

Chapter 16

Acid-Base Equilibria

I) Prop. of Acidic & Basic Soln's.

A) Acids (Protonic)

- 1) Sour taste
- 2) turn blue litmus red
- 3) react w. active metals to liberate H_2
- 4) Neutralize metal oxides & hydroxides to form salts & H_2O
- 5) Aqueous soln's conduct electricity

B) Bases

- 1) Bitter taste
- 2) Slippery feeling
- 3) turn red litmus blue
- 4) Neutralize acids to form salts & H_2O
- 5) Aqueous soln's. conduct electricity

II) Arrhenius Theory

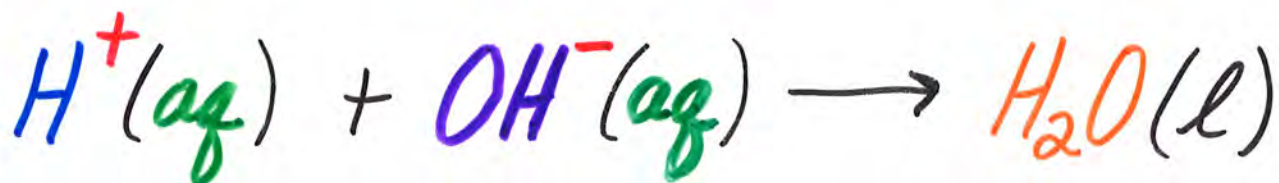
Acid: contain H & produce H^+ ions
in aqueous soln's.

Base: produce OH^- ions
in aqueous soln's.

Acidic soln: $[H^+] > [OH^-]$

Basic soln: $[OH^-] > [H^+]$

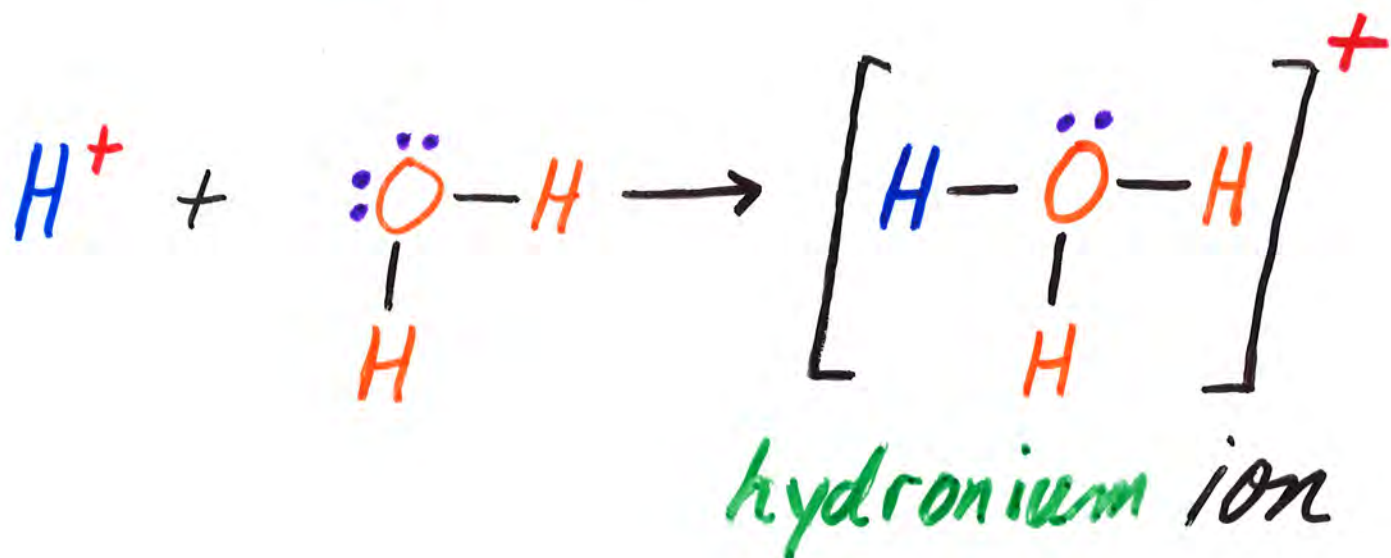
A) Neutralization



III) Hydrated Hydrogen Ion (H_3O^+)

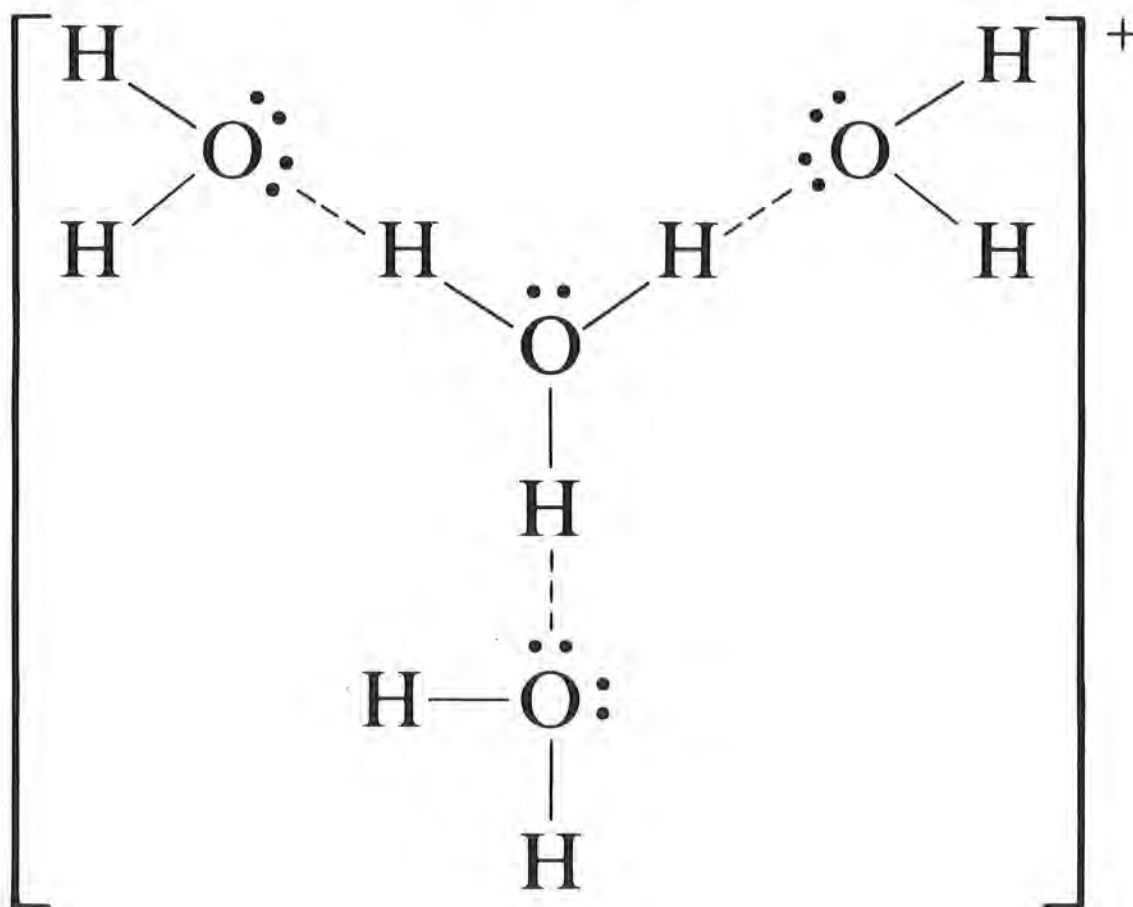
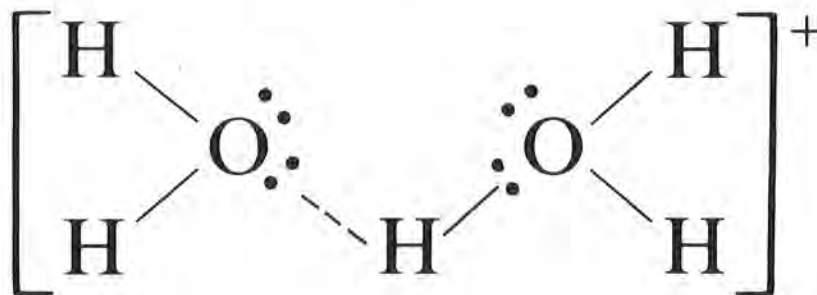


