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 ⟶

Small K_c = more reactants ⟵

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

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

Value of K_c in the reverse direction

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

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 6.2×10^{-13}.

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

I	.001M	.002M	0
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!

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

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

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

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

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

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

K_c is related to pressure

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

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 $K_p = 1.9 \times 10^{-3}$/atm and 25°C

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

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

$$* \quad \Delta N = -1$$

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

$$K = 298$$

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

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

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

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

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

<u>Reaction quotient (Q)</u> – 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 →

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

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

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

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

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

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 ←

	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:

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

LARGE K, CAN'T IGNORE!

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

Calculate the concentrations of all the species at equilibrium.

	H_2	F_2	HF
I	1.0	2.0	0
C	−x	−x	+2x
E	1−x	2−x	2x

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

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

$$x = \frac{-(-345) \pm \sqrt{(-345)^2 - [4(111\cdot 230)]}}{2\cdot 111} \rightarrow \frac{345 \pm \sqrt{16905}}{222} = .968 \text{ or } \cancel{2.19}$$

$$[H_2] = 1-x = \boxed{.032}$$
$$[F_2] = 2-x = \boxed{1.032}$$
$$[HF] = 2x = \boxed{1.936}$$

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?*

$$K_p = K_c\,(R\cdot T)^{\Delta N}$$
$$= 100\cdot[(.08206)(298)]^0$$
$$= 100 \qquad Q = K$$

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

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

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

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

$$x = .03232 \text{ or } -\cancel{.0687}$$

$$[H_2] = .01+x = \boxed{.04232}$$
$$[I_2] = .005+x = \boxed{.03732}$$
$$[HI] = .5-2x = \boxed{.435}$$

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 X 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 X 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	0
→	C_1	−.10	−.10	+.10
	E_1	0	1.9	.10
←	C_2	+X	+X	−X
	E_2	X	1.9+X	.10−X

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

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

$\frac{-2091 \pm 2091.1054}{2200}$ $X = 4.8 \times 10^{-4}$ or $\cancel{-1.9}$

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

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

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

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 X 10^{-8}? PbI_2(s) → Pb^{2+}(aq) + 2 I^-(aq)

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

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

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

EX 16: If the *Ksp* of aluminum hydroxide is 2 X 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? $K_{sp} = 1.2 \text{ X } 10^{-5}$? What if it is in 0.10 *M* silver nitrate instead of water?

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

$AgNO_3$ ADDS ANOTHER Ag^+!

Ksp IS SMALL, CAN DISREGARD X!

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

$AgNO_3 \rightarrow Ag^{+1} + NO_3^{-1}$
.1M .1M

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

$BaCl_2 + Na_2SO_4 \rightarrow \underset{?}{\underset{\uparrow}{BaSO_{4(s)}}} + NaCl_{(aq)}$ $BaSO_4 \rightarrow Ba^{2+} + SO_4^{-2}$

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

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

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

$\boxed{Q = 1.9\times10^{-4} > K_{sp} \therefore \text{YES, PPT FORMS}}$

EX 19: 100 mL of 0.0004 *M* $Mg(NO_3)_2$ is mixed with 100 mL of 0.0002 *M* NaOH ($K_{sp} = 8.9 \text{ X } 10^{-12}$). Does the magnesium precipitate?

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

$Mg^{2+} \rightarrow \frac{4\times10^{-4}\text{ mol }Mg^{2+}}{1\text{ L}} \Big| .1\text{ L} = \frac{4\times10^{-5}\text{ mol }Mg^{2+}}{.2\text{ L TOTAL}} = 2\times10^{-4}\text{ M }Mg^{2+}$

$OH^- \rightarrow \frac{2\times10^{-4}\text{ mol }OH^-}{1\text{ L}} \Big| .1\text{ L} = \frac{2\times10^{-5}\text{ mol }OH^-}{.2\text{ L TOTAL}} = 1\times10^{-4}\text{ M }OH^-$

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

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