AP Chem
Topic#9
Acid/Bases
General

Formula Page

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

weak acid, hydrogen ion, weak acid anion

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

$$\text{Percent Ionization} = \frac{[H^+]}{HA_{initial}} \times 100\%$$

Acid-Base General Properties

Acid - Latin (acidus) for "sour."

Alkali - Arabic for ashes (ashes dissolved in wate produce a solution that feels slippery and taste bitter.

Acids

- pH < 7
- $[H^+] > 1.0x10^{-7} M$
- $[H^+] > [OH^-]$
- blue litmus paper **red**
- taste sour
- corrosive
- react with bases to produce water and a salt
- phenolphthalein is **clear** in acidic solutions (pH < 7)
- react with active metals (Zn, Fe, alkali, alkaline earth, etc.) to produce hydrogen gas and a soluble ionic compound.
- hydronium ion is present in great quantities (one can use either $[H^+]$ or $[H_3O^+]$ to represent the concentration of hydrogen ion in solution
- Strong acids are strong electrolytes
- Weak acids are weak elecrolytes
- React with carbonates to produce $CO_2(g)$
- React with sulfides to produce $H_2S(g)$

Bases

- pH > 7
- $[H+] < 1.0 \times 10^{-7} M$
- $[OH^-] > [H^+]$
- red litmus paper **blue**
- tast bitter
- feels slippery
- react with bases to produce water and a salt
- phenolphthalein is **pink** in basic solutions (pH > 7
- Strong bases are strong electrolytes
- Weak bases are weak elecrolytes

Acids/Bases
Topic#9

Acid-Base Theories

Acid - Latin (acidus) for "sour."
Alkali - Arabic for ashes (ashes dissolved in wate produce a solution that feels slippery and taste bitte

Arrhenius Acids/Bases:

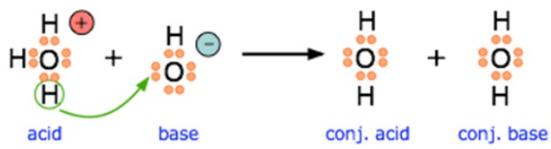
- Acids produce hydrogen ions in aqueous solutions, while bases produce hydroxide ions.
- Only applies to aqueous solutions and allows for only one kind of base - the hydroxide ion.
  - Strong acids:
    - Binary: hydrochloric acid, $HCl(aq)$, hydrobromic acid, $HBr(aq)$, and hydroiodic acid,$HI(aq)$
    - Oxyacids: nitric acid, $HNO_3(aq)$, sulfuric acid, $H_2SO_4(aq)$, chloric acid, $HClO_3(aq)$, and perchloric acid, $HClO_4(aq)$
  - Strong bases:
    - Group I hydroxides: $LiOH(aq)$, $NaOH(aq)$, $KOH(aq)$, $RbOH(aq)$, $CsOH(aq)$
    - Middle 3 Group II hydroxides: $Ca(OH)_2(aq)$, $Sr(OH)_2(aq)$, and $Ba(OH)_2(aq)$

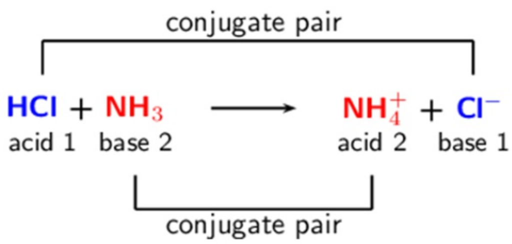
MEMORIZE THE STRONG ACIDS AND BASES!!!!

Acid-Base Theories

Bronsted-Lowry Acids/Bases (BL)

- Acid donates a proton (proton donor)
- Base accepts a proton (proton acceptor)
  - After an acid donates a proton, it becomes a conjugate base as a product in an acid-base reaction.
  - After a base accepts a proton, it becomes a conjugate acid as a product in an acid-base reaction.
    - General BL acid-base equation: A + B ⇔ CB + CA
    - Conjugate acid-base pair: H_2O and OH^-, H_3O^+ and H_2O, HNO_2 and NO_2^-

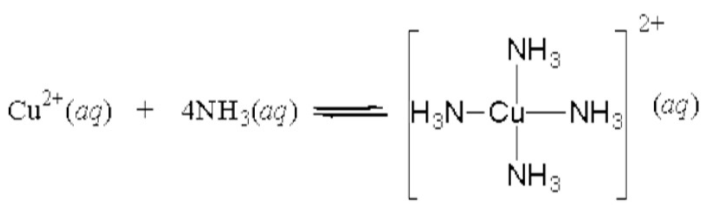


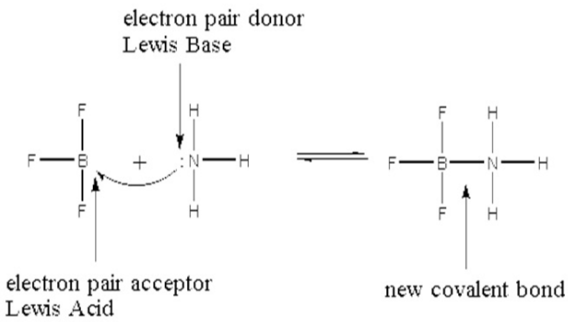


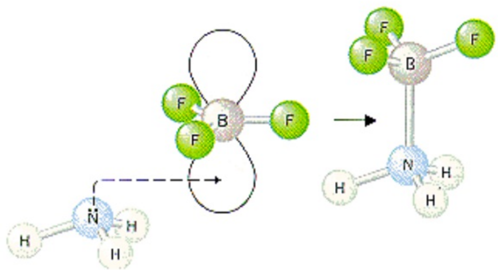
Acid-Base Theories

Lewis Acids/Bases

- Acid is an electron pair acceptor.
  - All transition metal ions are Lewis acids.
- Base is an electron pair donor.