H^+ strongly hydrated in aq. soln.



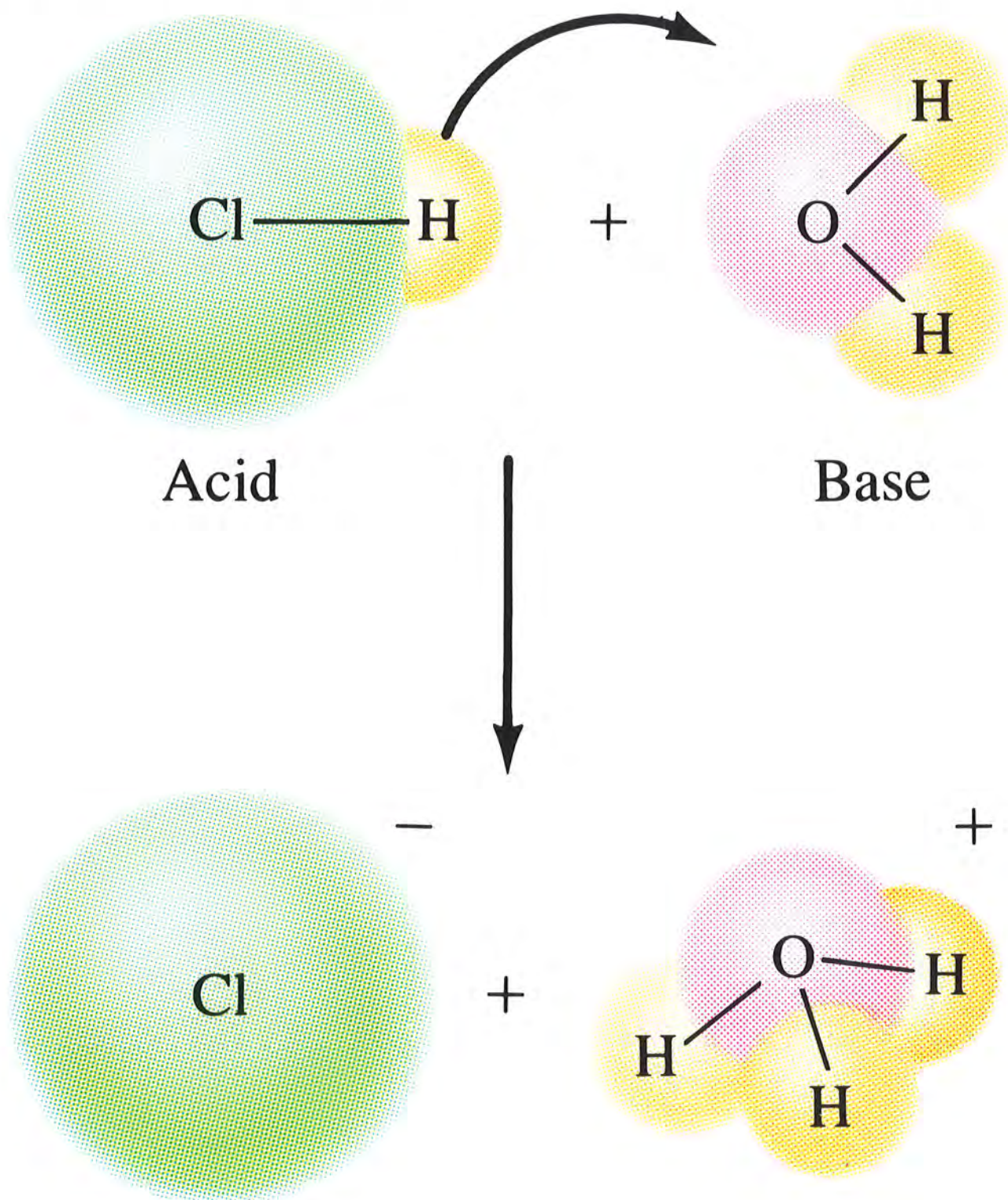
Transparency 113

Figure 16.1 The hydrated proton



Transparency 114

Figure 16.2 Proton transferred from HCl to H₂O

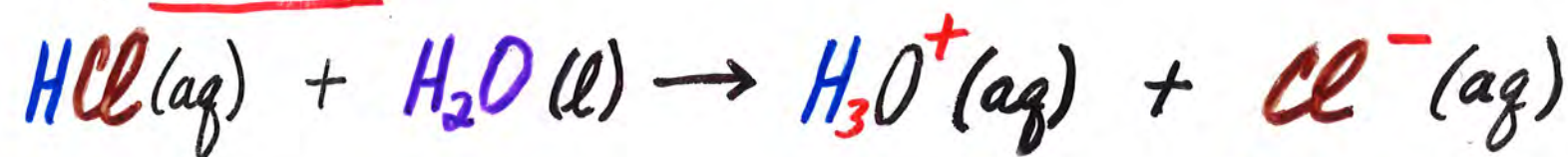


IV) Brønsted-Lowry Theory

Acid: H^+ donor

Base: H^+ acceptor

A) Acids



acid base acid base

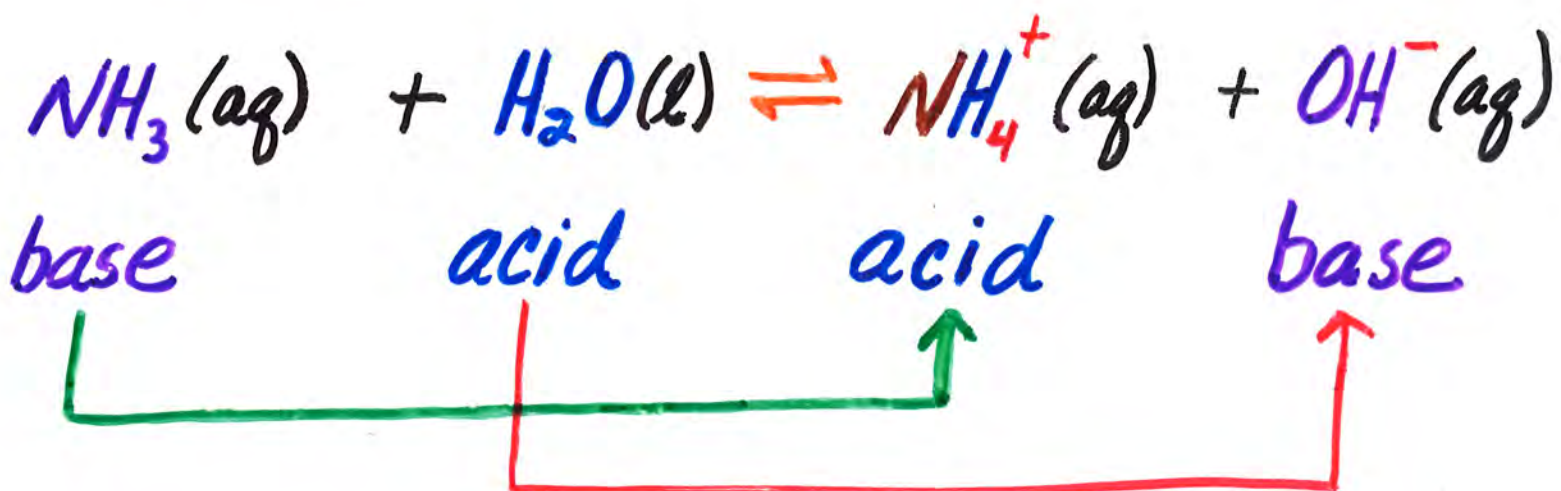


Conjugate Acid-Base Pairs

HCl : acid Cl^- : conjugate base

H_2O : base H_3O^+ : conjugate acid

B) Bases

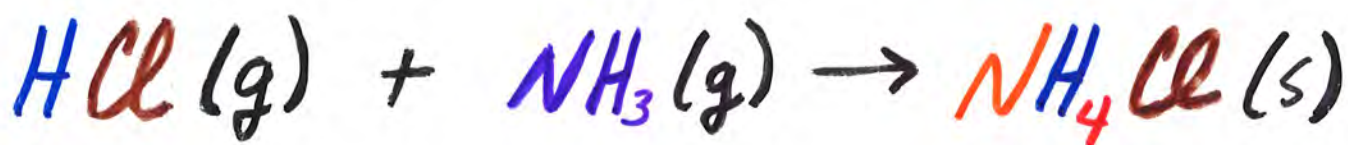


NH_3 : base NH_4^+ : conjugate acid

H_2O : acid OH^- : conjugate base

C) Nonaqueous Acid-Base Rx's

Acid-Base rx. involves transfer of H^+ from acid to base

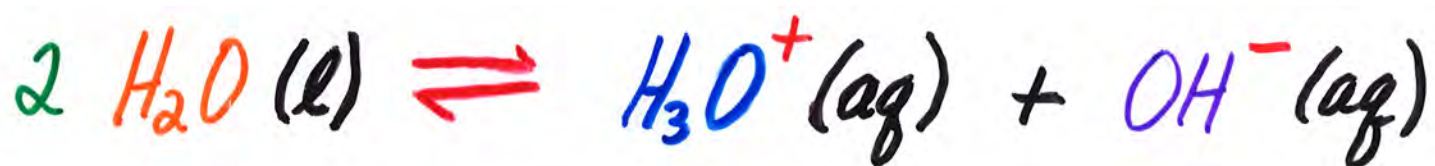


D) Auto ionization of H_2O

H_2O is Amphoteric (amphiprotic)

- Acts as acid or base

H_2O can autoionize (self-ionize)



or



IV a) Relative Strengths of Acids & Bases

