

Acids: taste sour

Bases: "alkalis" taste bitter, feel slippery

Arrhenius concept: (limited to aqueous soln)

Acids: produce hydrogen ions in solution

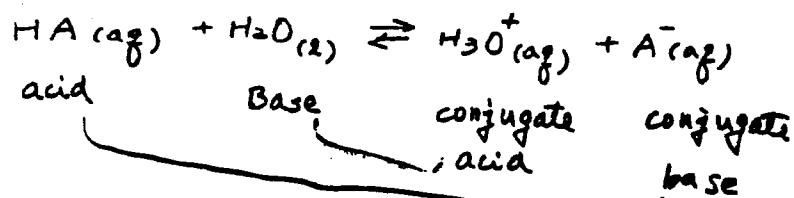
Bases: produce hydroxide ions

Bronsted-Lowry model: (not limited to aqueous soln)

Acids: proton donor

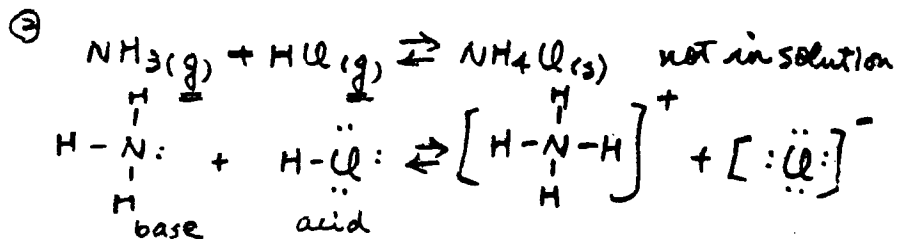
Bases: proton acceptor

例 1: ①



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

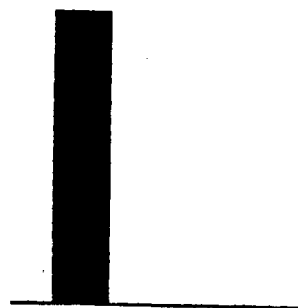
acid dissociation constant



Before dissociation

After dissociation, at equilibrium

HA Strong Acid



H⁺ A⁻



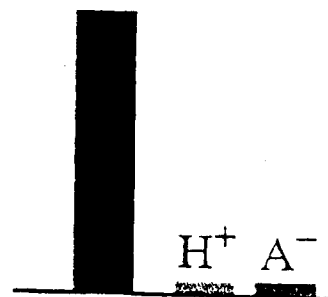
(a)

HA

weak acid



HA

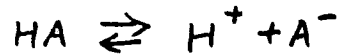


(b)

Figure 14.4

Graphical representations of strong and weak acid equilibria

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14-3

strong acid : equilibrium lies far to the right
 (a strong acid yields a weak conjugate base)

weak acid : equilibrium lies far to the left
 (a weak acid yields a relatively strong base conjugate)

See Fig. 14.1 & 14.2

Table 14.1

property	strong Acid	Weak Acid
Ka value	Ka is large	Ka is small
Equilibrium conc of H ⁺	[H ⁺] ≈ [HA] ₀	[H ⁺] ≪ [HA] ₀
strength of conjugate base	A ⁻ much weaker base than H ₂ O	A ⁻ much stronger base than H ₂ O

Common strong acids :

- sulfuric acid (H₂SO₄)
 - hydrochloric acid (HCl)
 - nitric acid (HNO₃)
 - perchloric acid (HClO₄)
- } 100% dissociated in H₂O