Acid-Base Theories

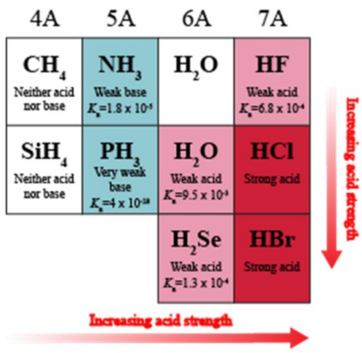
Acid dissociation constant, K_a, is a measure of the strength of an acid.

- The strength of an acid depends on how readily it can donate a hydrogen, H, to another species.
  - A K_a > 1 indicates a strong acid (SA)
    - **SA** include HI(*aq*), HBr(*aq*), HCl(*aq*), HNO_3(*aq*), $HClO_4$(*aq*), $HClO_3$(*aq*) and H_2SO_4(*aq*).
    - SA ionize 100% into H^+ (H_3O^+, hydronium) and the acid anion (A^-)
    - Written as a complete reaction: HCl(*aq*) → H^+(*aq*) + Cl^-(*aq*) with K_a >> 1
    - In binary acids (an acid with just two elements, one being H) (H-X), the strength of the acid depends on the strength of the bond between the H and the second element. To determine relative strength, use the size of the atom attached to H. The larger the atom attached to H, the weaker the bond between the H and other atom. Weaker bonds makes it easier for water to remove the hydrogen.
      - Please order from weakest to strongest: HI(*aq*), HCl(*aq*), and HBr(*aq*)
    - In oxyacids (H-O-X), the strength of the acid depends on the number of oxygens attached to the X element. As the number of oxygens increases, the O-H bond becomes weaker and more polarized, so the H is more easily removed by water.
      - **Please order from weakest to strongest**: $HClO_3$(aq), $HClO_2$(*aq*), HClO(*aq*) and $HClO_4$(*aq*).
    - What if the X is the only difference between the acids (HOCl vs HOBr)?
      - Then the strength of the acid depends on the EN values of the X. The greater the EN value, the greater the attraction of electrons. This weakens the O-H bond resulting in a higher acid strength.
        - **Please order from weakest to strongest**: HOCl(*aq*), HOI(*aq*), and HOBr(*aq*).

Acid Strength Due to Structure

Table 14.7 | Bond Strengths and Acid Strengths for Hydrogen Halides

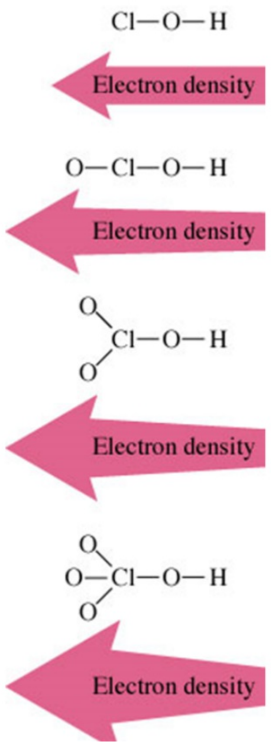
H—X Bond	Bond Strength (kJ/mol)	Acid Strength in Water
H—F	565	Weak
H—Cl	427	Strong
H—Br	363	Strong
H—I	295	Strong

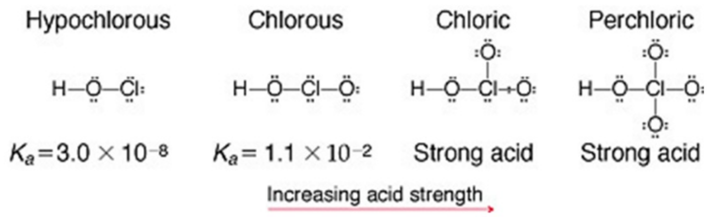


strength dependent on bond length

strength dependent on the electronegativity of central atom

Acid Strength Due to Structure





The O-H bond becomes more polar as the number of oxygens around the central atom increases.

Acid Strength Due to Structure

Factors Affecting Acid Strength

In oxyacids, in which an -OH is bonded to another atom, Y, the more electronegative Y is, the more acidic the acid.

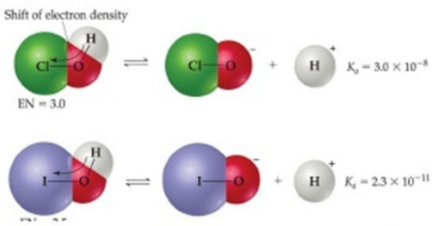
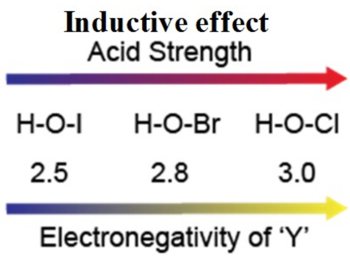


TABLE 16.6 ■ Electronegativity Values (EN) of Y and Acid-Dissociation Constants

Acid	EN of Y	K_a
HClO	3.0	3.0×10^{-8}
HBrO	2.8	2.5×10^{-9}
HIO	2.5	2.3×10^{-11}



Acids and Bases

Weak Acids

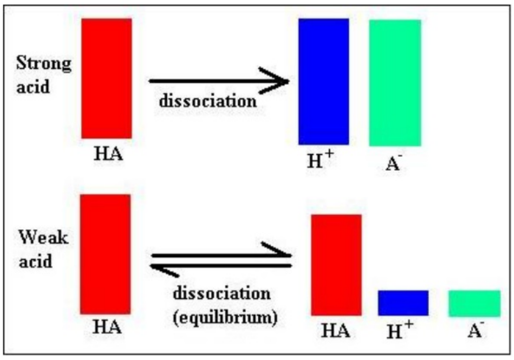
- A $K_a < 1$ indicates a weak acid (WA)
  - WA include $HCN(aq)$, $HNO_2(aq)$, $HF(aq)$, $H_3PO_4(aq)$, $HSO_4^-(aq)$, $HOCl(aq)$, $HClO_2(aq)$, $CH_3COOH(aq)$ ($HC_2H_3O_2(aq)$), and $NH_4^+(aq)$.
    - These are the most common WA used on the test.
  - WA only partially ionize (usually under 10%), so WA are in a state of equilibrium.
    - Written as an equilibrium: $HCN(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + CN^-(aq)$ with a $K_a = 6.2\text{x}10^{-10}$

