Chem 1515
Problem Set #7
Fall 2001

Name______________________

TA Name ____________________

Lab Section #_____

ALL work must be shown to receive full credit. **Due at the beginning of lecture on Wednesday, October 24, 2001.**

PS7.1. Given the reaction

$$3O_2(g) + 4NH_3(g) \rightleftarrows 6H_2O(g) + 2N_2(g)$$

Initially (before any reaction occurs) a 1.00 liter reaction vessel at some temperature contains 0.502 moles of O_2 and 0.791 moles of NH_3 and no water or nitrogen. Consider the following:

a) If 0.245 moles of O_2 react, how many moles of NH_3 must react and how many moles of H_2O and N_2 are formed? How many moles of O_2, NH_3, H_2O and N_2 remain after completion of the reaction?

	$3O_2$ +	$4NH_3$ ⇄	$6H_2O$ +	$2N_2$
initial	**.502**	**.791**	**0**	**0**
change	**-.245**	**-.327**	**+.490**	**+.165**
moles remaining(final)	**.257**	**.464**	**.490**	**.1263**

Note: the change row was determined using the reaction stoichiometry calculations below,

$$0.245 \text{ mol } O_2 \left(\frac{4 \text{ mol } NH_3}{3 \text{ mol } O_2}\right) = 0.327 \text{ mol } NH_3 \text{ reacting}$$

$$0.245 \text{ mol } O_2 \left(\frac{6 \text{ mol } H_2O}{3 \text{ mol } O_2}\right) = 0.490 \text{ mol } H_2O \text{ formed}$$

$$0.245 \text{ mol } O_2 \left(\frac{2 \text{ mol } N_2}{3 \text{ mol } O_2}\right) = 0.163 \text{ mol } N_2 \text{ formed}$$

The moles remaining row is determined by adding the moles reacting or forming (change row) to the initial amount of each species.

b) If 0.304 moles of NH_3 react, how many moles of O_2 must react and how many moles of H_2O and N_2 are formed? How many moles of O_2, NH_3, H_2O and N_2 remain after completion of the reaction?

	$3O_2$ +	$4NH_3$ ⇄	$6H_2O$ +	$2N_2$
initial	**.502**	**.791**	**0**	**0**
change	**-.228**	**-.304**	**+.456**	**+.152**
moles remaining(final)	**.274**	**.487**	**.456**	**.152**

Note: the change row was determined using the reaction stoichiometry calculations below,

$$0.304 \text{ mol } NH_3 \left(\frac{3 \text{ mol } O_2}{4 \text{ mol } NH_3}\right) = 0.327 \text{ mol } O_2 \text{ reacting}$$

$$0.304 \text{ mol } NH_3 \left(\frac{6 \text{ mol } H_2O}{4 \text{ mol } NH_3}\right) = 0.490 \text{ mol } H_2O \text{ formed}$$

$$0.304 \text{ mol } NH_3 \left(\frac{2 \text{ mol } N_2}{4 \text{ mol } NH_3}\right) = 0.152 \text{ mol } N_2 \text{ formed}$$

c) If '**3x**' moles of O_2 react, how many moles of NH_3 must react and how many moles of H_2O and N_2 are formed(in terms of '**x**')? How many moles of O_2, NH_3, H_2O and N_2 remain after completion of the reaction?

	$3O_2$	+ $4NH_3$ ⇄	$6H_2O$ +	$2N_2$
initial	**.502**	**.791**	**0**	**0**
change	**-3x**	**-4x**	**+6x**	**+2x**
moles remaining(final)	**.502-3x**	**.791-4x**	**0+6x**	**0+2x**

d) If 0.503 moles of H_2O are formed, how many moles of N_2 are formed and how many moles of O_2 and NH_3 must react? How many moles of O_2, NH_3, H_2O and N_2 remain after completion of the reaction?