acid strength

conjugate base strength

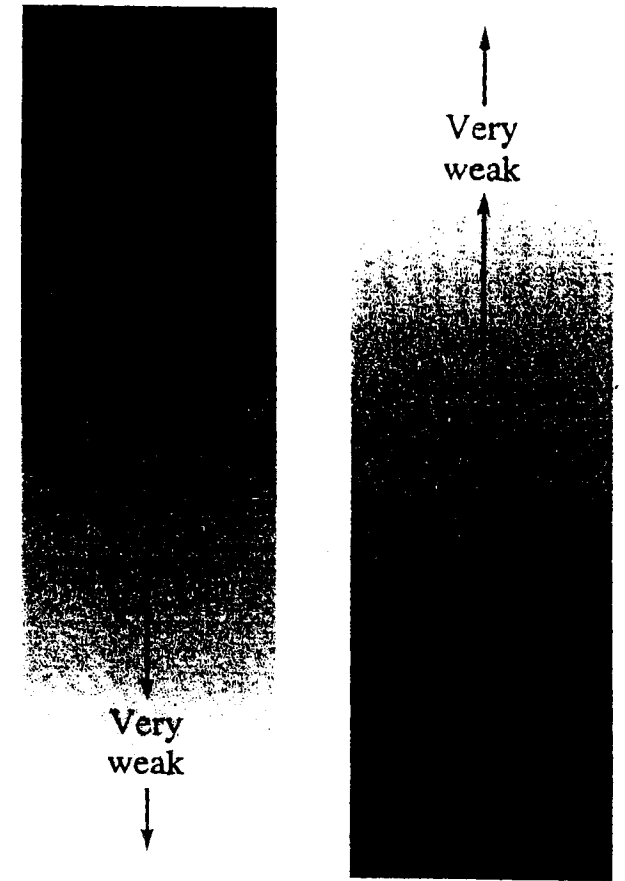
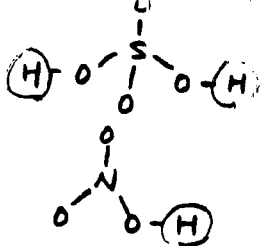
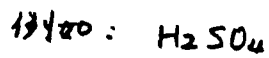


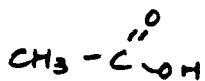
Figure 14.5
 Acid strength versus conjugate base strength

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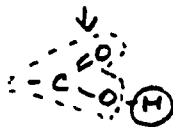


organic acids: w/ a carbon atom backbone,
common contain the carboxyl group

13/20: acetic acid



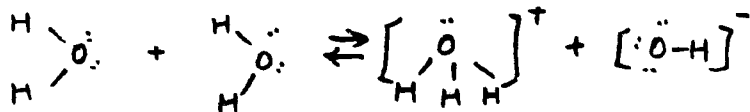
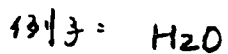
benzoic acid



Monoprotic Acid: (those having one acidic proton)

K_a ~~13~~: see Table 14.2

Amphoteric: a substance ~~to~~ behaves as
an acid or as a base



autodionization

13

Table 14.2

Formula	Name	Value of K_a^*
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
$HC_2H_2ClO_2$	Monochloroacetic acid	1.35×10^{-3}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
$HC_2H_3O_2$	Acetic acid	1.8×10^{-5}
$[Al(H_2O)_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}
$HOCl$	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HOC_6H_5	Phenol	1.6×10^{-10}

*The units of K_a are mol/L but are customarily omitted.

Increasing acid strength

Figure 14.2

Values of K_a for some common monoprotic acids

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-]$$

dissociation const for water

$$= 1.0 \times 10^{-14} \text{ mol}^2/\text{L}^2 \text{ at } 25^\circ\text{C}$$

1. a neutral solution, where $[H^+] = [OH^-]$
2. a acidic solution, where $[H^+] > [OH^-]$
3. a basic solution, where $[H^+] < [OH^-]$

