Homework #1

Chapter 6

Chemical Equilibrium

2. Assume the reaction is A + B → C + D. It is given that K=9 and $K = \frac{[C][D]}{[A][B]}$. At the start of the reaction, before equilibrium is reached, there are 8 A molecules, 8 B molecules, and no C or D molecules. Therefore, $Q = \frac{[C][D]}{[A][B]} = \frac{(\frac{0}{V})(\frac{0}{V})}{(\frac{8}{V})(\frac{8}{V})} = 0$. In order for Q to equal K and the system to be at equilibrium 6 A and 6 B molecules must react to form 6 C and 6 D molecules. Leaving 2 A and 2 B molecules unreacted $\left(K = \frac{[C][D]}{[A][B]} = \frac{(\frac{6}{V})(\frac{6}{V})}{(\frac{2}{V})(\frac{2}{V})} = 9\right)$.

10. a) The reaction of interest is N_2+ $3H_2$ → $2NH_3$.
   Red = NH_3 (This is the only line that increases with time.)
   Green = H_2 (This line decreases faster that the N_2 line.)
   Blue = N_2

   b) Initially there is only H_2 and N_2 in the system therefore, in order to reach equilibrium some of the H_2 and N_2 will convert to NH_3. This results in the green, and blue lines (representing H_2 and N_2) decreasing as time goes on. Since there is no NH_3 to start with the red line (representing NH_3) must increase as time goes on. The slope of the lines represents how fast the levels of the substances change. The larger the coefficient in the chemical equation the steeper the slope will be, therefore, the green line (H_2) is the steepest because it has a coefficient of 3, followed by red (NH_3) which has a coefficient of 2, and finally blue line (N_2) which has a coefficient of 1.

   c) Equilibrium is reached when the concentration of the species is not changing which is represented by flat horizontal line. This happens about 2/3 of the way on the time axis.

11. At equilibrium the forward rate of the reaction equals the reveres rate of the reaction. The general expression for the equilibrium constant is $K = \frac{products}{reactants}$ therefore, the larger the K the more product that are present at equilibrium. If K equals 1 there will be equal amounts of products and reactants at equilibrium. Therefore, the reaction involving the NOCl as the reactant has lost of reactants at equilibrium and the reaction involving NO as the reactant has lots or products at equilibrium.

13. The equilibrium constant for both case is $K = \frac{[H_2][CO_2]}{[H_2O][CO]}$
   Since the temperature, and volume are the same in both cases and the stoichiometric coefficients are all one (with 1 mole of either both reactants or both products added) there will be only one way (1 set of concentrations) to get the equilibrium constant to be the same for both cases. Therefore, at equilibrium both flasks will have the same composition of materials in them.

21. a) $K = \frac{[H_2O]}{[NH_3]^2[CO_2]}$
   $K_P = \frac{P_{H_2O}}{P_{NH_3}^2 P_{CO_2}}$

   b) $K = [N_2][Br_2]^3$
   $K_P = P_{N_2} P_{Br_2}^3$

c) $K = [O_2]^3$

$K_P = P_{O_2}^3$

d) $K = \frac{[H_2O]}{[H_2]}$

$K_P = \frac{P_{H_2O}}{P_{H_2}}$

24. $K_P = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}}$

$PV = nRT$ $\qquad \frac{P}{RT} = \frac{n}{v}$ (concentration)

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left(\frac{[SO_3]}{RT}\right)^2}{\left(\frac{[SO_2]}{RT}\right)^2\left(\frac{[O_2]}{RT}\right)} = RTK_P = (0.08206)(1{,}100)(0.25) = 23$$

25. Given

At equilibrium

[CH_3OH]=0.15 M, [CO]=0.24 M, [H_2]=1.1 M

T=327˚C=327+273.15=600.K

$$K = \frac{[CO][H_2]^2}{[CH_3OH]} = \frac{(0.24)(1.1)^2}{(0.15\ )} = 1.9 \qquad K_P = \frac{P_{CO}P_{H_2}^2}{P_{CH_3OH}}$$

$PV = nRT$ $\qquad P = \frac{n}{v}RT$

$$K = \frac{\frac{P_{CO}}{RT}\left(\frac{P_{H_2}}{RT}\right)^2}{\frac{P_{CH_3OH}}{RT}} = \frac{1}{(RT)^2}\frac{P_{CO}P_{H_2}^2}{P_{CH_3OH}} = \frac{1}{(RT)^2}K_P$$

$$K_P = K(RT)^2 = (1.9)\big((0.08206)(600.)\big)^2 = 4{,}700$$

26. Given:

$H_2(g) + Br_2(g) \leftrightharpoons 2HBr(g)$

$K_{P_1} = \frac{P_{HBr}^2}{P_{H_2}P_{Br_2}} = 3.5 \times 10^4\ at\ 1{,}495K$

a) $HBr(g) \leftrightharpoons ½H_2(g) + ½Br_2(g)$

$K_{P_2} = \frac{P_{H_2}^{\frac{1}{2}}P_{Br_2}^{\frac{1}{2}}}{P_{HBr}} = \frac{1}{\sqrt{K_{P_1}}} = \frac{1}{\sqrt{3.5\times10^4}} = 0.0053$

b) $2HBr(g) \leftrightharpoons H_2(g) + Br_2(g)$

$K_{P_3} = \frac{P_{H_2}P_{Br_2}}{P_{HBr}^2} = \frac{1}{K_{P_1}} = \frac{1}{3.5\times10^4} = 2.9 \times 10^{-5}$

c) $½H_2(g) + ½Br_2(g) \leftrightharpoons HBr(g)$

$K_{P_4} = \frac{P_{HBr}}{P_{H_2}^{\frac{1}{2}}P_{Br_2}^{\frac{1}{2}}} = \sqrt{K_{P_1}} = \sqrt{3.5 \times 10^4} = 190$

