1. Calculate the pH of each solution:

a. 0.010 M $HClO_4$

strong acid so $[H^+] = 0.010$ M $pH = -\log(.010) = \boxed{2.00}$

b. 0.0010 M $Ba(OH)_2$

$[Ba^{+2}] = .0010$ M $[OH^-] = .0020$ M

$pOH = -\log(.0020) = 2.70$

$pH = 14 - pOH = \boxed{11.30}$

c. 0.040 M LiH

$H^{-1} + H_2O \rightarrow H_{2(g)} + OH^{-1}$

so $[OH^-] = .040$ M $pOH = -\log(.040) = 1.40$

$pH = 14 - pOH = \boxed{12.60}$

d. 0.040 M Li_2O

$O^{-2} + H_2O \rightarrow 2OH^-$ $pOH = -\log(.080) = 1.10$

so $[OH^-] = 0.080$ M $pH = 14 - pOH = \boxed{12.90}$

e. What was the % ionization for each of the above solutions? $\boxed{100\%}$ (strong acids/bases)

2. Calculate the pH, $[H^{+1}]$, and % ionization of acetic acid in each case:

a. 0.90 M $HC_2H_3O_2$ $HC_2H_3O_2 \rightleftharpoons H^{+1} + C_2H_3O_2^{-1}$

$(K_a = 1.8 \times 10^{-5})$

	$HC_2H_3O_2$	H^{+1}	$C_2H_3O_2^{-1}$
I	0.90	0	0
Δ	$-x$	$+x$	$+x$
E	$.90-x$	x	x

assume x << 0.90

$\dfrac{x^2}{.90} = 1.8 \times 10^{-5}$

$x = [H^+] = \boxed{.0040 \text{ M}}$ [H+]

$K_a = \dfrac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$

$\dfrac{x^2}{.90-x} = 1.8 \times 10^{-5}$

$pH = -\log(.0040) = \boxed{2.40}$ pH

$\dfrac{.00402}{0.90} \times 100 = \boxed{0.45\%}$ ioniz ation

b. 0.0010 M $HC_2H_3O_2$ (same "rxn" as above)

$\dfrac{x^2}{.0010-x} = 1.8 \times 10^{-5}$

plug in:

$\dfrac{x^2}{.0010 - .0001342} = 1.8 \times 10^{-5}$

assume x << .0010

$\dfrac{x^2}{.0010} = 1.8 \times 10^{-5}$

$x = .0001248$

again: x = .0001255

x = .0001255 ✓

$x = .0001342$ M

too big to actually "neglect" since has a SF in 4th decimal place, as does .0010 M.

$\boxed{[H^+] = .00013 \text{ M}}$

$pH = -\log(.0001255)$

$\boxed{pH = 3.90}$

$\dfrac{.0001255}{.0010} \times 100 = 12.546 \rightarrow \boxed{13\%}$ ionization

3. Calculate the pH, $[H^{+1}]$, and % ionization of the weak in each case. Use your answers to fill in lines A-D in the chart in #4.

A. 0.20 M Cyanic acid (HCNO) ($Ka = 3.5 \times 10^{-4}$)

$$HCNO \rightleftarrows H^{+1} + CNO^{-1}$$
$$.20 - x \qquad x \qquad x$$
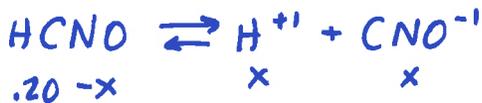
$$Ka = \frac{[H^+][CNO^-]}{[HCNO]} \qquad \frac{x^2}{.20-x} = 3.5 \times 10^{-4} \qquad \text{assume} \atop x \ll .20 \longrightarrow \frac{x^2}{.20} = 3.5 \times 10^{-4}$$

$$x = .008367 \, M \quad \text{too big to neglect..}$$

$$\frac{x^2}{.20 - .008367} = 3.5 \times 10^{-4} \quad \text{replug in}$$

$$x = .008190, \qquad x = .008194, \quad .008193..$$

$\boxed{[H^+] = .0082 \, M}$

$pH = -\log(.008193) = \boxed{2.09} \, pH$

$\frac{.008193}{.20} \times 100 = \boxed{4.1 \% \, ion}$

B. A solution that is 0.20 M HCNO and 0.10 M NaCNO

$$HCNO \rightleftarrows H^{+1} + CNO^{-1}$$
$$0.20 - x \qquad x \qquad 0.10 + x$$
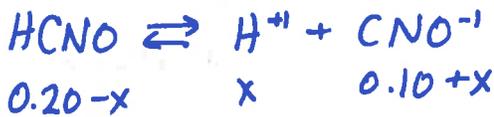
$$Ka = \frac{x(0.10+x)}{(.20-x)} = 3.5 \times 10^{-4} \qquad \text{assume } x \ll .10, .20$$

$$\frac{x(.10)}{(.20)} = 3.5 \times 10^{-4} \qquad x = \boxed{.00070 \, M \, H^+}$$

$$pH = -\log(.00070)$$

$$\boxed{pH = 3.15}$$

C. 0.20 Molar propionic acid, $HC_3H_5O_2$ ($Ka = 1.3 \times 10^{-5}$)

$$HC_3H_5O_2 \rightleftarrows H^{+1} + C_3H_5O_2^{-1}$$
$$.20 - x \qquad x \qquad x$$

$$\frac{x^2}{.20-x} = 1.3 \times 10^{-5} \qquad \frac{x^2}{.20} = 1.3 \times 10^{-5}$$
$$\text{assume} \atop x \ll .20$$

$$\frac{.00070}{.20} \times 100 = \boxed{0.35 \% \atop ioniz.}$$
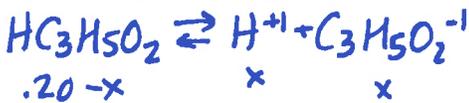
$\boxed{x = .0016 \, M \, H^{+1}}$

$pH = -\log(.001612) = \boxed{2.79} \, pH$

$\frac{.001612}{.20} \times 100 = \boxed{0.81 \%}$

D. A solution that is 0.20 M $HC_3H_5O_2$ and 0.10 M $KC_3H_5O_2$

$$HC_3H_5O_2 \rightleftarrows H^{+1} + C_3H_5O_2^{-1}$$
$$.20 - x \qquad x \qquad .10 + x$$
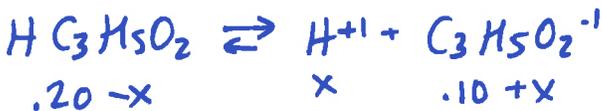
$$\frac{x(.10+x)}{.20 - x} = 1.3 \times 10^{-5}$$

assume $x \ll .10, .20$

$$\frac{x(.10)}{.20} = 1.3 \times 10^{-5}$$

or if you "iterate" 1 time thru, you get 0.80 % .. either ok.

$$x = \boxed{2.6 \times 10^{-5} M} = \boxed{H^{+1}}$$

$pH = -\log(2.6 \times 10^{-5}) = \boxed{4.59} \, pH$

$\frac{2.6 \times 10^{-5}}{.20} \times 100 = \boxed{0.013 \% \, ioniz.}$

Solution	$[H^{+1}]$	pH	% ionization
A. 0.20 M Cyanic acid (HCNO) (Ka = 3.5 x 10⁻⁴)	.0082 M	2.09	4.1 %
B. A solution that is 0.20 M HCNO and 0.10 M NaCNO	.00070 M	3.15	0.35 %
C. 0.20 Molar propionic acid, $HC_3H_5O_2$ (Ka = 1.3 x 10⁻⁵)	.0016 M	2.79	0.80 %
D. A solution that is 0.20 M $HC_3H_5O_2$ and 0.10 M $KC_3H_5O_2$	2.6×10⁻⁵ M	4.59	0.013 %
E. 0.0020 Molar propionic acid, $HC_3H_5O_2$	0.00050	3.30	2.5 %
F. A solution that is 0.0020 M $HC_3H_5O_2$ and 0.0010 M $KC_3H_5O_2$	0.000026	4.59	0.13%

4. a. Use your answers to problem 3 to complete the first four lines of the chart.

b. Compare Solution A to Solution C.
For a given acid molarity, how does the Ka of the acid affect the [H+], percent ionization, and pH?