Ex. 14.3 page 665 & 14.4 page 666

at 25°C , calculate $[H^+]$ and $[OH^-]$

a. $1.0 \times 10^{-5} \text{ M } OH^-$

b. $1.0 \times 10^{-7} \text{ M } OH^-$

c. $10.0 \text{ M } H^+$

Sol: $K_w = 1.0 \times 10^{-14}$ at 25°C

$$[H^+][OH^-] = K_w$$

a. $[H^+] \cdot (1.0 \times 10^{-5}) = 1.0 \times 10^{-14}$

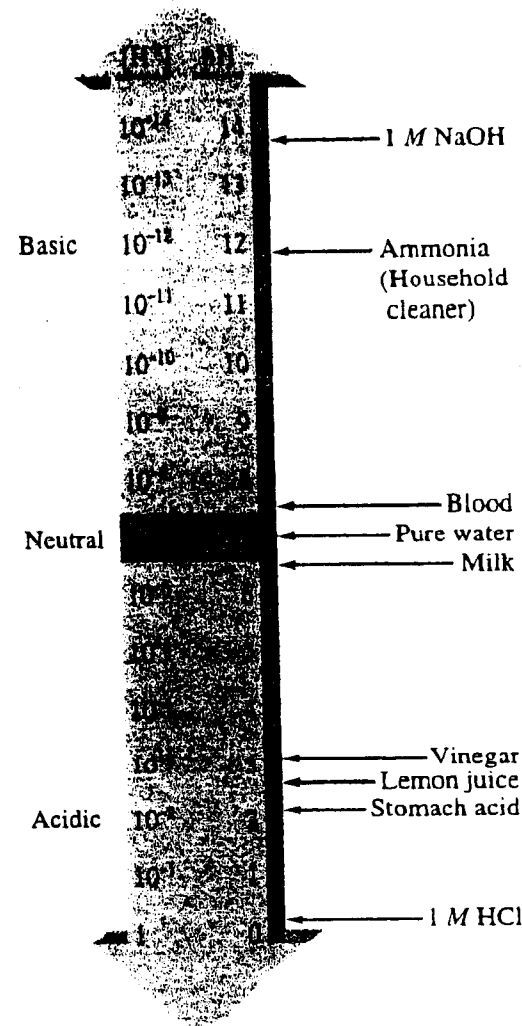
$$[H^+] = 1.0 \times 10^{-9} \quad [H^+] < [OH^-] \text{ basic}$$

b. $[H^+][1.0 \times 10^{-7}] = 1.0 \times 10^{-14}$

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

c. $[10.0][OH^-] = 1.0 \times 10^{-14}$

$$[OH^-] = 1.0 \times 10^{-15} \quad [H^+] > [OH^-] \text{ acidic}$$



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$$pH = -\log [H^+] \quad pOH = -\log [OH^-]$$

the number of decimal places in the log
= the number of significant figures in the original number

例如: $[H^+] = 1.0 \times 10^{-9} M$

2位有效数字

$$pH = -\log [H^+] = 9.00$$

2位小数点以下有效数字

Fig 14. B page 667

pH 增加 1, $[H^+]$ 变为 $1/10$ 倍

pH 减少 1, $[H^+]$ 变为 10 倍

Ex. 14.5 calculate pH and pOH at 25°C

a. $1.0 \times 10^{-3} M OH^-$

b. $1.0 M H^+$

sol. a. $[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11}$

$$pH = -\log [H^+] = -\log (1.0 \times 10^{-11}) = 11$$

$$pOH = 14 - pH = 3 \quad (\text{at } 25^\circ C)$$

取 log

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

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

$$-\log K_w = -\log [H^+] - \log [OH^-]$$

$$pK_w = pH + pOH$$

at 25°C $K_w = 1.0 \times 10^{-14}$

$$pK_w = 14 = pH + pOH$$

Ex. 14.6

The pH of a sample of human blood = 7.41 at 25°C. Calculate pOH, $[H^+]$, and $[OH^-]$ for the sample.

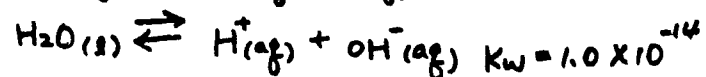
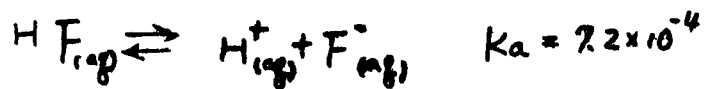
sol. $pH + pOH = 14.00$

$$pOH = 14.00 - 7.41 = 6.59$$

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

$$[H^+] = 10^{-pH} = 10^{-7.41} = 3.9 \times 10^{-8} M$$

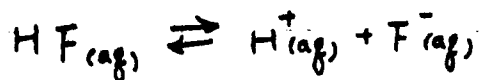
$$[OH^-] = 10^{-pOH} = 10^{-6.59} = 2.6 \times 10^{-7} M$$



