and so on
- Ka values are denoted Ka_1, Ka_2, Ka_3
- The acid formed in the successive steps becomes progressively weaker (It is more difficult to remove H+ from a negatively charged species

# Polyprotic acid

- $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$$Ka_1 = 4.3 \times 10^{-7}$$

- $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

$$Ka_2 = 4.3 \times 10^{-10}$$
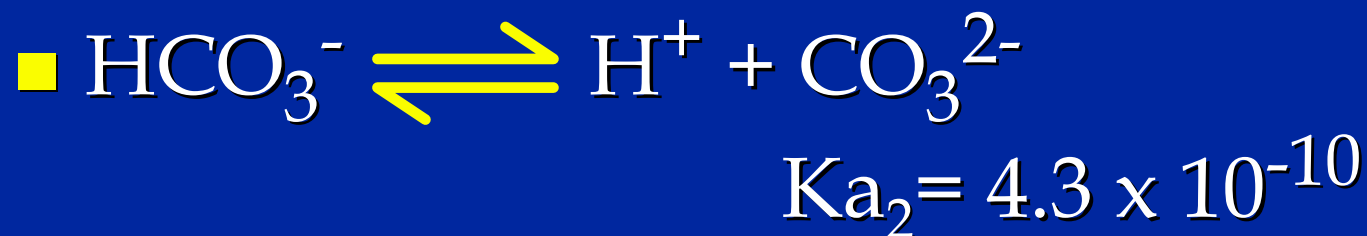
- The conjugate base HCO_3^- in the first step is an acid in the second.

- In calculations we can normally ignore the second dissociation.

Phosphoric acid, H_3PO_4

- ## H_3PO_4 is a triprotic acid

- ## $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; $K_{a1} = 7.5 \times 10^{-3}$

- ## $H_2PO_4^- \rightleftharpoons H^+ + HPO4^{2-}$; $K_{a2} = 6.2 \times 10^{-8}$

- ## $HPO4^{2-} \rightleftharpoons H^+ + PO4^{3-}$; $K_{a3} = 4.8 \times 10^{-13}$

- ## $H_3PO_4 >> H_2PO_4^- >> HPO4^{2-}$
- ## For pH calculation only the first dissociation step contributes to $[H^+]$

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$$
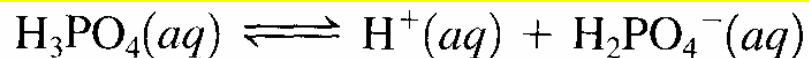
where
$$K_{a_1} = 7.5 \times 10^{-3} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$$

The ICE table is:

	$H_3PO_4(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$H_2PO_4^-(aq)$
Initial:	5.0		0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$5.0 - x$		x		x

$$K_{a_1} = 7.5 \times 10^{-3} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{(x)(x)}{5.0 - x} \approx \frac{x^2}{5.0}$$

$$x \approx 1.9 \times 10^{-1}$$

Since 1.9×10^{-1} is less than 5% of 5.0, the approximation is acceptable, and

$$[H^+] = x = 0.19\ M$$
$$pH = 0.72$$

So far we have determined that

$$[H^+] = [H_2PO_4^-] = 0.19 \, M$$

and

$$[H_3PO_4] = 5.0 - x = 4.8 \, M$$

The concentration of HPO_4^{2-} can be obtained by using the expression for K_{a_2}:

$$K_{a_2} = 6.2 \times 10^{-8} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

where

$$[H^+] = [H_2PO_4^-] = 0.19 \, M$$

Thus
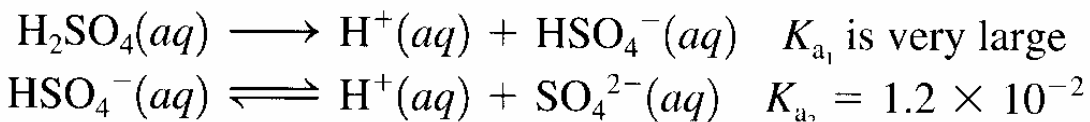
$$[HPO_4^{2-}] = K_{a_2} = 6.2 \times 10^{-8} \, M$$

To calculate $[PO_4^{3-}]$, we use the expression for K_{a_3} and the values of $[H^+]$ and $[HPO_4^{2-}]$ calculated previously:

$$K_{a_3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.8 \times 10^{-13} = \frac{0.19[PO_4^{3-}]}{(6.2 \times 10^{-8})}$$

$$[PO_4^{3-}] = \frac{(4.8 \times 10^{-13})(6.2 \times 10^{-8})}{0.19} = 1.6 \times 10^{-19} \, M$$

Sulfuric Acid

Sulfuric acid is unique among the common acids in that it is *a strong acid in its first dissociation step and a weak acid in its second step:*

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq) \quad K_{a_1} \text{ is very large}$$

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \quad K_{a_2} = 1.2 \times 10^{-2}$$

Sample Exercise 14.16 illustrates how to calculate the pH for sulfuric acid solutions.