27. $2N_2(g) + O_2(g) \leftrightharpoons 2N_2O(g)$

	N_2	O_2	N_2O
Equilibrium (mol)	2.80×10^{-4}	2.50×10^{-5}	2.00×10^{-2}
Equilibrium $\left(M = \frac{n}{V}\right)$	1.40×10^{-4}	1.25×10^{-5}	1.00×10^{-2}

$$K = \frac{[N_2O]^2}{[N_2]^2[O_2]} = \frac{(1.00 \times 10^{-2})^2}{(1.40 \times 10^{-4})^2(1.25 \times 10^{-5})} = 4.08 \times 10^8$$

$$Q = \frac{[N_2O]^2}{[N_2]^2[O_2]} = \frac{(0.200)^2}{(2.00 \times 10^{-4})^2(0.00245)} = 4.08 \times 10^8$$

Since Q=K the system is at equilibrium

28. $N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g)$

$$K_P = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = \frac{(3.1 \times 10^{-2})^2}{(8.5 \times 10^{-1})(3.1 \times 10^{-3})^3} = 3.8 \times 10^4$$

$$Q_P = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = \frac{(0.0167)^2}{(0.525)(0.00761)^3} = 1.21 \times 10^3$$

No the system is not at equilibrium. There are too many reactants, therefore, the reaction will proceed in the forward direction to reach equilibrium.

31. $3Fe(s) + 4H_2O(g) \leftrightharpoons Fe_3O_4(s) + 4H_2(g)$

$$K_P = \frac{P_{H_2}^4}{P_{H_2O}^4}$$

Calculate pressure of H_2

$$P_{H_2O} = 15.0 torr \left(\frac{1\ atm}{760\ torr}\right) = 0.0197\ atm$$

$$P_{tot} = P_{H_2} + P_{H_2O} = 36.3\ torr \left(\frac{1\ atm}{760\ torr}\right) = 0.0478\ atm$$

$$P_{H_2} = P_{tot} - P_{H_2O} = 0.0478\ atm - 0.0197\ atm = 0.0281\ atm$$

$$K_P = \frac{P_{H_2}^4}{P_{H_2O}^4} = \frac{(0.0281)^4}{(0.0197)^4} = 4.14$$

33. $PCl_5(g) \leftrightharpoons PCl_3(g) + Cl_2(g)$

	PCl_5	PCl_3	Cl_2
Initial (atm)	0.50	0	0
Change (atm)	-x	+x	+x
Equilibrium (atm)	0.50-x	x	x

$$P_{tot} = P_{PCl_5} + P_{PCl_3} + P_{Cl_2} = 0.50 - x + x + x = 0.84\ atm$$

$$x = 0.34\ atm$$

$$P_{PCl_5} = 0.50\ atm - 0.34\ atm = 0.16\ atm$$

$$P_{PCl_3} = P_{Cl_2} = 0.34\ atm$$

$$K_P = \frac{P_{PCl_3}P_{Cl_2}}{P_{PCl_5}} = \frac{(0.34)(0.34)}{(0.16)} = 0.72$$

$$K = \frac{[PCl_3][O_2]}{[PCl_5]}$$

$PV = nRT$ $\qquad \frac{P}{RT} = \frac{n}{v}$ (concentration)

$$K = \frac{[PCl_3][O_2]}{[PCl_5]} = \frac{\frac{P_{PCl_3}}{RT}\frac{P_{Cl_2}}{RT}}{\frac{P_{PCl_5}}{RT}} = \frac{1}{RT}K_P = \frac{1}{(0.08206)(523)}(0.72) = 0.017$$

35. $2SO_3(g) \leftrightharpoons 2SO_2(g) + O_2(g)$

	SO_3	SO_2	O_2
Initial (mol)	12.0	0	0
Initial $\left(M = \frac{n}{V}\right)$	4.00	0	0
Change (M)	-2x	+2x	+x
Equilibrium (mol)	?	3.0	?
Equilibrium $\left(M = \frac{n}{V}\right)$	4.00-2x	$\frac{3.0\ mol}{3.0\ L} = 1.0\ M = 2x$	x

From SO_2 we see that x = 0.50 M

Therefore calculate the concentrations at equilibrium

$$[SO_3] = 4.00 - 2x = 4.00 - 2(0.50) = 3.0\ M$$
$$[SO_2] = 2x = 2(0.50) = 1.0\ M$$
$$[O_2] = x = 0.5\ M$$
$$K = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{(1.0)^2(0.50)}{(3.0)^2} = 0.056$$