Acid-Base rx. is competition for H^+

Stronger Acid: lose H^+ more readily

Stronger Base: accept H^+ more readily

H_3O^+ : strongest acid that can exist in aqueous soln.

- acids stronger than H_3O^+ completely transfer H^+ to H_2O to form H_3O^+

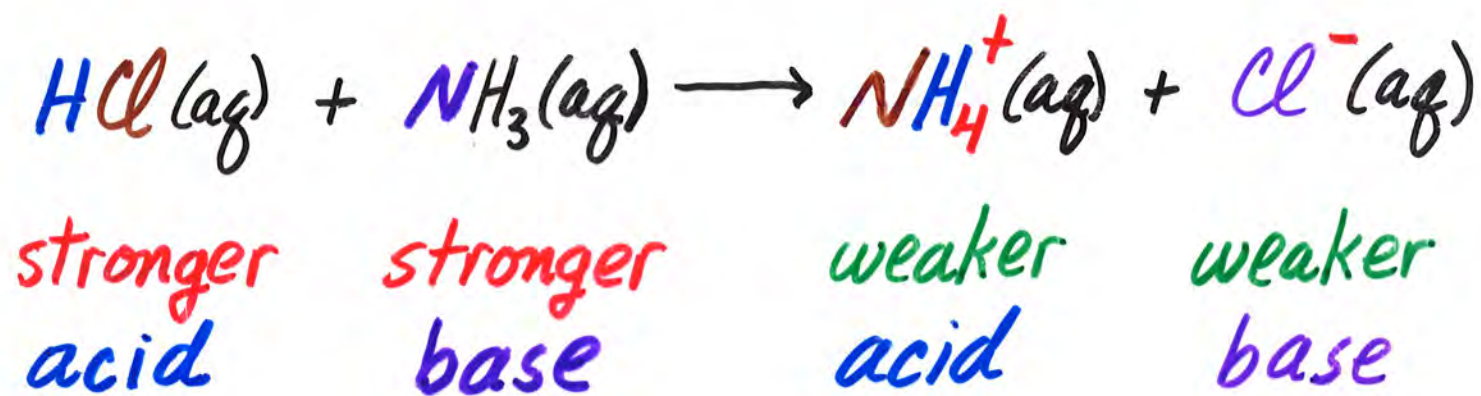
OH^- : strongest base in aqueous soln.

- bases stronger than OH^- completely react w. H_2O to form OH^-

	ACID	BASE			
100 percent ionized in H ₂ O	Strong	HCl	Cl ⁻	Negligible	
		H ₂ SO ₄	HSO ₄ ⁻		
		HNO ₃	NO ₃ ⁻		
Acid strength increases ↑		H ⁺ (aq)	H ₂ O		
	Weak		HSO ₄ ⁻	SO ₄ ²⁻	Weak
			H ₃ PO ₄	H ₂ PO ₄	
			HF	F ⁻	
			HC ₂ H ₃ O ₂	C ₂ H ₃ O ₂	
			H ₂ CO ₃	HCO ₃ ⁻	
			H ₂ S	HS ⁻	
			H ₂ PO ₄ ⁻	HPO ₄ ²⁻	
			NH ₄ ⁺	NH ₃	
			HCO ₃ ⁻	CO ₃ ²⁻	
			HPO ₄ ²⁻	PO ₄ ³⁻	
	H ₂ O	OH ⁻			
Negligible		HS ⁻	S ²⁻	Strong	
		OH ⁻	O ₂ ⁻		
		H ₂	H ⁻		
				100 percent protonated in H ₂ O	

Base strength increases ↓

B) Predicting Direction of Rx.



