In Class Exercise for Chapter 13 - 14

1. Methanol (CH_3OH) is manufactured in the presence of a ZnO/Cr_2O_3 catalyst through the following equation:

$$CO_{(g)} + 2H_{2(g)} \xrightleftharpoons{ZnO/Cr_2O_3} CH_3OH_{(g)} \quad \Delta H^\circ = -91 kJ$$

Does the amount of methanol increase, decrease, or remain the same when an equilibrium mixture of the above reaction is subjected to the following changes:

$$CO_{(g)} + 2H_{2(g)} \xrightleftharpoons{ZnO/Cr_2O_3} CH_3OH_{(g)} + \Delta H^\circ$$

(a) the temperature is increased – goes toward reactants, $[CH_3OH]$ decreases

(b) the volume is decreased – more gaseous moles on reactant side, goes toward products, $[CH_3OH]$ increases

(c) helium is added – not involved in the eq so no change in $[CH_3OH]$

(d) CO is added – goes toward products, $[CH_3OH]$ increases

(e) hydrogen is removed – goes toward reactants, $[CH_3OH]$ decreases

2. In the gas phase at 400°C, isopropyl alcohol decomposes to acetone and H_2 gas by:

$$(CH_3)_2 CHOH_{(g)} \rightleftharpoons (CH_3)_2 CO_{(g)} + H_{2(g)} \quad \Delta H^\circ = 57.3 kJ$$

Does the amount of hydrogen gas increase, decrease, or remain the same when the equilibrium mixture is subjected to the following changes:

$$(CH_3)_2 CHOH_{(g)} + \Delta H^\circ \rightleftharpoons (CH_3)_2 CO_{(g)} + H_{2(g)}$$

(a) the temperature is increased – goes toward products, $[H_2]$ increases

(b) the volume is increased – more gaseous moles on product side so goes toward product, $[H_2]$ increases

(c) Ar is added – no change in $[H_2]$

(d) Acetone is added – goes toward reactants, $[H_2]$ decreases

(e) Isopropyl alcohol is added – goes toward products, $[H_2]$ increases

3. At a certain temperature, K_p = 1.42 for the reaction shown below. Calculate the equilibrium partial pressures and the total pressure if the initial partial pressures are $P_{PCl_5} = 3.00\, atm$, $P_{PCl_3} = 2.00\, atm$, $P_{Cl_2} = 1.50\, atm.$

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

	$PCl_{5(g)}$	$PCl_{3(g)}$	$Cl_{2(g)}$
Initial	3.00	2.00	1.50
Change	-x	+x	+x
Eq	3.00 - x	2.00+x	1.50+x

$$K_P=\frac{P_{PCl_{3(g)}}P_{Cl_{2(g)}}}{P_{PCl_{5(g)}}}=1.42=\frac{(2.00+x)(1.50+x)}{(3.00-x)}\rightarrow x^2+4.92x-1.26=0\rightarrow x=\frac{-4.92\pm\sqrt{(4.92)^2-4(1)(-1.26)}}{2(1)}$$

$x=0.244\ atm$ or ~~$x=-5.16\ atm$~~

$P_{PCl_{5(g)},eq}=3.00-x=2.76\ atm$; $P_{PCl_{3(g)},eq}=2.00+x=2.24\ atm$; $P_{Cl_{2(g)},eq}=1.50+x=1.74\ atm$; $P_{Tot}=6.74\ atm$

4. Calculate the pH of solutions prepared by:

(a) dissolving 0.20 g of sodium hydroxide in water to give 100.0 mL solution

$$\left(0.20\ g\times\frac{1\ mol\ NaOH}{39.998\ g}\times\frac{1\ mol\ OH^-}{1\ mol\ NaOH}\right)\Big/0.1000\ L=0.050\ M$$

$$pH=14+\log\left[OH^-\right]=12.70$$

(b) dissolving 1.26 g of pure nitric acid in water to give 0.500 L solution

$$\left(1.26\ g\times\frac{1\ mol\ HNO_3}{63.018\ g}\times\frac{1\ mol\ H^+}{1\ mol\ HNO_3}\right)\Big/0.5000\ L=0.040\ M$$