37. $H_2O(g) + Cl_2O(g) \leftrightharpoons 2HOCl(g)$

$$K = \frac{[HOCl]^2}{[H_2O][Cl_2O]} = 0.0900$$

a) Calculate the molarities

$$[HOCl] = \frac{n}{V} = \frac{1.0\ mol}{1.0\ L} = 1.0\ M$$
$$[H_2O] = \frac{n}{V} = \frac{0.10\ mol}{1.0\ L} = 0.10\ M$$
$$[Cl_2O] = \frac{n}{V} = \frac{0.10\ mol}{1.0\ L} = 0.10\ M$$
$$Q = \frac{[HOCl]^2}{[H_2O][Cl_2O]} = \frac{(1.0)^2}{(0.10)(0.10)} = 1.0 \times 10^2$$

Q >K therefore, there are too many products and the reverse reaction will occur to reach equilibrium (or reaction will go to the left).

b) Calculate the molarities

$$[HOCl] = \frac{n}{V} = \frac{0.084\ mol}{2.0\ L} = 0.042\ M$$
$$[H_2O] = \frac{n}{V} = \frac{0.98\ mol}{2.0\ L} = 0.49\ M$$
$$[Cl_2O] = \frac{n}{V} = \frac{0.080\ mol}{2.0\ L} = 0.040\ M$$
$$Q = \frac{[HOCl]^2}{[H_2O][Cl_2O]} = \frac{(0.042)^2}{(0.040)(0.49)} = 0.090$$

System is at equilibrium.

c) Calculate the molarities

$$[HOCl] = \frac{n}{V} = \frac{0.24\ mol}{3.0\ L} = 0.083\ M$$
$$[H_2O] = \frac{n}{V} = \frac{0.56\ mol}{3.0\ L} = 0.19\ M$$
$$[Cl_2O] = \frac{n}{V} = \frac{0.0010\ mol}{3.0\ L} = 3.3 \times 10^{-4}\ M$$

$$\text{H}Q = \frac{[HOCl]^2}{[H_2O][Cl_2O]} = \frac{(0.083)^2}{(0.19)(3.3\times10^{-4})} = 110$$

Q >K therefore, there are too many products and the reverse reaction will occur to reach equilibrium (or reaction will go to the left).

38. $H_2O(g) + Cl_2O(g) \leftrightharpoons 2HOCl(g)$

$$K = K_P = \frac{P_{HOCl}^2}{P_{H_2O}P_{Cl_2O}} = 0.0900$$

a) $$Q_P = \frac{P_{HOCl}^2}{P_{H_2O}P_{Cl_2O}} = \frac{(1.00)^2}{(1.00)(1.00)} = 1.00$$

$Q_P > K_P$, therefore, there are too many products and the reverse reaction will occur to reach equilibrium (or reaction will go to the left).

b) $$P_{HOCl} = 21.0\ torr\left(\frac{1\ atm}{760\ torr}\right) = 0.0276\ atm$$

$$P_{H_2O} = 200.\ torr\left(\frac{1\ atm}{760\ torr}\right) = 0.263\ atm$$

$$P_{Cl_2O} = 49.8\ torr\left(\frac{1\ atm}{760\ torr}\right) = 0.0655\ atm$$

$$Q_P = \frac{P_{HOCl}^2}{P_{H_2O}P_{Cl_2O}} = \frac{(0.0276)^2}{(0.263)(0.0655)} = 0.0442$$

$Q_P < K_P$, therefore, there are too many reactants and the forward reaction will occur to reach equilibrium (or reaction will go to the right).

Note: Pressures were converted to atm. If you plugged in the pressure in torr you would have gotten the same answer. This works for this problem because there are the same number of moles of gas on the product and the reactants side of the equation. If there were different number of moles on the product and the reactants side of the reaction you would have to plug the pressure in in atm.

c) $$P_{HOCl} = 20.0\ torr\left(\frac{1\ atm}{760\ torr}\right) = 0.0263\ atm$$

$$P_{H_2O} = 296\ torr\left(\frac{1\ atm}{760\ torr}\right) = 0.389\ atm$$

$$P_{Cl_2O} = 15.0\ torr\left(\frac{1\ atm}{760\ torr}\right) = 0.0198\ atm$$

$$Q_P = \frac{P_{HOCl}^2}{P_{H_2O}P_{Cl_2O}} = \frac{(0.0263)^2}{(0.389)(0.0198)} = 0.0898$$

System is essentially at equilibrium

43. $H_2O(g) + Cl_2O(g) \leftrightharpoons 2HOCl(g)$

$$K = \frac{[HOCl]^2}{[H_2O][Cl_2O]} = 0.090$$

a)