The pH of Sulfuric Acid

Calculate the pH of a 1.0 *M* H_2SO_4 solution.

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-$$

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}$$
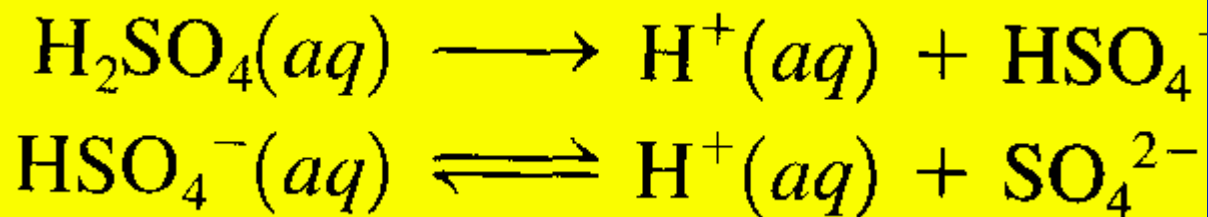
- The first two ions are produced by the complete first dissociation step of H_2SO_4.

- The concentration of H^+ in this solution will be at least 1.0 M, since this amount is produced by the first dissociation step of H_2SO_4.

- We must now answer this question: Does the HSO_4^- ion dissociate enough to produce a significant contribution to the concentration of H^+?

- This question can be answered by calculating the equilibrium concentrations for the dissociation reactions of HSO_4^-

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

where
$$K_{a_2} = 1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$$

	$HSO_4^-(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$SO_4^{2-}(aq)$
Initial:	1.0		1.0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$1.0 - x$		$1.0 + x$		x

Note that $[H^+]_0$ is not equal to zero, as it usually is for a weak acid, because the first dissociation step has already occurred. Substituting the equilibrium concentra-

~~first dissociation step has already occurred~~. Substituting the equilibrium concentrations into the expression for K_{a_2} and making the usual approximation give

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(1.0 + x)(x)}{1.0 - x} \approx \frac{(1.0)(x)}{(1.0)}$$

Thus
$$x \approx 1.2 \times 10^{-2}$$

Since 1.2×10^{-2} is 1.2% of 1.0, the approximation is valid according to the 5% rule. Note that x is not equal to $[H^+]$ in this case. Instead,

$$[H^+] = 1.0\ M + x = 1.0\ M + (1.2 \times 10^{-2})\ M$$
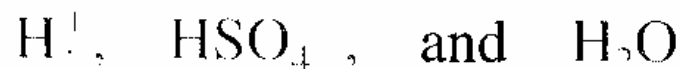$$= 1.0\ M \quad \text{(to the correct number of significant figures)}$$

Thus the dissociation of HSO_4^- does not make a significant contribution to the concentration of H^+, and

$$[H^+] = 1.0\ M \quad \text{and} \quad pH = 0.00$$

The pH of Sulfuric Acid

Calculate the pH of a $1.00 \times 10^{-2}\ M\ H_2SO_4$ solution.

The major species in solution are

$$H^+, \quad HSO_4^-, \quad \text{and} \quad H_2O$$

	$HSO_4^-(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$SO_4^{2-}(aq)$
Initial:	0.0100		0.0100		0
			From dissociation of H_2SO_4		
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.0100 - x$		$0.0100 + x$		x

Substituting the equilibrium concentrations into the expression for K_{a_2} gives

$$1.2 \times 10^{-2} = K_{a_2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(0.0100 + x)(x)}{(0.0100 - x)}$$

Substituting the equilibrium concentrations into the expression for K_{a_2} gives

$$1.2 \times 10^{-2} = K_{a_2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(0.0100 + x)(x)}{(0.0100 - x)}$$

If we make the usual approximation, then $0.0100 + x \approx 0.0100$ and $0.0100 - x$ 0.0100, and we have

$$1.2 \times 10^{-2} = \frac{(0.0100 + x)(x)}{(0.0100 - x)} \approx \frac{(0.0100)x}{(0.0100)}$$

The calculated value of x is

$$x = 1.2 \times 10^{-2} = 0.012$$

This value is larger than 0.010, clearly a ridiculous result. Thus we cannot make usual approximation and must instead solve the quadratic equation. The express

$$1.2 \times 10^{-2} = \frac{(0.0100 + x)(x)}{(0.0100 - x)}$$

leads to
$$(1.2 \times 10^{-2})(0.0100 - x) = (0.0100 + x)(x)$$
$$(1.2 \times 10^{-4}) - (1.2 \times 10^{-2})x = (1.0 \times 10^{-2})x + x^2$$
$$x^2 + (2.2 \times 10^{-2})x - (1.2 \times 10^{-4}) = 0$$