The acid with a higher Ka will have a higher % ionization and a higher molarity of H^{+1}, and will ∴ have a lower pH. (more acidic!)

✓ and C to D, E to F...

c. Compare Solution A to Solution B. For a given acid molarity, how does the presence of the conjugate base affect the affect the [H+], percent ionization, and pH?

When the conjugate base is "added," the % ionization and the molarity of H^{+1} decrease, so the pH increases (more basic / less acidic)

d. Compare Solution C to Solution E.
For a given acid, how does the acid molarity affect the percent ionization?

The higher the overall acid molarity, the lower the % ionization.

$K_b = 1.8 \times 10^{-5}$

5. Determine the pH of each of these solutions.

a. 2.0 Molar ammonia (NH_3)

$$NH_3 + H_2O \rightleftarrows NH_4^{+1} + OH^{-1}$$
$$2.0 - x \qquad\qquad x \qquad\quad x$$

$$K_b = \frac{[NH_4^{+1}][OH^-]}{[NH_3]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{2.0 - x}$$

assume $x \ll 2.0$

$$\frac{x^2}{2.0} = 1.8 \times 10^{-5}$$

$$x = [OH^-] = .0060\ M$$

$$pOH = -\log(.0060) = 2.22$$

$$pH = 14 - pOH = \boxed{11.78}$$

b. A solution that contains ammonia dissolved at 2.0 Molar, and ammonium chloride dissolved at 1.0 Molar.

$$NH_3 + H_2O \rightleftarrows NH_4^{+1} + OH^{-1}$$
$$2.0 - x \qquad\qquad 1.0 + x \qquad x$$

$$K_b = \frac{x(1.0 + x)}{(2.0 - x)} = 1.8 \times 10^{-5}$$

assume $x \ll 1.0, 2.0$

$$\frac{x(1.0)}{(2.0)} = 1.8 \times 10^{-5}$$

$$x = 3.6 \times 10^{-5} M = [OH^-]$$

$$pOH = -\log(3.6 \times 10^{-5}) = 4.44$$

$$pH = 14 - pOH = \boxed{9.56}$$

c. 0.80 Molar pyridine

$$C_5H_5N + H_2O \rightleftarrows C_5H_5NH^{+1} + OH^{-1}$$
$$.80 - x \qquad\qquad x \qquad\quad x$$
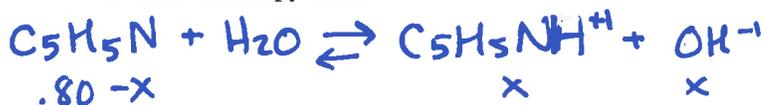
$$K_b = \frac{[C_5H_5NH^{+1}][OH^-]}{[C_5H_5N]} = 1.7 \times 10^{-9}$$

$$\frac{x^2}{.80 - x} = 1.7 \times 10^{-9}$$

ass. $x \ll .80$

$$\frac{x^2}{.80} = 1.7 \times 10^{-9}$$

$$x = [OH^-] = 3.69 \times 10^{-5}$$

$$\boxed{pH = 9.57}$$

d. A solution containing 0.10 M pyridine, and 0.080 Molar pyridinium chloride. (C_5H_5NHCl)

$$C_5H_5N + H_2O \rightleftarrows C_5H_5NH^{+1} + OH^{-1}$$
$$.10 - x \qquad\qquad .080 + x \qquad x$$
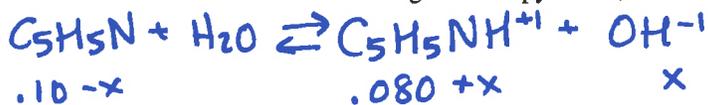
$$K_b = \frac{x(.080 + x)}{(.10 - x)} = 1.7 \times 10^{-9}$$

ass $x \ll .10, .080$

$$\frac{x(.080)}{(.10)} = 1.7 \times 10^{-9}$$

$$x = [OH^-] = 2.125 \times 10^{-9}\ M$$

$$pOH = 8.67, \quad \boxed{pH = 5.33}$$

**6a.** Draw the Lewis dot structure of each molecule or ion: (all have 32 v.e.)

phosphoric acid $\qquad$ $H_2PO_4^{-1}$ $\qquad\qquad$ HPO_4^{-2} $\qquad\qquad$ PO_4^{-3}
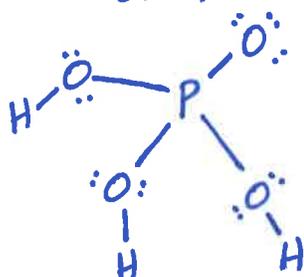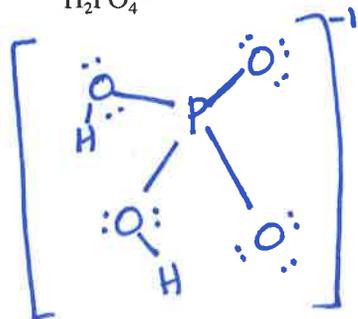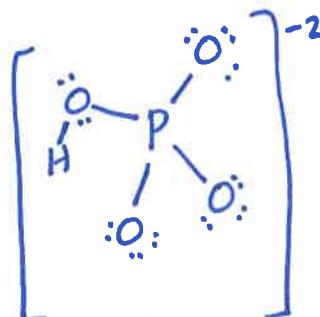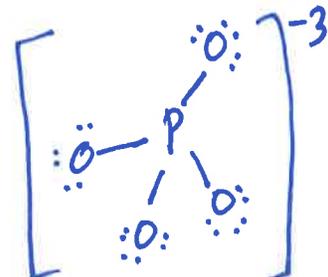
H_3PO_4

(I emphasized the octet rule over formal charges)

$K_{a1} = .0075$ $\qquad$ $K_{a2} = 6.2 \times 10^{-8}$ $\qquad$ $K_{a3} = 4.2 \times 10^{-13}$

6b. Calculate $[H_3PO_4]$, $[H_2PO_4^{-1}]$, $[HPO_4^{-2}]$, $[PO_4^{-3}]$, $[H^+]$, and pH in a 0.15 Molar solution of phosphoric acid.