	H_2O	Cl_2O	HOCl
Initial (g)	1.0	2.0	0
Initial $\left(n = \frac{m}{M_x}\right)$	0.055	0.023	0
Initial $\left(M = \frac{n}{V}\right)$	0.055	0.023	0
Change (M)	-x	-x	+2x
Equilibrium (M)	0.055-x	0.023-x	2x

$$K = \frac{[HOCl]^2}{[H_2O][Cl_2O]} = \frac{(2x)^2}{(0.0550 - x)(0.023 - x)} = 0.090$$

$$\frac{4x^2}{0.0013 - 0.078x + x^2} = 0.090$$
$$4x^2 = 1.17 \times 10^{-4} - 0.0070x + 0.090x^2$$
$$-3.91x^2 - 0.0070x + 1.17 \times 10^{-4} = 0$$
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{0.0070 \pm \sqrt{4.9 \times 10^{-5} - -0.0018}}{-7.82} = -0.0064\ and\ 0.0046$$
The molarity cannot be negative, therefore, the x = 0.0046 M
With guess and check x = 0.00457
Concentrations at equilibrium
$$[H_2O] = 0.055\ M - 0.0046\ M = 0.050\ M$$
$$[Cl_2O] = 0.023\ M - 0.0046\ M = 0.018\ M$$
$$[HOCl] = 2(0.0046\ M) = 0.0092\ M$$

b)

	H_2O	Cl_2O	HOCl
Initial (mol)	0	0	1.0
Initial $\left(M = \frac{n}{V}\right)$	0	0	0.50
Change (M)	x	x	-2x
Equilibrium (M)	x	x	0.50-2x

$$K = \frac{[HOCl]^2}{[H_2O][Cl_2O]} = \frac{(0.50 - 2x)^2}{(x)(x)} = 0.090$$
$$\frac{4.0x^2 - 2.0x + 0.25}{x^2} = 0.090$$
$$4.0x^2 - 2.0x + 0.25 = 0.0904x^2$$
$$3.91x^2 - 2.0x + 0.25 = 0$$
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{2.0 \pm \sqrt{4.0 - 3.91}}{7.82} = 0.29\ and\ 0.22$$
Since the concentration of HOCl was only 0.50 M to start with you cannot subtract more than 0.50 M. Therefore, the answer must be 0.22
If you use guess and check x = 0.217, 0.22 with correct significant figures
Concentrations at equilibrium
$$[H_2O] = [Cl_2O] = 0.22\ M$$
$$[HOCl] = 0.50\ M - 2(0.22\ M) = 0.06\ M$$

44. $K = \frac{[HF]^2}{[H_2][F_2]} = \frac{(0.400)^2}{(0.0500)(0.0100)} = 320.$

Calculate Q after adding 0.200 mol of F_2
$$Q = \frac{[HF]^2}{[H_2][F_2]}$$
Concentration of F_2 added
$$[F_2] = \frac{0.200\ mol}{5.00\ L} = 0.0400\ M$$
Calculate the initial F_2 concentration
$$[F_2] = \frac{0.200\ mol}{5.00\ L} = 0.0400\ M$$
$$[F_2] = 0.0100\ M + 0.0400\ M = 0.0500\ M$$

$$Q = \frac{(0.400)^2}{(0.0500)(0.0500)} = 64.0$$

Q<K, therefore, reaction will proceed toward products

	H_2	F_2	HF
Initial (M)	0.0500	0.0500	0.400
Change (M)	-x	-x	+2x
Equilibrium (M)	0.0500-x	0.0500-x	0.400+2x

$$K = \frac{[HF]^2}{[H_2][F_2]} = \frac{(0.400 + 2x)^2}{(0.0500 - x)(0.0500 - x)} = 320.$$

$$\sqrt{\frac{(0.400 + 2x)^2}{(0.0500 - x)^2}} = \sqrt{320.}$$

$$\frac{0.400 + 2x}{0.0500 - x} = 17.9$$

$$0.400 + 2x = 0.895 - 17.9x$$

$$19.9x = 0.495$$

$$x = 0.0249$$

$$[H_2] = [F_2] = 0.0500\ M - 0.0249\ M = 0.0251\ M$$

$$[HF] = 0.400\ M + 2(0.0249\ M) = 0.450\ M$$

45. $2SO_2(g) + O_2(g) \leftrightharpoons 2SO_3(g)$

$$K_P = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}} = 0.25$$

	SO_2	O_2	SO_3
Initial (atm)	0.50	0.50	0
Change (atm)	-2x	-x	+2x
Equilibrium (atm)	0.50-2x	0.50-x	2x

$$K_P = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}} = \frac{(2x)^2}{(0.50-2x)^2(0.50-x)} = 0.25$$

Using guess and check x = 0.0621 atm, 0.062 with correct significant figures

Partial pressures at equilibrium

$$P_{SO_2} = 0.50\ atm - 2(0.062\ atm) = 0.38\ atm$$

$$P_{O_2} = 0.50\ atm - 0.062\ atm = 0.44\ atm$$

$$P_{SO_3} = 2(0.062\ atm) = 0.12\ atm$$

46. $N_2(g) + O_2(g) \leftrightharpoons 2NO(g)$

$$K = \frac{[N_2O]^2}{[N_2][O_2]} = 0.050$$

$$K_P = \frac{P_{NO}^2}{P_{N_2}P_{O_2}}$$

$PV = nRT$ $\quad\quad \frac{P}{RT} = \frac{n}{v}$ (concentration)

$$K = \frac{\left(\frac{P_{NO}}{RT}\right)^2}{\left(\frac{P_{N_2}}{RT}\right)\left(\frac{P_{O_2}}{RT}\right)} = \frac{P_{NO}^2}{P_{N_2}P_{O_2}} = K_P = 0.050$$

