Acids and Bases
Definitions and Strengths

I. Systems of acids and bases.

A. Arrhenius system.

1. **Acid**: any substance that dissociates in H_2O to give **hydronium ions** (H_3O^+).

a. Must have H in formula. The general formula is H_nX. The acidic hydrogens are written first in the formula.

b. Examples.

1) Monoprotic - one acidic proton.

HNO_3	Nitric acid
HCl	Hydrochloric acid
HBr	Hydrobromic acid
$HC_2H_3O_2$	Acetic acid

2) Diprotic - two acidic protons.

H_2SO_4	Sulfuric acid
H_2SO_3	Sulfurous acid

3) Triprotic - three acidic protons

H_3PO_4	Orthophosphoric acid (Phosphoric acid).

c. Acids are covalent substances that react with a water molecule to give H_3O^+

$$HCl + H_2O \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

Shorthand notation : $HCl \longrightarrow H^+ + Cl^-$ (H_3O^+ written as H^+).

d. The acids can be either strong acids (100% dissociated) or weak acids (partially dissociated).

Strong: $HCl + H_2O \longrightarrow H_3O^+(aq) + Cl^-(aq)$ (100%)

Weak: $HNO_2(aq) + H_2O \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$ (*not* 100%)

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = 7.2x10^{-4}$$

2. **Base**: any substance that dissociates in H_2O to give OH^- ions. The general formula is $M(OH)_n$.

a. Arrhenius bases are ionic compounds where OH^- is the anion.

b. All are strong but many have low solubility.

c. Examples: NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$, $Al(OH)_3$

Some bases, such as $Al(OH)_3$, are more complex in structure and composition than the formula would indicate.

3. Limitations of the Arrhenius system.

a. Many substances dissolve in water to give acidic or basic solutions but do not have the classical acid or base formulas.

b. Example: A solution of K_2O in H_2O is identical with a solution of KOH in H_2O. However , according to the Arrhenius system K_2O cannot be classified as a base in that it does not have OH^- 's in its formula.

B. Brönsted-Lowry System.

1. Acid = proton donor. Must have a H in its formula.
2. Base = proton acceptor.
   a. Must possess a lone pair of electrons to form a coordinate covalent bond with a H^+.
   b. An acid-base reaction is the transfer of a proton from an acid to a base.
3. Conjugate acid-base pairs.
   a. After an acid transfers a proton, the molecule or ion left has a lone pair of electrons and is therefore a base - the conjugate base of the original acid. After a base accepts a proton, it is converted into an acid - the conjugate acid of the original base.
   b. Examples.

$$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{NH_3} \rightleftharpoons \underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{OH^-}$$

$$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{OH^-}$$ (Self dissociation reaction of water)

$$\underset{\text{base}}{H_2O} + \underset{\text{acid}}{HCl} \longrightarrow \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{Cl^-}$$

4. Relative strengths of acids and bases.
   a. Strong acids will yield weak conjugate bases and weak acids will give strong conjugate bases. The following page is a table that lists some conjugate acid-base pairs, arranged in order of decreasing acid strength.
   b. In a reaction of an acid with a base below it in the table, the proton transfer will be complete, that is, the reaction will essentially go to completion. The reaction of an acid with a base above will result in an equilibrium reaction; the larger the separation, the more unfavorable is the equilibrium.

Relative Strengths of Acid-Base Pairs

	Conjugate Acid	Conjugate Base	
Strongest Acid	$HClO_4$	ClO_4^-	Weakest Base
↑	HI	I^-	↓
	HBr	Br^-	
	HCl	Cl^-	
	H_2SO_4	HSO_4^-	
	$HClO_3$	ClO_3^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	
	HSO_4^-	SO_4^{2-}	
	H_2SO_3	HSO_3^-	
	$HClO_2$	ClO_2^-	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	HSO_3^-	SO_3^{2-}	
	$HClO$	ClO^-	
	NH_4^+	NH_3	
	H_2O_2	HO_2^-	
	H_2O	OH^-	
	NH_3	NH_2^-	
Weakest Acid	OH^-	O^{2-}	Strongest Base

c. Solvent leveling effect.

1) The first seven acids in the Table are all above the base H_2O and will transfer their protons 100% to H_2O. Thus, these are the strong acids that are completely dissociated in water.

2) Note that in an aqueous solution the strongest acid that can exist is H_3O^+. All acids stronger will dissociate 100%. Therefore, in aqueous solution, there are no experimental differences in the strengths of the first seven acids; they are all 100% dissociated.