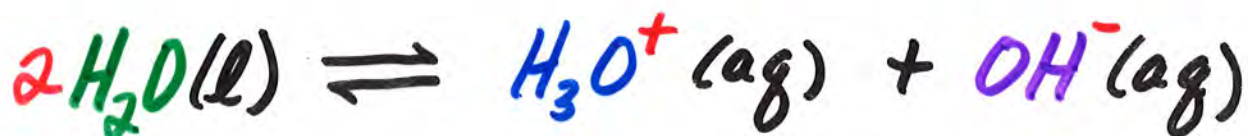
proceeds in direction of
weaker acid & base

stronger Acid \Rightarrow weaker conj. Base

stronger Base \Rightarrow weaker conj. Acid

I) Autoionization of H_2O

H_2O can autoionize (self-ionize)



or



$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

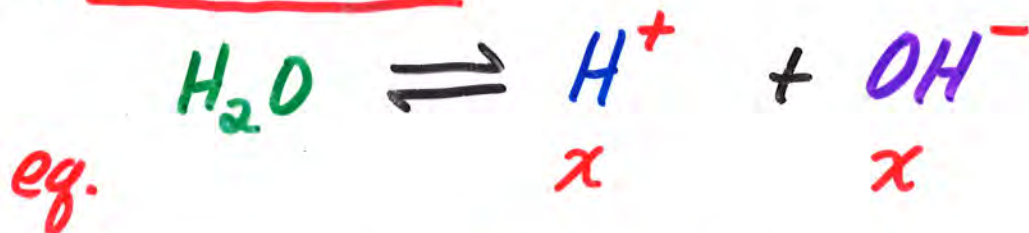
$$K_c [H_2O] = \boxed{K_w = [H^+][OH^-]}$$

Ion-Product Constant for H_2O

At 25°C

$$K_w = 1.0 \times 10^{-14}$$

A) Pure H₂O



$$K_w = [\text{H}^+][\text{OH}^-] = x^2 = 1.0 \times 10^{-14}$$

$$[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

Neutral

B) Acidic Soln.

$$[\text{H}^+] > [\text{OH}^-] \quad \text{or} \quad [\text{H}^+] > 1.0 \times 10^{-7} \text{ M}$$

C) Basic Soln.

$$[\text{OH}^-] > [\text{H}^+] \quad \text{or} \quad [\text{OH}^-] > 1.0 \times 10^{-7} \text{ M}$$

II) pH Scale

$[H^+] + [OH^-]$ in range $10^0 - 10^{-14}$ M

Convert to convenient scale:

$$pH = -\log [H^+]$$

pH in range 0 - 14

pH = 7 Neutral

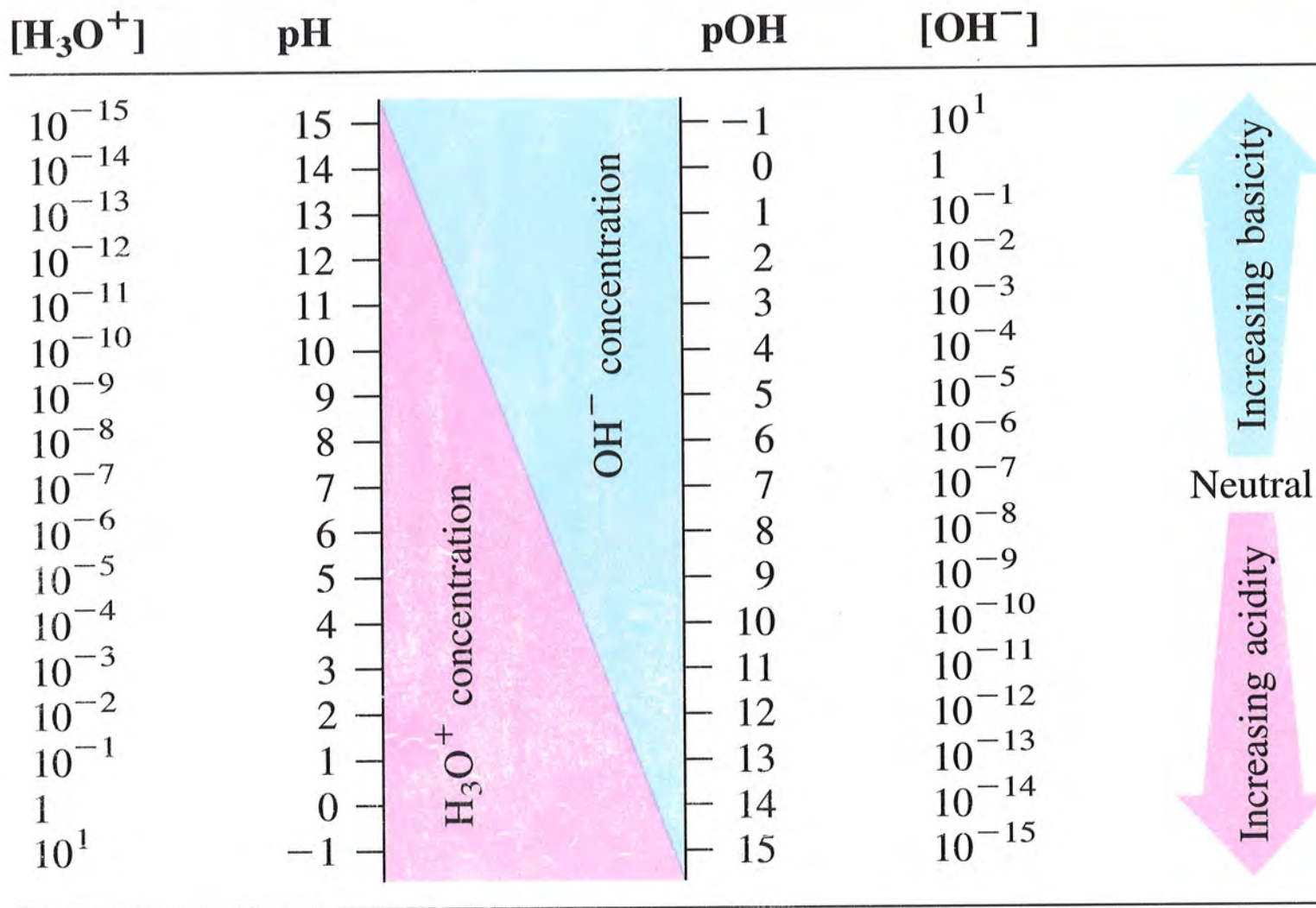
pH < 7 Acidic

pH > 7 Basic

pH dec. as $[H^+]$ inc.