	N_2	O_2	NO
Initial (atm)	0.80	0.20	0
Change (atm)	-x	-x	+2x
Equilibrium (atm)	0.80-x	0.20-x	2x

$$K_P = \frac{P_{NO}^2}{P_{N_2}P_{O_2}} = \frac{(2x)^2}{(0.80-x)(0.20-x)} = 0.050$$

$$\frac{4x^2}{x^2 - 1.0x + 0.16} = 0.050$$

$$4x^2 = 0.050x^2 - 0.050x + 0.0080$$

$$3.95x^2 + 0.050x - 0.0080 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.050 \pm \sqrt{0.0025 - -0.126}}{-7.90} = -0.052 \text{ and } 0.039$$

The pressure cannot be negative therefore the x= 0.039

Using guess and check x = 0.0392, 0.039 with correct significant figures

Calculate the pressure of NO

$$P_{NO} = 2x = 2(0.039 atm) = 0.078 atm$$

49. $2CO_2(g) \leftrightharpoons 2CO(g) + O_2(g)$

$$K = \frac{[CO]^2[O_2]}{[CO_2]^2} = 2.0 \times 10^{-6}$$

	CO_2	CO	O_2
Initial (mol)	2.0	0	0
Initial $\left(M = \frac{n}{V}\right)$	0.40	0	0
Change (M)	-2x	+2x	+x
Equilibrium (M)	0.40-2x	2x	x

$$K = \frac{[CO]^2[O_2]}{[CO_2]^2} = \frac{(2x)^2 x}{(0.40-2x)^2} = 2.0 \times 10^{-6}$$

This is a very small equilibrium constant therefore try assuming that 2x is much less than 0.40 therefore assume 0.40-2x = 0.40

$$K = \frac{4x^3}{0.40^2} = 2.0 \times 10^{-6}$$

$$x = 0.0043\ M$$

Test to make sure that this is a good assumption (5% rule)

$$\frac{Amount\ Gained/Lost}{Original\ Conentration} 100\% = \frac{2(0.0043)}{0.40} = 2.15\%$$

Since it is less than 5% the assumption was good.

Concentrations at Equilibrium

$$[CO_2] = 0.40\ M - 2(0.0043\ M) = 0.39\ M$$

$$[CO] = 2(0.0043\ M) = 0.0086\ M$$

$$[O_2] = 0.0043\ M$$

50. $N_2O_4(g) \leftrightharpoons 2NO_2(g)$

$$K_P = \frac{P_{NO_2}^2}{P_{N_2O_4}} = 0.25$$

a)

	N_2O_4	NO_2
Initial (atm)	4.5	0
Change (atm)	-x	+2x
Equilibrium (atm)	4.5-x	2x

$$K_P = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{(2x)^2}{(4.5-x)} = 0.25$$

$$4x^2 = 1.1 - 0.25x$$

$$4x^2 + 0.25x - 1.1 = 0$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-0.25 \pm \sqrt{0.063 - -18}}{8} = 0.50\ and - 0.56$$

The pressure cannot be negative, therefore, x = 0.50 atm

Using guess and check x = 0.500, 0.50 with correct significant figures

Partial pressures at equilibrium

$$P_{NO_2} = 2(0.50\ atm) = 1.0\ atm$$

$$P_{N_2O_4} = 4.5\ atm - 0.5\ atm = 4.0\ atm$$

b)

	N_2O_4	NO_2
Initial (atm)	0	9.0
Change (atm)	+x	-2x
Equilibrium (atm)	x	9.0-2x

$$K_P = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{(9.0-2x)^2}{x} = 0.25$$

$$4x^2 - 36x + 81 = 0.25x$$

$$4x^2 - 36.25x + 81 = 0$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{36.25 \pm \sqrt{1{,}314 - 1{,}296}}{8} = 5.0\ and\ 4.0$$

If x=5.0 the pressure of NO_2 at equilibrium would be negative, therefore, x = 4.0

Using guess and check x = 4.00 atm, 4.0 with correct significant figures

Partial pressures at equilibrium

$$P_{NO_2} = 9.0\ atm - 2(4.0\ atm) = 1.0\ atm$$

$$P_{N_2O_4} = 4.0\ atm$$

c) No it does not matter which direction equilibrium is reached.

d) If the volume is decreased by ½ then the pressure will increase by 2.

