UNIT 7 – CHAPTER 13 STUDENT NOTES: EQUILIBRIUM

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

$$N_{2(g)} + 3\ H_{2(g)} \longleftrightarrow 2\ NH_{3(g)}$$

Law of mass action – describes the equilibrium condition

$$K_c = \frac{[NH_3]^2}{[N_2]^1 \cdot [H_2]^3}$$

Large K_c = more products $\longrightarrow$

Small K_c = more reactants $\longleftarrow$

Calculate the value of K_c if: $[N_2] = 0.85\ M$, $[H_2] = 0.0031\ M$, $[NH_3] = 0.031\ M$

$\rightarrow$ $K_c = \dfrac{[.031]^2}{[.85]^1 \cdot [.0031]^3} = \boxed{3.8 \times 10^4\ \dfrac{L^2}{MOL^2}}$

Value of K_c in the reverse direction

$\leftarrow$ $K_c = \dfrac{[.85]^1 \cdot [.0031]^3}{[.031]^2} = \dfrac{1}{3.8 \times 10^4} = \boxed{2.6 \times 10^{-5}\ \dfrac{MOL^2}{L^2}}$

EX 1: Calculate the equilibrium concentrations of all the reactants and products for the following reaction: $N_{2(g)} + O_{2(g)} \longleftrightarrow 2\ NO_{(g)}$ $K_c = 4.1 \times 10^{-4}$

The initial amounts of reactants are N_2 = 0.50 moles and 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 PCl_3 and 0.00870 moles of PCl_5. It followed this equation:

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

When equilibrium was reached, it was found that 0.002 moles of 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 X 10^{-13}.

$$N_{2(g)} + 3H_{2(g)} \longleftrightarrow 2NH_{3(g)}$$

I	.001M	.002M	∅
C	−x	−3x	+2x
E	.001−x	.002−3x	2x

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

$K_c = 6.2\times10^{-13} = \frac{(2x)^2}{(.001-\cancel{x})^1\cdot(.002-\cancel{3x})^3} \rightarrow 6.2\times10^{-13} = \frac{4x^2}{8\times10^{-12}} \rightarrow (6.2\times10^{-13})\cdot(8\times10^{-12}) = 4x^2 \rightarrow 4.96\times10^{-24} = 4x^2$

$x^2 = 1.24\times10^{-24}$

$x = 1.11\times10^{-12}$

$[N_2] = .001 - x = \boxed{.001}$

$[H_2] = .002 - 3x = \boxed{.002}$

$[NH_3] = 2x = \boxed{2.22\times10^{-12}}$

<u>K_c is related to pressure</u>

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

K_c = concentrations [ ]

K_p = pressures P_{gas}

T = Kelvin

R = 0.08206

ΔN = coefficients (prod - reactants)

EX 4: Given the equation: $2\ NO_{(g)} + Cl_{2(g)} \rightarrow 2\ NOCl_{(g)}$

Calculate K_c if K_p = 1.9 X 10^{-3}/atm and 25°C

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

$\Delta N = (2-3)$

* $\Delta N = -1$

* $K = °C + 273$

$K = 298$

$1.9\times10^{-3} = K_c \cdot [(.08206)(298)]^{-1}$

$1.9\times10^{-3} = K_c \cdot .04089$

$\boxed{K_c = 4.6\times10^{-2}}$

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.

$CaCO_{3(s)} \longleftrightarrow CaO_{(s)} + CO_{2(g)}$ $K_c = \frac{\cancel{[CaO]} \cdot [CO_2]}{\cancel{[CaCO_3]}} \rightarrow K_c = [CO_2]^1$

$PCl_{5(s)} \longleftrightarrow PCl_{3(l)} + Cl_{2(g)}$ $K_c = [Cl_2]^1$

$CuSO_4 \cdot 5\,H_2O_{(s)} \longleftrightarrow CuSO_{4(s)} + 5\,H_2O_{(g)}$ $K_c = [H_2O]^5$

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 products

EX 6: From the following reaction:

$N_{2(g)} + 3\,H_{2(g)} \longleftrightarrow 2\,NH_{3(g)}$ $K_c = 0.06\ L^2/mol^2$

$K_c = \frac{[NH_3]^2}{[N_2] \cdot [H_2]^3}$

	#1	#2	#3
$[NH_3]$	0.001 *M*	0.0002 *M*	0.0001 *M*
$[N_2]$	0.00001 *M*	0.000015 *M*	5.0 *M*
$[H_2]$	0.002 *M*	0.354 *M*	0.01 *M*

Which direction will the equilibrium shift in the three trials?

#1 $Q = \frac{[.001]^2}{[.00001]^1 \cdot [.002]^3} = \frac{.000001}{(.00001)(8\times10^{-9})} = 1.3\times10^7$ Q>K, So ←

#2 $Q = \frac{[.0002]^2}{[1.5\times10^{-5}]^1 \cdot [.354]^3} = \frac{4.0\times10^{-8}}{6.7\times10^{-7}} = .06$ Q=K, SO IT IS AT EQUILIBRIUM

#3 $Q = \frac{[.0001]^2}{[5]^1 \cdot [.01]^3} = \frac{1\times10^{-8}}{5\times10^{-6}} = .002$ Q<K, SO →

EX 7: From the following reaction:

$$H_{2(g)} + F_{2(g)} \longleftrightarrow 2\ HF_{(g)} \qquad K_c = 115\ L^2/mol^2$$

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.