$$pOH = -\log [OH^-]$$

Table 18-3 Relationships Among $[H_3O^+]$, pH, pOH, and $[OH^-]$



A) Ex: Find relationship between
pH, pOH, + K_w

K_w

B) Ex 2: What is $[H^+]$, $[OH^-]$,
pH & pOH at $0^\circ C$.
 $K_w = 1.2 \times 10^{-15}$ at $0^\circ C$

	pH	$[H^+]$	$[OH^-]$	pOH
	14	1×10^{-14}	1×10^{-0}	0
NaOH, 0.1M -----	13	1×10^{-13}	1×10^{-1}	1
Household bleach -----	12	1×10^{-12}	1×10^{-2}	2
Household ammonia -----	11	1×10^{-11}	1×10^{-3}	3
Lime water -----	10	1×10^{-10}	1×10^{-4}	4
Milk of magnesia -----	9	1×10^{-9}	1×10^{-5}	5
Borax -----	8	1×10^{-8}	1×10^{-6}	6
Baking soda -----	7	1×10^{-7}	1×10^{-7}	7
Egg white, sea water -----	6	1×10^{-6}	1×10^{-8}	8
Human blood, tears -----	5	1×10^{-5}	1×10^{-9}	9
Milk -----	4	1×10^{-4}	1×10^{-10}	10
Saliva -----	3	1×10^{-3}	1×10^{-11}	11
Rain -----	2	1×10^{-2}	1×10^{-12}	12
Black coffee -----	1	1×10^{-1}	1×10^{-13}	13
Banana -----	0	1×10^0	1×10^{-14}	14
Tomatoes -----				
Wine -----				
Cola, vinegar -----				
Lemon juice -----				
Gastric juice -----				

VIII) Measuring pH

1) pH meter

Voltage varies w. pH

Use voltmeter calibrated
to give pH

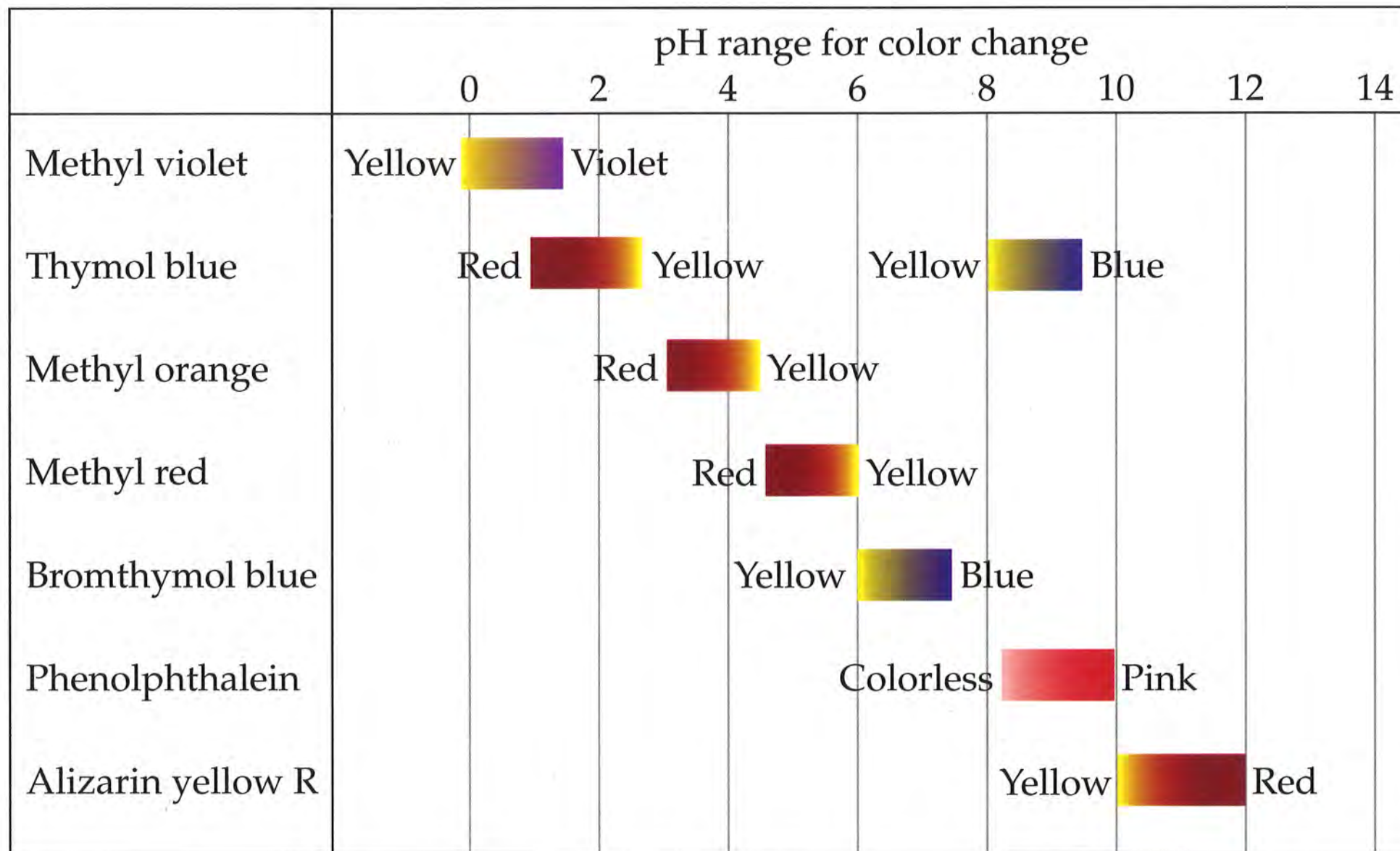
2) Indicators

Substances that exist in
either acid or base forms
which have diff. colors.

Change colors over small
pH ranges

Semi quantitative measure
of pH

pH Ranges of Common Acid-Base Indicators

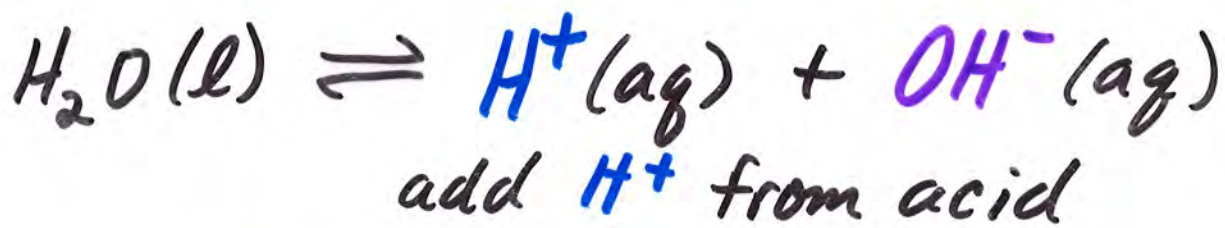


III) Strong Acids

Strong electrolytes

Completely **ionize**

Ignore $[H^+]$ due to
autoionization of H_2O



$$[H^+]_{\text{auto.}} < 1.0 \times 10^{-7} M$$

$$\therefore [H^+] = [HB]_0$$

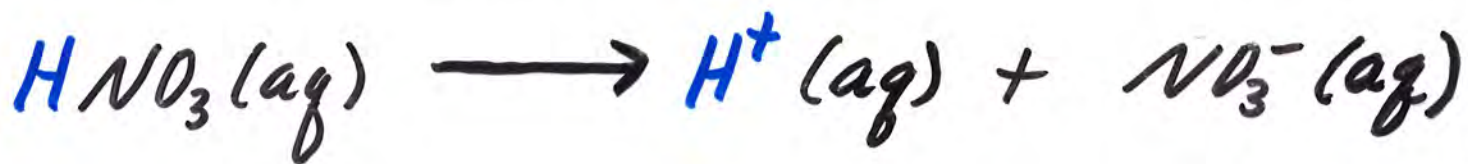
\uparrow
acid

NOTE: common strong acids

HCl , HBr , HI , HNO_3 , $HClO_4$, $HClO_3$

H_2SO_4 (1st H^+ only)