3) In the same way, the strongest base that can exist in water is OH^-, the anionic species in the self dissociation. Therefore, NH_2^- and O^{2-} can not exist in aqueous solution.

d. Classical weak acids are those that fall between H_3O^+ and H_2O in the above list.

Examples:

Hydrogen sulfate $HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$ $K_a = 1.3 \times 10^{-2}$

Hydrofluoric acid $HF + H_2O \rightleftharpoons H_3O^+ + F^-$ $K_a = 7.1 \times 10^{-4}$

Acetic acid $HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$ $K_a = 1.8 \times 10^{-5}$

Hydrogen sulfite $HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}$ $K_a = 6.3 \times 10^{-8}$

Note: The closer the conjugate acid is to the base, H_2O, the larger the value of K_a

C. Lewis System.

1. Acid = any substance that can accept an electron pair in forming a coordinate covalent bond.

a. A Lewis acid must have a fairly low energy vacant, or easily vacated orbital.

b. Examples.

H^+ (vacant 1s orbital)

BF_3 (vacant 2p orbital on B)

Ni^{2+}(vacant 3d, 4s, and 4p orbitals)

SO_3 (the S—O π bond is easily broken)

c. Acid are **electrophiles** because they react readily with electron pair donors.

2. Base = any substance that can donate an electron pair in forming a coordinate covalent bond.

a. A Lewis base must have a lone pair of electrons. This is the same as a Brönsted-Lowry base.

b. The base is a **nucleophile**.

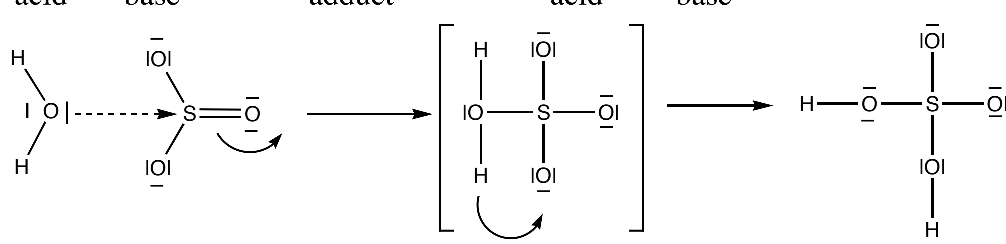
3. The reaction of an acid and a base is the formation of a coordinate covalent bond.

a. $H^+ + NH_3$ --------> NH_4^+
acid base adduct

b. $BF_3 + NH_3$ -------> $F_3B\text{-}NH_3$
acid base adduct

c. $Ni^{2+} + 6NH_3$ -------> $Ni(NH_3)_6^{2+}$
acid + base adduct

d. $SO_3 + H_2O$ --------> H_2SO_4
acid base



II. Acid - Base Strength.

A. Strength of Brönsted-Lowry oxyacids.

1. In an oxyacid, the acidic proton is bonded to an oxygen; the group is –X–O–H

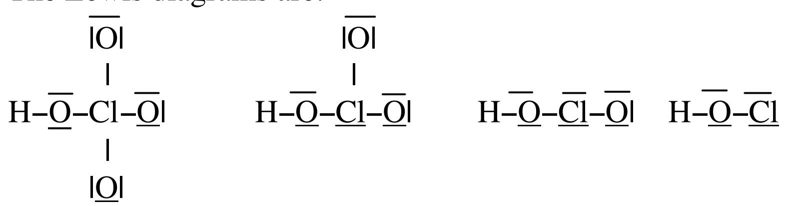
Any interaction that will polarize the O–H bond electron density towards the O will facilitate heteronuclear cleavage to give H^+ and X–O^- and increase acid strength.

a. The strength of an oxyacid will increase as the electronegativity (χ) of X is increased. Another way of stating this is to note the an increase in the positive direction of the charge/size ratio of X will increase acid strength.

b. Consider the oxychloro acids. The acid strength decreases in the order

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

1) The Lewis diagrams are:



2) In going from HClO to $HClO_4$, highly electronegative O's are being placed on the central Cl, this will increase the electronegative of the Cl and, hence, increase the strength of the acid.

3) Either the oxidation number of the Cl or its formal charge can be used to follow these changes. As more O's are added the oxidation number of the Cl increases (from +1 in HClO to +7 in $HClO_4$). Therefore, acid strength increases as the oxidation number of the central atom increases. The formal charge of the Cl increases from 0 in HOCl to +3 in $HClO_4$.