This equation can be solved using the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where $a = 1$, $b = 2.2 \times 10^{-2}$, and $c = -1.2 \times 10^{-4}$. Use of the quadratic formula gives one negative root (which cannot be correct) and one positive root,
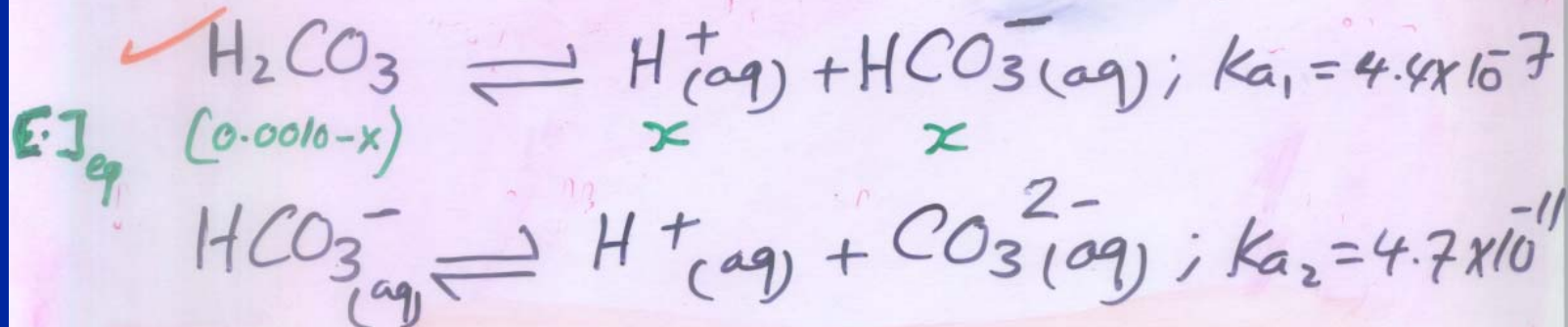
$$x = 4.5 \times 10^{-3}$$

Thus
$$[H^+] = 0.0100 + x = 0.0100 + 0.0045 = 0.0145$$

and
$$pH = 1.84$$

Note that in this case the second dissociation step produces about half as many H^+ ions as the initial step does.

Example

Calculate pH of a 0.0010 M solution of carbonic acid, H_2CO_3.

$$H_2CO_3 \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)} \; ; \; Ka_1 = 4.4 \times 10^{-7}$$

$[\;]_{eq}$ $(0.0010-x)$ $\quad\quad x \quad\quad\quad x$

$$HCO_3^-{}_{(aq)} \rightleftharpoons H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \; ; \; Ka_2 = 4.7 \times 10^{-11}$$

* First dissociation is predominant!

* Thus, it is responsible for the pH of
  Solution.

* The acid is treated as a weak
  monoprotic acid (1st step only).

$$Ka_1 = \frac{x^2}{0.0010-x} \implies x = 2.1 \times 10^{-5} M$$

$$pH = -\log 2.1 \times 10^{-5} = 4.68$$

** pH of a Solution of weak polyprotic acid is
fixed by the First Dissociation Step

Acid-Base Properties of Salts

- Salts are ionic compounds.

- Ionic compounds containing a cation other than H^+ and anion other than OH^- or O^{2-}

- The ions of salts behave as acids or bases

Salts that produce neutral solutions

- Salts of the cation of strong bases and the anion of strong acids are neutral (have no effect on the pH of the solution); pH =7.00

- for example NaCl, KNO_3

- There is no equilibrium for strong acids and bases.

- We ignore the reverse reaction.

Salts that produce basic solutions

- If the anion of a salt is the conjugate base of a weak acid its aqueous solution will be basic

- In an aqueous solution of NaF

- The major species are Na^+, F^-, and H_2O

- $F^- + H_2O \rightleftharpoons HF + OH^-$

- $$K_b = \frac{[HF][OH^-]}{[F^-]}$$

- but $$K_a = \frac{[H^+][F^-]}{[HF]}$$

Salts that produce basic solutions

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

Salts that produce basic solutions

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

Salts that produce basic solutions

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

Salts that produce basic solutions

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

- $K_a \times K_b = [OH^-][H^+]$

Salts that produce basic solutions

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

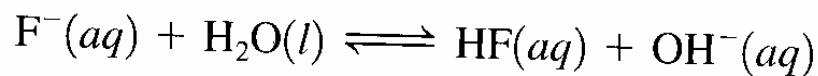- $K_a \times K_b = [OH^-][H^+]$
- $K_a \times K_b = K_W$

Salts as Weak Bases

Calculate the pH of a 0.30 M NaF solution. The K_a value for HF is 7.2×10^{-4}.