	$3O_2$	+ $4NH_3$ ⇄	$6H_2O$ +	$2N_2$
initial	**.502**	**.791**	**0**	**0**
change	**-.252**	**-.335**	**+.503**	**+.168**
moles remaining(final)	**.250**	**.456**	**.503**	**.168**

Note: the change row was determined using the reaction stoichiometry calculations below,

$$0.503 \text{ mol } H_2O \left(\frac{3 \text{ mol } O_2}{6 \text{ mol } H_2O}\right) = 0.252 \text{ mol } O_2 \text{ reacting}$$

$$0.503 \text{ mol } H_2O \left(\frac{4 \text{ mol } NH_3}{6 \text{ mol } H_2O}\right) = 0.335 \text{ mol } NH_3 \text{ formed}$$

$$0.503 \text{ mol } H_2O \left(\frac{2 \text{ mol } N_2}{6 \text{ mol } H_2O}\right) = 0.168 \text{ mol } N_2 \text{ formed}$$

PS7.2. Write the equilibrium expression for each of the following chemical equations;

a) $N_{2(g)} + O_{2(g)} \rightleftarrows 2NO_{(g)}$ $\quad K_c = \frac{[NO]^2}{[N_2]^1[O_2]^1}$ or $K_p = \frac{P^2_{NO}}{P^1_{N_2} \cdot P^1_{O_2}}$

b) $2NO_{(g)} + O_{2(g)} \rightleftarrows 2NO_{2(g)}$ $\quad K_c = \frac{[NO_2]^2}{[O_2]^1[NO]^2}$ or $K_p = \frac{P^2_{NO_2}}{P^1_{O_2} \cdot P^2_{NO}}$

c) $N_{2(g)} + 2O_{2(g)} \rightleftarrows 2NO_{2(g)}$ $\quad K_c = \frac{[NO_2]^2}{[N_2]^1[O_2]^2}$ or $K_p = \frac{P^2_{NO_2}}{P^1_{N_2} \cdot P^2_{O_2}}$

d) $2N_2O_{(g)} + O_{2(g)} \rightleftarrows 4NO_{(g)}$ $\quad K_c = \frac{[NO]^4}{[N_2O]^2[O_2]^1}$ or $K_p = \frac{P^4_{NO}}{P^2_{N_2O} \cdot P^1}$

PS7.3. In each of the following you are given the equation for an equilibrium system and the magnitude of the equilibrium constant. Calculate the new equilibrium constant for the reaction in the alternative form;

	Equilibrium reaction	Equilibrium constant	Alternative reaction
a)	$N_2(g) + O_2(g) \rightleftarrows 2NO(g)$	4.7×10^{-31}	$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftarrows NO(g)$

$$\mathbf{K_{alternative} = \sqrt{K} = \sqrt{4.7 \times 10^{-31}} = 6.86 \times 10^{-16}}$$

b)	$CO_2(g) + H_2(g) \rightleftarrows CO(g) + H_2O(g)$	1.4	$CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$

$$\mathbf{K_{alternative} = \frac{1}{K} = \frac{1}{1.4} = 7.14 \times 10^{-1}}$$

c)	$6ClO_3F(g) \rightleftarrows 2ClF(g) + 4ClO(g) + 7O_2(g) + 2F_2(g)$	32.6	$\frac{1}{3}ClF(g) + \frac{2}{3}ClO(g) + \frac{7}{6}O_2(g) + \frac{1}{3}F_2(g) \rightleftarrows ClO_3F(g)$

$$\mathbf{K_{alternative} = \frac{1}{\sqrt[6]{K}} = \frac{1}{\sqrt[6]{32.6}} = 5.59 \times 10^{-1}}$$

PS7.4. Equilibrium constants for the following reactions have been determined at 298 K:

$N_2(g) + O_2(g) \rightleftarrows 2NO(g)$ $\quad K_1 = 4.7 \times 10^{-31}$

$2NO_2(g) \rightleftarrows 2NO(g) + O_2(g)$ $\quad K_2 = 4.35 \times 10^{-13}$

Calculate K (at the same temperature) for the reaction

$\frac{1}{2}N_2(g) + O_2(g) \rightleftarrows NO_2(aq)$ $\quad K_3 = ?$

To solve
We need to reverse the second equation;
$\mathbf{2NO(g) + O_2(g) \rightleftarrows 2NO_2(g)}$
Then we can add the two equations together;