If $[\text{HF}]_0 = 1.00 \text{ M}$ initial concentration
calculate pH value of the solution at equilibrium

Sol:

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = 7.2 \times 10^{-4}$$



1 M

1-x

x

x

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = 7.2 \times 10^{-4} = \frac{x^2}{1-x}$$

If $x \ll 1$, then $K_a = \frac{x^2}{1}$

$$\therefore x = \sqrt{K_a} = 2.7 \times 10^{-2}$$

Now 驗算

$$\frac{x}{[\text{HF}]_0} = \frac{2.7 \times 10^{-2} \text{ M}}{1 \text{ M}} = 2.7\% \text{ (can be ignored)}$$

$$\text{pH} = -\log(2.7 \times 10^{-2}) = 1.57$$

漂白水的成分 hypochlorite ion (OCl^-)
Calculate pH of a 0.100 M aqueous soln of hypochlorous acid.

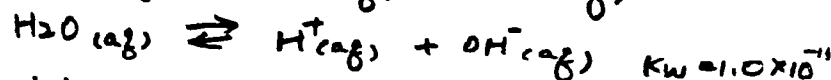
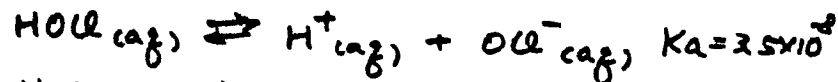
Sol:

Step 1. List the major species.

HOCl (weak acid)

H_2O

Step 2 choose the species that can produce H^+
and write balanced equations for the reactions producing H^+



Step 3 Using the values of equilibrium constants for the reactions you have written, decide which equilibrium will dominate in producing H^+

HOCl is much stronger

Step 4 write the equilibrium expression

$$K_a = 3.5 \times 10^{-8} = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]}$$

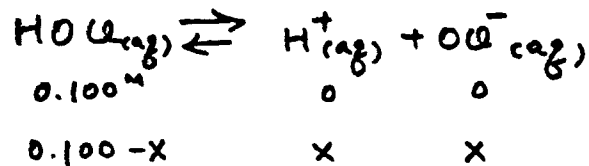
step 6 Define the change needed to achieve equilibrium, that is, define x

$$[HOCl]_0 = 0.100 M \quad [OCl^-]_0 = 0 \quad [H^+]_0 \approx 0$$

x = the amount of HOCl that dissociates in reaching equilibrium

step 7 Write the equilibrium concs in terms of x

step 8 Substitute the equilibrium concs into the equilibrium expression



$$K_a = 3.5 \times 10^{-8} = \frac{x^2}{0.100 - x}$$

step 9 Solve x , (% assuming $[HA]_0 - x \approx [HA]_0$)

step 10 Using 5% rule to verify whether the approx. is valid.

$$x = \sqrt{K_a(0.100 - x)} \approx \sqrt{K_a(0.100)} = 5.9 \times 10^{-5}$$

$$\frac{x}{[HA]_0} = \frac{5.9 \times 10^{-5}}{0.100} = 0.059\% < 5\%$$

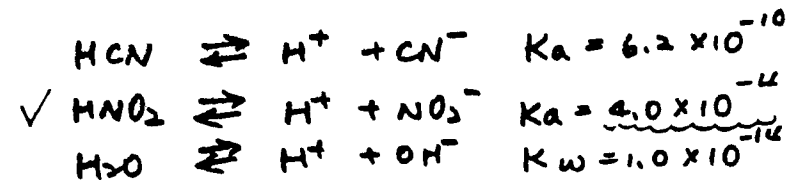
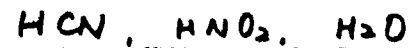
$$pH = -\log[H^+] = -\log(x) = 4.23$$

The pH of a Mixture of Weak Acids

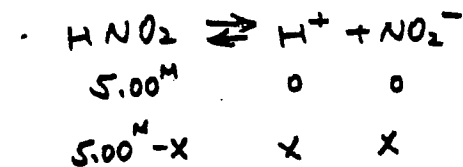
Sample Ex. 14.9

Calculate pH of a soln that contains $1.00 M$ HCN ($K_a = 6.2 \times 10^{-10}$) & $5.00 M$ HNO₂ ($K_a = 4.0 \times 10^{-4}$) also calculate the conc. of cyanide ion (CN⁻) in soln at equilibrium

