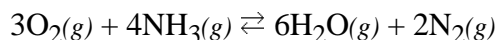


ALL work must be shown to receive full credit. **Due at the beginning of lecture on Wednesday, October 24, 2001.**

PS7.1. Given the reaction



Initially (before any reaction occurs) a 1.00 liter reaction vessel at some temperature contains 0.502 moles of O₂ and 0.791 moles of NH₃ and no water or nitrogen.

Consider the following:

- a) If 0.245 moles of O₂ react, how many moles of NH₃ must react and how many moles of H₂O and N₂ are formed? How many moles of O₂, NH₃, H₂O and N₂ remain after completion of the reaction?

	3O₂	+	4NH₃	⇌	6H₂O	+	2N₂
	initial		.502		.791		0
	change		-.245		-.327		+.490
moles remaining(final)			.257		.464		.490
					.163		.1263

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

$$0.245 \text{ mol O}_2 \left(\frac{4 \text{ mol NH}_3}{3 \text{ mol O}_2} \right) = 0.327 \text{ mol NH}_3 \text{ reacting}$$

$$0.245 \text{ mol O}_2 \left(\frac{6 \text{ mol H}_2\text{O}}{3 \text{ mol O}_2} \right) = 0.490 \text{ mol H}_2\text{O formed}$$

$$0.245 \text{ mol O}_2 \left(\frac{2 \text{ mol N}_2}{3 \text{ mol O}_2} \right) = 0.163 \text{ mol N}_2 \text{ formed}$$

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 NH₃ react, how many moles of O₂ must react and how many moles of H₂O and N₂ are formed? How many moles of O₂, NH₃, H₂O and N₂ remain after completion of the reaction?

	3O₂	+	4NH₃	⇌	6H₂O	+	2N₂
	initial		.502		.791		0
	change		-.228		-.304		+.456
moles remaining(final)			.274		.487		.456
					.152		.152

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

$$0.304 \text{ mol NH}_3 \left(\frac{3 \text{ mol O}_2}{4 \text{ mol NH}_3} \right) = 0.228 \text{ mol O}_2 \text{ reacting}$$

$$0.304 \text{ mol NH}_3 \left(\frac{6 \text{ mol H}_2\text{O}}{4 \text{ mol NH}_3} \right) = 0.456 \text{ mol H}_2\text{O formed}$$

$$0.304 \text{ mol NH}_3 \left(\frac{2 \text{ mol N}_2}{4 \text{ mol NH}_3} \right) = 0.152 \text{ mol N}_2 \text{ formed}$$

- c) If '3x' moles of O₂ react, how many moles of NH₃ must react and how many moles of H₂O and N₂ are formed (in terms of 'x')? How many moles of O₂, NH₃, H₂O and N₂ remain after completion of the reaction?

	3O₂	+ 4NH₃	⇌	6H₂O	+ 2N₂
	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 H₂O are formed, how many moles of N₂ are formed and how many moles of O₂ and NH₃ must react? How many moles of O₂, NH₃, H₂O and N₂ remain after completion of the reaction?

	3O₂	+ 4NH₃	⇌	6H₂O	+ 2N₂
	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,

$$0.503 \text{ mol H}_2\text{O} \left(\frac{3 \text{ mol O}_2}{6 \text{ mol H}_2\text{O}} \right) = 0.252 \text{ mol O}_2 \text{ reacting}$$

$$0.503 \text{ mol H}_2\text{O} \left(\frac{4 \text{ mol NH}_3}{6 \text{ mol H}_2\text{O}} \right) = 0.335 \text{ mol NH}_3 \text{ formed}$$

$$0.503 \text{ mol H}_2\text{O} \left(\frac{2 \text{ mol N}_2}{6 \text{ mol H}_2\text{O}} \right) = 0.168 \text{ mol N}_2 \text{ formed}$$