$$H_3PO_4 \rightleftarrows H^{+1} + H_2PO_4^{-1}$$
$$0.15 - x \qquad x \qquad x$$

$$H_2PO_4^{-1} \rightleftarrows H^{+1} + HPO_4^{-2}$$
$$.030 - y \qquad .030 + y \qquad y$$
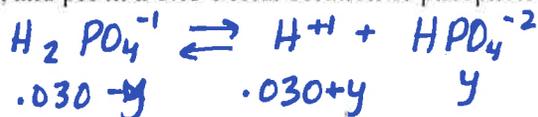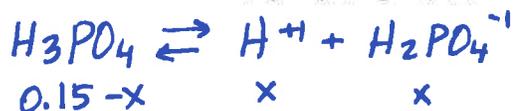
$$K_{a1} = \frac{x^2}{.15 - x} = .0075$$

(this is a big K_a so I'm just gonna do quadratic...)

$$x^2 = .0075(.15 - x) = .001125 - .0075\,x$$

$$x^2 + .0075\,x - .001125 = 0$$

$$x = \frac{-.0075 \pm \sqrt{(.0075)^2 - 4(1)(-.001125)}}{2(1)}$$

$$x = 0.030 \text{ M} \quad \text{or} \quad \cancel{-.0375}$$

$$\boxed{[H^+] = [H_2PO_4^-] = 0.030 \text{ M}}$$
$$[H_3PO_4] = 0.15 - .030 = 0.12 \text{ M } H_3PO_4$$
$$pH = -\log(.030) = 1.52$$

$$K_{a2} = \frac{(.030 + y)(y)}{(.030 - y)} = 6.2 \times 10^{-8}$$

assume $y \ll .030$

$$\frac{(.030)y}{.030} = 6.2 \times 10^{-8} \qquad y = 6.2 \times 10^{-8}$$

$$\boxed{\text{so } [HPO_4^{-2}] = 6.2 \times 10^{-8} \text{ M}}$$

($[H^+]$ is still $\approx .030$)

$$HPO_4^{-2} \rightleftarrows H^{+1} + PO_4^{-3}$$
$$6.2 \times 10^{-8} - z \qquad .030 + z \qquad z$$

$$K_{a3} = \frac{z(.030 + z)}{6.2 \times 10^{-8} - z} = 4.2 \times 10^{-13}$$

assume $z \ll 6.2 \times 10^{-8}, .030$

$$\boxed{z = 8.7 \times 10^{-19} \text{ M } PO_4^{-3}}$$

7. a. Calculate the pH of 0.20 M NaF

$$F^{-1} + H_2O \rightleftarrows HF + OH^{-1}$$
$$0.20 - x \qquad x \qquad x$$

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

$$K_b \text{ of } F^{-1} = \frac{K_w}{K_a(HF)} = \frac{10^{-14}}{6.8 \times 10^{-4}} = 1.4706 \times 10^{-11}$$

$$\frac{x^2}{0.20 - x} = 1.4706 \times 10^{-11}$$

assume $x \ll 0.20$

$$\frac{x^2}{.20} = 1.4706 \times 10^{-11}$$

$$x = 1.715 \times 10^{-6} \text{ M}$$

$$pOH = -\log[OH^-] = -\log(1.715 \times 10^{-6})$$
$$pOH = 5.77$$
$$pH = 14 - pOH = \boxed{8.23}$$

b. Calculate the pH of 0.40 M NH_4Cl

$$NH_4^{+1} \rightleftarrows H^{+1} + NH_3$$
$$0.40 - x \qquad x \qquad x$$
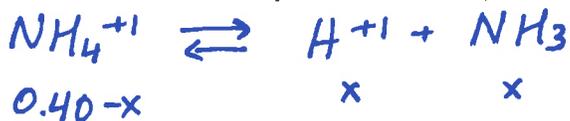
$$K_a = \frac{[H^+][NH_3]}{[NH_4^{+1}]} = \frac{x^2}{.40 - x} = 5.5(6) \times 10^{-10}$$

$$K_a(NH_4^{+1}) = \frac{K_w}{K_b(NH_3)} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.5(6) \times 10^{-10}$$

ass. $x \ll .40$

$$\frac{x^2}{.40} = 5.5(6) \times 10^{-10}$$

$$x = 1.4(9) \times 10^{-5} \text{ M } H^{+1}$$

$$pH = -\log[H^+]$$
$$pH = -\log(1.49 \times 10^{-5})$$
$$\boxed{pH = 4.83}$$

7c. What mass of solid NH_4Cl must be dissolved into water, in order to make 60.0 mL of solution with a pH of 4.42?

As shown in (7b), NH_4^{+1} is a weak acid with a Ka of $5.5(6) \times 10^{-10}$.

I'll start by finding the **molarity** of NH_4^{+1} needed to make pH of 4.42.

$$NH_4^{+1} \rightleftarrows NH_3 + H^{+1}$$

$$Ka = \frac{[NH_3][H^{+1}]}{[NH_4^{+1}]} = 5.5(6) \times 10^{-10}$$

* the 2.602 M would be $[NH_4^{+}]$ when it is at equilibrium, once the NH_4^{+1} has ionized. but since $3.8 \times 10^{-5} << 2.6$ M, we'll ignore any difference between "initial" and "equilibrium" values of NH_4^{+1}!

If pH = 4.42, $[H^+] = 10^{-4.42} = 3.8(02) \times 10^{-5} M$

$[NH_3] = [H^+]$ acc to stoichiometry, so:

$$\frac{(3.802 \times 10^{-5})(3.802 \times 10^{-5})}{[NH_4^{+1}]} = 5.5(6) \times 10^{-10}$$

$$[NH_4^{+1}] = 2.6(02) M. *$$

$$\left(\frac{2.602 \text{ mole } NH_4Cl}{Litre}\right)(0.0600 L)\left(\frac{53.4913 g}{1 mole}\right) = \boxed{8.4 g \text{ } NH_4Cl \text{ needed.}}$$

8. Calculate $[H_3AsO_4]$, $[H_2AsO_4^{-1}]$, $[HAsO_4^{-2}]$, $[AsO_4^{-3}]$, $[H^{+1}]$, and pH in 0.20 Molar H_3AsO_4.