Sol:



$$K_a(HNO_2) = 4.0 \times 10^{-4} = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

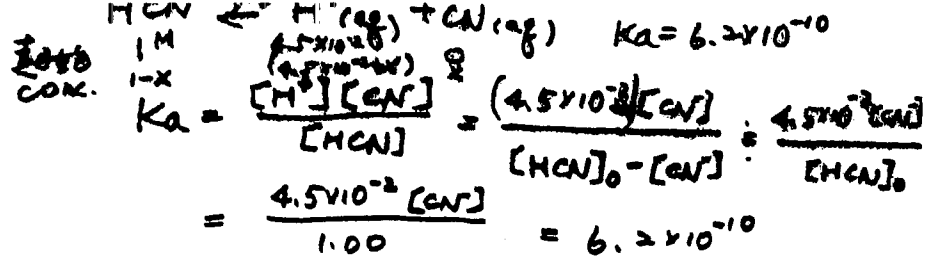


$$K_a = \frac{x^2}{5.00 - x} \approx \frac{x^2}{5.00}$$

$$\therefore pH = -\log x = 1.35$$

$$x = \sqrt{5.00 \cdot K_a} = 4.5 \times 10^{-2}$$

($\frac{4.5 \times 10^{-2}}{5} \times 100\% = 0.9\%$)



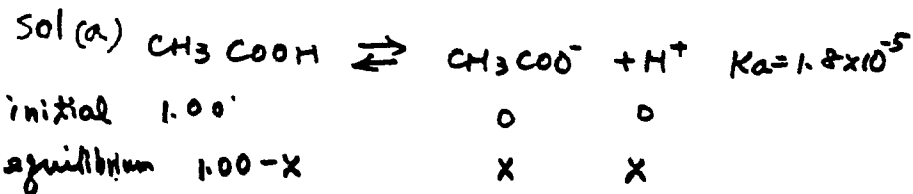
$$[\text{CN}^-] = 1.4 \times 10^{-8} \#$$

Percent dissociation

$$\text{Percent dissociation} = \frac{\text{amount dissociated}}{\text{initial conc.}} \times 100\%$$

sample Ex. 14.10.

calculate the percent dissociation of acetic acid ($K_a = 1.8 \times 10^{-5}$) in each of the following solns. (a) 1.00 M $\text{HC}_2\text{H}_3\text{O}_2$
 (b) 0.100 M $\text{HC}_2\text{H}_3\text{O}_2$



$$K_a = \frac{x^2}{1.00 - x} \approx \frac{x^2}{1.00} \quad \therefore x = 4.2 \times 10^{-3} \text{ M}$$

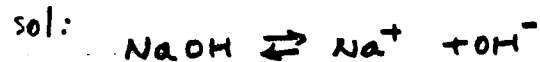
$$\frac{4.2 \times 10^{-3}}{1.00} \times 100\% = 0.42\% \#$$

All the hydroxides of Group 1A elements (alkaline) are strong bases (LiOH , NaOH , KOH , RbOH , and CsOH)

all the hydroxides of Group 2A element (alkaline earth) are strong bases (Ca(OH)_2 , Ba(OH)_2 , and Sr(OH)_2)

Sample Ex. 14.12 (page 682)

Calculate the pH of a $5.0 \times 10^{-2} \text{ M}$ NaOH soln



$K = \infty$

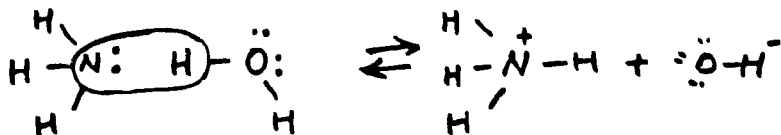
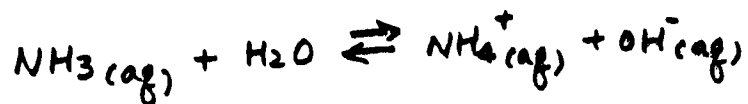
$[\text{OH}^-] = 5.0 \times 10^{-2}$

