

## UNIT 7 – CHAPTER 13 STUDENT NOTES: EQUILIBRIUM

Chemical equilibrium – State where the concentration [ ] of all reactants and products remain constant with time.



Law of mass action – describes the equilibrium condition

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2]^1 \cdot [\text{H}_2]^3}$$

Large  $K_c$  = more products  $\longrightarrow$   
Small  $K_c$  = more reactants  $\longleftarrow$

Calculate the value of  $K_c$  if:  $[\text{N}_2] = 0.85 \text{ M}$ ,  $[\text{H}_2] = 0.0031 \text{ M}$ ,  $[\text{NH}_3] = 0.031 \text{ M}$

$$\rightarrow K_c = \frac{[0.031]^2}{[0.85]^1 \cdot [0.0031]^3} = 3.8 \times 10^4 \frac{\text{L}^2}{\text{mol}^2}$$

Value of  $K_c$  in the reverse direction

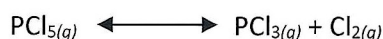
$$\leftarrow K_c = \frac{[0.85]^1 \cdot [0.0031]^3}{[0.031]^2} = \frac{1}{3.8 \times 10^4} = 2.6 \times 10^{-5} \frac{\text{mol}^2}{\text{L}^2}$$

EX 1: Calculate the equilibrium concentrations of all the reactants and products for the following reaction:



The initial amounts of reactants are  $\text{N}_2 = 0.50$  moles and  $\text{O}_2 = 0.86$  moles and it reacts in a 2-liter container.

EX 2: A reaction in a 1-liter container had the following amounts: 0.298 moles  $\text{PCl}_3$  and 0.00870 moles of  $\text{PCl}_5$ . It followed this equation:



When equilibrium was reached, it was found that 0.002 moles of  $\text{Cl}_2$  had formed. A) Calculate the concentrations of all species at equilibrium and B) calculate the value of  $K_c$ .

EX 3: Nitrogen reacts with hydrogen to form ammonia. If 0.001 M nitrogen reacts with 0.002 M hydrogen, calculate the concentrations of all the species at equilibrium.  $K_c$  for this reaction is  $6.2 \times 10^{-13}$ .

	$\text{N}_2(g)$	$3\text{H}_2(g)$	$2\text{NH}_3(g)$
I	0.001M	0.002M	0
C	-x	-3x	+2x
E	0.001-x	0.002-3x	2x

\* X IS SO SMALL IT IS NEGLIGIBLE IF YOU ARE ADDING OR SUBTRACTING IT. YAY!

$$K_c = 6.2 \times 10^{-13} = \frac{(2x)^2}{(0.001-x) \cdot (0.002-3x)^3} \rightarrow 6.2 \times 10^{-13} \approx \frac{4x^2}{6 \times 10^{-12}} \rightarrow (6.2 \times 10^{-13}) \cdot (8 \times 10^{-12}) = 4x^2 \rightarrow 4.96 \times 10^{-24} = 4x^2$$

$$x^2 = 1.24 \times 10^{-24} \rightarrow x = 1.11 \times 10^{-12}$$

$$[\text{N}_2] = 0.001 - x \approx 0.001$$

$$[\text{H}_2] = 0.002 - 3x \approx 0.002$$

$$[\text{NH}_3] = 2x = 2.22 \times 10^{-12}$$

$$K_p = K_c \cdot (R \cdot T)^{\Delta n}$$

$K_c$  is related to pressure

$K_c$  = concentrations [ ]

$K_p$  = pressures  $P_{\text{gas}}$

T = Kelvin

R = 0.08206

$\Delta n$  = coefficients (prod - reactants)

EX 4: Given the equation:  $2 \text{NO}(g) + \text{Cl}_2(g) \rightarrow 2 \text{NOCl}(g)$