$$pH=-\log\left[H^+\right]=1.40$$

(c) diluting 40.0 mL of 0.075 M $Ba(OH)_2$ to a volume of 300.0 mL

$$\left(40.0\ mL\times\frac{1\ L}{1000\ mL}\times\frac{0.075\ mol\ Ba(OH)_2}{1\ L}\times\frac{2\ mol\ OH^-}{1\ mol\ Ba(OH)_2}\right)\Big/0.3000\ L=0.020\ M$$

$$pH=14+\log\left[OH^-\right]=12.30$$

(d) mixing equal volume of 0.20 M HCl and 0.50 M HNO_3

$$\left(1\ L\times\frac{0.20\ mol\ HCl}{1\ L}\times\frac{1\ mol\ H^+}{1\ mol\ HCl}+1\ L\times\frac{0.50\ mol\ HNO_3}{1\ L}\times\frac{1\ mol\ H^+}{1\ mol\ HNO_3}\right)\Big/2L=0.35M$$

$$pH=-\log\left[H^+\right]=0.46$$

5. Lactic acid ($C_3H_6O_3$), which occurs in sour milk and foods such as sauerkraut, is a weak monoprotic acid. The pH of 0.10 M solution of lactic acid is 2.43. What is the value of K_a for this acid?

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

	HA	H^+	A^-
Initial	0.10	0	0
Change	-x	+x	+x
Eq	0.10 - x	+x	+x

$$pH=2.43\rightarrow\left[H^+\right]=10^{-2.43}=0.00372\,M\ \ H^+=x$$

$$K_a=\frac{x^2}{0.10-x}=\frac{(0.00372)^2}{0.10-0.00372}=1.44\times10^{-4}$$

6. Aniline ($C_6H_5NH_2$) is an organic base used in the manufacture of dyes. Calculate the pH and concentrations of all species present in a 0.15 M solution of aniline ($K_b = 4.3 \times 10^{-10}$).

$$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$$

	$C_6H_5NH_2$	$C_6H_5NH_3^+$	OH^-
Initial	0.15	0	0
Change	-x	+x	+x
Eq	0.15 - x	+x	+x

$$K_b = \frac{x^2}{0.15 - x} = 4.3\times10^{-10} \text{ assume x} \ll 0.15 \rightarrow 4.3\times10^{-10} \sim \frac{x^2}{0.15}$$

$$x = 8.03\times10^{-6}M \text{ ck assumption: } \frac{8.03\times10^{-6}}{0.15}\times100\% = 0.005\% < 5\%$$

assumption is therefore valid

$$\left[C_6H_5NH_2\right] \sim 0.15M;\ \left[C_6H_5NH_3^+\right] = \left[OH^-\right] = 8.03\times10^{-6}M$$

$$pH = 14 + \log\left[OH^-\right] = 8.90$$

7. Calculate the pOH and the concentrations of all species in a solution prepared by mixing equal volumes of 0.2 M HCl and 0.6 M H_2SO_4 ($K_{a2} = 1.2 \times 10^{-2}$).

we have two strong acids which completely dissociate:

$$HCl \rightarrow H^+ + Cl^- \text{ and } H_2SO_4 \rightarrow H^+ + HSO_4^-$$

$$\text{Initially: } \left[H^+\right] = \frac{1\,\text{L}\times0.2\,\frac{mol}{L} + 1\,\text{L}\times0.6\,\frac{mol}{L}}{2L} = 0.4\,\frac{mol}{L} \text{ and } \left[HSO_4^-\right] = \frac{1\,\text{L}\times0.6\,\frac{mol}{L}}{2L} = 0.3\,\frac{mol}{L}$$

since is a polyprotic acid we use the equation below to determine eq:

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

	HSO_4^-	H^+	SO_4^{2-}
Initial	0.30	0.4	0
Change	-x	+x	+x
Eq	0.30 - x	0.4+x	+x

$$K_a = \frac{\left[H^+\right]\left[SO_4^{2-}\right]}{\left[HSO_4^-\right]} = \frac{x(0.4+x)}{0.3-x} = 1.2\times10^{-2} \rightarrow x^2 + 0.412x - 0.0036 = 0$$

$$x = \frac{-0.412 \pm \sqrt{0.412^2 - 4(1)(-0.0036)}}{2} \rightarrow x = 0.0085M \text{ or } x = \text{-}0.420M$$

$$\left[HSO_4^-\right] = 0.3 - x = 0.291M \rightarrow 0.3M$$

$$\left[H^+\right] = 0.4 + x = 0.409M \rightarrow 0.4M$$

$$\left[SO_4^{2-}\right] = 0.009M$$

$$pOH = 14 - pH = 14 + \log\left[H^+\right] = 13.60$$

8. Calculate the pH of 0.020 M solution of $NaNO_3$ (K_a is super huge). What about the pH of a 0.020 M $NaNO_2$ solution (4.5×10^{-4})?

$$NaNO_3 \rightarrow \underbrace{Na^+}_{\text{conj acid NaOH}} + \underbrace{NO_3^-}_{\text{conj base } HNO_3} \qquad pH = 7.0$$

$NaNO_2 \rightarrow Na^+ + NO_2^-$ in water we get $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$

	NO_2^-	HNO_2	OH^-
Initial	0.20	0	0
Change	-x	+x	+x
Eq	0.20 - x	+x	+x

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{4.5\times10^{-4}} = 2.22\times10^{-11} = \frac{x^2}{0.20-x} \sim \frac{x^2}{0.20}$$

$$x = 2.11\times10^{-6} M \quad \text{ck assumption: } \frac{2.11\times10^{-6}}{0.2}\times100\% = 0.001\% < 5\%$$

$$pH = 14 + \log\left[OH^-\right] = 8.32$$

9. Follow the directions given below and for each case explain your reasoning.

(a) arrange each group of compounds in order of decreasing acid strength

(i) H_2O, H_2S, H_2Se

As we go down a column we increase polarizability and reduce EN
$H_2Se > H_2S > H_2O$

(ii) $HClO_3$, $HClO$, $HClO_2$

Acidity increases with # of O-atoms: $HClO_3 > HClO_2 > HClO$

(iii) PH_3, H_2S, HCl

Across a row from left to right we increase EN – make sure we have an acid: $HCl > H_2S > PH_3$

(b) identify the weakest acid for each set below.

(i) $\boxed{H_2SO_3}$, $HClO_3$, $HClO_4$ the strongest acid is $HClO_4$ since it has both the most EN central atom as well as the largest number of O-atoms; since Cl is more EN than S, $HClO_3$ is a stronger acid than H_2SO_3

(ii) $\boxed{NH_3}$, H_2O, H_2S EN decreases going across a row from right to left

(iii) $B(OH)_3$, $Al(OH)_3$, $\boxed{Ga(OH)_3}$ for an oxoacid, acid strength decreases with decreasing EN of the central atom – since Ga is the least EN $Ga(OH)_3$ is the weakest acid

(c) Identify the stronger base in each of the following pairs.

(i) $\boxed{ClO_2^-}$ vs. ClO_3^-

(ii) $\boxed{HSO_4^-}$ vs. $HSeO_4^-$

(iii) HS^- vs. $\boxed{OH^-}$

(iv) $\boxed{HS^-}$ vs. Br^-

10. If the percent dissociation of a 0.1 M solution of HNO_3 is actually 99.6%, what is the K_a for this acid?

$$\% \; dissociation = \frac{\left[H^{+}\right]}{\left[HNO_{3}\right]} \times 100\% \rightarrow 0.996 = \frac{x^{2}}{0.1} \rightarrow x = 0.0996M$$

$$K_{a} = \frac{x^{2}}{0.1 - x} = \frac{0.0996^{2}}{0.1 - 0.0996} = 28$$