$\text{pH} = -\log(2 \times 10^{-13})$

$= 12.70$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-2}} = 2 \times 10^{-13}$$

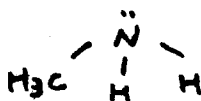
Base is proton "acceptor"



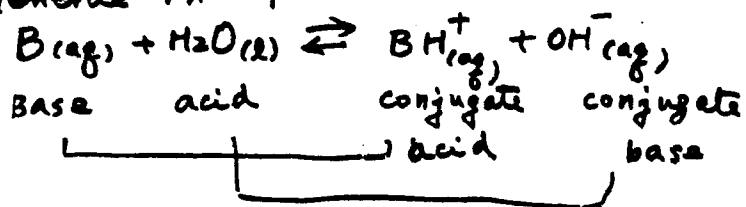
Amines will produce OH^- like NH_3

Ex. methylamine

Pyridine



General rx of a base:



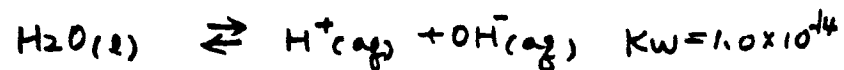
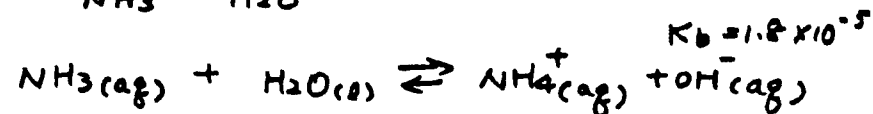
$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

Table 14.3 K_b values

Calculate pH of a 15.0 M soln of NH_3
($K_b = 1.8 \times 10^{-5}$)

Sol: main species:

NH_3 H_2O



$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x \cdot x}{15.0 - x}$$

$$\approx \frac{x^2}{15.0} \quad \therefore x \approx 1.6 \times 10^{-2} = [\text{OH}^-]$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{1.6 \times 10^{-2}} = 6.3 \times 10^{-13} \text{ M}$$

$$\text{pH} = -\log(6.3 \times 10^{-13}) = 12.20$$

§ 14.7 polyprotic Acids

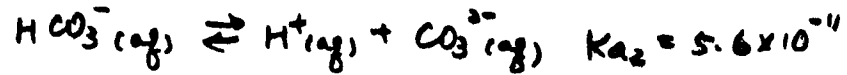
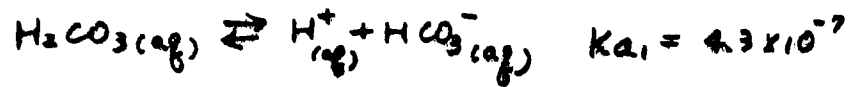
H_2SO_4 sulfuric acid

H_3PO_4 phosphoric acid

H_2CO_3 carbonic acid

a polyprotic acid dissociate "one proton" at a time in a "step-wise" manner.

13440: carbonic acid

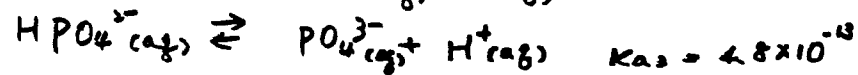
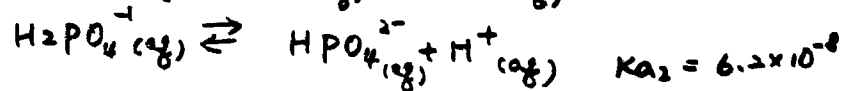
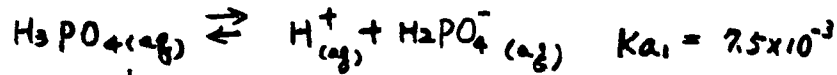


A typical weak polyprotic acid

$$K_{a1} > K_{a2} > K_{a3} \dots$$

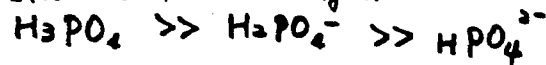
Table 14.4 Step-wise dissociation Consts.