Calculate  $K_c$  if  $K_p = 1.9 \times 10^{-3}/\text{atm}$  and  $25^\circ\text{C}$

$$K_p = K_c \cdot (R \cdot T)^{\Delta n}$$

$$\Delta n = (2 - 3)$$

$$* \Delta n = -1$$

$$* K = ^\circ\text{C} + 273$$

$$K = 298$$

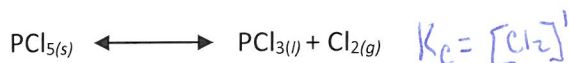
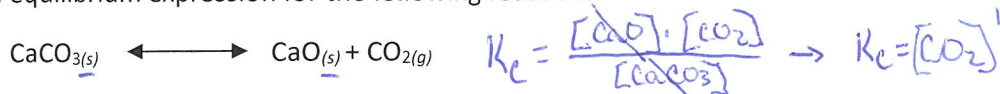
$$1.9 \times 10^{-3} = K_c \cdot [(0.08206)(298)]^{-1}$$

$$1.9 \times 10^{-3} = K_c \cdot 0.4089$$

$$K_c = 4.6 \times 10^{-2}$$

Equilibrium expressions involving concentrations or pressures only involve substances that change from initial to equilibrium conditions. A pure substance (liquid) or solid changes amount, but not concentration.

EX 5: Write the equilibrium expression for the following reactions.



Equilibrium predicts several things:

1) Extent of the reaction

$K_c$  larger than 1 – mostly products

$K_c$  smaller than 1 – mostly reactants

2) Shift of equilibrium

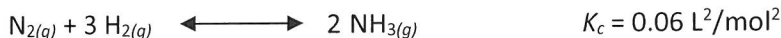
Reaction quotient (Q) – used if [ ] are not zero

$Q = K_c$  – no shift, system is in equilibrium

$Q > K_c$  – shift to left, large [ ] of products

$Q < K_c$  – shift to right, large [ ] of reactants

EX 6: From the following reaction:



	#1	#2	#3
[NH <sub>3</sub> ]	0.001 M	0.0002 M	0.0001 M
[N <sub>2</sub> ]	0.00001 M	0.000015 M	5.0 M
[H <sub>2</sub> ]	0.002 M	0.354 M	0.01 M

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2] \cdot [\text{H}_2]^3}$$

Which direction will the equilibrium shift in the three trials?

$$\#1 \quad Q = \frac{[0.001]^2}{[0.00001]^1 \cdot [0.002]^3} = \frac{0.000001}{(0.00001)(8 \times 10^{-9})} = 1.3 \times 10^7 \quad Q > K, \text{ So } \leftarrow$$

$$\#2 \quad Q = \frac{[0.0002]^2}{[1.5 \times 10^{-5}]^1 \cdot [0.354]^3} = \frac{4.0 \times 10^{-8}}{6.7 \times 10^{-7}} = .06 \quad Q = K, \text{ So IT IS AT EQUILIBRIUM}$$

$$\#3 \quad Q = \frac{[0.0001]^2}{[5]^1 \cdot [0.01]^3} = \frac{1 \times 10^{-8}}{5 \times 10^{-6}} = .002 \quad Q < K, \text{ So } \rightarrow$$

EX 7: From the following reaction:



Calculate the concentration of all species if 3.0 moles of each reactant and 3.0 moles of the product are added to a 1.5-liter container.

$$K_c = 115 = \frac{[\text{HF}]^2}{[\text{H}_2]^1 [\text{F}_2]^1}$$

\*  $\frac{3.0 \text{ mol}}{1.5 \text{ L}} = 2.0 \text{ M}$  FOR EACH

\* WHICH DIRECTION? \*

$$Q = \frac{(2.0)^2}{(2.0)^1 \cdot (2.0)^1} = 1 \quad Q < K, \text{ SO } \rightarrow$$

	$\text{H}_2$	$\text{F}_2$	$\text{HF}$
I	2.0	2.0	2.0
C	-x	-x	+2x
E	2-x	2-x	2+2x

$$K_c = \frac{(2+2x)^2}{(2-x) \cdot (2-x)} \rightarrow \sqrt{115} = \sqrt{\frac{(2+2x)^2}{(2-x)^2}} \rightarrow 10.7 = \frac{2+2x}{2-x}$$