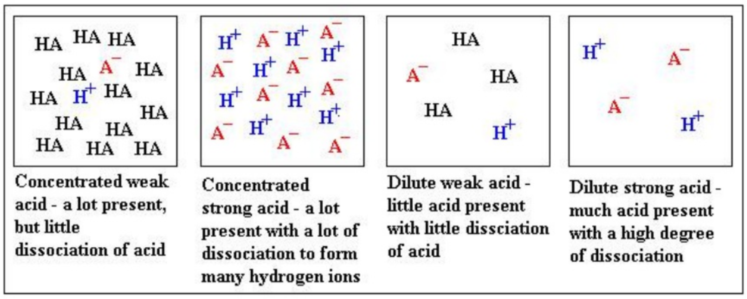
      ≃ 99%   1% ionizes
    - General equation for a weak acid: $\underset{\text{weak acid}}{HA} \rightleftarrows \underset{\text{hydrogen ion}}{H^+} + \underset{\text{weak acid anion}}{A^-}$
    - Equilibrium expression for a weak acid: $K_a = \frac{[H^+][A^-]}{[HA]}$

No.	Acid	K_a	pK_a
1	Hydroiodic acid (HI)	3.16x10⁹	-9.5
2	Hydrobromic acid (HBr)	1.0x10⁹	-9
3	Hydrochloric acid (HCl)	1.0x10⁶	-6
4	Sulfuric acid (H_2SO_4)	1.0x10³	-3
5	Hydronium ion (H_3O^+)	55	-1.74
6	Nitric acid (HNO_3)	28.2	-1.45
7	Trifluoroacetic acid (CF_3COOH)	5.62x10⁻¹	0.25
8	Oxalic acid (HOOC–COOH)	5.37x10⁻²	1.27
9	Acetic acid (CH_3COOH)	1.75x10⁻⁵	4.76

Weak Acids

Quatities of HA, H^+, and A^- @ equilibrium: SA vs. WS





Acids/Bases
Topic#9

Formula Page

HA ⇄
weak acid hydr

K_a =

Various Ways to Describe Acid Strength

Property	**Strong Acid (SA)**	**Weak Acid (WA)**
K_a	large	small
Position of the ionization equilibrium	far to the right	far to the left
Equilibrium concentration of $[H^+]$ compared to $[HA]_o$	$[H^+] \cong [HA]_o$	$[H^+] << [HA]_o$
Strength of conjugate base compared to water	A^- much weaker base than water*	A^- much stronger base than water**
*Does not react with water	$A^- + H_2O \rightarrow NR$	
**Does react with water		$A^- + H_2O \Leftrightarrow HA + OH^-$

Note: When an ion is a stronger base or acid than water, hydrolysis of water by the ion occurs. This is a Bronsted-Lowry acid base reaction

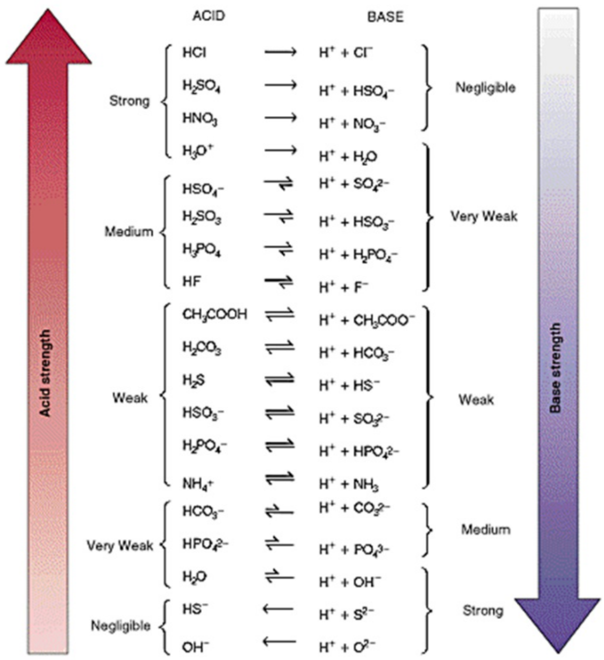
- an anion reacts with H_2O to form OH^- ions or a cation reacts with H_2O to form H_+ ions
- the acid/base strength of an ion depends on its parent acid or base. The stronger the parent acid/base the weaker the conjugate base/acid. Ex. F^- comes from HF which is a weak acid so F^- is a stronger conjugate base than Cl- which comes from the parent acid, HCl.

Formula Page

Acid Strength Conjugate Base Strength

As the strength of the acid, increases the strength of the conjugate base decreases. In other words, the *ability* of the conjugate base to react with water decreases as the strength of its acid increases.

- Cl- is a very weak base (does not react with water.
- F^- is a strong enough base to react with water to create HF molecules and OH^- ions.



Acid-Base Theories

Acids-Bases Sample WS#1 - Introduction to Acid-Bases

1. Write the simple dissociation (ionization) reaction with water for each of the following acids and label the acid (A), base (B), conjugate base (CB), and conjugate acid (CA):

a. hydrochoric acid (HCl) $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

b. acetic acid (ethanoic acid) ($HC_2H_3O_2$ and CH_3COOH)

$CH_3COOH(aq) + H_2O \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
A, B, CB, CA

c. the ammonium ion (NH_4^+)

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
A, B, CA

d. the anilinium ion ($C_6H_5NH_3^+$)

$C_6H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_2(aq) + H_3O^+(aq)$
A, B, CB, CA

e. methyl amine (CH_3NH_2)