Phosphoric Acid



$$\frac{K_{a1}}{K_{a2}} \approx 10^5 \quad \frac{K_{a2}}{K_{a3}} \approx 10^5$$

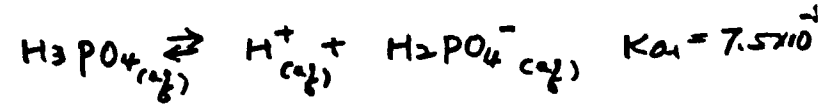
∴ Relative Acid Strength



sample ex. 14.13

Calculate pH of a 5.0 M H_3PO_4 and the concs of H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-}

sol: major species: H_3PO_4 & H_2O



$$5.0 \text{ M} \quad 0 \quad 0$$

$$5.0 - x \quad x \quad x$$

$$K_{a1} = \frac{x^2}{5.0 - x} = 7.5 \times 10^{-3}$$

$$x = 1.9 \times 10^{-1} \text{ M}$$

$$[\text{H}^+] = x = 0.19 \text{ M} \quad \text{pH} = -\log(0.19) = 0.72$$

$$[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.19 \text{ M}$$

$$[\text{H}_3\text{PO}_4] = 5.0 \text{ M} - 0.19 \text{ M} = 4.8 \text{ M}$$

$$\Rightarrow K_{a2} = \frac{6.2 \times 10^{-8}}{(0.19 - x)} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \quad \begin{array}{l} \text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-} \\ 0.19 \quad 0.19 \\ 0.19 - x \quad 0.19 + x \end{array}$$

$$\therefore [\text{HPO}_4^{2-}] = K_{a2} = \frac{6.2 \times 10^{-8}}{0.19} = 3.3 \times 10^{-7} \text{ M}$$

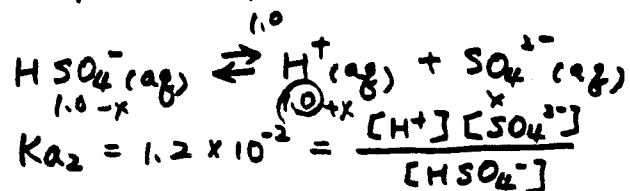
$$K_{a3} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 4.8 \times 10^{-13} = \frac{0.19 [\text{PO}_4^{3-}]}{3.3 \times 10^{-7}}$$

$$[\text{PO}_4^{3-}] = 1.6 \times 10^{-19} \text{ M}$$

Ex. 14.16 Calculate $\hat{\text{pH}}$ of $1.0 \text{ M H}_2\text{SO}_4$

sol:

main species: H^+ , HSO_4^- & H_2O



$$\begin{array}{ccc} 1.0 \text{ M} & & 1.0 \\ 1.0 - x & & 1.0 + x \quad x \end{array}$$

$$K_{a2} = \frac{x(1.0+x)}{1.0-x} = 1.2 \times 10^{-2}$$

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

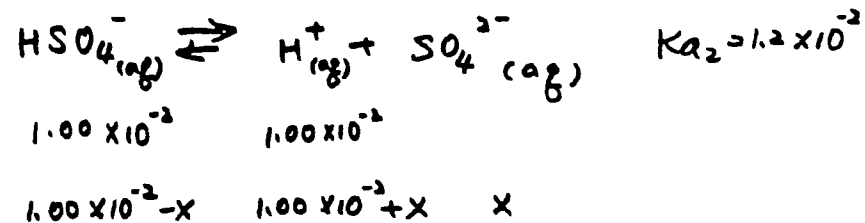
$$\therefore [\text{H}^+] = 1.0 \text{ M} + x = 1.0 \text{ M} + (1.2 \times 10^{-2}) \text{ M} \approx 1.0 \text{ M}$$