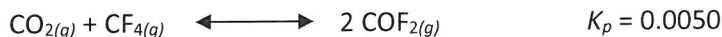
$$21.4 - 10.7x = 2 + 2x \rightarrow 19.4 = 12.7x \rightarrow x = 1.53$$

$$[\text{H}_2], [\text{F}_2] = 2-x \rightarrow \boxed{0.47 \text{ M } \text{H}_2, \text{F}_2}$$

$$[\text{HF}] = 2+2x \rightarrow \boxed{5.06 \text{ M } \text{HF}}$$

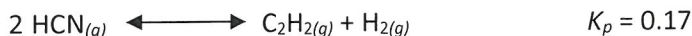
**Intermediate values of K – 5% rule**

EX 8: Carbonyl fluoride,  $\text{COF}_2$ , is an important intermediate for organic fluorine compounds. It can be prepared by the following reaction:



At  $1000^\circ\text{C}$ ,  $K_p$  for this reaction is 0.0050. What are the partial pressures of all the gases at equilibrium when the initial partial pressures of  $\text{CO}_2$  and  $\text{CF}_4$  are 0.713 atm?

EX 9: Hydrogen cyanide, a highly toxic gas, can decompose to cyanogen and hydrogen gas:



What are the partial pressures of all gases at equilibrium if initial partial pressures are  $P_{\text{C}_2\text{H}_2} = 0.32 \text{ atm}$ ,  $P_{\text{H}_2} = 0.32 \text{ atm}$ ,  $P_{\text{HCN}} = 0.45 \text{ atm}$ ? \* WHICH DIRECTION? \*

$$Q = \frac{(0.32)^1 \cdot (0.32)^1}{(0.45)^2} = 0.50 \quad Q > K, \text{ SO } \leftarrow$$

	$\text{HCN}$	$\text{C}_2\text{H}_2$	$\text{H}_2$
I	.45	.32	.32
C	+2x	-x	-x
E	.45+2x	.32-x	.32-x

$$K_p = 0.17 = \frac{(0.32-x)^2}{(0.45+2x)^2} \rightarrow \sqrt{0.17} = \sqrt{\frac{(0.32-x)^2}{(0.45+2x)^2}}$$

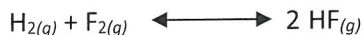
$$0.4123 = \frac{0.32-x}{0.45+2x} \rightarrow 0.32-x = 0.1855 + 0.8246x$$

$$1.8246x = 0.1345 \rightarrow x = 0.0737$$

$$P_{\text{HCN}} = 0.45 + 2x = \boxed{0.5974}$$

$$P_{\text{C}_2\text{H}_2}, P_{\text{H}_2} = 0.32 - x = \boxed{0.246}$$

EX 10: 3.0 moles of H<sub>2</sub> and 6.0 moles of F<sub>2</sub> are placed into a 3.0-liter container and is allowed to reach equilibrium according to the following equation:



$$K_c = 115$$

Calculate the concentrations of all the species at equilibrium.

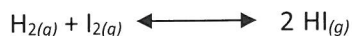
	H <sub>2</sub>	F <sub>2</sub>	HF
I	1.0	2.0	0
C	-x	-x	+2x
E	1-x	2-x	2x

$$K_c = 115 = \frac{(2x)^2}{(1-x)(2-x)} \rightarrow 115 = \frac{4x^2}{2-3x+x^2} \rightarrow 230 - 345x + 115x^2 = 4x^2$$

$\frac{3.0 \text{ mol}}{3 \text{ L}} = 1 \text{ M}$      $\frac{6.0 \text{ mol}}{3 \text{ L}} = 2 \text{ M}$   
 $115x^2 - 345x + 230 = 4x^2$      $* -b \pm \sqrt{b^2 - 4ac}$   
 $x = \frac{-(-345) \pm \sqrt{(-345)^2 - 4(111)(230)}}{2(111)} \rightarrow \frac{345 \pm \sqrt{16905}}{222} = \frac{345 \pm 130}{222}$

$[\text{H}_2] = 1-x = 0.032$   
 $[\text{F}_2] = 2-x = 1.032$   
 $[\text{HF}] = 2x = 1.936$

EX 11: A container holds HI at 0.50 atm, H<sub>2</sub> at 0.01 atm, and I<sub>2</sub> at 0.005 atm and reacts according to the following reaction:



$$K_c = 100$$

Calculate the partial pressures of all species when the reaction reaches equilibrium. \*WHICH DIRECTION?\*

