8th Homework: Reading, M&F, ch. 15, pp. 570-574, 605-607, 574-584, 598-602 (theories of acids & bases; acid & base strength; acidic, basic and neutral ions; pH, pOH, K_w; pH of strong acids and bases. Problems: M&F, ch. 15, #27-29, 31, 32, 36-39, 43, 67-69, 79. Nakon, ch. 18, #46, 53.

V. Aqueous Equilibria: Acids and Bases.

A. Theories of acids and bases.

1. <u>Arrhenius theory of acids and bases</u>. (useful only in water)

Acids dissociate in water to produce H^+ ions; bases dissociate in water to produce OH^- ions. Hence, HCl is an acid, NaOH is a base.

2. <u>Bronsted-Lowry theory of acids and bases</u>. (more general and the one we'll use)

Acids can donate a proton (H^+) to another substance; bases can accept a proton from another substance. Hence, acid-base reactions are proton-transfer reactions.

Ex. $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$ (K is large, almost 100% products)
HCl is the proton donor (acid), H_2O is the proton acceptor (base).
Ex. $HF + H_2O \rightleftharpoons H_3O^+ + F^-$ (K is small, almost 100% reactants)
acid base
Ex. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ (K is small, almost 100% reactants)
base acid
The extent of the reaction is not important in the definition, HCl & HF are both acids.

Reverse the reactions - the products are also an acid and a base:
Ex. $H_3O^+ + F^- \rightleftharpoons HF + H_2O$
acid base
Ex. $NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$
acid base

In any B-L acid-base reaction, there are two <u>conjugate acid-base pairs</u>. The conjugate acids contain the extra proton, the conjugate base does not:
Ex. $HF + H_2O \rightleftharpoons H_3O^+ + F^-$ (conj. acid-base pairs are HF/F^- and H_3O^+/H_2O)
acid base acid base
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Ex. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ (conj. acid-base pairs are NH_4^+/NH_3 and H_2O/OH^-)
base acid acid base

Note that some substances (e.g., H_2O) can be either an acid or a base, <u>depending on the reaction</u>.

Answers to the following given in class.
(i) Identify the conjugate acids of the following substances: (a) H_2O, (b) NO_3^-, (c) O^{2-}, (d) N_2H_4,
(ii) Identify the conjugate bases of the following substances: (a) H_2O, (b) HBr, (c) HCO_3^-, (d) NH_3.
(iii) Identify the acids and bases and the conjugate acid/base pairs in the following reactions:

$$H_2SO_3 + OH^- \rightleftharpoons HSO_3^- + H_2O$$

$$SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + OH^-$$

3. <u>Lewis theory of acids and bases</u> (even more general, but less useful for this course)

An acid can accept a lone pair of electrons from another substance; a base can donate a lone pair of electrons to another substance. (Note: it helps to show non-bonding electron pairs)

Ex. $HF + :OH_2 \rightleftharpoons H:OH_2^+ + F^-$ (normally written as H_3O^+)
Lewis acid base

All B-L acids are also Lewis acids; all B-L bases are Lewis bases. However, consider the following:
Ex. $BCl_3 + :NH_3 \rightleftharpoons Cl_3B:NH_3$ (the boron accepts an electron pair from the nitrogen)
Lewis acid base

Ex. All reactions between a metal cation (a Lewis acid) and a ligand (a Lewis base).
$Cu^{2+} + 6\ :OH_2 \rightleftharpoons [Cu(:OH_2)_6]^{2+}$ (normally written as $Cu(H_2O)_6^{2+}$)
Lewis acid base

Identify the Lewis acid and Lewis base in the following reactions (answers given in lecture):
(a) $AlCl_3 + Cl^- \rightleftharpoons AlCl_4^-$
(b) $2NH_3 + Ag^+ \rightleftharpoons Ag(NH_3)_2^+$

B. B-L acid and base strength.

B-L acid-base reactions are essentially a competition for a proton. Strong acids tend to force other substances to accept protons, strong bases tend to pull protons off other substances. In every acid-base reaction, the equilibrium lies towards the side of the weaker acid and base:

Ex.	HBr +	H_2O	⇌	H_3O^+ +	Br^-	(K large, ~100% products)
	stronger acid	stronger base		weaker acid	weaker base	

This leads to the general rule: <u>the stronger the acid, the weaker the conjugate base, and visa-versa</u>.

<u>Relative strengths of conjugate acids and bases in water</u>

<u>Conjugate Acid</u>	<u>Conjugate Base</u>
HCl (strong acid, ~100% dissociated in water)	Cl^- (very weak base, ~0% protonated in water)
HF (weak acid, slightly dissociated in water)	F^- (weak base, slight tendency to accept a proton from water)
CH_3COOH (weak acid)	CH_3COO^- (weak base)
NH_4^+ (weak acid)	NH_3 (weak base)
OH^- (very weak acid, ~0% dissociated in water)	O^{2-} (strong base, ~100% protonated in water)

Please note, MEMORIZE and appreciate the following consequences of the above trends. The first step in many of the acid/base problems is <u>recognizing whether you are dealing with an acid or a base, and whether it is strong or weak</u>.