$\mathbf{N_2(g) + O_2(g) \rightleftarrows 2NO(g)} \quad \mathbf{K_1 = 4.7 \times 10^{-31}}$

$\mathbf{2NO(g) + O_2(g) \rightleftarrows 2NO_2(g)} \quad \mathbf{K_{2new} = \frac{1}{K_2} = \frac{1}{4.35 \times 10^{-13}}}$

$\mathbf{N_2(g) + 2O_2(g) \rightleftarrows 2NO_2(g)} \quad \mathbf{K_1 \cdot \frac{1}{K_2}}$

Now multiply the equation by 1/2 to get

$\mathbf{\frac{1}{2}N_2(g) + O_2(g) \rightleftarrows NO_2(g)}$

$$\mathbf{\sqrt{\frac{K_1}{K_2}} = \sqrt{\frac{4.7 \times 10^{-31}}{4.35 \times 10^{-13}}} = 1.04 \times 10^{-9}}$$

PS7.5. The reaction

$$NOBr(g) \rightleftarrows NO(g) + \frac{1}{2}Br_2(g)$$

has been carefully studied at 350 ˚C and the K_c is 0.079. Calculate Q and determine which direction (left-to-right or right-to-left) will the reaction proceed to establish equilibrium under each of the following initial conditions?

a) $[NOBr]_o = 0.100$ M : $[NO]_o = 0$: $[Br_2]_o = 0$

$$\mathbf{Q = \frac{[NO]_{init}[Br_2]^{1/2}}{[NOBr]_{init}} = \frac{(O)(O)^{1/2}}{.1} = 0: Q < K_c: L \rightarrow R}$$

b) $[NOBr]_o = 0$: $[NO]_o = 0.100$ M : $[Br_2]_o = 0.100$ M

$$\mathbf{Q = \frac{[NO]_{init}[Br_2]^{1/2}}{[NOBr]_{init}} = \frac{(.1)(.1)^{1/2}}{0} = \text{very large} : Q > K_c : R \rightarrow L}$$

c) $[NOBr]_o = 0.100$ M : $[NO]_o = 0$: $[Br_2]_o = 0.100$ M

$$\mathbf{Q = \frac{[NO]_{init}[Br_2]^{1/2}}{[NOBr]_{init}} = \frac{(0)(.1)^{1/2}}{0} = 0: Q < K_c: L \rightarrow R}$$

d) $[NOBr]_o = 0.100$ M : $[NO]_o = 0.100$ M : $[Br_2]_o = 0.100$ M

$$\mathbf{Q = \frac{[NO]_{init}[Br_2]^{1/2}}{[NOBr]_{init}} = \frac{(0.1)(.1)^{1/2}}{0.1} = .316: Q > K_c : R \rightarrow L}$$

e) $[NOBr]_o = 0.200$ M : $[NO]_o = 0.0500$ M : $[Br_2]_o = 0.100$ M

$$\mathbf{Q = \frac{[NO]_{init}[Br_2]^{1/2}}{[NOBr]_{init}} = \frac{(0.05)(.1)^{1/2}}{0.2} = .079: Q = K_c : \text{at equilibrium}}$$

PS7.6. Consider the reaction

$$2H_2S(g) + 3O_2(g) \rightleftarrows 2H_2O(g) + 2SO_2(g)$$

for which $\Delta H_{rxn} = -1036$ kJ. Predict how the $[H_2O]$ will change when the equilibrium is disturbed by;

a) Addition of O_2
$[H_2O]$ will increase

b) Addition of SO_2
$[H_2O]$ will decrease

c) Addition of a catalyst
$[H_2O]$ will not change

d) Decrease in temperature
$[H_2O]$ will increase

e) Decrease in the volume of the reaction container
$[H_2O]$ will increase

PS7.7. In the manufacture of ammonia from its elements hydrogen must be produced on site. An important source of hydrogen is the reforming of methane at high temperature. The reaction which describes the reforming of methane is;

$$CH_4(g) + 2H_2O(g) \rightleftarrows CO_2(g) + 4H_2(g)$$

a) A mixture of 1.00 mol of methane and 1.00 mol of water are heated to 1000 K in a 10.0 L flask. The mixture was allowed to reach equilibrium. The amount of unreacted methane was found to be 11.2 g. Calculate the amount of hydrogen at equilibrium.