	H <sub>2</sub>	I <sub>2</sub>	HI
I	.01	.005	.5
C	+x	+x	-2x
E	.01+x	.005+x	.5-2x

$$K_p = 100 = \frac{(0.5-2x)^2}{(0.01+x)(0.005+x)} \rightarrow 100 = \frac{0.25-2x+4x^2}{0.00005+0.015x+x^2}$$

$$100x^2 + 1.5x + 0.005 = 0.25 - 2x + 4x^2$$

$$96x^2 + 3.5x - 0.245 \rightarrow \frac{-3.5 \pm \sqrt{(3.5)^2 - 4(96)(-0.245)}}{2(96)} \rightarrow \frac{-3.5 \pm \sqrt{94.2025}}{192}$$

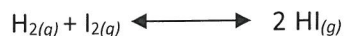
$K_p = K_c (R \cdot T)^{\Delta n}$   
 $= 100 \cdot [(0.08206)(298)]^0$   
 $= 100 \quad (Q=K)$

$[\text{H}_2] = 0.01+x = 0.04232$   
 $[\text{I}_2] = 0.005+x = 0.03732$   
 $[\text{HI}] = 0.5-2x = 0.435$

$x = 0.03232$   
~~0.0687~~

**Equilibrium with large values of K**

EX 12: In a 5.00-liter container, 15.7 grams of H<sub>2</sub> and 295 grams of I<sub>2</sub> are allowed to reach equilibrium according to the following equation:



$$K_c = 701$$

Calculate the equilibrium concentration of all the species at equilibrium.

EX 13: At a particular temperature, the equilibrium constant for the gas-phase reaction between carbon monoxide and oxygen to produce carbon dioxide is  $5.0 \times 10^3$  L/mol. Calculate the concentrations of all species at equilibrium if 2.0 moles each of CO and O<sub>2</sub> are placed in a 5.0-liter vessel and allowed to come to equilibrium.

EX 14: At a certain temperature,  $K_c = 1.1 \times 10^3$  L/mol for the reaction:



Calculate the concentrations of all species if 0.10 moles Fe(NO<sub>3</sub>)<sub>3</sub> is added to 1.0 liters of 2.0 M KSCN.

	Fe <sup>3+</sup>	SCN <sup>-</sup>	FeSCN <sup>2+</sup>
I	.10	2.0	0
C <sub>1</sub>	-.10	-.10	+.10
E <sub>1</sub>	0	1.9	.10
C <sub>2</sub>	+x	+x	-x
E <sub>2</sub>	x	1.9+x	.10-x

$K_c = 1100 = \frac{(.10-x)}{(x) \cdot (1.9+x)} \rightarrow 1100 = \frac{(.10-x)}{1.9x+x^2} \rightarrow .10-x = 2090x + 1100x^2$   
 $1100x^2 + 2091x - .10 \rightarrow \frac{-2091 \pm \sqrt{(2091)^2 - 4(1100)(-.10)}}{2(1100)} \rightarrow \frac{-2091 \pm \sqrt{4372281}}{2200}$   
 $\frac{-2091 \pm 2091.1054}{2200} \quad x = 4.8 \times 10^{-4} \text{ or } x = 9$   
 $[\text{Fe}^{3+}] = x = 4.8 \times 10^{-4} \text{ M}$   
 $[\text{SCN}^{-}] = 1.9+x = 1.9 \text{ M}$   
 $[\text{FeSCN}^{2+}] = .10-x = .10 \text{ M}$

**Calculating solubility constant and determining solubility from  $K_{sp}$**

A solubility constant is calculated by concentrations in your Q value. Large  $K_{sp}$  means more soluble.

EX 15: What is the solubility of PbI<sub>2</sub>,  $K_{sp} = 1.4 \times 10^{-8}$ ?  $\text{PbI}_2(\text{s}) \rightarrow \text{Pb}^{2+}(\text{aq}) + 2 \text{I}^{-}(\text{aq})$

$$\text{PbI}_2 \rightarrow \text{Pb}^{2+} + 2 \text{I}^{-}$$

$$K_{sp} = 1.4 \times 10^{-8} = \frac{[\text{Pb}^{2+}][\text{I}^{-}]^2}{1(\text{solid})} \rightarrow 1.4 \times 10^{-8} = 4x^3 \rightarrow 3.5 \times 10^{-9} = x^3$$