4) This only holds for the oxychloro acids. Hydrochloric acid, HCl, does not fit into this sequence.

c. Since electronegativity decreases as one goes down a group in the Periodic Table, the strengths of the oxyacids will decrease as you go down a group, provided the oxidation number does not change.

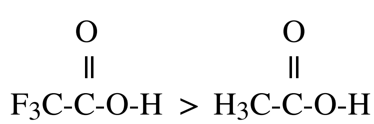
Example:

$$HNO_3 > H_3PO_4 > H_3AsO_4 \text{ (all have a +5 oxidation number)}$$

$$\chi_N > \chi_P > \chi_{As}$$

d. Electronegative groups may be introduced near the O–H bond to increase acid strength.

Example:



2. Transition form acidic to basic oxides in a group in the Periodic Table.

a. Consider the group 15 oxides where the group 15 element is in a +3 oxidation state.

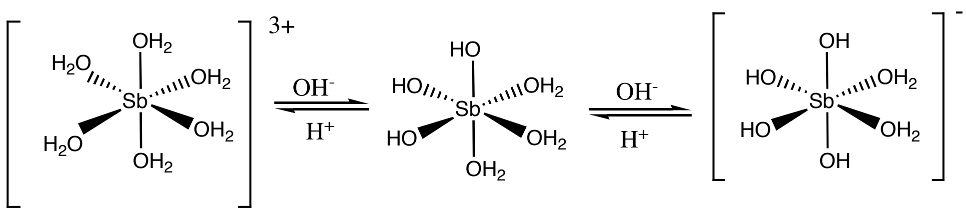
Oxide _____________Hydrolysis Product_________

formula	formula	property
N_2O_3	HNO_2	weak acid
P_2O_3	H_3PO_3	weaker acid
As_2O_3	H_3AsO_3	weakest acid
Sb_2O_3	$Sb(OH)_3$	amphoteric hydroxide
Bi_2O_3	$Bi(OH)_3$	basic hydroxide

b. Amphoteric hydroxides = hydroxides that are insoluble in water but will dissolve in either an acid or a base.

1) $Sb(OH)_3$ is amphoteric

$$Sb^{3+} \xleftarrow{H^+} Sb(OH)_3(s) \xrightarrow{OH^-} Sb(OH)_4^-$$



Sb^{3+} $\quad$ $Sb(OH)_3(s)$ $\quad$ $Sb(OH)_4^-$

2) In amphoteric hydroxides the central nonoxygen atom has a charge/size ratio between that for an acid and a base.

3. Polyprotic acids: as more H^+'s are removed, the resulting acids become weaker.

a. Example:

$$H_3PO_4 > H_2PO_4^- > HPO_4^{2-}$$

b. It becomes increasingly more difficult to remove H^+ ions from more negative substances.

B. Strength of the hydrogen halide acids.

1. Acid strength is directly related to the strength of the H–X bond. The stronger the H–X bond, the weaker the acid. This dominates in variations in a group.

2. For the group 17 hydrides ------Increasing acid strength------>

	HF	<	HCl	<	HBr	<	HI
K_a:	6.6×10^{-4}		1.3×10^{6}		10^{8}		10^{9}
H–X bond energy (kJ/mol):	569		431		368		297

C. χ is important when comparing binary acids within a Period

Example. Acid strength: $HF > H_2O > NH_3 > CH_4$

$(\chi_x - \chi_H)$: $1.8 > 1.2 > 0.8 > 0.4$

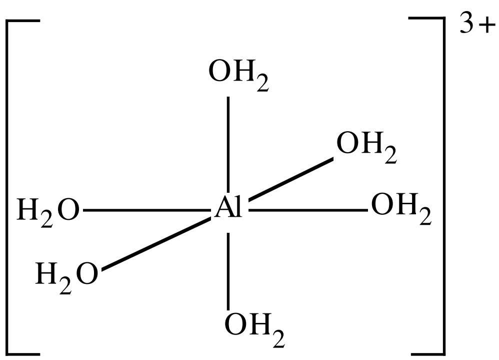
D. Base Strength.