Ka_1 of $H_3AsO_4 = .0056$, $Ka_2 = 1.0 \times 10^{-7}$, $Ka_3 = 3.0 \times 10^{-12}$

$$H_3AsO_4 \rightleftarrows H^{+1} + H_2AsO_4^{-1}$$
$$0.20 - x \qquad x \qquad x$$
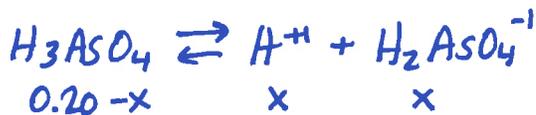
$$Ka_1 = \frac{x^2}{.20 - x} = 0.0056$$

$x^2 = (.20 - x)(.0056) = .00112 - .0056 x$

$x^2 + .0056 x - .00112 = 0$

$x = 0.030783 M$ or $-.0364 M$

$$\boxed{[H^+] = [H_2AsO_4^-] = 0.031 M}$$

pH = $-\log(.030783) = \boxed{1.51}$ pH

$[H_3AsO_4] = .20 - x = .20 - .030783$

$$\boxed{[H_3AsO_4] = 0.17 M}$$

$$H_2AsO_4^- \rightleftarrows H^{+1} + HAsO_4^{-2}$$
$$.03078 - y \qquad .03078 + y \qquad y$$
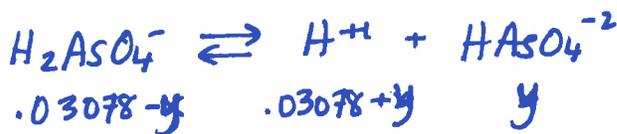
$$Ka_2 = \frac{(.03078 + y)(y)}{(.03078 - y)} = 1.0 \times 10^{-7}$$

ass. $y << .03078$

$$\frac{(.03078)(y)}{.03078} = 1.0 \times 10^{-7}$$

$$\boxed{y = 1.0 \times 10^{-7} M = [HAsO_4^{-2}]}$$

$$HAsO_4^{-2} \rightleftarrows H^{+1} + AsO_4^{-3}$$
$$1.0 \times 10^{-7} - z \qquad .03078 + z \qquad z$$
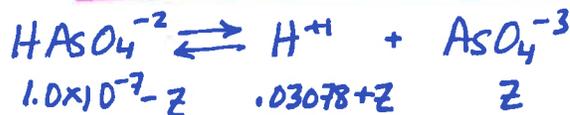
$$Ka_3 = \frac{(.03078 + z)(z)}{1.0 \times 10^{-7} - z} = 3.0 \times 10^{-12}$$

assume $z << .030, 1.0 \times 10^{-7}$

$$z = \boxed{[AsO_4^{-3}] = 9.7 \times 10^{-18} M}$$

9. Several "species" are shown below. Three of the them are "amphoteric" (and "amphiprotic").

PO_4^{-3} $H_2C_2O_4$ (HC$_3$H$_4$O$_2^{-1}$) NH_4^{+1} (HPO$_4^{-2}$) $C_3H_4O_2^{-2}$ CO_3^{-2} (H$_2$PO$_4^{-1}$)

a. Circle the three species that are amphiprotic.
**b.** For the first (left) two that you circled, complete the reactions below!

first species acting as an acid:

$\underline{HC_3H_4O_2^{-1}}$ + H$_2$O ------> $\underline{C_3H_4O_2^{-2} \quad + \quad H_3O^{+1}}$

first species acting as a base:

$\underline{HC_3H_4O_2^{-1}}$ + H$_2$O ------> $\underline{H_2C_3H_4O_2 \quad + \quad OH^{-1}}$

second species acting as an acid:

$\underline{HPO_4^{-2}}$ + H$_2$O ------> $\underline{PO_4^{-3} \quad + \quad H_3O^{+1}}$

second species acting as a base:

$\underline{HPO_4^{-2}}$ + H$_2$O ------> $\underline{H_2PO_4^{-1} \quad + \quad OH^{-1}}$
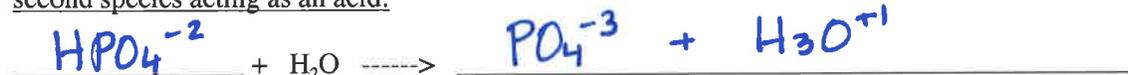
10. Consider the acids HClO$_2$, HClO$_3$, and HNO$_2$.
a. Which of these is the strongest acid? Which is the weakest?
(Use numbers to justify your answer as needed.)

HClO$_3$ = strong, so $Ka = \infty$
Ka of HClO$_2$ = 1.1×10^{-2}
Ka of HNO$_2$ = 4.5×10^{-4}

$HClO_3$ = strongest acid
HNO_2 = weakest acid   (HClO$_2$ and HNO$_2$ are weak, but HNO$_2$ is weaker)

b. If you had a 0.10 Molar solution of each acid, which solution would have the highest pH? Which would have the lowest pH?

all will be acidic, but HClO$_3$ is most acidic, so will have the lowest pH.
HNO$_2$ is least acidic, so will have the highest.
KClO$_3$ = lowest pH pH.

c. If you have 0.10 M solutions of KClO$_2$, KClO$_3$, and KNO$_2$,
Which solution would have the lowest pH, and which would have the highest pH? Explain.
KNO$_2$ = highest pH

K^{+1} ion is neutral, so disregard.

HClO$_3$ = strong, so its conjugate base, ClO$_3^{-1}$, will be neutral. (pH 7)
HNO$_2$ and HClO$_2$ are weak acids, so NO$_2^{-1}$ and ClO$_2^{-1}$ are basic. (pH > 7)
Since HNO$_2$ is a weaker acid, NO$_2^{-1}$ will be a stronger base than ClO$_2^{-1}$ (highest pH)

11. Classify each compound as acidic, basic, or neutral:

CH$_3$CH$_2$CH$_2$CH$_2$OH neutral (alcohol)

CH$_3$CH$_2$CH$_2$COOH C-ö-H acidic

CH$_3$CH$_2$CH$_2$CH$_2$NH$_2$ basic (amine)

HNO$_2$ acidic

LiNO$_2$ basic

LiNO$_3$ neutral

11, cont'd: Classify each as acidic, basic, or neutral:

H_2SO_3 **acidic**

MgH_2 **basic (H^{-1} is basic)**

H_2S **acidic**

Na_2SO_3 **basic**

NH_3 **basic**

NH_4Br **acidic**   (NH_4^{+1} is the conjugate acid of NH_3)

KCl **neutral**

NaF **basic**   (F^{-1} is the conj. base of a weak acid, HF)

$BaCO_3$ **basic**

CaO **basic ($CaO + H_2O \rightarrow Ca(OH)_2$)**

CH_3NH_2 **basic (amine)**

CH_3NH_3Cl **$CH_3NH_3^{+1} / Cl^{-1}$** **acidic**

CH_3OH **neutral (alcohol)**

KOH **basic (K^{+1}/OH^{-1})**

CH_3COOH (circled) **acidic**

$LiCH_3COO$ **Li^{+1}/CH_3COO^{-1} basic**

---

12. Carbonic acid has a K_{a1} of 4.3×10^{-7}, and a K_{a2} of 5.6×10^{-11}.
Calculate Keq for each of these equations.

a. H_2CO_3 <----> $HCO_3^{-1} + H^{+1}$ $Keq = K_{a1} = 4.3 \times 10^{-7}$

b. HCO_3^{-1} <----> $CO_3^{-2} + H^{+1}$ $Keq = K_{a2} = 5.6 \times 10^{-11}$

c. H_2CO_3 <----> $2H^{+1} + CO_3^{-2}$ ← sum of (a) and (b) so $Keq = K_{a1} \cdot K_{a2}$
$$= 2.4 \times 10^{-17}$$

d. $HCO_3^{-1} + H_2O$ <----> $OH^{-1} + H_2CO_3$ K_b of $HCO_3^{-1} = \dfrac{K_w}{K_a(H_2CO_3)} = \dfrac{10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$