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

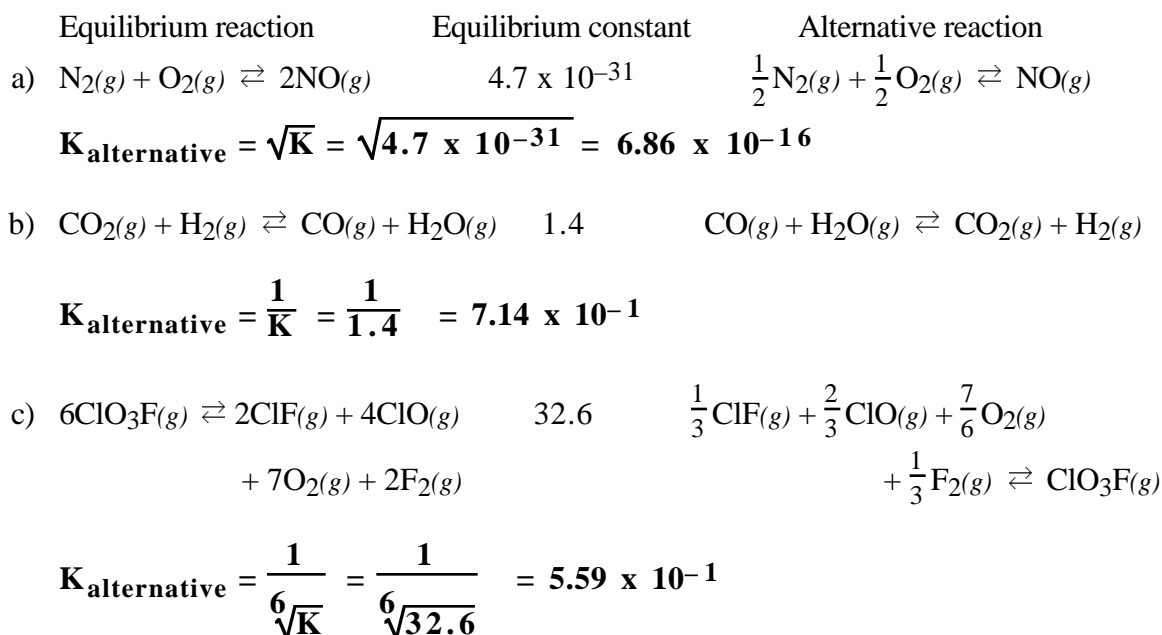
$$\text{a) } \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \quad K_c = \frac{[\text{NO}]^2}{[\text{N}_2]^1[\text{O}_2]^1} \quad \text{or} \quad K_p = \frac{P^2_{\text{NO}}}{P^1_{\text{N}_2} \cdot P^1_{\text{O}_2}}$$

$$\text{b) } 2\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g) \quad K_c = \frac{[\text{NO}_2]^2}{[\text{O}_2]^1[\text{NO}]^2} \quad \text{or} \quad K_p = \frac{P^2_{\text{NO}_2}}{P^1_{\text{O}_2} \cdot P^2_{\text{NO}}}$$

$$\text{c) } \text{N}_2(g) + 2\text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g) \quad K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2]^1[\text{O}_2]^2} \quad \text{or} \quad K_p = \frac{P^2_{\text{NO}_2}}{P^1_{\text{N}_2} \cdot P^2_{\text{O}_2}}$$

$$\text{d) } 2\text{N}_2\text{O}(g) + \text{O}_2(g) \rightleftharpoons 4\text{NO}(g) \quad K_c = \frac{[\text{NO}]^4}{[\text{N}_2\text{O}]^2[\text{O}_2]^1} \quad \text{or} \quad K_p = \frac{P^4_{\text{NO}}}{P^2_{\text{N}_2\text{O}} \cdot P^1_{\text{O}_2}}$$

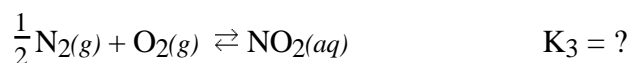
PS7.3. In each of the following you are given the equation for an equilibrium system and the magnitude of the equilibrium constant. Calculate the new equilibrium constant for the reaction in the alternative form;



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

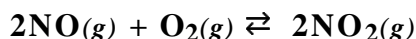


Calculate K (at the same temperature) for the reaction

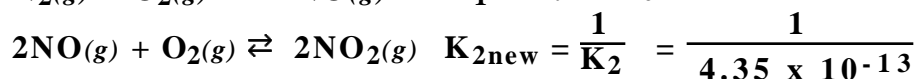
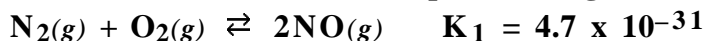


To solve

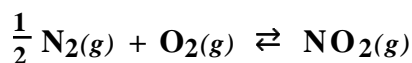
We need to reverse the second equation;



Then we can add the two equations together;

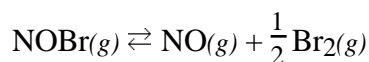


Now multiply the equation by 1/2 to get



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

PS7.5. The reaction



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) $[\text{NOBr}]_o = 0.100 \text{ M} : [\text{NO}]_o = 0 : [\text{Br}_2]_o = 0$

$$Q = \frac{[\text{NO}]_{\text{init}}[\text{Br}_2]^{1/2}}{[\text{NOBr}]_{\text{init}}} = \frac{(0)(0)^{1/2}}{.1} = 0: Q < K_c: L \rightarrow R$$

b) $[\text{NOBr}]_o = 0 : [\text{NO}]_o = 0.100 \text{ M} : [\text{Br}_2]_o = 0.100 \text{ M}$

$$Q = \frac{[\text{NO}]_{\text{init}}[\text{Br}_2]^{1/2}}{[\text{NOBr}]_{\text{init}}} = \frac{(.1)(.1)^{1/2}}{0} = \text{very large} : Q > K_c : R \rightarrow L$$

c) $[\text{NOBr}]_o = 0.100 \text{ M} : [\text{NO}]_o = 0 : [\text{Br}_2]_o = 0.100 \text{ M}$

$$Q = \frac{[\text{NO}]_{\text{init}}[\text{Br}_2]^{1/2}}{[\text{NOBr}]_{\text{init}}} = \frac{(0)(.1)^{1/2}}{0} = 0: Q < K_c: L \rightarrow R$$