$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$
B, A, CA, CB

Acid-Base Theories

Bronsted-Lowry Acid-Base Reactions Practice Problems

2. Identify the acid (A), base (B), conjugate base (CB), and conjugate acid (CA) in each of the following reactions.

a. $NH_3(aq) + HNO_2(aq) \Leftrightarrow NO_2^-(aq) + NH_4^+(aq)$
B A CB CA

b. $H_2PO_4^-(aq) + HCl(aq) \rightarrow H_3PO_4(aq) + Cl^-(aq)$
B A CA CB

c. $CH_3NH_3^+(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + CH_3NH_2(aq)$
A B CA CB

d. $H_2PO_4^-(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + HPO_4^{2-}(aq)$
A B CA CB

Amphoteric Species

- A species that can act as a BL acid or base
- Has the ability to donate a proton, H+, (acid) or accept a proton (base).
- Examples include $H_2PO_4^{1-}$, HPO_4^{2-}, H_2O, HS^{1-}, HSO_4^{1-},

Acid-Base Theories

Acid-Base Reaction Product Prediction Practice Problems

3. Predict the products of the following acid-base reactions and identify the acid (A), base (B), conjugate base (CB), and conjugate acid (CA).

a. $PO_4^{3-}(aq) + H_2O(l) \rightarrow$ $HPO_4^{2-}(aq) + OH^-(aq)$
B A CA CB

b. $HS^-(aq) + NH_3(aq) \rightarrow$ $S^{2-}(aq) + NH_4^+(aq)$
A B CB CA

c. $NH_4^+(aq) + S^{2-}(aq) \rightarrow$ $NH_3(aq) + HS^-(aq)$
A B CB CA

Acid-Base Theories

Relative Base Strength Practice Problems

4. Arrange the following species according to their strengths as bases: H_2O, F-, Cl-, NO_2^-, and CN^-.
K_a (HF) = 7.2×10^{-4}, K_a (HCl) >> 1, K_a (HNO_2) = 4.0×10^{-4}, and K_a (HCN) = 6.2×10^{-10}

(1) Order according to acid strength.

$HCl > HF > HNO_2 > HCN$

(2) Write the A⁻ of the acid (The conjugate base) and reverse the symbol.

$Cl^- < F^- < NO_2^- < CN^-$

(3) Place H_2O between the CB it will react with and the first CB it does not react with.

$Cl^- < H_2O < F^- < NO_2^- < CN^-$

Calculating pH/pOH/[H_3O^+]/[OH^-]

Self Ionization of Water @ 25°C
K_w = [H^+] x [OH^-] = 1.0x10^{-14}
Neutral solution: [H^+] = [OH^-]
Acidic solution: [H^+] > [OH^-]
Basic solution: [H^+] < [OH^-]

Acids-Bases Sample WS#2 - pH/pOH/[H_3O^+]/[OH^-]

[H^+] and [OH^-] Practice Problems

1. Calculate [H^+] or [OH^-] as required for each of the following solutions at 25°C, and state whether the solution is neutral, acidic, or basic.

a. 1.0x10^{-5}*M* OH^-

$[H_3O^+] = \frac{K_w}{[OH^-]}$
$= \frac{1.0\times10^{-14}}{1.0\times10^{-5}} =$
$= 1.0\times10^{-9}$ M
basic

b. 1.0x10^{-7}*M* OH^-

$[OH^-] = \frac{K_w}{[H_3O^+]}$
$= \frac{1.0\times10^{-14}}{1.0\times10^{-7}}$
$= 1.0\times10^{-7}$ M H_3O^+
neutral

c. 10.0*M* H^+

$[H_3O^+]$ = 10.0 M
$[OH^-] = \frac{1\times10^{-14}}{10}$
$= 1\times10^{-15}$ M
Acidic

Acid-Base Theories

Self Ionization of Water @ 25ºC
$K_w = [H^+] \times [OH^-] = 1.0 \times 10^{-14}$
Neutral solution: $[H^+] = [OH^-]$
Acidic solution: $[H^+] > [OH^-]$
Basic solution: $[H^+] < [OH^-]$

Acids-Bases Sample WS#2 - pH/pOH/[H_3O^+]/[OH^-]

2. At 60ºC, the value of K_w is 1.0×10^{-13}.
   a. Using Le Chatelier's principle, predict whether the reaction $2H_2O(l) \Leftrightarrow H_3O^+(aq) + OH^-(aq)$ is exothermic or endothermic.
   b. Calculate $[H^+]$ and $[OH^-]$ in a neutral solution at 60ºC.

(a.) Since the K_w increased from 1.0×10^{-14} to 1.0×10^{-13} with an increase of temperature from 25° C to 60°C, the ionization of water is endothermic.

(b.) $[H^+][OH^-] = 1.0 \times 10^{-13}$

$x^2 = 1.0 \times 10^{-13}$

$x = \sqrt{1.0 \times 10^{-13}}$

$x = 3.2 \times 10^{-7}$

$3.2 \times 10^{-7}\ M = [H^+] = [OH^-]$

Acid-Base Theories

The pH Scale

- 0-14
- pH is the measure of the hydrogen content of a solution.
- Best method of measuring pH is by using a pH meter.
- pH < 7; acidic solution
- pH> 7; basic solution
- pH = $-\log[H^+]$
- pOH = $-\log[OH^-]$
- pH + pOH = 14
- $[H^+] = 10^{-pH}$
- $[OH^-] = 10^{-pOH}$

Acid-Base Theories

Calculations involving pH/pOH Practice Problems

3. Calculate pH and pOH:

a. $1.0x10^{-3} M\ OH^-$

c. $3.0x10^{-4} M\ H^+$

b. $1.0 M\ OH^-$

d. $5.5x10^{-4} M\ OH^-$

Acid-Base Theories

4. The pH of a sample of human blood was measured to be 7.41 at 25°C. Calculate pOH, [H^+], and [OH^-] for the sample.

C
3.