1. Recall that a strong acid will yield a weak conjugate base. Therefore, any interaction that increase the strength of an acid will decrease the strength of its conjugate base. All the changes listed in A. and B. that increase acid strength can be used to rationalize the decrease in the strength of the conjugate base.
2. In general for a substance to be a good base the base site must have a lone pair of electrons in a readily available, well oriented (hybridized) orbital.
   a. $NH_3 > PH_3$; the N lone pair is in a smaller more hybridized orbital than is the P lone pair.
   b. $NH_3 > H_2O$; $\chi_N < \chi_O$ therefore the N lone pair is more available the are the O lone pairs.
   c. $NH_3 > NH_2NH_2 > NH_2OH$; putting more electronegative groups on the N will decrease its basicity.

IV. Acidities of Aqueous Solutions.

A. Substances that dissolve in H_2O to give **acidic** solutions.

1. Arrhenius Acids.
2. Nonmetal Oxides.
   a. Example: $SO_3 + H_2O \longrightarrow H_2SO_4$
   b. Nonmetal oxides **Hydrolyze** to give an Arrhenius Acid.
      Hydrolysis = Reaction with H_2O to give an acidic or a basic solution.
   c. Nonmetal oxide is an **acid anhydride**.
3. Salts with small highly charged cations. Metal cations with a +3 charge.
   a. Example: $AlCl_3$ will dissolve in H_2O to give an acidic solution. Due to the Al^{3+} ion. $Al^{3+}(aq) = [Al(H_2O)_6]^{3+}$, it's sturcture is



The high charge/size ratio of the Al^{3+} ion causes the electron density in the O–H bond to be polarized towards the oxygen. Thus, a bound H_2O is more acidic than is a water molecule in the bulk solvent. Therefore, $Al(H_2O)_6^{3+}$ is acidic, as shown in the following reaction.

$$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H_3O^+$$

b. Any cation will polarize the electron density in a bound water molecule, but only the +3 ions have charge/size ratios large enough to materially increase the acidity of their salts.

4. Ammonium salts. Ammonia, NH_3, is a weak base ($K_b = 1.8x10^{-5}$). Therefore, NH_4^+ is acidic, it will hydrolyze as follows.

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

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = 5.6x10^{-10}$$

B. Substances that Dissolve in H_2O to give **Basic** Solutions.

1. Arrhenius Bases.
2. Salts whose anions are anions of weak acids.

a. HNO_2 is a weak acid ($K_a = 7.2x10^{-4}$). Therefore, $NaNO_2$ will dissolve in H_2O to give a basic solution, due to the hydrolysis of the NO_2^- which is basic.

b. $$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$$

$$K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]} = 1.4x10^{-11}$$

3. Metal Oxides.

a. Example. $Na_2O + H_2O \longrightarrow 2\ NaOH \longrightarrow 2\ Na^+ + 2\ OH^-$

b. Metal oxides = base anhydrides.

c. Reactions of anhydrides. They "neutralize" one another the same as do their acids and bases.

$$H_2SO_4 + 2\ NaOH \longrightarrow Na_2SO_4 + 2\ H_2O$$

$$SO_3 + Na_2O \longrightarrow Na_2SO_4$$

4. Ammonia-type Bases.

a. Ammonia = $|NH_3$ It is basic due to the lone pair on the N.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

b. Can substitute any single bonding groups (R) for the H's and still maintain its basic character. Therefore, |NR_3 is also basic.

$$NR_3 + H_2O \rightleftharpoons R_3NH^+ + OH^-$$

ACIDS-BASES
PROBLEMS

1. Consider the following list of substances. Classify each substance as an acid or base (or neither) in the Arrhenius system, Brönsted-Lowry, and Lewis systems.

$H_2PO_4^-$ NH_2^- SO_2 $CH_3NH_3^+$ BaO BH_3 HI

2. Given the following list of solutes, KNO_3, P_2O_5, FeI_3, $NaNO_2$, KClO, Li_2O

   a. Which one(s), if any will dissolve in water to give acidic solutions ?

   b. Which one(s), if any, will dissolve in water to give basic solutions ?

   c. Which one(s), if any, will dissolve in water to give neutral solutions ?

3. Compare and contrast the Brönsted-Lowry and the Lewis System of acids and bases. What definition, that of the acid or that of the base, has under gone the greatest change in going from one system to the other. Do the same for the Arrhenius and the Brönsted-Lowry systems.

4. Which one of the following will be the stronger acid ? (Justify your choice)

   a. $HBrO_2$ or HBrO. b. HIO or HClO c. H_2S or HS^-. d. CH_3OH or Cl_3COH.

   e. H_2O_2 or H_2O f. $Mg(H_2O)_6^{2+}$ or $Ba(H_2O)_6^{2+}$. g. H_2SO_4 or HSO_3F

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5. Account for the fact that $CH_3CH_2O^-$ is much more basic than is $CH_3C\text{-}O^-$.