(i) List of strong acids: HCl, HBr, HI, HNO_3, $HClO_4$, H_2SO_4. Their conjugate bases are so weak that they do not accept protons in water. Cl^-, Br^-, I^-, NO_3^-, ClO_4^- are <u>neutral anions</u> (Special case: HSO_4^- is borderline strong/weak acid; SO_4^{2-} is essentially neutral).

(ii) List of strong bases: $M(OH)_n$ (metal hydroxides). The metal cations are <u>neutral</u> (Na^+, Ca^{2+}, etc.)

(iii) <u>All weak acids have weak conjugate bases. Similarly, all weak bases have weak conjugate acids</u>.

Ex. HNO_2 is a weak acid, NO_2^- is a weak base (note: anions not listed above are generally weak bases).

Ex. CH_3NH_2 is a weak base, $CH_3NH_3^+$ is a weak acid (neutral organic compounds with N are generally weak bases. If there is an H and a + charge on the N, it is a weak acid).

You can now predict whether a SALT is neutral, acidic or basic.
Ex. NaCl is neutral (neutral metal cation Na^+, neutral anion Cl^-)
Ex. KCN is basic (neutral metal cation K^+, weak base anion CN^-)
Ex. NH_4NO_3 is acidic (acidic cation NH_4^+, neutral anion NO_3^-)

C. Water dissociation, pH and pOH.

Water can act as an acid and a base. In particular,

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ (conj. acid-base pairs are H_2O/OH^- and H_3O^+/H_2O)
acid base acid base

It is customary to represent H_3O^+ as simply H^+. The <u>water dissociation equilibrium</u> is:

$H_2O \rightleftharpoons H^+ + OH^-$ $K_w = [H^+][OH^-]$ (note the absence of $[H_2O]$)

where K_w is the <u>ion-product constant for water</u>. At 25°C, $K_w = 1.0\times10^{-14}$ (MEMORIZE!). In pure neutral water (no added acids or bases), $[H^+] = [OH^-] = \sqrt{K_w} = 1.0\times10^{-7}$ M.

The water dissociation equilibrium is valid for an aqueous solution with any amount of added acid or base. Hence, if $[H^+]$ increases, $[OH^-]$ decreases proportionally, and visa-versa. An aqueous solution is acidic if $[H^+] > \sqrt{K_w}$; it is basic if $[H^+] < \sqrt{K_w}$.

Ex. Water exposed to air at 25°C has an H^+ conc. of 3×10^{-6} M. What is $[OH^-]$? Is the water acidic, neutral or basic? $1.0\times10^{-14} = (3\times10^{-6})[OH^-]$; $[OH^-] = 3\times10^{-9}$ M; the water is acidic.

Because $[H^+]$ and $[OH^-]$ can vary over many orders-of-magnitude, we define a logarithmic scale:

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

and

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

Note the following trends (valid at 25°C):

$[H^+]$	pH	$[OH^-]$	pOH
10 M	−1	10^{-15} M	15
1 M	0	10^{-14} M	14
10^{-7} M	7	10^{-7} M	7
10^{-14} M	14	1 M	0
10^{-15} M	15	10 M	−1

Note that (a) pH and pOH are usually positive, but can be negative, and (b) at 25°C:

☞$pH + pOH = 14.00$☜

Ex. What is the pH and pOH of water exposed to air at 25°C? Since $[H^+] = 3\times10^{-6}$ M,
$pH = -\log(3\times10^{-6}) = -(-5.522878...) = 5.5$; $pOH = 14.00 - 5.5 = 8.5$
Note on sig. fig.: when taking a log of a NUMBER, the number of digits past the decimal in the answer equals the number of sig. fig. in the NUMBER.

Ex. The pH of grapefruit juice is 3.76. What is $[H^+]$?
$[H^+] = 10^{-pH} = 10^{-3.76} = 1.7378008...\times10^{-4}$ M $= 1.7\times10^{-4}$ M
Note on sig. fig.: when taking an antilog of a NUMBER, the number of sig. fig. in the answer equals the number of digits past the decimal in the NUMBER.
<u>DON'T FORGET TO CHANGE THE SIGN OF THE NUMBER BEFORE TAKING THE ANTI-LOG!! BE SURE TO PUT THE ANSWER IN SCIENTIFIC NOTATION BEFORE READING IT FROM THE CALCULATOR!</u>

D. pH Calculations: strong acids and bases.

Because strong acids and bases are 100% dissociated to ions, the conc. of H^+ and OH^- are readily calculated and then converted to pH and/or pOH.

Ex. What is the pH of 0.050 M $HClO_4$? of 6.0 M HCl?
$[H^+] = 0.050$ M; $pH = -\log(0.050) = 1.30$
$[H^+] = 6.0$ M; $pH = -\log(6.0) = -0.78$

Ex. What is the pH of 0.020 M KOH? of 0.010 M $Ba(OH)_2$?
$[OH^-] = 0.020$ M; $pOH = -\log(0.020) = 1.70$; $pH = 14.00 - 1.70 = 12.30$
$[OH^-] = 2(0.010\text{ M}) = 0.020$ M (watch the stoichiometry!!); $pOH = -\log(0.020) = 1.70$; $pH = 14.00 - 1.70 = 12.30$