$x = 1.5 \times 10^{-3}$

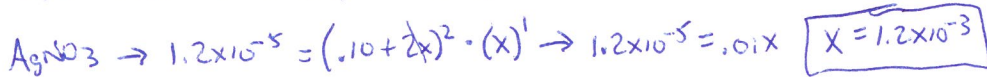
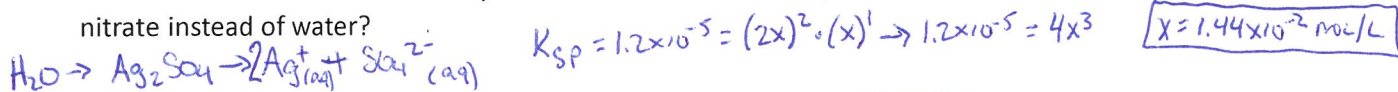
EX 16: If the  $K_{sp}$  of aluminum hydroxide is  $2 \times 10^{-32}$  and the  $[\text{Al}^{3+}] = .5 \text{ M}$ , what is the concentration of the other ion?

$$\text{Al}(\text{OH})_3 \rightarrow \text{Al}^{3+} + 3 \text{OH}^{-}$$

$$K_{sp} = 2 \times 10^{-32} = \frac{[.5][3x]^3}{1} \rightarrow x^3 = 1.48 \times 10^{-33}$$

$x = 1.14 \times 10^{-11} \text{ M}$

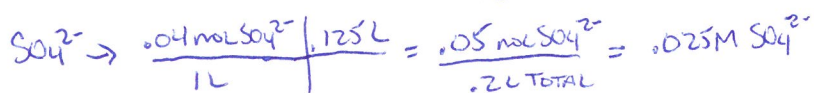
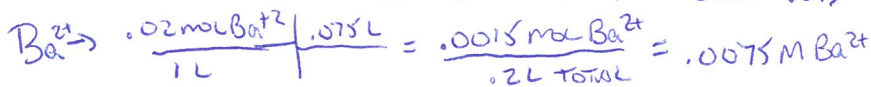
EX 17: What is the molar solubility of silver sulfate in water?  $K_{sp} = 1.2 \times 10^{-5}$ ? What if it is in 0.10 M silver nitrate instead of water?



\*  $AgNO_3$  ADDS ANOTHER  $Ag^+$ !

\*  $K_{sp}$  IS SMALL, CAN DISREGARD!

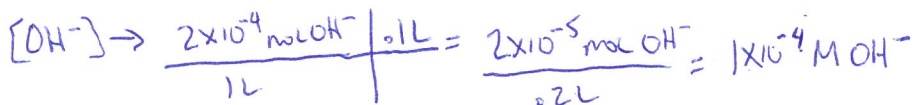
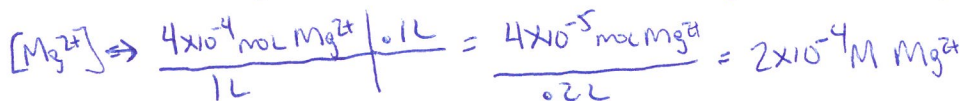
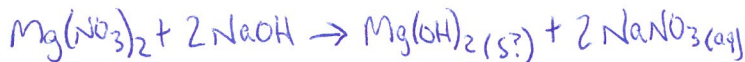
EX 18: 75 mL of 0.02 M  $BaCl_2$  is mixed with 125 mL of 0.04 M  $Na_2SO_4$  ( $K_{sp} = 1.5 \times 10^{-9}$ ). Does the barium precipitate?



$Q = [Ba^{2+}]^1 \cdot [SO_4^{2-}]^1 = (.0075) \cdot (.025)$

$Q = 1.9 \times 10^{-4} > K_{sp} \therefore \text{YES, PPT FORMS}$

EX 19: 100 mL of  $Mg(NO_3)_2$  is mixed with 100 mL  $NaOH$  ( $K_{sp} = 8.9 \times 10^{-12}$ ). Does the magnesium precipitate?



$Q = [Mg^{2+}]^1 \cdot [2OH^-]^2 \rightarrow (2 \times 10^{-4}) \cdot (2 \times 10^{-4})^2$

$Q = 8 \times 10^{-12} < K_{sp} \therefore \text{NO, PPT DOES NOT FORM}$