Ex: Calc. $[H^+]$, $[OH^-]$, pH, pOH
in 0.050 M HNO_3



IV) Strong Bases

a) Soluble Hydroxides of IA & IIA Metals

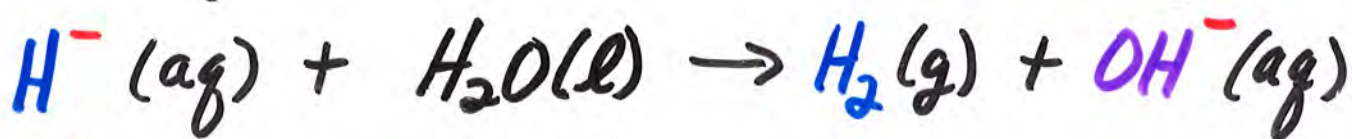
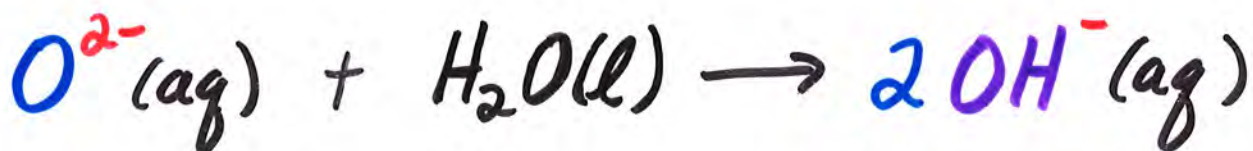
Completely dissociate

NaOH , KOH : 1 OH^- / formula unit

$\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$: 2 OH^- / F.U.

b) Basic Anions

Anions that react w. H_2O to produce OH^-



Na_2O , NaH , Li_3N

Ex: Calc. $[H^+]$, $[OH^-]$, pH, + pOH for
a 0.020 M Na_2O soln.



$$[OH^-] =$$

$$pOH =$$

$$[H^+] = \frac{K_w}{[OH^-]} =$$

$$pH =$$

or

$$pH + pOH =$$

$$pH =$$

$$[H^+] =$$

* # digits to right of decimal pt.
in pH is # sig. fig.

II) Weak Acid

Do **not** completely ionize



$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

Acid-Ionization Constant



weaker acid \Rightarrow smaller K_a

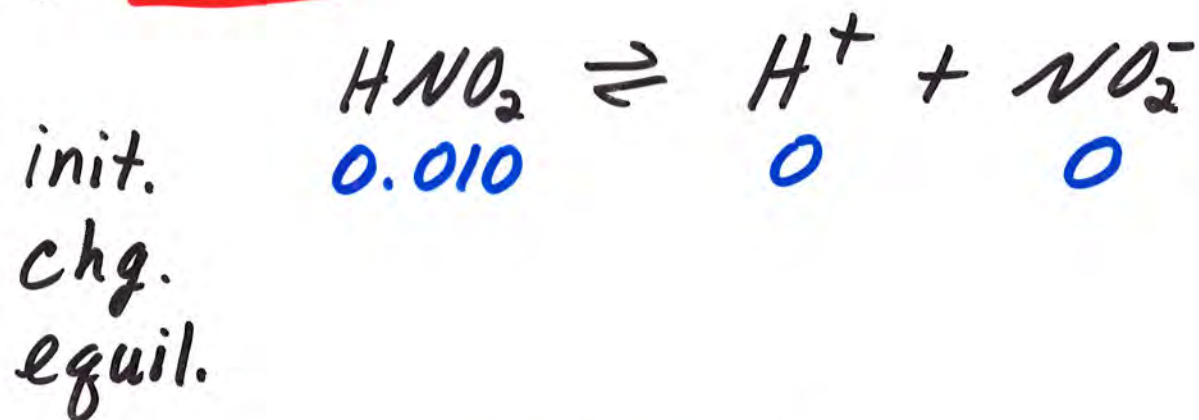
less ionization

Ebbing, GENERAL CHEMISTRY, Third Edition
 Table 16.2 Acid-ionization constants

Substance	Formula	K_a
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	1.7×10^{-5}
Benzoic acid	$\text{HC}_7\text{H}_5\text{O}_2$	6.3×10^{-5}
Boric acid	H_3BO_3	5.9×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}
	HCO_3^-	4.8×10^{-11}
Cyanic acid	HCNO	3.5×10^{-4}
Formic acid	HCHO_2	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrofluoric acid	HF	6.8×10^{-4}
Hydrogen sulfate ion	HSO_4^-	1.1×10^{-2}
Hydrogen sulfide	H_2S	8.9×10^{-8}
	HS^-	$1.2 \times 10^{-13}\dagger$
Hypochlorous acid	HClO	3.5×10^{-8}
Nitrous acid	HNO_2	4.5×10^{-4}
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	5.6×10^{-2}
	HC_2O_4^-	5.1×10^{-5}
Phosphoric acid	H_3PO_4	6.9×10^{-3}
	H_2PO_4^-	6.2×10^{-8}
	HPO_4^{2-}	4.8×10^{-13}
Phosphorous acid	H_2PHO_3	1.6×10^{-2}
	HPO_3^-	7×10^{-7}
Propionic acid	$\text{HC}_3\text{H}_5\text{O}_2$	1.3×10^{-5}
Pyruvic acid	$\text{HC}_3\text{H}_3\text{O}_3$	1.4×10^{-4}
Sulfurous acid	H_2SO_3	1.3×10^{-2}
	HSO_3^-	6.3×10^{-8}

B) Ex 2: Calc. $[H^+]$ in 0.010 M HNO_2

1) Table



$$2) K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} = \frac{x^2}{(0.010 - x)} = 4.5 \times 10^{-4}$$

3) Solve for x

Assume:

4) Calc. Error

5) Two Choices

a) Successive Approx.

use x value calc. & substitute
in $(0.010 - x)$ & solve for
 x in numerator

$$\frac{x^2}{(0.010 - 0.0021)} = 4.5 \times 10^{-4}$$

$$x = [H^+] = 1.88 \times 10^{-3}$$

Repeat until change in x
is $<$ # of sig. fig.

$$\frac{x^2}{(0.010 - 0.00188)} = 4.5 \times 10^{-4}$$

$$x = [H^+] = 1.91 \times 10^{-3}$$

b) Use quadratic formula

$$x^2 + (4.5 \times 10^{-4})x - 4.5 \times 10^{-6} = 0$$

$$x = \frac{-(4.5 \times 10^{-4}) \pm \sqrt{(2.0 \times 10^{-7}) + (1.8 \times 10^{-5})}}{2}$$