Givn
pH = 7.41
25°C

NTK
pOH = 14 − pH
[H^+] = 10^{-pH}
[OH^-] = 10^{-pOH}

Unk
pOH = 6.59
[H^+] = 3.9×10^{-8} M
[OH^-] = 2.6×10^{-7} M

Solve: pOH = 14 − 7.41 = 6.59
[H^+] = $10^{-7.41}$ = 3.8×10^{-8} M
[OH^-] = $10^{-6.59}$ = 2.6×10^{-7} M

Acid-Base Theories

Calculating the pH of Strong Acids/Bases Practice Problems

5. a. Calculate the pH and pOH of 0.10*M* HNO_3
   b. Calculate the pH and pOH of 1.0x10^{-10}*M* HCl
   c. Calculate the pH and pOH of 0.030*M* HI
   d. Calculate the pH and pOH of 0.10*M* NaOH
   e. Calculate the pH and pOH of 0.00450*M* KOH
   f. Calculate the pH and pOH of 0.030*M* $Ca(OH)_2$

f. $[OH^-] = 2 \times 0.030 = 0.060$
pOH = $-\log(0.060) = 1.22$
pH = 14 − 1.22 = 12.78

$[OH^-] = [B]$

a. $[H^+] = [HA]$ pH = 1.00
$[H^+] = 0.10M$ pOH = 13.00

d. $[OH^-] = .10$ pOH = 1.00
pH = 13.00

e. $[OH^-] = 0.00450$ pOH = $-\log(OH^-)$
pOH = $-\log(0.0045)$
pOH = 2.347
pH = 14 − 2.347
= 11.653

b. $[H^+] = 1.0 \times 10^{-10}$ pH = 10
pOH = 4

c. $[H^+] = 0.030$ pH = $-\log(0.030) = 1.52$
pOH = 14 − 1.52 = 12.48

Acid-Base Theories

Percent Ionization

- Amount of acid/base that has ionized
- SA/SB ionize 100%
- WA/WB ionize under 10%, with most under 5%
- % ionized = $\frac{[H^+]}{[HA]_o}$ x 100% or $\frac{[OH^-]}{[B]_o}$ x 100%
- Rule: under 5% ionization you can get rid of the +x when solving for an equilibrium concentration of H^+ or other species.
- Use K_a to solve for $[H^+]$ or K_b to solve for [OH-].

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

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2}{[HA]}$$

$$[H^+] = \sqrt{K_a[HA]}$$

$$B + H_2O \leftrightarrow BH^+ + OH$$

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{[OH^-]^2}{[B]_o}$$

$$[OH^-] = \sqrt{K_b[B]}$$

Percent Ionization (Dissociation) Practice Problem

6. Calculate the percent dissociation of acetic acid ($K_a = 1.8x10^{-5}$) in each of the following solutions.

a. 1.00*M* $HC_2H_3O_2$ (Ans: 0.42%)

$[H^+] = \sqrt{(K_a)[HA]_o} = \sqrt{(1.8x10^{-5})(1)} = 0.0042$

% ionized = $\frac{[H^+]}{[HA]_o}$ x 100% = $\frac{0.0042}{1.00}$ x 100% = **0.42% ionized**

b. 0.100*M* $HC_2H_3O_2$ (Ans: 1.3%)

$[H^+] = \sqrt{(1.8x10^{-5})(0.100)} = 0.00134$

$\frac{0.00134}{0.100}$ x 100% = **1.3% ionized**

Acid-Base Theories

Calculating the pH of a Weak Acid

- set up as an equilibrium
- $[H^+] = (K_a \times [HA]_o)^{1/2}$ $[H^+] = \sqrt{K_a [HA]}$
- Check for % ionization
- If less than 5% you are OK, if not set up equilibrium expression and use quadratic equation.
  - $\% \text{ ionization} = \frac{[H^+]}{[HA]_o} \times 100\%$

Calculating Percent Ionization

- Percent ionization = $\frac{[H_3O^+]_{eq}}{[HA]_{initial}} \times 100$
- In this example,

  $[H_3O^+]_{eq} = 4.2 \times 10^{-3}\ M$

  $[HCOOH]_{initial} = 0.10\ M$

Percent ionization = $\frac{4.2 \times 10^{-3}}{0.10} \times 100$

$= 4.2\%$

Acid-Base Theories

pH of a Weak Acid Practice Problems

7. Calculate the pH of a 0.100*M* aqueous solution of HOCl (hypochlorous acid) ($K_a = 3.5 \times 10^{-8}$). (Ans: 4.23)

Major species: $HOCl$ / H_2O

Species producing H^+: $HOCl_{(aq)} \rightleftharpoons H^+ + OCl^-_{(aq)}$

Write Equil Exp for dominant rxn: $K_a = \frac{[H^+][OCl^-]}{[HOCl]}$

Set up RICE table:

Use $[H^+] = \sqrt{K_a [HA]}$ $= [H^+] = \sqrt{(3.5 \times 10^{-8})(0.1)} = 5.9 \times 10^{-5} M$

Check 5% rule: $\frac{5.9 \times 10^{-5}}{0.1} \times 100\% = 0.059\%$

Solve for pH: $pH = -\log(5.9 \times 10^{-5}) = \underline{4.229}$

Acid-Base Theories

$HCN \rightleftharpoons H^+ + CN^-$
$HNO_2 \rightleftharpoons H^+ + NO_2^-$

pH of a Weak Acid Mixture Practice Problems

8. Calculate the pH that contains 1.00*M* HCN ($K_a = 6.22 \times 10^{-10}$) and 5.00*M* HNO_2 ($K_a = 4.0 \times 10^{-4}$). Also calculate the concentrations of cyanide ion (CN^-) in this solution at equilibrium. (Ans: 1.35 and $1.4 \times 10^{-8}M$)

Major species: HCN / H_2O / HNO_2

Species producing H^+: HNO_2

Write Equil Exp for dominant rxn: $K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$

Set up RICE table:

Use $[H^+] = (K_a \times [HA]_o)^{1/2}$: $[H^+] = \sqrt{4.0 \times 10^{-4} (5)} = 4.47 \times 10^{-2} M$