e. $CO_3^{-2} + H_2O$ <----> $OH^{-1} + HCO_3^{-1}$
K_b of $CO_3^{-2} = \dfrac{K_w}{K_a(HCO_3^-)} = \dfrac{K_w}{5.6 \times 10^{-11}} = 1.8 \times 10^{-4}$

f. $HCO_3^{-1} + OH^{-1}$ <----> $H_2O + CO_3^{-2}$
this is the reverse of (e). $Keq = \dfrac{5.6 \times 10^{-11}}{K_w} = 5600$

g. $CO_3^{-2} + 2H^{+1}$ <----> H_2CO_3
this is the reverse of (c). $Keq = \left(\dfrac{1}{K_{a1} \cdot K_{a2}}\right) = 4.2 \times 10^{16}$

h $HCO_3^{-1} + H^{+1}$ <----> H_2CO_3
this is the reverse of (a). $Keq = \dfrac{1}{K_{a1}} = \dfrac{1}{4.3 \times 10^{-7}} = 2.3 \times 10^6$

i. $CO_3^{-2} + H^{+1}$ <----> HCO_3^{-1}
this is the reverse of (b). $Keq = \dfrac{1}{K_{a2}} = \left(\dfrac{1}{5.6 \times 10^{-11}}\right) = 1.8 \times 10^{10}$

**13.** Ascorbic acid (vitamin C) has the formula $C_6H_8O_6/H_2C_6H_6O_6$.
Its structure is shown to the right.
(Note: Citric acid doesn't actually have the "acid" functional
group, does it?! The alcohol functional group isn't usually acidic,
but in this case the first and second Hs fall off of "alcoholic" oxygens.
The first Ka (K_{a1}) is for the bottom left hydrogen,
and the second Ka (K_{a2}) is the for the bottom right hydrogen.
Ascorbic acid has a K_{a1} of 8.0×10^{-5}, and a K_{a2} of 1.6×10^{-12}.
a. Calculate pKa1 and pKa2.

$$pKa_1 = -\log(Ka_1) = -\log(8.0 \times 10^{-5}) = \boxed{4.10} \ pKa_1$$

$$pKa_2 = -\log(Ka_2) = -\log(1.6 \times 10^{-12}) = \boxed{11.80} \ pKa_2$$

Consider the compound sodium ascorbate (aka sodium hydrogen ascorbate), $NaHC_6H_6O_6$.
Sodium ascorbate and ascorbic acid/vitamin C are both used as food additives, as antioxidants.
When sodium ascorbate dissolves in water, it splits into Na^{+1} and $HC_6H_6O_6^{-1}$.
b. $HC_6H_6O_6^{-1}$ is amphoteric. Determine the Ka and the Kb values of this ion.

$$Ka = Ka_2 \ of \ H_2C_6H_6O_6 = \boxed{1.6 \times 10^{-12}} \ Ka$$

$$Kb \ (HC_6H_6O_6^{-1}) = \frac{Kw}{Ka(H_2C_6H_6O_6)} = \frac{10^{-14}}{8.0 \times 10^{-5}} = 1.25 \times 10^{-10} \rightarrow \underline{\underline{1.3 \times 10^{-10}}} \ Kb$$

c. Based on the answers to b, calculate the pH of a 0.086 Molar solution of $NaHC_6H_6O_6$.

$Kb > Ka$ so it is more basic than acidic. do Kb calc.

$$HC_6H_6O_6^{-1} + H_2O \rightleftarrows OH^{-1} + H_2C_6H_6O_6 \qquad \boxed{pH = 8.52}$$
$$.086-x \qquad\qquad\qquad\qquad x \qquad\qquad x$$

$$Kb = \frac{x^2}{.086-x} = 1.2(5) \times 10^{-10} \qquad \frac{x^2}{.086} = 1.2(5) \times 10^{-10}$$
$$\leftarrow assume \ x << .086 \qquad\qquad x = 3.28 \times 10^{-6}$$

14. The structure of citric acid ($C_6H_8O_7$ or $H_3C_6H_5O_7$) is shown to the right.
The pKa1, pKa2, and pKa3 values of this acid are 3.13, 4.78, and 6.40.
a. Circle the three acidic hydrogens in the picture.
b. Calculate Ka1, Ka2, and Ka3 of citric acid.

$$Ka_1 = 10^{-pKa_1} = 10^{-3.13} = \boxed{7.4 \times 10^{-4}} \ Ka_1$$

$$Ka_2 = 10^{-pKa_2} = 10^{-4.78} = \boxed{1.7 \times 10^{-5}} \ Ka_2 \qquad Ka_3 = 10^{-pKa_3} = 10^{-6.40} = \boxed{4.0 \times 10^{-7}} \ Ka_3$$

c. Determine the Ka and Kb values of the ion $HC_6H_5O_7^{-2}$.

$$Ka = Ka_3 \ of \ citric \ acid = \boxed{4.0 \times 10^{-7}} \ Ka$$

$$Kb = \frac{Kw}{Ka(H_2C_6H_5O_7^{-1})} = \frac{10^{-14}}{1.6(596) \times 10^{-5}} = \boxed{6.0 \times 10^{-10}} \ Kb$$

d. Write the chemical reaction that corresponds to the Ka value of this ion (show the ion reacting with water.)

$$HC_6H_5O_7^{-2} + H_2O \rightleftarrows H_3O^{+1} + C_6H_5O_7^{-3}$$

e. Write the chemical reaction that corresponds to the Kb value of this ion (show the ion reacting with water.)

$$HC_6H_5O_7^{-2} + H_2O \rightleftarrows OH^{-1} + H_2C_6H_5O_7^{-1}$$

f. If $K_2HC_6H_5O_7$ dissolves into water, with the pH of the solution be greater, less than, or equal to 7?
Justify your answer. $\boxed{less \ than \ 7.}$ $Ka > Kb$ so it is more acidic than basic.

15. Ethanol has a pKa of 15.9,
a. Calculate Ka of ethanol.

$$Ka = 10^{-pKa} = 10^{-15.9} = 1.26 \times 10^{-16} \text{ or } \approx \boxed{1 \times 10^{-16}}$$

b. We generally classify alcohols as neutral, not as acidic. (Vitamin C is an exception to this, as seen in #12). Does it make sense to classify ethanol as neutral? Explain.

I'd say so! 1×10^{-16} is a very small Ka, so ethanol does not release a significant amount of H^{+1} ions in ionization.

For comparison:
H_2O has a Kw of 1.0×10^{-14}
Kw is essentially the Ka of water! So ethanol is even less acidic than H_2O

c. The ethoxide ion is $C_2H_5O^{-1}$. If sodium ethoxide dissolves into water, will the resulting solution be acidic, basic, or neutral? Explain.