6. Draw the Lewis diagrams for and give the hybridization of the nonhydrogen atoms in BH_3, NH_3, and their adduct molecule.

7. Write the conjugate acid and conjugate base for HS^- .

8. Identify the conjugate acid-base pairs in the following reactions.

   a. $NH_3 + HSO_4^- \text{ ----> } NH_4^+ + SO_4^{2-}$

   b. $PH_3 + O^{2-} \text{ ----> } PH_2^- + OH^-$

9. Consider the following solutes;

   a) $LiNO_3$ b) KNO_2 c) NH_4Cl d) P_2O_5 e) K_2O f) $Cr(NO_3)_3$

   (1) Which ones would produce acidic solution when dissolved in water?

   (2) Which ones would produce basic solutions in water?

(3) Which ones would produce neutral solutions in water?

10. Consider 0.10 M aqueous solutions of the following solutes. List these in order of increasing acidity.

a) $NaNO_3$ b) $NaNO_2$ c) HNO_2 d) NH_3 e) NH_4NO_3 f) HNO_3 g) NaOH

ACIDS-BASES
PROBLEMS (ANSWERS)

1. Consider the following list of substances. Classify each substance as an acid or base (or neither) in the Arrhenius system, general solvent system (water solvent), Brönsted-Lowry, and Lewis systems.

(AA=Arrhenius acid; AB=Arrhenius base; BA=Brönsted acid;BB=Brönsted base; LA=Lewis acid; LB=Lewis base)

$H_2PO_4^-$	NH_2^-	SO_2	$CH_3NH_3^+$	BaO	BH_3	HI
AA						AA
BA,BB	BA,BB	BB	BA	BB	BA	BA,BB
LB	LB	LA,LB		LB	LA	LB

2. Given the following list of solutes, KNO_3, P_2O_5, FeI_3, $NaNO_2$, KClO, Li_2O
   a. Which one(s), if any will dissolve in water to give acidic solutions ? P_2O_5, FeI_3
   b. Which one(s), if any, will dissolve in water to give basic solutions ? $NaNO_2$, KClO, Li_2O
   c. Which one(s), if any, will dissolve in water to give neutral solutions ? KNO_3
3. Compare and contrast the Brönsted-Lowry and the Lewis System of acids and bases. What definition, that of the acid or that of the base, has under gone the greatest change in going from one system to the other. Do the same for the Arrhenius and the Brönsted-Lowry systems. (See notes)
4. Which one of the following will be the stronger acid ? (Justify your choice)(answer in **bold**)
   a. **$HBrO_2$** or HBrO. b. HIO or **HClO** c. **H_2S** or HS^-. d. CH_3OH or **Cl_3COH**.
   e. **H_2O_2** or H_2O f. **$Mg(H_2O)_6^{2+}$** or $Ba(H_2O)_6^{2+}$. g. H_2SO_4 or **HSO_3F**.

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5. Account for the fact that $CH_3CH_2O^-$ is much more basic than is $CH_3C\text{-}O^-$ ($\chi_O > \chi_H$)
6. Draw the Lewis diagrams for and give the hybridization of the nonhydrogen atoms in BH_3, NH_3, and their adduct molecule. (see notes in BH_3 sp^2 in adduct B = N = sp^3 = N in sp^3)
7. Write the conjugate acid and conjugate base for HS^-. (CA = H_2S, CB = S^{2-})
8. Identify the conjugate acid-base pairs in the following reactions.
   a. $NH_3 + HSO_4^- \text{---->} NH_4^+ + SO_4^{2-}$
   base acid acid base
   b. $PH_3 + O^{2-} \text{---->} PH_2^- + OH^-$
   acid base base acid

9. Consider the following solutes;

a) $LiNO_3$ b) KNO_2 c) NH_4Cl d) P_2O_5 e) K_2O f) $Cr(NO_3)_3$

(1) Which ones would produce acidic solution when dissolved in water? NH_4Cl, P_2O_5, $Cr(NO_3)_3$

(2) Which ones would produce basic solutions in water? KNO_2, K_2O

(3) Which ones would produce neutral solutions in water? $LiNO_3$

10. Consider 0.10 M aqueous solutions of the following solutes. List these in order of increasing acidity.

$HNO_3 < HNO_2 < NH_4NO_3 < NaNO_3 < NaNO_2 < NH_3 < NaOH$