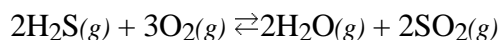
d) $[\text{NOBr}]_o = 0.100 \text{ M} : [\text{NO}]_o = 0.100 \text{ M} : [\text{Br}_2]_o = 0.100 \text{ M}$

$$Q = \frac{[\text{NO}]_{\text{init}}[\text{Br}_2]^{1/2}}{[\text{NOBr}]_{\text{init}}} = \frac{(0.1)(.1)^{1/2}}{0.1} = .316: Q > K_c : R \rightarrow L$$

e) $[\text{NOBr}]_o = 0.200 \text{ M} : [\text{NO}]_o = 0.0500 \text{ M} : [\text{Br}_2]_o = 0.100 \text{ M}$

$$Q = \frac{[\text{NO}]_{\text{init}}[\text{Br}_2]^{1/2}}{[\text{NOBr}]_{\text{init}}} = \frac{(0.05)(.1)^{1/2}}{0.2} = .079: Q = K_c : \text{at equilibrium}$$

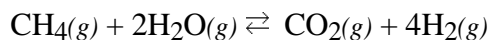
PS7.6. Consider the reaction



for which $\Delta H_{\text{rxn}} = -1036 \text{ kJ}$. Predict how the $[\text{H}_2\text{O}]$ will change when the equilibrium is disturbed by;

- Addition of O_2
 $[\text{H}_2\text{O}]$ will increase
- Addition of SO_2
 $[\text{H}_2\text{O}]$ will decrease
- Addition of a catalyst
 $[\text{H}_2\text{O}]$ will not change
- Decrease in temperature
 $[\text{H}_2\text{O}]$ will increase
- Decrease in the volume of the reaction container
 $[\text{H}_2\text{O}]$ 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;



- 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

	$\text{CH}_4(g)$	+ $2\text{H}_2\text{O}(g)$	\rightleftharpoons	$\text{CO}_2(g)$	$4\text{H}_2(g)$
I	0.100 M	0.100 M		0	0
C					
E	0.0775 M				

From this information we can calculate the change in the $[\text{CH}_4]$.

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

	$\text{CH}_4(g)$	+ $2\text{H}_2\text{O}(g)$	\rightleftharpoons	$\text{CO}_2(g)$	$4\text{H}_2(g)$
I	0.100 M	0.100 M		0	0
C	-0.0225 M				
E	0.0775 M				

Using the stoichiometry we can calculate $[\text{H}_2\text{O}]$ reacting and the $[\text{CO}_2]$ and $[\text{H}_2]$ forming.

$$0.0225 \text{ M CH}_4 \left(\frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol CH}_4} \right) = 0.0450 \text{ M}$$

$$0.0225 \text{ M CH}_4 \left(\frac{1 \text{ mol CO}_2}{1 \text{ mol CH}_4} \right) = 0.0225 \text{ M}$$

$$0.0225 \text{ M CH}_4 \left(\frac{4 \text{ mol H}_2}{1 \text{ mol CH}_4} \right) = 0.0900 \text{ M}$$

	$\text{CH}_4(g)$	+ $2\text{H}_2\text{O}(g)$	\rightleftharpoons	$\text{CO}_2(g)$	$4\text{H}_2(g)$
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				

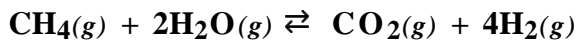
Then we can calculate the concentrations at equilibrium;

	$\text{CH}_4(g)$	+ $2\text{H}_2\text{O}(g)$	\rightleftharpoons	$\text{CO}_2(g)$	$4\text{H}_2(g)$
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.

$$K_c = \frac{[\text{CO}_2] [\text{H}_2]^4}{[\text{CH}_4] [\text{H}_2\text{O}]^2} = \frac{[0.0225] [0.0900]^4}{[0.0775] [0.0550]^2} = 6.30 \times 10^{-3}$$

c) Calculate ΔH° for the reaction



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

$$\Delta H_{\text{rxn}}^\circ = \sum n \Delta H_f^\circ (\text{products}) - \sum m \Delta H_f^\circ (\text{reactants})$$

$$\Delta H_{\text{rxn}}^\circ = \left(1 \text{ mol} \left(-393.5 \frac{\text{kJ}}{\text{mol}}\right) + 4 \text{ mol} \left(0 \frac{\text{kJ}}{\text{mol}}\right)\right) - \left(1 \text{ mol} \left(-74.9 \frac{\text{kJ}}{\text{mol}}\right) + 2 \text{ mol} \left(-241.8 \frac{\text{kJ}}{\text{mol}}\right)\right)$$

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

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

- i) add a catalyst (**no effect**) iv) increase T to 1200 K (**increase**)
- ii) add CH_4 (**increase**) v) transfer mixture to a 15.0 L flask (**increase**)
- iii) remove CO_2 (**increase**)