	N_2O_4	NO_2
Initial (atm)	9	0
Change (atm)	-x	+2x
Equilibrium (atm)	9-x	2x

$$K_P = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{(2x)^2}{(9-x)} = 0.25$$

$$4x^2 = 2.25 - 0.25x$$

$$4x^2 + 0.25x - 2.25 = 0$$
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.25 \pm \sqrt{0.063 - -36}}{8} = 0.72\ and - 0.78$$
The pressure cannot be negative, therefore, x = 0.72 atm
Using guess and check x = 0.720, 0.72 with correct significant figures
Partial pressures at equilibrium
$$P_{NO_2} = 2(0.72\ atm) = 1.4\ atm$$
$$P_{N_2O_4} = 9.0\ atm - 0.72\ atm = 8.3\ atm$$

54. $Fe^{3+}(aq) + SCN^{-}(aq) \leftrightarrows FeSCN^{2+}(aq)$
$$K = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = 1.1 \times 10^3$$

	Fe^{3+}	SCN^-	$FeSCN^{2+}$
Initial $\left(M = \frac{n}{V}\right)$	0.020	0.10	0
Change (M)	-x	-x	+x
Equilibrium (M)	0.020-x	0.10-x	x

$$K = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{x}{(0.020 - x)(0.10 - x)} = 1.1 \times 10^3$$
$$\frac{x}{x^2 - 0.12x + 0.0020} = 1.1 \times 10^3$$
$$x = 1.1 \times 10^3 x^2 - 132x + 2.2$$
$$1.1 \times 10^3 x^2 - 133x + 2.2 = 0$$
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{133 \pm \sqrt{17{,}700 - 9{,}680}}{2{,}200} = 0.10\ and\ 0.020$$
The molarity cannot be negative, therefore, x = 0.020
Using guess and check x = 0.01978, 0.020 with correct significant figures
Concentrations at equilibrium
$$[Fe^{3+}] = 0.020\ M - 0.020\ M = 0\ M$$
$$[SCN^-] = 0.10\ M - 0.020\ M = 0.08\ M$$
$$[FeSCN^{2+}] = 0.020\ M$$

56. If the volume of the reaction vessel is increased the overall pressure of the system drops causing the partial pressures of all the gases to drop. To compensate for this, equilibrium shifts in the direction that has the most gas molecules. If both sides have the same number of gas molecules, then there will be no change in equilibrium. If an inert gas is added to the system it causes the total pressure to go up by whatever the partial pressure of the inert gas is. However, the partial pressures of the gases in the reaction remain unchanged, causing the system to remain at equilibrium.

58. a) Adding water increases volume and shifts equilibrium to the side with the great number of moles of aqueous solution.

Equilibrium shifts toward reactants (left).

b) Adding $AgNO_3$ will cause AgSCN to precipitate out of solution, therefore, more reactants will form.

Equilibrium shifts toward reactants (left).

c) Adding FeOH will cause $Fe(OH)_3$ to precipitate out of solution, therefore, more reactants will form.

Equilibrium shifts toward reactants (left).

d) Add $Fe(NO_3)_3$ causes more Fe^{3+} ion to be in solution which shifts equilibrium away from reactants.

Equilibrium shifts toward products (right).

59. When sodium hydroxide is added to the beaker it produces OH^- ions in solution, which bond with the H^+ ions to form H_2O. Removing H^+ ions from solution causes equilibrium to shift to the products (right). Since CrO_4^{2-} is yellow in color, as more CrO_4^{2-} forms the solution turns yellow.

61. a) Equilibrium shifts to the products (right).

b) Equilibrium shifts to the products (right).

c) When an inert gases is added and the volume remains the same the partial pressures of the other gases in the system do not change. Therefore, there is no shift in equilibrium.

d) For exothermic reactions (heat in the products side) when the temperature is increased the equilibrium shifts to the reactants (left).

e) When the volume of the container is decreased equilibrium shifts to the side of the reaction with the overall fewer number of gas molecule. If the same number of gas molecules are present on both sides no shift in equilibrium occurs. Therefore, no shift in equilibrium occurs.

62. a) Equilibrium shifts to the reactants (left).

b) For endothermic reactions (heat on reactants side) when the temperature is increased equilibrium shifts to products (right).

c) Adding an inert gas does not affect the partial pressure of the gases. Therefore, there is no shift in equilibrium.

d) Equilibrium shifts to the products (right).

e) When the volume of the container is increased equilibrium shifts to the side of the reaction with the overall larger number of gas molecules. Therefore, equilibrium shifts to the products (right).

63. a) Equilibrium shifts toward reactants (left).

b) Equilibrium shifts toward products (right).

c) Equilibrium shifts toward reactants (left).

d) Adding an inert gas does not affect the partial pressure of the gases. Therefore, there is no shift in equilibrium.

e) When the volume of the container is increased, equilibrium shifts to the side of the reaction with the larger number of gas molecules. If the same number of gas molecules are present on both sides no shift in equilibrium occurs. Therefore, no shift in equilibrium occurs.

f) For an exothermic reaction the heat is on the products side. Therefore, decreasing the heat will cause the equilibrium to shift to the products side.

Equilibrium shifts toward products (right)

65. a) Equilibrium shifts to reactants (left) more SO_3 forms.

b) When the pressure is decreased equilibrium shifts to the toward the side with the overall fewer gas molecules. Equilibrium shifts to the reactants (left) more SO_3 forms.

c) Adding an inert gas does not affect the partial pressure of the gases. Therefore, there is no shift in equilibrium; the amount of SO_3 stays the same.

d) For endothermic reactions (heat on reactants side) when the temperature is decreased equilibrium shifts to reactants (left); more SO_3 forms.

e) Equilibrium shifts to the products (right); moles of SO_3 decreases.