neg. root gives neg. $[H^+]$

- doesn't make sense

use (+) root

$$x = [H^+] = 1.9 \times 10^{-3} M$$



$$[H^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a[HB]}}{2}$$

C) Degree & % Ionization

$$\text{Degree of ionization} = \frac{[H^+]}{[HB]_0}$$

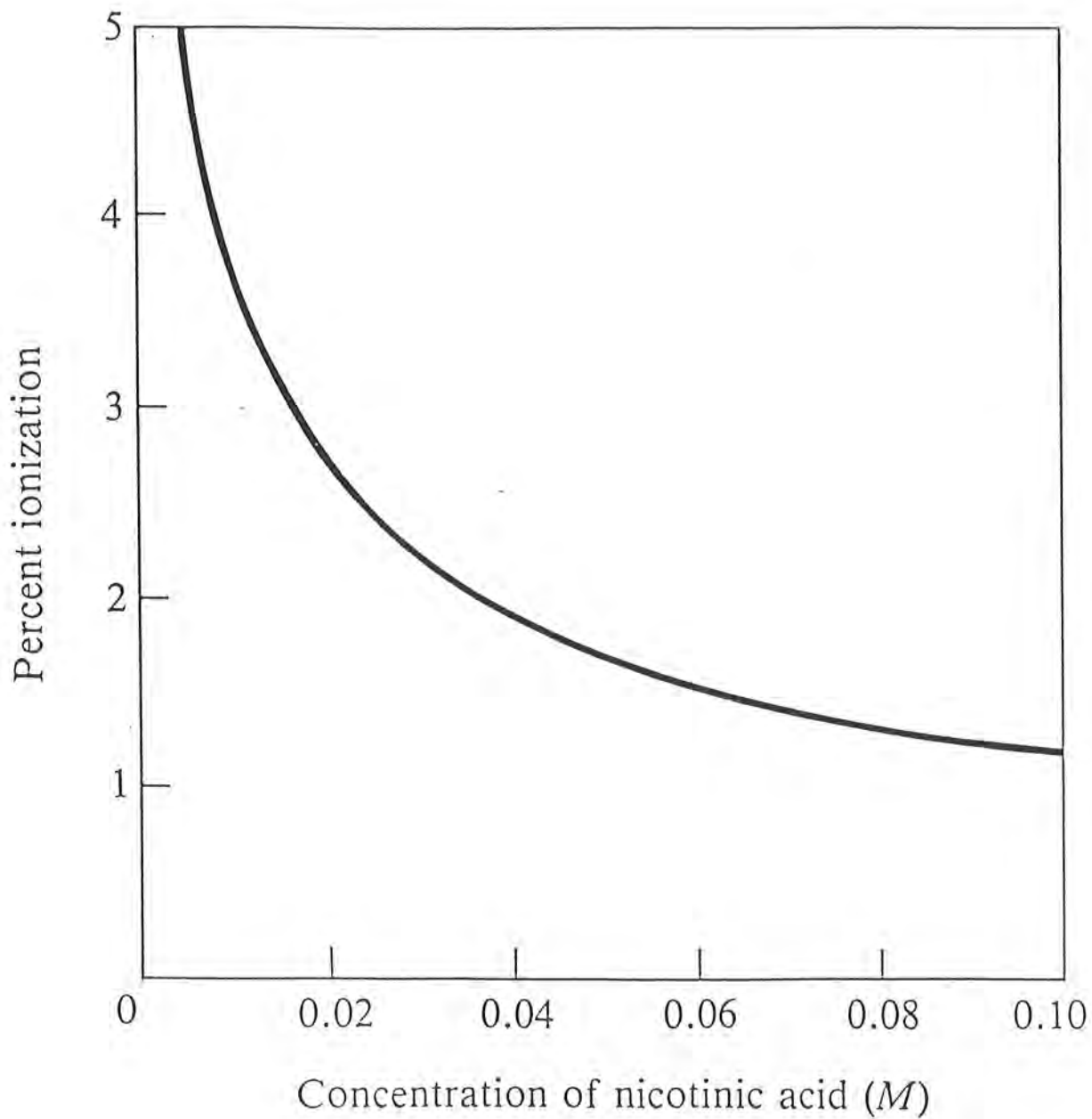
$$\% \text{ ionization} = \frac{[H^+]}{[HB]_0} \times 100\%$$

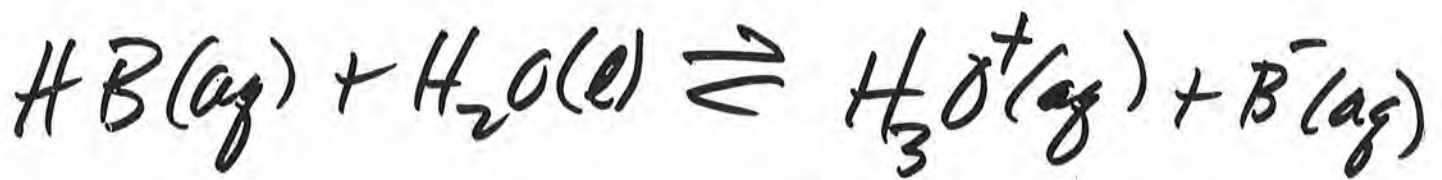
1) Ex 1: For 0.010 M HNO₂

2) Ex 2: For 3.0 M HNO₂

Figure 16.7

Variation of percent ionization of a weak acid with concentration





$$K_a = \frac{[\text{H}_3\text{O}^+]_{\text{aq}} [\text{B}^-]_{\text{aq}}}{[\text{HB}]_0}$$

$$Q = \frac{[\text{H}_3\text{O}^+]_i [\text{B}^-]_i}{[\text{HB}]_i}$$

$$= \frac{\frac{1}{2} [\text{H}_3\text{O}^+]_0 \cdot \frac{1}{2} [\text{B}^-]_0}{\frac{1}{2} [\text{HB}]_0}$$

$$= \frac{\frac{1}{4}}{\frac{1}{2}} \frac{[\text{H}_3\text{O}^+]_0 [\text{B}^-]_0}{[\text{HB}]_0}$$

$$Q = \frac{1}{2} K_a$$

$$Q < K_a$$

D) When can the assumption be made?

Generally, if

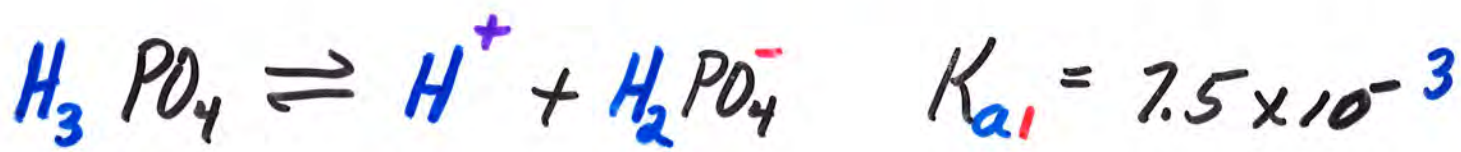
$$\frac{K_a}{[HB]} \lesssim 10^{-3}$$

then error is $\approx 5\%$

VI) Polyprotic Acids

More than 1 acidic hydrogen (ionizable proton) per molecule

H_3PO_4 - stepwise ionization



1st ionization stronger than 2nd which is stronger than 3rd

Easier to remove H^+ from uncharged molecule than from a negative ion.

1) What are conc. of all ions & H_3PO_4 in 6.0 M soln. of H_3PO_4 ?