The major species in solution are

$$Na^+, F^-, \quad \text{and} \quad H_2O$$
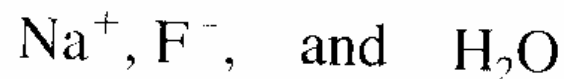
Since HF is a weak acid, the F^- ion must have a significant affinity for protons, and the dominant reaction will be

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$
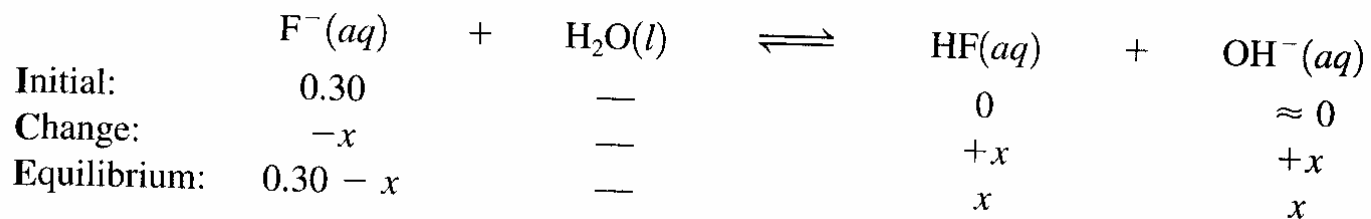
which yields the K_b expression

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

The value of K_b can be calculated from K_w and the K_a value for HF:

$$K_b = \frac{K_w}{K_a \text{ (for HF)}} = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$$

	$F^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$HF(aq)$	+	$OH^-(aq)$
Initial:	0.30		—		0		≈ 0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$0.30 - x$		—		x		x

Thus
$$K_b = 1.4 \times 10^{-11} = \frac{[HF][OH^-]}{[F^-]} = \frac{(x)(x)}{0.30 - x} \approx \frac{x^2}{0.30}$$
and

$$x \approx 2.0 \times 10^{-6}$$

The approximation is valid by the 5% rule, so

$$[OH^-] = x = 2.0 \times 10^{-6} \, M$$
$$pOH = 5.69$$
$$pH = 14.00 - 5.69 = 8.31$$

As expected, the solution is basic.

Salts that produce acidic solutions

- A salt with a cation that is a conjugate acid of a weak base and an anion of a strong acid produce acidic solution

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

- Calculate the pH of a solution of 0.10 M NH_4Cl (the K_b of NH_3 1.8 x 10^{-5}).

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

The major species in solution are

$$NH_4^+, \quad Cl^-, \quad and \quad H_2O$$

Note that both NH_4^+ and H_2O can produce H^+. The dissociation reaction for the NH_4^+ ion is

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

for which

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

Note that although the K_b value for NH_3 is given, the reaction corresponding to K_b is not appropriate here, since NH_3 is not a major species in the solution. Instead, the given value of K_b is used to calculate K_a for NH_4^+ from the relationship

$$K_a \times K_b = K_w$$

Thus

$$K_a \text{ (for } NH_4^+) = \frac{K_w}{K_b \text{ (for } NH_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

We solve the weak acid problem in the usual way:

	$NH_4^+(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$NH_3(aq)$
Initial:	0.10		≈ 0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.10 - x$		x		x

$$5.6 \times 10^{-10} = K_a = \frac{[H^+][NH_3]}{[NH_4^+]} = \frac{(x)(x)}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x \approx 7.5 \times 10^{-6}$$

The approximation is valid by the 5% rule, so

$$[H^+] = x = 7.5 \times 10^{-6}\ M \qquad \text{and} \qquad pH = 5.13$$

Acidic salts containing highly charged metal ions

- When solid aluminum chloride ($AIC1_3$) is dissolved in water, the resulting solution is significantly acidic.
- Although the Al^{3+} ion is not itself a Bronsted-Lowry acid, the hydrated ion $Al(H_2O)_6^{3+}$ formed in water is a weak acid

$$Al(H_2O)_6^{3+}(aq) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + H^+(aq)$$

- The high charge on the metal ion polarizes the O-H bonds in the attached water molecules, making the hydrogens in these water molecules more acidic than those in free water molecules.
- Typically, the higher the charge on the metal ion, the stronger the acidity of the hydrated ion.

Calculate the pH of a 0.010 M $AlCl_3$ solution. The K_a value for $Al(H_2O)_6^{3+}$ is 1.4 × 10^{-5}.

SOLUTION

The major species in solution are

$$Al(H_2O)_6^{3+}, \quad Cl^-, \quad \text{and} \quad H_2O$$

Since the $Al(H_2O)_6^{3+}$ ion is a stronger acid than water, the dominant equilibrium is

$$Al(H_2O)_6^{3+}(aq) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + H^+(aq)$$
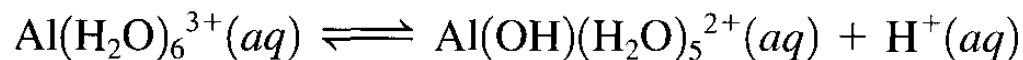
and
$$1.4 \times 10^{-5} = K_a = \frac{[Al(OH)(H_2O)_5^{2+}][H^+]}{[Al(H_2O)_6^{3+}]}$$

This is a typical weak acid problem, which we can solve with the usual procedure:

	$Al(H_2O)_6^{3+}(aq)$	$\rightleftharpoons$	$Al(OH)(H_2O)_5^{2+}(aq)$	$+$	$H^+(aq)$
Initial:	0.010		0		≈ 0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.010 - x$		x		x

Thus

$$1.4 \times 10^{-5} = K_a = \frac{\left[Al(OH)(H_2O)_5^{2+}\right]\left[H^+\right]}{\left[Al(H_2O)_6^{3+}\right]} = \frac{(x)(x)}{0.010 - x} \approx \frac{x^2}{0.010}$$

$$x \approx 3.7 \times 10^{-4}$$

Since the approximation is valid by the 5% rule,

$$\left[H^+\right] = x = 3.7 \times 10^{-4}\, M \quad \text{and} \quad pH = 3.43$$

Salts of anions of weak acids and cations of weak bases

- So far we have considered salts in which only one of the ions has acidic or b properties.
- For many salts, such as ammonium acetate $(NH_4C_2H_3O_2)$, both ions can affect the pH of the aqueous solution.
- We can predict whether the solution will be basic, acidic, or neutral by comp ring the Ka value for the acidic ion with the Kb value for the basic ion.
- If the Ka for the acidic ion is larger than the Kb value for the basic ion, the solution will be acid
- If the Kb value is larger than the Ka value, the solution will be basic.
- Equal Ka and Kb values mean a neutral solution.

Qualitative prediction of pH for solutions of salts with acidic cation and basic anion

- $K_a > K_b$ acidic NH_4F pH = 6.2

- $K_a < K_b$ basic $AlPO_4$ pH = 8.7

- $K_a = K_b$ Neutral $NH_4C_2H_5O_2$ pH = 7.0

Acidity and basicity of amphiprotic Solutions

- HCO_3- (aq) + $H_2O(l)$ ⇌ H_3O^+(aq)

$$Ka = 4.7 \times 10^{-11}$$

- HCO_3^- (aq) + H_2O H_2CO_3(aq) + OH^-(aq)

$$Kb = 2.3 \times 10^{-8}$$

- Since Ka < Kb , the solution of $NaHCO_3$ is Basic (pH = 8.3)

Predict whether an aqueous solution of each of the following salts will be acidic, basic, or neutral.

a. $NH_4C_2H_3O_2$ **b.** NH_4CN **c.** $Al_2(SO_4)_3$

SOLUTION

a. The ions in solution are NH_4^+ and $C_2H_3O_2^-$. As we mentioned previously, K_a for NH_4^+ is 5.6×10^{-10} and K_b for $C_2H_3O_2^-$ is 5.6×10^{-10}. Thus K_a for NH_4^+ is equal to K_b for $C_2H_3O_2^-$, and the solution will be neutral (pH = 7).

b. The solution will contain NH_4^+ and CN^- ions. The K_a value for NH_4^+ is 5.6 $\times$ 10^{-10} and

$$K_b(\text{for } CN^-) = \frac{K_w}{K_a \,(\text{for } HCN)} = 1.6 \times 10^{-5}$$

Since K_b for CN^- is much larger than K_a for NH_4^+, CN^- is a much stronger base than NH_4^+ is an acid. This solution will be basic.

c. The solution will contain $Al(H_2O)_6^{3+}$ and SO_4^{2-} ions. The K_a value for $Al(H_2O)_6^{3+}$ is 1.4×10^{-5}, as given in Sample Exercise 14.20. We must calculate K_b for SO_4^{2-}. The HSO_4^- ion is the conjugate acid of SO_4^{2-}, and its K_a value is K_{a_2} for sulfuric acid, or 1.2×10^{-2}. Therefore,

$$K_b \,(\text{for } SO_4^{2-}) = \frac{K_w}{K_{a_2} \,(\text{for sulfuric acid})}$$
$$= \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-2}} = 8.3 \times 10^{-13}$$

This solution will be acidic, since K_a for $Al(H_2O)_6^{3+}$ is much greater than K_b for SO_4^{2-}.

Acid-Base Properties of Salts

Cation	Anion	Acidic or Basic	Example
neutral	neutral	neutral	NaCl
neutral	conj base of weak acid	basic	NaF **KCN, NaC$_2$H$_5$O$_2$**
conj acid of weak base	neutral	acidic	NH$_4$Cl
conj acid of weak base	conj base of weak acid	depends on K_a & K_b values	Al$_2$(SO$_4$)$_3$

Acid-Base Properties of Some Common Ions in Water Solution

	SPECTATOR		BASIC		ACIDIC
Anion	Cl^- Br^- **I^-**	NO_3^- ClO_4^- SO_4^{2-} *From strong acids*	$C_2H_3O_2^-$ F^- CO_3^{2-} S^{2-} PO_4^{3-}	CN^- NO_2^- HCO_3^- HS^- HPO_4^{2-} *(From Weak acids)*	HSO_4^- $H_2PO_4^-$ HPO_4^{2-} *(From Poly protic acids)*
Cation	Li^+ Na^+ K^+ *From strong bases*	Ca^{2+} Ba^{2+}	none		Mg^{2+} Al^{3+} NH_4^+ transition metal ions

These ions do not affect pH

All Cations except those of Group I & Heavier Group II.