$\boxed{\text{Basic.}}$ $C_2H_5O^{-1}$ is the conjugate base of an <u>extremely</u> weak acid. the weaker the acid, the stronger the conjugate base. (and Na^{+1} ion is neutral)

16a. Draw the dot structures of HNO_2 and of HNO_3.
HNO_2 (18) HNO_3 (24)
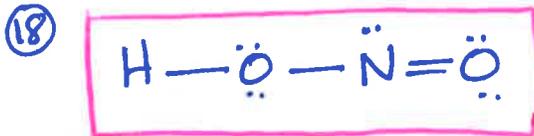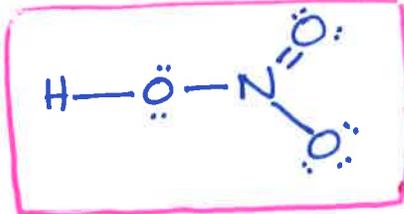
b. HNO_3 is a strong acid, but HNO_2 is a weak acid. Explain why having the extra oxygen causes HNO_3 to be more strongly acidic than HNO_2!

oxygen is very electronegative, so as more oxygens are attached to X, the more the e- in the H-O bond in the acid are pulled away from H; the H-O bond becomes more polar when more oxygens are present on X.
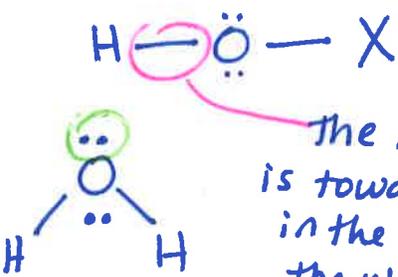
The more polar this H-O bond is toward the O/ the more the e- in the bond are pulled away from the H, the weaker the H-O bond... and the more likely the H^+ is to leave, and stick to the (lone pair) on H_2O

c. $HAsO_2$ has a similar dot structure to HNO_2. Which acid should be expected to be stronger? $\boxed{HNO_2.}$

(N is more electronegative than As. having a more EN "X" atom in the acid increases the polarity of the H-O bond in $\rightarrow$ HOO-X.)

17a. Classify each ionic compound shown here as acidic or neutral. $\rightarrow$ H-O bond in

$AlBr_3$	NaI	$Zn(ClO_4)_2$	$Cu(NO_3)_2$	$Ba(ClO_3)_2$
Acidic	Neutral	acidic	acidic	neutral

| $NiBr_2$	$CrCl_3$	KCl	SnI_4
acidic	acidic	neutral	acidic

(all of the anions are conj. bases of strong acids, so are neutral. IA and IIA cations are neutral, other metal cations are generally <u>acidic</u>.)

Fe^{+2} or Fe^{+3} surrounded by H$_2$O:

17b. FeCl$_2$ and FeCl$_3$ are both acidic. Which is more strongly acidic?
Explain why this compound is more strongly acidic.

FeCl$_3$ is more acidic; Fe^{+3} is more acidic than Fe^{+2} due to its larger positive charge. The e- in the H$_2$O's O-H bonds are attracted to the positive charge of the metal cation. The higher the cation's charge, the stronger the attractive force, and the more polar the H-O bond becomes (since the electrons in the bond are being pulled even further away from the H). the more polar the H-O bond, the more likely the H is to leave its molecule and stick to another H$_2$O molecule, so [H$_3$O$^+$] increases.

for ex, this H can stick to the <mark>lone pair</mark> *on this "passerby" H$_2$O.*

The sexy one.
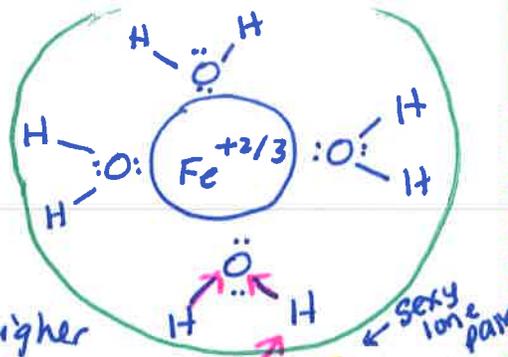
18. For each pair, circle the compound that will be more acidic (lower pH) when dissolved into water. (Assume the same molarity for each compound. You should be able to do this *without* Ka/Kb values)

(you don't have to explain on the HW) on #18

HBr is a strong acid
(HBr) or HBrO   HBrO is a weak acid

The more oxygens, the stronger the (weak)acid. Assuming they both contain O.
(HBrO$_3$) or HBrO
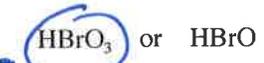
NaBrO or (HBrO)   HBrO is acidic / NaBrO is basic
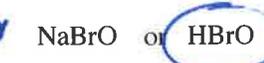
(HF) or KH   HF is acidic. KH is basic (H^{-1} ion)

Same # oxygens but Br is more electronegative than I
(HBrO$_3$) or HIO$_3$
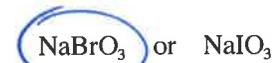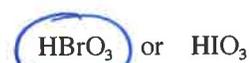
(NaBrO$_3$) or NaIO$_3$ ← Both are basic, but since HIO$_3$ is a weaker acid than HBrO$_3$, IO$_3^{-1}$ is a stronger base, so NaIO$_3$ is more basic.

NH$_4^{+1}$ is acidic. NH$_3$ is basic
(NH$_4$Cl) or NH$_3$
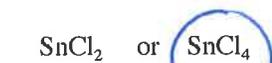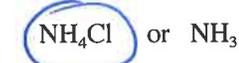
SnCl$_2$ or (SnCl$_4$)   Both acidic, but Sn^{+4} vs Sn^{+2} (higher charge → more acidic)

IA and IIA ions are neutral. other cations are generally acidic
MgBr$_2$ or (CuBr$_2$)
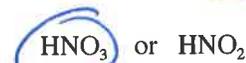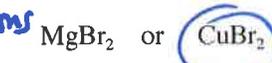
(HNO$_3$) or HNO$_2$ HNO$_3$ is stronger due to the extra O (HNO$_3$ is a strong acid)

neutral → (NaNO$_3$) or NaNO$_2$ ← basic

S is more EN than Se
(H$_2$SO$_3$) or H$_2$SeO$_3$
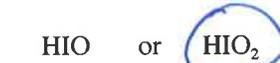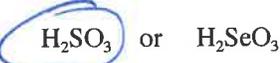
HIO or (HIO$_2$)   More O → more acidic since both contain O
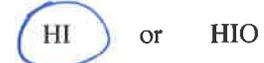
strong acid
(HI) or HIO ← weak acid

19. Classify each of these as a *strong electrolyte*, *weak electrolyte*, or *non electrolyte*.

a. Covalent compounds that aren't acids. (examples: CH_3OH, $C_{12}H_{22}O_{11}$, $C_3H_8O_2$, $C_5H_{10}(OH)_2$)

non electrolytes.

b. Strong Acids (List 3 or more examples: HCl HBr HI HNO_3 $HClO_4$ $HClO_3$ H_2SO_4

strong electrolytes

c. Weak Acids (List 3 or more examples: HF, HNO_2, $HClO_2$, $HClO$, $HC_2H_3O_2$, ...

weak electrolytes

d. Ionic Compounds. (Examples: $NaBr$, $Ca(NO_3)_2$, $MgSO_4$)

strong electrolytes.