3 equil. in 5 unknowns

a) simplifying assumptions

1) Use fact that:

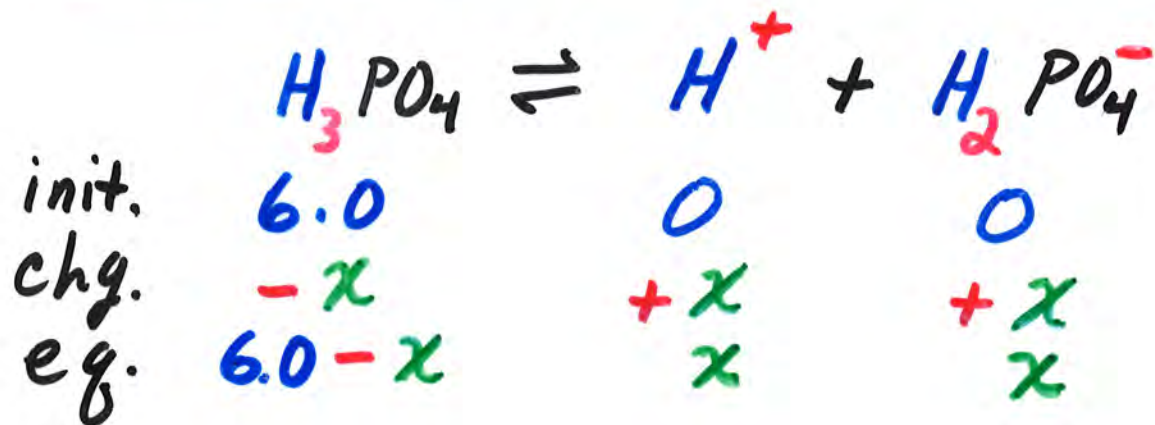
$$K_{a1} \gg K_{a2} \gg K_{a3}$$

- essentially, all H^+ is from 1st ionization

2) $[\text{H}_2\text{PO}_4^-]$ produced in 1st step is **not** significantly **reduced** in 2nd step.

- likewise $[\text{HPO}_4^{2-}]$ in 2nd step

b) Setup table & find $[H^+] + [H_2PO_4^-]$



$$K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{x^2}{(6.0-x)} = 7.5 \times 10^{-3}$$

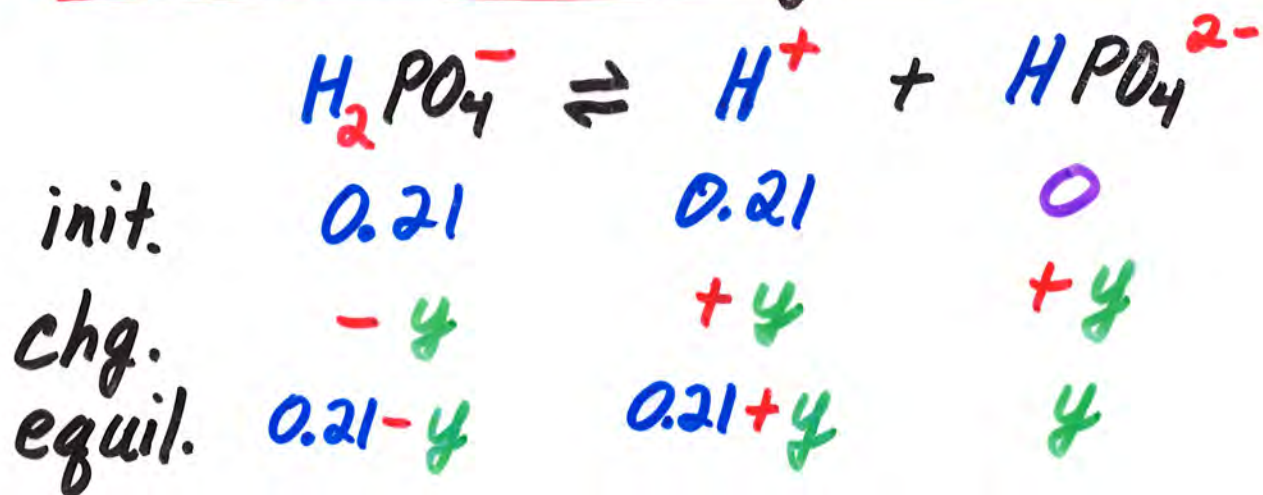
assume $6.0 - x \approx 6.0$

$$x = [H^+] = [H_2PO_4^-] = 0.21 \text{ M}$$

3.5 % error (okay)

$$[H_3PO_4] = 5.8 \text{ M}$$

c) Find $[HPO_4^{2-}]$ using 2nd step



$$K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.2 \times 10^{-8}$$

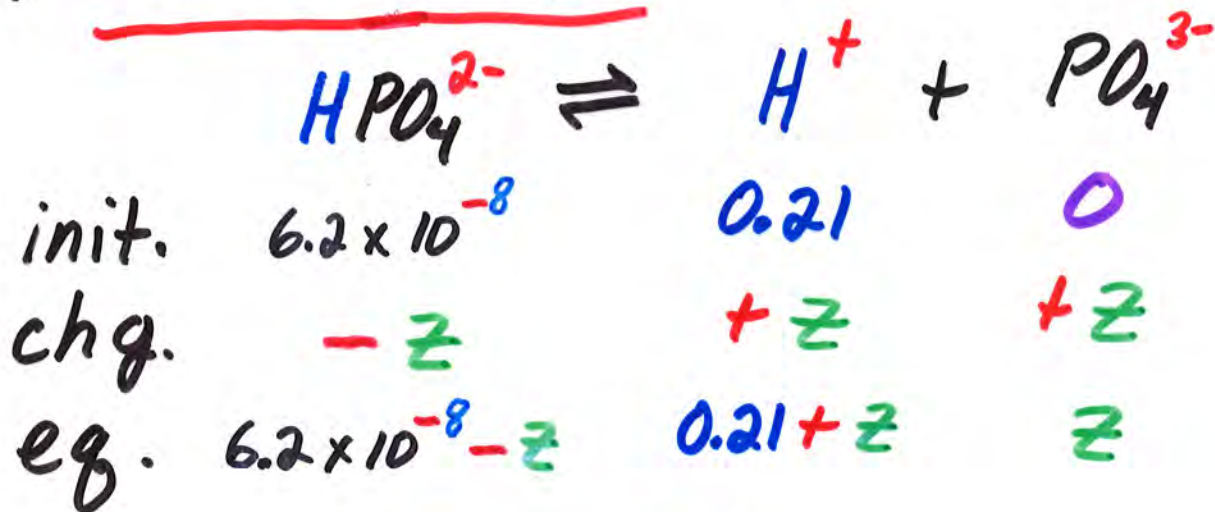
$$\frac{(0.21)[HPO_4^{2-}]}{(0.21)} = 6.2 \times 10^{-8}$$

$$[HPO_4^{2-}] = 6.2 \times 10^{-8} = K_{a2}$$

General Rule: Conc. of anion formed in 2nd ionization step equals K_{a2} if K_{a2} is small + acid is the only solute

$$[\text{anion}]_2 = K_{a2}$$

d) Find $[PO_4^{3-}]$



$$K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.2 \times 10^{-13}$$

$$\frac{(0.21)[PO_4^{3-}]}{(6.2 \times 10^{-8})} = 4.2 \times 10^{-13}$$

$$[PO_4^{3-}] = 1.2 \times 10^{-19}$$

Note:

$$K_{a3} = \frac{[H^+]_1 [PO_4^{3-}]}{K_{a2}}$$

$$[PO_4^{3-}] = \frac{K_{a2} \cdot K_{a3}}{[H^+]}$$