72. a)

$Na_2O(s) \leftrightharpoons 2Na(l) + \frac{1}{2}O_2(g)$ $\quad K_1$

$\underline{2Na(l) + O_2(g) \leftrightharpoons Na_2O_2(s)}$ $\quad \frac{1}{K_3}$

$Na_2O(s) + \frac{1}{2}O_2(g) \leftrightharpoons Na_2O_2(s)$ $\quad \frac{K_1}{K_3} = \frac{2\times10^{-25}}{5\times10^{-29}} = 4\times10^{3}$

b)

$NaO(g) \leftrightharpoons Na(l) + \frac{1}{2}O_2(g)$ $\quad K_2$

$Na_2O(s) \leftrightharpoons 2Na(l) + \frac{1}{2}O_2(g)$ $\quad K_1$

$\underline{2Na(l) + O_2(g) \leftrightharpoons Na_2O_2(s)}$ $\quad \frac{1}{K_3}$

$NaO(g) + Na_2O(s) \leftrightharpoons Na_2O_2(s) + Na(l)$ $\quad \frac{K_1K_2}{K_3} = \frac{(2\times10^{-25})(2\times10^{-5})}{5\times10^{-29}} = 0.08$

c)

$2(NaO(g) \leftrightharpoons Na(l) + \frac{1}{2}O_2(g))$ $\quad K_2^2$

$\underline{2Na(l) + O_2(g) \leftrightharpoons Na_2O_2(s)}$ $\quad \frac{1}{K_3}$

$2NaO(g) \leftrightharpoons Na_2O_2(s)$ $\quad \frac{K_2^2}{K_3} = \frac{(2\times10^{-5})^2}{5\times10^{-29}} = 8\times10^{18}$

73.

$NO(g) + O(g) \rightleftharpoons NO_2(g)$ $\quad \frac{1}{K_1}$

$\underline{NO_2(g) + O_2(g) \rightleftharpoons O_3(g) + NO(g)}$ $\quad \frac{1}{K_2}$

$O_2(g) + O(g) \rightleftharpoons O_3(g)$ $\quad K = \frac{1}{K_1K_2} = \frac{1}{(6.8\times10^{-49})(5.8\times10^{-34})} = 2.5\times10^{81}$

75. $3H_2(g) + N_2(g) \leftrightharpoons 2NH_3(g)$

	H_2	N_2	NH_3
Equilibrium (M)	5.0	8.0	4.0
Initial (M)	x	y	0 M
Change (M)	-3z	-z	+z
Equilibrium (M)	x-3z = 5.0	y-z = 8.0	2z = 4.0

Looking at the change in NH_3 concentration will allow for z to be solved for

2z = 4.0 M

z= 2.0 M

Calculate the initial concentration of N_2

y - z = 8.0 y - 2.0 = 8.0 y = 10.0 M

Calculate the initial concentration of H_2

x - 3z = 8.0 x – 3(2.0) = 5.0 x = 11.0 M

76. $3H_2(g) + N_2(g) \leftrightharpoons 2NH_3(g)$

$$K_P = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = 5.3 \times 10^5$$

	H_2	N_2	NH_3
Initial (M)	0	0	x
Change (M)	+3z	+z	-2z
Equilibrium (M)	3z	z	x-2z=$\frac{x}{2}$=0.50x z=$\frac{x}{4}$
Equilibrium (M)	0.75x	0.25x	0.50x

Note when the amount of NH_3 drops to 50% so does the partial pressure

$$K_P = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = \frac{(0.5x)^2}{(0.25x)(0.75x)^3} = 5.3 \times 10^5$$

$$2.37\frac{1}{x^2} = 5.3 \times 10^5$$

$$x = 0.0021$$

The original partial pressure of NH_3 is 0.0021atm

79. $PCl_5(g) \leftrightharpoons PCl_3(g) + Cl_2(g)$

$P_{tot} = P_{PCl_5} + P_{PCl_3} + P_{Cl_2} = 358.7torr\left(\frac{1\,atm}{760\,torr}\right) = 0.4720\,atm$ (at equilibrium)

a)

	PCl_5	PCl_3	Cl_2
Initial (g)	2.4156	0	0
Initial $\left(n = \frac{m}{M_X}\right)$	0.011601	0	0
Initial $\left(P = \frac{nRT}{V}\right)$	0.24894	0	0
Change (atm)	-x	+x	+x
Equilibrium (atm)	0.24894-x	x	x

Therefore

$$P_{tot} = P_{PCl_5} + P_{PCl_3} + P_{Cl_2} = 0.24894 - x + x + x = 0.4720$$

$$x = 0.2231$$

$$P_{PCl_5} = 0.2489\,atm - x = 0.2489\,atm - 0.2231\,atm = 0.0258\,atm$$

$$P_{PCl_3} = P_{Cl_2} = x = 0.2231\,atm$$

$$K_P = \frac{P_{PCl_3}P_{Cl_2}}{P_{PCl_5}} = \frac{(0.2231)(0.2231)}{0.0258} = 1.93$$

b)