R	HCN	$\rightleftharpoons$ H^+	$+ CN^-$
I	1	4.47×10^{-2}	0
C	$1 - x$	$4.47 \times 10^{-2} + x$	$+x$
E	$1 - x$	$4.47 \times 10^{-2} + x$	x

Check 5% rule:

Solve for pH: $pH = -\log(4.47 \times 10^{-2}) = 1.35$

$K_a = \frac{[H^+][CN^-]}{[HCN]}$

$\frac{(1)(6.22 \times 10^{-10})}{(4.47 \times 10^{-2})} = [CN^-] = 1.3 \times 10^{-8} M$

Acid-Base Theories

Calculating K_a from Percent Dissociation Practice Problems

9. Lactic acid ($HC_3H_5O_3$) is a waste product that accumulates in muscle tissue during exercise, leading to pain and a feeling of fatigue. In a 0.100*M* aqueous solution, lactic acid is 3.7% dissociated. Calculate the value of K_a for this acid. (Ans: $1.4x10^{-4}$)

Given
0.100M HA

0.100
x 0.037
0.0037 M H+ + A-

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

K_a = ______

	HA	⇌	H+	+ A-
R	HA		H+	A-
I	0.100		0	0
C	-x		+x	+x
E	0.100-x		0.0037	0.0037

$K_a = \frac{(0.0037)(0.0037)}{0.1} = 1.4 \times 10^{-4}$

$K_a = \frac{(0.0037)(0.0037)}{0.0963} = 1.4 \times 10^{-4}$

Acid-Base Theories

Bases

- Strong Bases (SB) completely dissociate
  - All are ionic compounds (LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$)
  - $NaOH(s) \rightarrow Na^{+}(aq) + OH^{-}(aq)$
  - $[B]_o = [OH^-]_E$
- Weak Bases (WB) partially dissociate (ionic compound: $Mg(OH)_2(s) \Leftrightarrow Mg^{2+}(aq) + 2OH^{-}(aq)$) or ionize (molecular compound, $CH_3NH_2(aq) + H_2O(l) \Leftrightarrow CH_3NH_3^{+}(aq) + OH^{-}(aq)$)
  (methyl amine)
- WB need to be set up in a RICE table
- The $[OH^-]$ can be calculated by using the K_b (measure of the base strength).
- $K_w = K_a \times K_b = 1.0 \times 10^{-14}$ NH_3/NH_4^+

$$B_{(aq)} + H_2O_{(aq)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

$$[OH^-] = \sqrt{K_b[B]}$$

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

Acid-Base Theories

Topic#9 Sample WS#3 - pH of Bases Practice Problems

1. Calculate the pH of a $5.0x10^{-2}$ *M* NaOH solution. (Ans: 12.70)

Gvn
$[NaOH] = [OH^-] = 5.0x10^{-2}$

NTK
$pOH = -\log[OH^-]$
$pH = 14 - pOH$

Unk
$pH = 12.70$

Solve: $pOH = -\log(5.0x10^{-2}) = 1.30$ $pH = 14 - 1.30 = 12.70$

2. Calculate the pH, pOH, and percent ionization of a 15.0*M* solution of NH_3 ($K_b = 1.8x10^{-5}$).
(Ans: 12.20, 1.80, and 0.11%))

3. (O

Gvn
$15.0M = [NH_3]_0$
$K_b = 1.8x10^{-5}$

NTK
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
$[OH^-] = \sqrt{K_b[B]_0}$

pH = 12.21
pOH = 1.79
%ion = 0.11%

Solve: $[OH^-] = \sqrt{(1.8x10^{-5})(15)} = 1.64x10^{-2} M\ OH^-$
$pOH = -\log(1.64x10^{-2}) = 1.79$
$pH = 14 - 1.79 = 12.21$

$\%ion = \frac{1.64x10^{-2}}{15} x100 = 0.11\%$

Acid-Base Theories

3. (OYO) Calculate the pH, pOH, and percent ionization of a 1.0*M* solution of methylamine (K_b = 4.38x10^{-4}).
(Ans: 12.32, 1.68, and 2.1%)

Gin
$[CH_3NH_2] = 1.0M$
$K_b = 4.38x10^{-4}$

NTK
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$
$[OH^-] = \sqrt{K_b[B]_0}$

UK
pH = 12.32
pOH = 1.68
%ion = 2.1%

Solve:
$[OH^-] = \sqrt{(4.38x10^{-4})(1.0)}$
$= 0.0209\ M\ OH^-$
$pOH = -\log(0.0209) = 1.68$
$pH = 14 - 1.68 = 12.32$

$\%ion = \frac{0.0209}{1} \times 100\%$
$= 2.1\%$

Acid-Base Theories

Polyprotic Acids

- acids with more than one acidic hydrogen
- most common: H_3PO_4, H_2SO_4, H_2SO_3, H_2CO_3, and $H_2C_2O_4$.
- Acids with more than one ionizable hydrogens, will ionize in steps.
  - Two acidic hydrogens, two equations with water
  - Three acidic hydrogens, three equations with water
- For each equation, a K_a value exists. $K_a = K_{a1} \times K_{a2}$ x etc.
- Generally, $K_{a1} > K_{a2} >$ etc.
- Can calculate pH, $[H^+]$, from first reaction for high concentrations of the acid.
- For low concentrations, check for 5% rule after first solution for $[H^+]$.

Consider the dissociation of phosphoric acid.

$H_3PO_{4(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + H_2PO_4^-{}_{(aq)}$ $K_{a1} = 7.5 \times 1$

$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + HPO_4^{2-}{}_{(aq)}$ $K_{a2} = 6.2 \times 1$

$HPO_4^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + PO_4^{3-}{}_{(aq)}$ $K_{a3} = 4.8 \times 1$

$K_a = 2.2\text{x}10^{-22}$

H^+, HSO_4^- HS^- HCO_3^{-1}

$NaHSO_4$

Table 14.4 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid*	H_2S	1.0×10^{-7}	$\sim 10^{-19}$	
Oxalic acid	$H_2C_2O_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}	

*The K_{a_2} value for H_2S is very uncertain. Because it is so small, the K_{a_2} value is very difficult to measure accurately.