20. For each reaction, below:
 - predict products for the reaction, including phase subscripts.
     (assume that any ionic compounds that form are soluble into water; no solids will form)
 -balance the equation
 -Under the rxn, write a balanced, **net ionic** equation for the reaction, including phase subscripts.
 (remember to only split up compounds that are **aqueous** and **strong electrolytes**!) ← So, ionic or a strong acid.

a. $Ca(OH)_{2(s)}$ + 2 $HNO_{3\ (aq)}$ --------> $Ca(NO_3)_{2(aq)}$ $+2H_2O_{(l)}$

$Ca(OH)_{2(s)} + 2H^{+1}_{(aq)} \longrightarrow Ca^{+2}_{(aq)} + 2H_2O_{(l)}$

b. $Ca(OH)_{2(s)}$ + $2HNO_{2(aq)}$ --------> $Ca(NO_2)_{2(aq)}$ $+2H_2O_{(l)}$

$Ca(OH)_{2(s)} + 2HNO_{2(aq)} \longrightarrow Ca^{+2}_{(aq)} + 2NO_2^{-1}_{(aq)} + 2H_2O_{(l)}$

c. $NaOH_{(aq)}$ + $HF_{(aq)}$ --------> $NaF_{(aq)}$ + $H_2O_{(l)}$

$OH^{-1}_{(aq)} + HF_{(aq)} \longrightarrow F^{-1}_{(aq)} + H_2O_{(l)}$

d. $NaOH_{(aq)}$ + $HCl_{(aq)}$ --------> $NaCl_{(aq)}$ + $H_2O_{(l)}$

$OH^{-1}_{(aq)} + H^{+1}_{(aq)} \longrightarrow H_2O_{(l)}$

e. $HC_2H_3O_{2(aq)}$ + $KOH_{(aq)}$ --------> $H_2O_{(l)}$ + $KC_2H_3O_2_{(aq)}$

$HC_2H_3O_{2(aq)} + OH^{-1}_{(aq)} \longrightarrow H_2O_{(l)} + C_2H_3O_2^{-1}_{(aq)}$
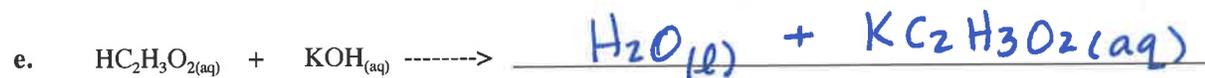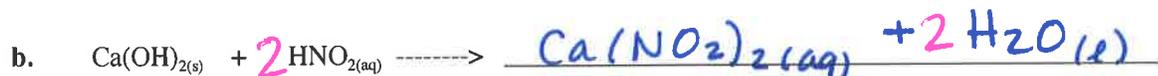
21. The following compounds have very low solubility into water.
a. Which compounds could dissolve more into acidic pH than into water? Circle them.
(Another way to ask this would be, which compounds will __react with acid, (so that the anion is "used up")__

(Zn(OH)$_2$) PbCl$_2$ (BaF$_2$) (MgCO$_3$) TlBr (AgCN) (MnS) CuI
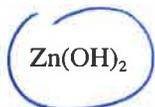
Cl^{-1}, Br^{-1}, and I^{-1} are conjugate bases of strong acids, so are not basic, and will not "stick to" H^{+1} ion.

b. For the compounds that will dissolve more into acid, write the net ionic equation for the reaction that would occur between the solid and H^{+1}. Include subscripts and balance.

$$Zn(OH)_{2(s)} + 2H^{+1}_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + 2H_2O_{(l)}$$

$$BaF_{2(s)} + 2H^{+1}_{(aq)} \longrightarrow Ba^{+2}_{(aq)} + 2HF_{(aq)}$$

OR $\Big\langle$
$$MgCO_{3(s)} + H^{+1}_{(aq)} \longrightarrow Mg^{+2}_{(aq)} + HCO_3^{-1}_{(aq)}$$
$$MgCO_3 + 2H^{+1}_{(aq)} \longrightarrow Mg^{+2}_{(aq)} + H_2CO_{3(aq)}$$
$\Big\rangle$ — could split into H_2O/CO_2

$$AgCN_{(s)} + H^{+1}_{(aq)} \longrightarrow Ag^{+1}_{(aq)} + HCN_{(aq)}$$

OR $\Big\langle$
$$MnS_{(s)} + H^{+1}_{(aq)} \longrightarrow Mn^{+2}_{(aq)} + HS^{-1}_{(aq)}$$
$$MnS_{(s)} + 2H^{+1}_{(aq)} \longrightarrow Mn^{+2}_{(aq)} + H_2S_{(aq)}$$
$\Big\rangle$
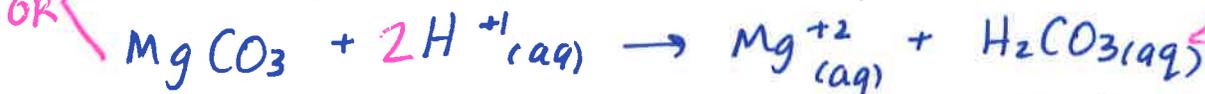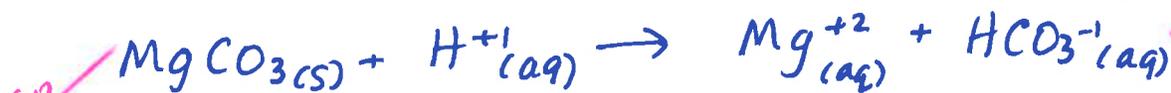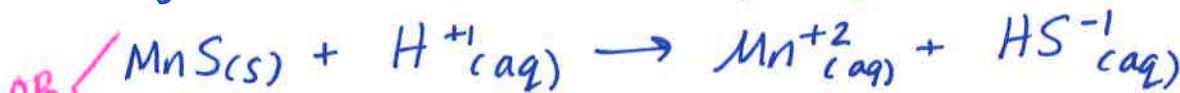
$\Big($ if you add H^{+1} to $PbCl_{2(s)}$, it won't work, since HCl would stay ionized, so Cl^{-1} isn't "removed" from soln. $\Big)$

a weak acid, like HF or H_2S, will stay together, mostly.

22. Zinc hydroxide has a Ksp of 1.2×10^{-17}.
If you have a solution in which $Zn^{+2}_{(aq)}$ is present at a concentration of 0.10 molar, what pH range is necessary to prevent precipitation of zinc hydroxide?

$$Zn(OH)_{2(s)} \rightleftarrows Zn^{+2}_{(aq)} + 2OH^{-1}_{(aq)}$$

$$K_{sp} = [Zn^{+2}][OH^-]^2$$

$$(.10)[OH^-]^2 = 1.2 \times 10^{-17}$$

$$\underline{[OH^-] = 1.095 \times 10^{-8} M}$$

must keep OH^- at or below this molarity to prevent precipitation.

$$pOH = -\log(1.095 \times 10^{-8}) = 7.96$$

$$pH = 14 - pOH = 6.04$$

must keep $\boxed{pH \text{ at or below } 6.04}$

(the lower the pH, the less OH^{-1} will be present)

23. CrF_3 has a Ksp of 6.6×10^{-11}.

$$CrF_{3(s)} \rightleftharpoons Cr^{+3}_{(aq)} + 3F^{-1}_{(aq)}$$

Suppose that HF (Ka = 0.00068) is dissolved at a fixed concentration of 0.10 Molar, and Cr^{+3} is dissolved at a concentration of 0.020 Molar. What pH range is necessary to avoid precipitation?