	PCl_5	PCl_3	Cl_2
Equilibrium (atm)	0.0258	0.2231	0.2231
Add (mol)	0	0	0.250
Add $\left(P = \frac{nRT}{V}\right)$	0	0	5.36
Initial (atm)	0.0258	0.2231	5.58
Change (atm)	+x	-x	-x
Equilibrium (atm)	0.0258+x	0.2231-x	5.58-x

$$K_P = \frac{P_{PCl_3}P_{Cl_2}}{P_{PCl_5}} = \frac{(0.2231 - x)(5.58 - x)}{0.0258 + x} = 1.93$$

$$\frac{x^2 - 5.80x + 1.24}{0.0258 + x} = 1.93$$
$$x^2 - 5.80x + 1.24 = 0.0498 + 1.93x$$
$$x^2 - 7.73x + 1.19 = 0$$
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{7.73 \pm \sqrt{(-7.63)^2 - 4(1)(1.19)}}{2(1)} = 7.57\ and\ 0.156$$

Since the pressure cannot be negative, therefore, x = 0.156
Using guess and check x = 0.1578 with significant figures x = 0.158
Partial pressure at equilibrium

$$P_{PCl_5} = 0.0258\ atm + x = 0.0258\ atm + 0.156\ atm = 0.182\ atm$$
$$P_{PCl_3} = 0.2231\ atm - x = 0.2231\ atm - 0.156\ atm = 0.067\ atm$$
$$P_{Cl_2} = 5.58\ atm - x = 5.58\ atm - 0.156\ atm = 5.42\ atm$$

81. Deteremine the equation of interest

$N_2O_4(g) \leftrightharpoons 2NO_2(g)$

Determine the expresion and value of K_P

$$K_P = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{(1.20)^2}{0.34} = 4.2$$

Determine the concentrations after volume doubled

$$PV = nRT \qquad P = \frac{nRT}{V}$$

Therefore, if the volume is doubled the pressure is cut in half
Initial (pressure after doubling volume)

$$P_{NO_2} = 1.20\ atm \qquad P_{N_2O_4} = 0.34\ atm$$

Determine the direction that the reaction will go
Le Chatelier principle states that if the volume is increased the reaction will proceed in the direction with the greater number of moles of gas (forward reaction).
Make ICE table

	N_2O_4	NO_2
Initial (atm)	0.17	0.600
Change (atm)	-x	+2x
Equilibrium (atm)	0.17-x	0.600+2x

Calculate the partial pressures after doubling volume

$$K_P = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{(0.600 + 2x)^2}{0.17 - x} = 4.2$$
$$4x^2 + 2.40x + 0.360 = 0.71 - 4.2x$$
$$4x^2 + 6.6x + 0.350 = 0$$
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-6.6 \pm \sqrt{43.6 - (-5.6)}}{8} = 0.052\ and - 1.7$$

Pressure cannot be negative, therefore, x = 0.052
Partial pressures at equilibrium

$$P_{NO_2} = 0.600atm + 2x = 0.600atm + 2(0.052\ atm) = 0.704\ atm$$
$$P_{N_2O_4} = 0.17\ atm - x = 0.17\ atm - 0.052\ atm = 0.12\ atm$$

82. a) $n_{PCl_5} = 2.450\ g\left(\frac{1\ mol\ PCl_5}{208.22\ g\ PCl_5}\right) = 0.01177\ mol\ PCl_5$

$$P = \frac{nRT}{V} = \frac{(0.01177\ mol)\left(0.08206\ \frac{L\cdot atm}{mol\cdot K}\right)(600.\ K)}{0.500\ L} = 1.16\ atm$$

b) $PCl_5(g) \leftrightharpoons PCl_3(g) + Cl_2(g)$

$$K = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{P_{PCl_3}}{RT}\frac{P_{PCl_2}}{RT}}{\frac{P_{PCl_5}}{RT}} = \frac{1}{RT}K_P = 11.5$$

$$K_P = (11.5)\left(0.08206\frac{L\cdot atm}{mol\cdot K}\right)(600K) = 566$$

	PCl_5	PCl_3	Cl_2
Initial (atm)	1.16	0	0
Change (atm)	-x	+x	+x
Equilibrium (atm)	1.16-x	x	x

$$K_P = \frac{xx}{1.16 - x} = 566$$

$$x^2 = 657 - 566x$$

$$x^2 + 566x - 657 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-566 \pm \sqrt{566^2 - 4(1)(-657)}}{2(1)} = 1.158\ and - 567.2$$

Pressure cannot be negative, therefore, x = 1.158

Using guess and check x = 1.15763, with correct significant figures x = 1.15

Calculate P_{PCl_5} at equilibrium

$$1.16\ atm - 1.15\ atm = 0.01\ atm$$

c) Calculate partial pressure of other gases

$$P_{PCl_3} = 1.15\ atm$$

$$P_{Cl_2} = 1.15\ atm$$

Calculate P_{tot}

$$P_{tot} = P_{PCl_5} + P_{PCl_3} + P_{Cl_2} = 0.01\ atm + 1.15\ atm + 1.15\ atm = 2.31\ atm$$

d) Initial: 1.16 atm

Final: 0.01 atm

Amount Dissociated

$$1.16\ atm - 0.01\ atm = 1.15\ atm$$

Percent Dissociated

$$\left(\frac{1.15}{1.16}\right)100\% = 99.1\%$$