$$\therefore \text{pH} = 0.00$$

EX. 14.17

calculate the pH of a $1.00 \times 10^{-2} \text{ M H}_2\text{SO}_4$

sol: major species: H^+ , HSO_4^- , & H_2O



$$K_{a2} = 1.2 \times 10^{-2} = \frac{x(0.01+x)}{0.01-x}$$

x 不可省略
 $x = 0.012$ 如省略
 $\gg 5\%$ of
 0.01

解 \Rightarrow 次方程式:

$$x^2 + 0.01x = (0.012 \times 0.01) - 0.012x$$

$$x^2 + 0.022x - 0.00012 = 0$$

$$x = 4.5 \times 10^{-3}$$

$$\therefore [\text{H}^+] = (1.00 \times 10^{-2}) + (4.5 \times 10^{-3}) = 0.0145$$

$$\text{pH} = 1.84$$

#

Salt: ionic compound

I. Neutral Salts (強酸強鹼的產物)

Salts that consist of the cations of strong bases and the anions of strong acids have no effect on $[H^+]$ when dissolved in water.

Ex. KCl , $NaCl$, $NaNO_3$, KNO_3
 $pH = 7$

II. Salts that produce basic solutions
(弱酸強鹼的產物)

Ex. $NaCH_3COO$

major species Na^+ , CH_3COO^- , and H_2O



base reacting with water to produce hydroxide ion and a conjugate acid

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$K_a \times K_b = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \times \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = [H^+][OH^-] = K_w$$

For any salt whose $\left\{ \begin{array}{l} \text{cation} - \text{neutral (e.g. } Na^+, K^+) \\ \text{anion} - \text{the conjugate base of a weak acid (e.g. } CH_3COO^-) \end{array} \right.$

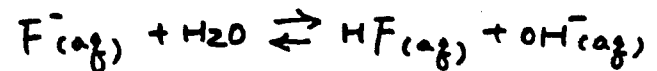
\rightarrow salt will be basic

Ex 14.18

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

Sol: major species Na^+ + F^- and H_2O

HF is a weak acid



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

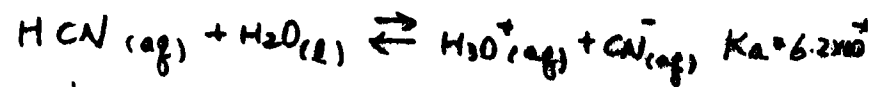
initial	$0.3 M$	0	0
Equil	$0.3 - x$	x	x

$$K_b = \frac{x^2}{0.3 - x} \approx \frac{x^2}{0.3} \quad x \approx 2.0 \times 10^{-6}$$

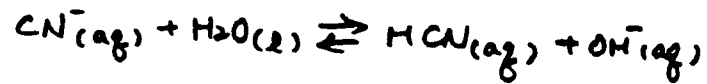
$$\therefore pOH = -\log x = 5.69$$

$$pH = 14 - pOH = 8.31$$

*



base strength: $\text{CN}^- > \text{H}_2\text{O}$



$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-4}} = 1.6 \times 10^{-5}$$

base strength: $\text{OH}^- > \text{CN}^-$

∴ base strength $\text{OH}^- > \text{CN}^- > \text{H}_2\text{O}$ (conjugate base of a weak acid)

Salts that produce Acidic Solution

Ex. NH_4Cl (強酸弱鹼)

salts in which $\left\{ \begin{array}{l} \text{anion} - \text{Cl}^-, \dots \\ \text{cation} - \text{conjugate acid of a weak base} \end{array} \right.$
 → produce acidic soln

Ex. 14-19 & 14-20 & 14-21

$K_a > K_b$ $\text{pH} < 7$ (acidic)

$K_b > K_a$ $\text{pH} > 7$ (basic)

$K_a = K_b$ $\text{pH} = 7$ (neutral)

Ex. 14-21

a. $\text{NH}_4\text{CH}_3\text{COO}$

b. NH_4CN

c. $\text{Al}_2(\text{SO}_4)_3$

sol: (a) K_a of $\text{NH}_4^+ = 5.6 \times 10^{-10}$

$$K_b \text{ of } \text{CH}_3\text{COO}^- = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

∴ $K_a = K_b$ soln will be neutral

see Table 14.6