$K_c = 115 = \frac{[HF]^2}{[H_2]^1 \cdot [F_2]^1}$

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

WHICH DIRECTION?

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

	H_2	F_2	HF
I	2.0	2.0	2.0
C	−x	−x	+2x
E	2−x	2−x	2+2x

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

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

$[H_2], [F_2] = 2 - x \rightarrow \boxed{.47\ M\ H_2, F_2}$

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

Intermediate values of K – 5% rule

EX 8: Carbonyl fluoride, COF_2, is an important intermediate for organic fluorine compounds. It can be prepared by the following reaction:

$$CO_{2(g)} + CF_{4(g)} \longleftrightarrow 2\ COF_{2(g)} \qquad K_p = 0.0050$$

At 1000°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 CO_2 and CF_4 are 0.713 atm?

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

$$2\ HCN_{(g)} \longleftrightarrow C_2H_{2(g)} + H_{2(g)} \qquad K_p = 0.17$$

What are the partial pressures of all gases at equilibrium if initial partial pressures are P_{C2H2} = 0.32 atm, P_{H2} = 0.32 atm, P_{HCN} = 0.45 atm?

WHICH DIRECTION?

$Q = \frac{(.32)^1 \cdot (.32)^1}{(.45)^2} = .50 \quad Q > K$, SO $\leftarrow$

	HCN	C_2H_2	H_2
I	.45	.32	.32
C	+2x	−x	−x
E	.45+2x	.32−x	.32−x

$K_p = .17 = \frac{(.32-x)^2}{(.45+2x)^2} \rightarrow \sqrt{.17} = \sqrt{\frac{(.32-x)^2}{(.45+2x)^2}}$

$.4123 = \frac{.32-x}{.45+2x} \rightarrow .32 - x = .1855 + .8246x$

$1.8246x = .1345 \rightarrow x = .0737$

$P_{HCN} = .45 + 2x = \boxed{.5974}$

$P_{C_2H_2}, P_{H_2} = .32 - x = \boxed{.246}$

EX 10: 3.0 moles of H_2 and 6.0 moles of F_2 are placed into a 3.0-liter container and is allowed to reach equilibrium according to the following equation:

LARGE K, CAN'T IGNORE!

$$H_{2(g)} + F_{2(g)} \longleftrightarrow 2\ HF_{(g)} \qquad K_c = 115$$

Calculate the concentrations of all the species at equilibrium.

$\boxed{\frac{3.0\text{ mol}}{3L} = 1M \qquad \frac{6.0\text{ mol}}{3L} = 2M}$

	H_2	F_2	HF
I	1.0	2.0	∅
C	$-x$	$-x$	$+2x$
E	$1-x$	$2-x$	$2x$

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

$\underset{A}{111x^2} \underset{B}{- 345x} \underset{C}{+ 230}$ $\quad * \frac{-b \pm \sqrt{(b)^2 - 4ac}}{2a}$

$x = \frac{-(-345) \pm \sqrt{(-345)^2 - [4(111 \cdot 230)]}}{2 \cdot 111} \rightarrow \frac{345 \pm \sqrt{16905}}{222} = .968$ or $\cancel{2.14}$

$[H_2] = 1 - x = \boxed{.032}$

$[F_2] = 2 - x = \boxed{1.032}$

$[HF] = 2x = \boxed{1.936}$

EX 11: A container holds HI at 0.50 atm, H_2 at 0.01 atm, and I_2 at 0.005 atm and reacts according to the following reaction:

$$H_{2(g)} + I_{2(g)} \longleftrightarrow 2\ HI_{(g)} \qquad K_c = 100$$

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

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

$= 100 \cdot [(.08206)(298)]^0$

$= 100 \quad Q = K$

	H_2	I_2	HI
I	.01	.005	.5
C	$+x$	$+x$	$-2x$
E	$.01+x$	$.005+x$	$.5-2x$

$K_p = 100 = \frac{(.5-2x)^2}{(.01+x)\cdot(.005+x)} \rightarrow 100 = \frac{.25 - 2x + 4x^2}{.00005 + .015x + x^2}$

$100x^2 + 1.5x + .005 = .25 - 2x + 4x^2$

$\underset{A}{96x^2} \underset{B}{+ 3.5x} \underset{C}{- .245} \rightarrow \frac{-3.5 \pm \sqrt{(3.5)^2 - 4(96 \cdot -.245)}}{2(96)} \rightarrow \frac{-3.5 \pm \sqrt{94.2025}}{192}$

$x = .03232$ or $-.\cancel{06}87$

$[H_2] = .01 + x = \boxed{.04232}$

$[I_2] = .005 + x = \boxed{.03732}$

$[HI] = .5 - 2x = \boxed{.435}$

Equilibrium with large values of K

EX 12: In a 5.00-liter container, 15.7 grams of H_2 and 295 grams of I_2 are allowed to reach equilibrium according to the following equation:

$$H_{2(g)} + I_{2(g)} \longleftrightarrow 2\ HI_{(g)} \qquad K_c = 701$$

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 5.0×10^3 L/mol. Calculate the concentrations of all species at equilibrium if 2.0 moles each of CO and O_2 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:

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \longleftrightarrow FeSCN^{2+}_{(aq)} \qquad K_c = 1100$$

Calculate the concentrations of all species if 0.10 moles $Fe(NO_3)_3$ is added to 1.0 liters of 2.0 *M* KSCN.