---

1. Consider the following Salts and indicate the types of anions & cations and acidity of solution

Salt	Cation	Anion	Solution of salt
NH_4I	NH_4^+ (acidic)	I^- (spect.)	Acidic
$Zn(NO_3)_2$	Zn^{2+} (acidic)	NO_3^- (Spect.)	Acidic
$KClO_4$	K^+ (Spect.)	ClO_4^- (Spect.)	Neutral
Na_3PO_4	Na^+ (Spect.)	PO_4^{3-} (basic)	Basic

14.9 The effect of structure on 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.**
- **$CHCl_3$ does not produce acidic aqueous solutions because C-H bond is both strong and nonpolar**
- **H-Cl in HCl(g) is stronger than C-H bond but much more polar thus it is acidic in aqueous solutions**
- **Thus, Strength and polarity of the X-H bond will decide for the acidity of species with H atom in aqueous solutions**
- **H-F > H-Cl > H-Br > H-I** **Strong acid**

most polar   **Least polar**

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
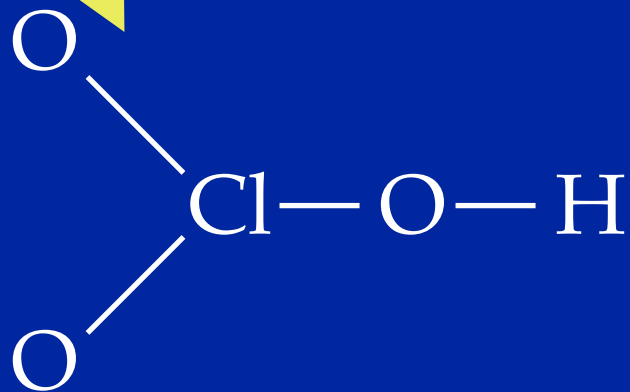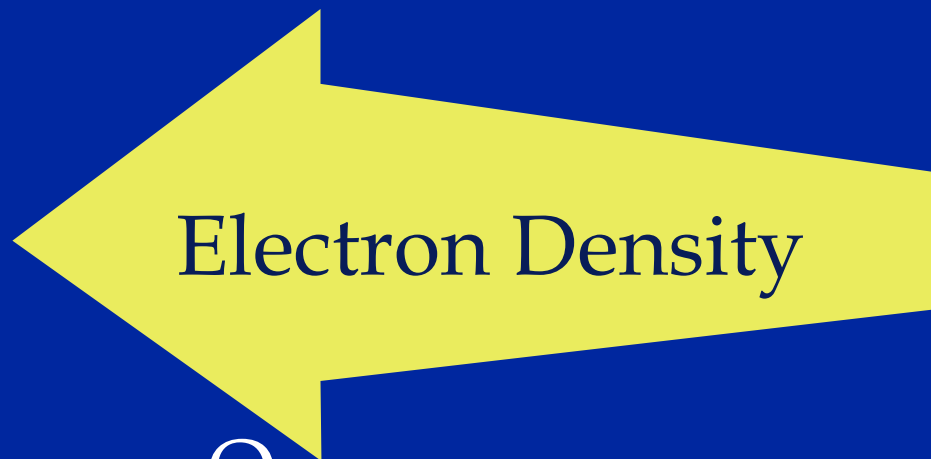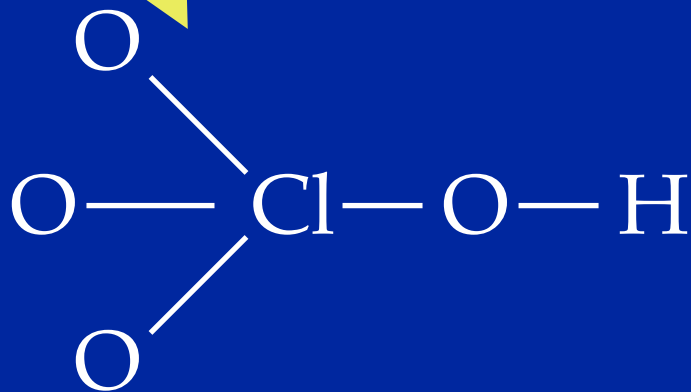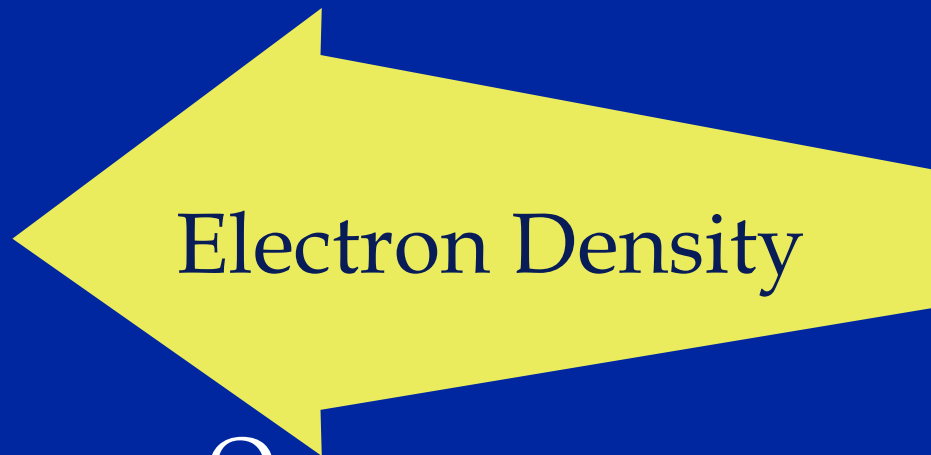- The oxygens pull electrons away from hydrogen