Using the initial information we can complete the table

	$CH_4(g)$	+ $2H_2O(g)$	⇄	$CO_2(g)$	$4H_2(g)$
I	**0.100 M**	**0.100 M**		**0**	**0**
C					
E	**0.0775 M**				

From this information we can calculate the change in the [CH_4].

$$0.100 - 0.0775 = 0.0225 \text{ M}$$

	$CH_4(g)$	+ $2H_2O(g)$	⇄	$CO_2(g)$	$4H_2(g)$
I	**0.100 M**	**0.100 M**		**0**	**0**
C	**-0.0225 M**				
E	**0.0775 M**				

Using the stoichiometry we can calculate [H_2O] reacting and the [CO_2] and [H_2] forming.

$$0.0225 \text{ M } CH_4 \left(\frac{2 \text{ mol } H_2O}{1 \text{ mol } CH_4}\right) = 0.0450 \text{ M}$$

$$0.0225 \text{ M } CH_4 \left(\frac{1 \text{ mol } CO_2}{1 \text{ mol } CH_4}\right) = 0.0225 \text{ M}$$

$$0.0225 \text{ M } CH_4 \left(\frac{4 \text{ mol } H_2}{1 \text{ mol } CH_4}\right) = 0.0900 \text{ M}$$

	$CH_4(g)$	+ $2H_2O(g)$	⇄	$CO_2(g)$	$4H_2(g)$
I	**0.100 M**	**0.100 M**		**0**	**0**
C	**-0.0225 M**	**-0.0450 M**		**0.0225 M**	**0.0900 M**
E	**0.0775 M**				

Then we can calculate the concentrations at equilibrium;

	$CH_4(g)$	+ $2H_2O(g)$	⇄	$CO_2(g)$	$4H_2(g)$
I	**0.100 M**	**0.100 M**		**0**	**0**
C	**-0.0225 M**	**-0.0450 M**		**0.0225 M**	**0.0900 M**
E	**0.0775 M**	**0.0550 M**		**0.0225 M**	**0.0900 M**

b) Calculate the magnitude of the equilibrium constant for the reaction at 1000 K.

$$\mathbf{K_c = \frac{[CO_2]\,[H_2]^4}{[CH_4]\,[H_2O]^2} = \frac{[0.0225]\,[0.0900]^4}{[0.0775]\,[0.0550]^2} = 6.30 \times 10^{-3}}$$

c) Calculate ΔH° for the reaction

$$\mathbf{CH_4(g) + 2H_2O(g) \rightleftarrows CO_2(g) + 4H_2(g)}$$

$$\mathbf{\Delta H_f^\circ \quad -74.9 \quad -241.8 \qquad -393.5 \quad -0 \qquad \left(\frac{kJ}{mol}\right)}$$

$$\mathbf{\Delta H_{rxn}^\circ = \Sigma\, n\Delta H_f^\circ\ (products) - \Sigma\, m\Delta H_f^\circ\ (reactants)}$$

$$\mathbf{\Delta H_{rxn}^\circ = \left(1\ mol\left(-393.5\ \frac{kJ}{mol}\right) + 4\ mol\left(0\ \frac{kJ}{mol}\right)\right)}$$

$$\mathbf{- \left(1\ mol\left(-74.9\ \frac{kJ}{mol}\right) + 2\ mol\left(-241.8\ \frac{kJ}{mol}\right)\right)}$$

$$\mathbf{\Delta H_{rxn}^\circ = +165\ kJ}$$

d) Describe the effect on the equilibrium amount of H_2 produced by each of the following actions;

i) add a catalyst **(no effect)**

ii) add CH_4 **(increase)**

iii) remove CO_2 **(increase)**

iv) increase T to 1200 K **(increase)**

v) transfer mixture to a 15.0 L flask **(increase)**