Acid-Base Theories

Calculating pH of Polyprotic Acids Practice Problems

4. Calculate the pH of a 5.0*M* H_3PO_4 solution and the equilibrium concentrations of the species H_3PO_4, $H_2PO_4^-$ HPO_4^{2-}, and PO_4^{3-}. (K_{a1} = 7.5x10^{-3}, K_{a2} = 6.2x10^{-8}, and K_{a3} = 4.8x10^{-13})
(Ans: pH = 0.72, [H^+] = [$H_2PO_4^{1-}$]=0.19*M*, [H_3PO_4] = 4.8*M*, [HPO_4^{2-}] = 6.2x10^{-8}, and [PO_4^{3-}] = 1.6x10^{-19})

(work on next page)

Acid-Base Theories

R	HPO_4^{2-}	⇌	H^+ +	PO_4^{3-}
I	6.2×10^{-8}		0.194	0
C	$-x$		$+x$	$+x$
E	$6.2\times10^{-8}-x$		$0.194+x$	x

$K_{a_3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.8\times10^{-13} = \frac{[0.194](PO_4^{3-})}{(6.2\times10^{-8})}$

$[PO_4^{3-}] = \frac{(4.8\times10^{-13})(6.2\times10^{-8})}{0.194}$

R	H_3PO_4	⇌	$H_2PO_4^-$ +	H^+
I	5.0		0	0
C	$-x$		$+x$	$+x$
E	$5.0-x$		x	x

$K_a = \frac{[H_2PO_4^-][H^+]}{[H_3PO_4]}$

$7.5\times10^{-3} = \frac{x^2}{5}$ $[H_2PO_4^-]$

$\sqrt{(5)7.5\times10^{-3}} = x = [H^+] = 0.194$

$\%im = \frac{0.194}{5}\times100\% = 3.9\%$

$pH = -\log(0.194) = 0.71$

$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^{1-} + H_3O^+$
$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$
$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$

$K_{a_1} = 7.5\times10^{-3}$
$K_{a_2} = 6.2\times10^{-8}$
$K_{a_3} = 4.8\times10^{-13}$

$[H^+] = [H_2PO_4^-] = 0.194$
$[H_3PO_4] = 5-x = 5-0.194 = 4.8$

	$H_2PO_4^-$	⇌	HPO_4^{2-} +	H^+
I	0.194		0	0.194
C	$-x$		$+x$	$+x$
E	$0.194-x$		x	$0.194+x$

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

$6.2\times10^{-8} = \frac{(x)(0.194)}{(0.194)}$

pH = 0.71
$[H_3PO_4]$ = 4.8 M
$[H_2PO_4^-]$ = 0.194 M
$[HPO_4^{2-}]$ = 6.2×10^{-8} M
$[PO_4^{3-}]$ = 1.5×10^{-19} M

Acid-Base Theories

Salt Hydrolysis

- A salt is created from an acid-base reaction (neutralization)
- Occurs when a salt dissolved in water changes the pH of water
- One of the ions from the salt reacts with water to form H^+ or OH^- ions.
- Cations from SB DO NOT react with water.
  a. Na^+, K^+, Ca^{2+}, Sr^{2+}, etc.
- Anions from SA DO NOT react with water.
  a. Cl^-, Br^-, NO_3^-, SO_4^{2-}, etc.

NaOH (SB)
$NaC_2H_3O_2$ basic
$HC_2H_3O_2$ (WA)

WB NH_4OH
NH_4Cl acidic
HCl (SA)

SA + SB --> neutral salt and water

SA + WB --> acidic salt and water
salt will lower the pH of the solution

$HCl + NH_4NO_3 \rightarrow HNO_3 + NH_4Cl$

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

SB + WA ---> basic salt and water
salt will raise the pH of the solution

$NaOH + HC_2H_3O_2 \rightarrow HOH + NaC_2H_3O_2$

$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$

WA + WB --> salt and water
salt affect on pH is determined by the K_a and K_b

Acid-Base Theories

How to do a "quick" determination of whether a salt will produce an acidic or basic solution.

1. Determine parent acid by adding an "H" to the anion.
   Ex. NaF, HF is a WA.
2. Determine parent base by adding "OH" to the cation.
   Ex. NaF, NaOH is a SB.
3. The "strong" part determines the nature of the solution.
   Ex. Since NaOH is a SB, the NaF solution is basic (pH>7).
   Why? Na^+ DOES not react with water while F^- does react with water:
   $F^-(aq) + H_2O(l) \rightarrow HF(aq) + OH^-(aq)$
4. If both parent acid/base are from weak acids/bases then you have to look at the K_a and K_b values of the parent acid or base.
   a. If the $K_a > K_b$ then the solution is acidic.
   b. If the $K_b > K_a$ then the solution is basic.

Table 14.5 Qualitative Prediction of pH for Solutions of Salts for Which Both Cation and Anion Have Acidic or Basic Properties

$K_a > K_b$	pH < 7 (acidic)
$K_b > K_a$	pH > 7 (basic)
$K_a = K_b$	pH = 7 (neutral)

Neutral Salts - a salt created from a SA and SB.
$NaNO_3$: $HNO_3 + NaOH$

Basic Salts - a salt created from a WA and a SB.
$KC_2H_3O_2$: $HC_2H_3O_2 + KOH$

Acidic Salts - a salt created form a SA and a WB.
NH_4Cl: $HCl + NH_4OH$

Example: What is the qualitative pH of $Fe(NO_3)_3$?

Acid-Base Theories

Determination of a Salt as Acidic, Basic, or Neutral Practice Problems.

5. Predict whether an aqueous solution of each of the following salts will be acidic, basic, or neutral. Prove with appropriate equations.
   a. $NaC_2H_3O_2$
   b. NH_4NO_3
   c. NH_4CN (K_a (HCN) = 6.2×10^{-10} and the K_b (NH_3) = 1.8×10^{-5})

(a) $NaC_2H_3O_2$ Parent Acid is $HC_2H_3O_2$ (WA)
Parent Base is NaOH (SB)
Since the parent base is strong and parent acid is weak, the salt will produce a basic solution.