Strength of oxyacids

Electron Density

Cl—O—H

Strength of oxyacids

$$O \quad — \quad Cl — O — H$$

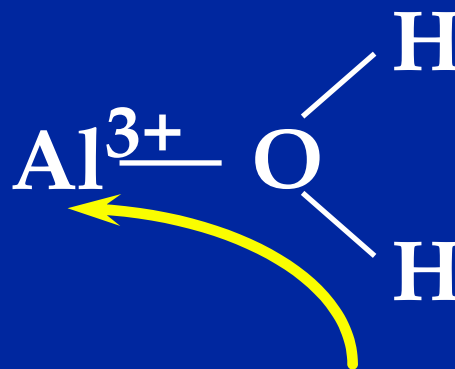# Strength of oxyacids

Electron Density

O

O—Cl—O—H
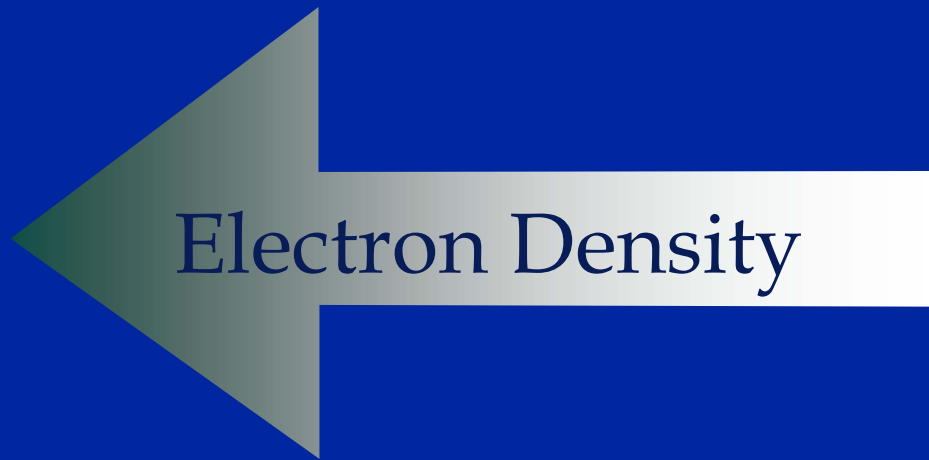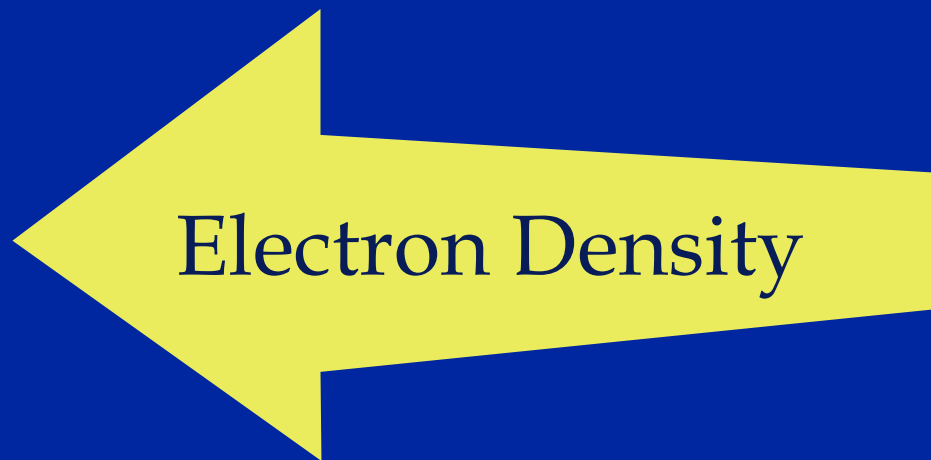
Strength of oxyacids

Hydrated metals

- **Highly charged metal ions pull the electrons of surrounding water molecules toward them.**