	Fe^{3+}	SCN^-	$FeSCN^{2+}$
I	.10	2.0	Ø
C_1	-.10	-.10	+.10
E_1	Ø	1.9	.10
C_2	+X	+X	-X
E_2	X	1.9+X	.10-X

$K_c = 1100 = \frac{(.10-x)^1}{(x)^1 \cdot (1.9+x)^1} \rightarrow 1100 = \frac{(.10-x)}{1.9x+x^2} \rightarrow .10 - X = 2090X + 1100X^2$

$\overset{a}{1100X^2} + \overset{b}{2091X} - \overset{c}{.10} \rightarrow \frac{-2091 \pm \sqrt{(2091)^2 - 4(1100)\cdot(-.10)}}{2(1100)} \rightarrow \frac{-2091 \pm \sqrt{4372281\,440}}{2200}$

$\frac{-2091 \pm 2091.1054}{2200}$ $X = 4.8 \times 10^{-4}$ or $\cancel{-X9}$

$[Fe^{3+}] = X = \boxed{4.8 \times 10^{-4} M}$

$[SCN^-] = 1.9 + x = \boxed{1.9 M}$

$[FeSCN^{2+}] = .10 - X = \boxed{.10 M}$

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_2, $K_{sp} = 1.4 \times 10^{-8}$? $PbI_2(s) \rightarrow Pb^{2+}(aq) + 2\,I^-(aq)$

$PbI_2 \longrightarrow Pb^{2+} + 2I^-$

$K_{sp} = 1.4 \times 10^{-8} = \frac{[X]^1 \cdot [2X]^2}{1\,(\text{solid})} \rightarrow 1.4 \times 10^{-8} = 4X^3 \rightarrow 3.5 \times 10^{-9} = X^3$

$\boxed{X = 1.5 \times 10^{-3}}$

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

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

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

$\boxed{X = 1.14 \times 10^{-11} M}$

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?

$H_2O \rightarrow Ag_2SO_4 \rightarrow 2Ag^+_{(aq)} + SO_4^{2-}{}_{(aq)}$ $K_{sp} = 1.2\times10^{-5} = (2x)^2 \cdot (x)^1 \rightarrow 1.2\times10^{-5} = 4x^3$ $\boxed{x = 1.44\times10^{-2}\ mol/L}$

$AgNO_3 \rightarrow 1.2\times10^{-5} = (.10 + \cancel{2x})^2 \cdot (x)^1 \rightarrow 1.2\times10^{-5} = .01x$ $\boxed{x = 1.2\times10^{-3}}$

*$AgNO_3$ 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?

$BaCl_2 + Na_2SO_4 \rightarrow BaSO_{4(s?)} + NaCl_{(aq)}$

$Ba^{2+} \rightarrow \frac{.02\ mol\ Ba^{+2}}{1\ L} \cdot .075\ L = \frac{.0015\ mol\ Ba^{2+}}{.2\ L\ TOTAL} = .0075\ M\ Ba^{2+}$

$SO_4^{2-} \rightarrow \frac{.04\ mol\ SO_4^{2-}}{1\ L} \cdot .125\ L = \frac{.05\ mol\ SO_4^{2-}}{.2\ L\ TOTAL} = .025\ M\ SO_4^{2-}$

$Q = [Ba^{2+}]^1 \cdot [SO_4^{-2}]^1$
$= (.0075) \cdot (.025)$
$\boxed{Q = 1.9\times10^{-4} > K_{sp} \therefore \text{YES, PPT FORMS}}$

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?

$Mg(NO_3)_2 + 2NaOH \rightarrow Mg(OH)_{2(s?)} + 2NaNO_{3(aq)}$

$[Mg^{2+}] \Rightarrow \frac{4\times10^{-4}\ mol\ Mg^{2+}}{1\ L} \cdot .1\ L = \frac{4\times10^{-5}\ mol\ Mg^{2+}}{.2\ L} = 2\times10^{-4}\ M\ Mg^{2+}$

$[OH^-] \rightarrow \frac{2\times10^{-4}\ mol\ OH^-}{1\ L} \cdot .1\ L = \frac{2\times10^{-5}\ mol\ OH^-}{.2\ L} = 1\times10^{-4}\ M\ OH^-$

$Q = [Mg^{2+}]^1 \cdot [2\ OH^-]^2 \rightarrow (2\times10^{-4}) \cdot (2\times10^{-4})^2$

$\boxed{Q = 8\times10^{-12} < K_{sp} \therefore \text{NO, PPT DOES NOT FORM}}$