(b) NH_4NO_3
Parent acid : HNO_3 (SA)
Parent base : NH_4OH (WB)
Since the parent acid is strong and the parent base is weak, the salt will produce an acidic solution.

(c) NH_4CN
Parent acid: HCN (WA)
Parent base: NH_4OH (WB)
($NH_3 + H_2O$)
K_a (HCN) < K_b (NH_3) the solution will be basic. This means CN^- is a more effect base than NH_4^+ is an effect acid.

Acid-Base Theories

6. What is the relative pH of a solution created by adding the salt, NH_4F, is added to water? (K_a (HF) = 7.2x10^{-4} and K_b (NH_3) = 1.8x10^{-5})

Parent acid: HF (WA)

Parent base: NH_4OH (WB) ($NH_3 + H_2O$)

$K_a(HF) > K_b(NH_3)$

The solution will be acidic, because NH_4^+ is a more effective acid than F^- is a base

$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$ $\quad K_b(F^-) = \frac{1.0\times10^{-14}}{7.2\times10^{-4}} = 1.4\times10^{-11}$

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$ $\quad K_a(NH_4^+) = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10}$

$5.6\times10^{-10} > 1.4\times10^{-11}$

$K_a(NH_4^+) > K_b(F^-)$

(acidic)

Acid-Base Theories

Hydrolysis Reactions (Anion/Cation Reaction with Water)

Write the hydrolysis reaction for the salt NaCN.

Parent acid:

Parent base:

Which is weak:

Use the anion of a weak acid or the cation of a weak base to write an equation based on its reaction with water.

Cation (conjugate acid) reacts be donating an H^+ TO water creating hydronium (H_3O^+).

$$B^+ + H_2O \rightarrow BH + H_3O^+$$

Anion (conjugate base) reacts by accepting an H^+ FROM water creating hydroxide (OH^-).

$$A^- + H_2O \rightarrow HA + OH^-$$

Determining pH of a Solution Involving Cation/Anion Hydrolysis

- Write out the hydrolysis equation and equilibrium expression, K_a (cation) or K_b (anion)
- Determine the K_a(cation reaction) or K_b(anion reaction) by using the equation $K_w = K_a \times K_b$
- Solve for $[H^+]$ or $[OH^-]$ using K_a/K_b
- Remember to use ($x10^{-4}$) rule for elimination of the +/-x
- Use this equation for solving for $[H^+]$: $[H^+] = \sqrt{K_a[HA]}$
- Use this equation for solving for $[OH^-]$: $[OH^-] = \sqrt{K_b[B]}$

Acid-Base Theories

Salt Hydrolysis Practice Problem

7. Write the hydrolysis reactions for the following salts:

a. KNO_2 KOH(SB) $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$ basic

b. NH_4NO_3 HNO_3(SA) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ acidic

c. CH_3NH_3Cl HCl(SA) $CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$ acidic

d. $NaClO_2$ NaOH(SB) $ClO_2^- + H_2O \rightleftharpoons HClO_2 + OH^-$ basic

Acid-Base Theories

Salts as Weak Bases Practice Problems

8. Calculate the pH of a 0.30*M* NaF solution. The K_a for HF is $7.2x10^{-4}$. (Ans: 8.31)

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

$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{7.2\times10^{-4}} = 1.4\times10^{-11}$

$[OH^-] = \sqrt{K_b[B]}$

$[OH^-] = \sqrt{(1.4\times10^{-11})(0.30)} = 2.0\times10^{-6}$

pOH = 5.70

pH = 14 - 5.70 = 8.30

Salts as Weak Acids Practice Problems

9. Calculate the pH of a 0.10*M* NH_4Cl solution. The K_b value for NH_3 is $1.8x10^{-5}$. (Ans: 5.13)

$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$

$K_a(NH_4^+) = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10}$

$[H^+] = \sqrt{K_a[HA]}$

$[H^+] = \sqrt{(5.6\times10^{-10})(0.10)}$

$[H^+] = 7.5\times10^{-6}$

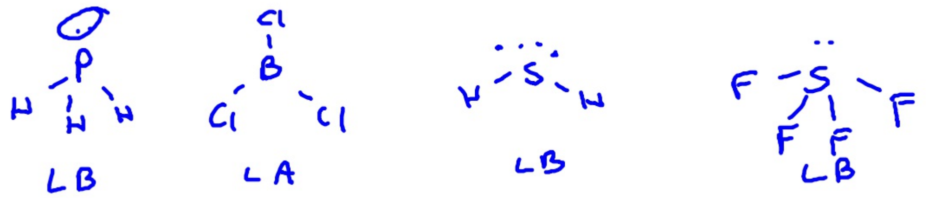
pH = $-\log(7.5\times10^{-6})$ = 5.12

10. Calculate the pH of 0.010*M* $AlCl_3$ solution. The K_a value for $Al(H_2O)_6^{3+}$ is $1.4x10^{-5}$ (Ans: 3.43)

Acids/Bases
Topic#9

Acid-Base Theories

11. Determine whether each of the following is a Lewis acid or base, draw structures as proof.
    (a) PH_3 (b) BCl_3 (c) H_2S (d) SF_4



pH<7

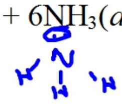
$HC_2H_3O_2$ / $C_2H_3O_2$
1.0 1.0

NH_3 / NH_4
1.0 1.0

12. For each reaction, identify the Lewis acid and base:

LA LB

(a) $Ni^{2+}(aq) + 6NH_3(aq) \rightarrow Ni(NH_3)_4^{2+}$



(b) $H^+(aq) + H_2O \leftrightarrow H_3O^+(aq)$

LA LB

PH_3

$5 + 3(1) = 8$ val
-6
2 val e⁻