$$K_{sp} = [Cr^{+3}][F^{-1}]^3 = 6.6 \times 10^{-11}$$

$$(.020)[F^-]^3 = 6.6 \times 10^{-11}$$

$$[F^-] = .001489 \, M \, (max)$$

$$HF \rightleftharpoons H^{+1} + F^{-1}$$

$$K_a = \frac{[H^+][F^-]}{[HF]} = .00068$$

$$\frac{[H^+](.001489)}{(.10 \, M)} = .00068 \qquad [H^+] = .04567$$

$$pH = -\log(.04567) = 1.34$$

must keep $\boxed{\text{pH at or below 1.34}}$

24. ZnS has a Ksp of 1.1×10^{-21}. CuS has a Ksp of 6.3×10^{-36}.
H_2S has a Ka1 and Ka2 of 1.0×10^{-7} and 1.3×10^{-13}. (these values may be incorrect on your Ka sheet?)
A solution has zinc ion dissolved at 0.0070 Molar, and H_2S is dissolved at a constant concentration of 0.020 Molar (it is held constant by bubbling H_2S gas through the solution at a constant gas pressure.)
a. What pH range is necessary to prevent the precipitation of ZnS?

$$K_{sp}(ZnS) = [Zn^{+2}][S^{-2}] = 1.1 \times 10^{-21}$$

$$(.0070)[S^{-2}] = 1.1 \times 10^{-21}$$

$$[S^{-2}]_{max} = 1.571 \times 10^{-19}$$

$$H_2S \rightleftharpoons H^{+1} + HS^{-1}$$
$$HS^{-1} \rightleftharpoons H^{+1} + S^{-2}$$
$$H_2S \rightleftharpoons 2H^{+1} + S^{-2}$$

$$K_{eq} = K_{a1} \cdot K_{a2} = 1.3 \times 10^{-20}$$

$$\frac{[H^+]^2[S^{-2}]}{[H_2S]} = 1.3 \times 10^{-20}$$

$$\frac{[H^+]^2(1.571 \times 10^{-19})}{(0.020)} = 1.3 \times 10^{-20}$$

$$[H^+] = 0.04068 \, M$$

keep pH at/below 1.39

b. If you do the same problem as above, but for CuS instead of ZnS, the result is a pH threshold of - 5.7.   What does this actually mean?

It is not possible to prevent precipitation with these concentrations of Cu^{+2} and H_2S. pH - 5.7 would mean that $H^{+1} = 10^{5.7}$ or $5 \times 10^5 \, M$ (not possible!)

25. Barium fluoride has a Ksp of 1.0×10^{-6}.
a. Write a net ionic equation for the reaction between solid barium fluoride and a solution nitric acid. Include subscripts and balance.

$$BaF_{2(s)} + 2H^{+1}_{(aq)} \longrightarrow Ba^{+2}_{(aq)} + 2HF_{(aq)}$$

$(BaF_2 \quad K_{sp} = 1.0 \times 10^{-6})$
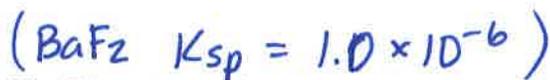
25b. What pH range is necessary to avoid precipitation, if barium ion is dissolved at 0.10 Molar, and HF is held at a constant molarity of 0.20 Molar?

K_{sp} of $BaF_2 = [Ba^{+2}][F^-]^2 = 1.0 \times 10^{-6}$

Ka of $HF = \dfrac{[H^+][F^-]}{[HF]} = .00068$

$(.10)[F^-]^2 = 1.0 \times 10^{-6}$

$[F^-]_{max} = 3.162 \times 10^{-3} M$

$\dfrac{[H^+](3.162 \times 10^{-3})}{(0.20)} = .00068$

$[H^+] = \ldots .04301 M$

keep pH at or below 1.37

26. Silver carbonate has a Ksp of 8.1 x 10^{-12}.
a. Write a net ionic equation for the reaction between solid silver carbonate and H^{+1} ion. Include subscripts and balance.
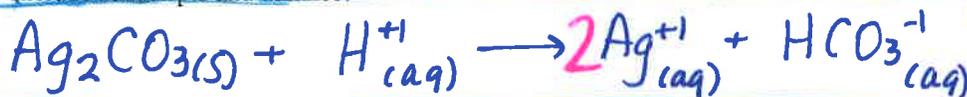
$Ag_2CO_{3(S)} + H^{+1}_{(aq)} \longrightarrow 2Ag^{+1}_{(aq)} + HCO_3^{-1}{}_{(aq)}$ ← or go to H_2CO_3

b. If H$_2$CO$_3$ is held constant at 0.010 Molar, what pH range is needed to keep silver ion dissolved at 0.10 M. **?**

$K_{sp} = [Ag^{+1}]^2[CO_3^{-2}] = 8.1 \times 10^{-12}$

$(.10)^2[CO_3^{-2}] = 8.1 \times 10^{-12}$

$[CO_3^{-2}]_{Max} = 8.1 \times 10^{-10} M$

$H_2CO_3: \quad Ka_1 = 4.3 \times 10^{-7}$
$\qquad\qquad Ka_2 = 5.6 \times 10^{-11}$

$H_2CO_3 \rightleftarrows H^{+1} + HCO_3^{-1}$
$HCO_3^{-1} \rightleftarrows H^{+1} + CO_3^{-2}$
_____
$H_2CO_3 \rightleftarrows 2H^{+1} + CO_3^{-2}$
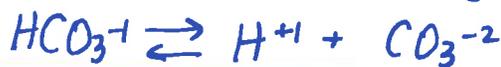
$Keq = Ka_1 \cdot Ka_2$

$\dfrac{[H^+]^2[CO_3^{-2}]}{[H_2CO_3]} = Ka_1 \cdot Ka_2 = 2.408 \times 10^{-17}$

$\dfrac{[H^+]^2(8.1 \times 10^{-10})}{(0.010)} = 2.408 \times 10^{-17}$

$[H^+] = 1.724 \times 10^{-5} M$ Keep pH at or below 4.76

27. Scandium hydroxide has a Ksp of 4.2 x 10^{-18}.
a. Scandium nitrate is dissolved into water so that the Sc^{+3}$_{(aq)}$ concentration is 0.15 Molar. Concentrated sodium hydroxide is added to the solution 1 drop at a time.. Assume that the volume of base is small enough that the molarity of Sc^{+3} remains at 0.15 Molar. At what pH will Sc(OH)$_3$ begin to precipitate?

$K_{sp} = [Sc^{+3}][OH^{-1}]^3$

$(0.15)[OH^-]^3 = 4.2 \times 10^{-18}$

$[OH^-]_{max} = 3.037 \times 10^{-6} M$

$pOH = -\log(3.037 \times 10^{-6}) = 5.52$

$pH = 14 - pOH = 8.48$

precipitation should begin right above pH 8.48

b. If Sc(OH)$_3$ solid does form, the precipitate can be cleared up by adding acid. Write the reaction that would occur between the H+1 and the precipitate. (Net ionic, balance, subscripts!)

$Sc(OH)_{3(S)} + 3H^{+1}_{(aq)} \longrightarrow Sc^{+3}_{(aq)} + 3H_2O_{(l)}$