- **Make it easier for H^+ to come off.**

$$Al^{3+} - O \begin{matrix} H \\ \\ H \end{matrix}$$

Effect of elctronegativity of –X on the strength of the oxyacid

- **For acids containing the H-O-X grouping, the greater the ability of X to draw electrons toward itself, the greater the acidity of the molecule.**

- **Electronegativity of X reflects its ability to attract the electrons involved in bonding**

**TABLE 14.9** Comparison of Electronegativity of X and K_a Value for a Series of Oxyacids

Acid	X	Electronegativity of X	K_a for Acid
HOCl	Cl	3.0	4×10^{-8}
HOBr	Br	2.8	2×10^{-9}
HOI	I	2.5	2×10^{-11}
HOCH$_3$	CH$_3$	2.3 (for carbon in CH$_3$)	$\sim 10^{-15}$

14.10 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.**
- $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$

14.11 The Lewis Acid-Base Model

- **Acids are electron pair acceptors.**
- **Bases are electron pair donors.**

$$F - B - F \text{ (with F above)} \qquad :N - H \text{ (with H above and below)}$$
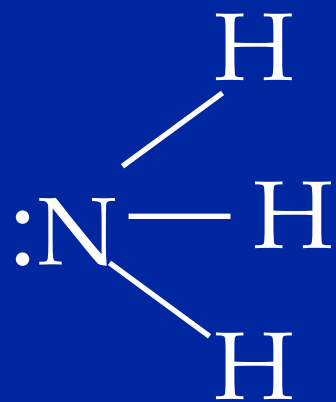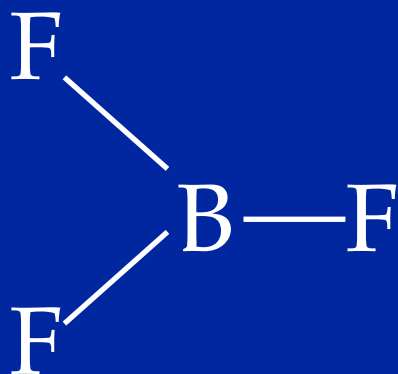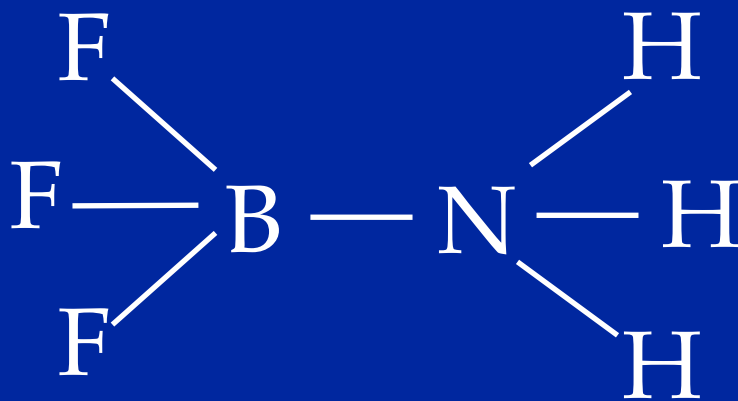
Lewis Acids and Bases

- Boron triflouride wants more electrons.
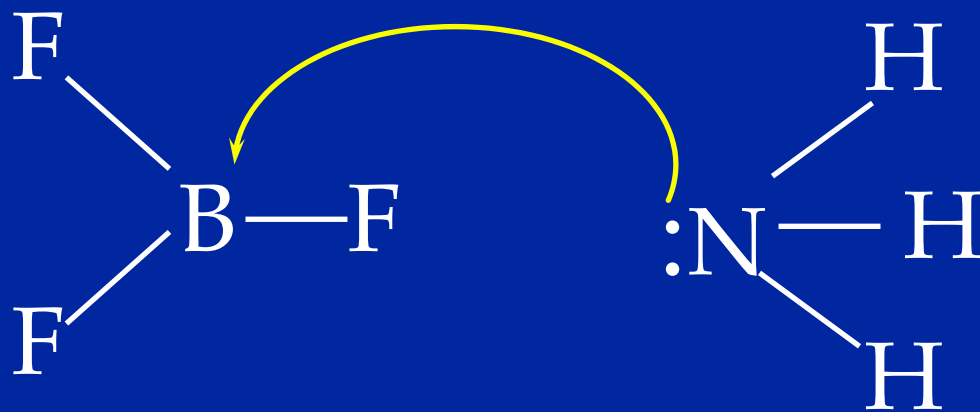
Lewis Acids and Bases

■ **Boron triflouride wants more electrons.**

■ **BF_3 is Lewis base NH_3 is a Lewis Acid.**

Lewis Acids and Bases

$$Al^{+3} + 6 \left(\ddot{O} \begin{array}{c} H \\ H \end{array} \right)$$

$$\left[Al - \left(\ddot{O} \begin{array}{c} H \\ H \end{array} \right)_6 \right]^{+3}$$