

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 $\longleftarrow$

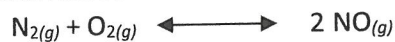
Calculate the value of K_c if: $[\text{N}_2] = 0.85 \text{ M}$, $[\text{H}_2] = 0.0031 \text{ M}$, $[\text{NH}_3] = 0.031 \text{ M}$

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

Value of K_c in the reverse direction

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

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



$$K_c = 4.1 \times 10^{-4}$$

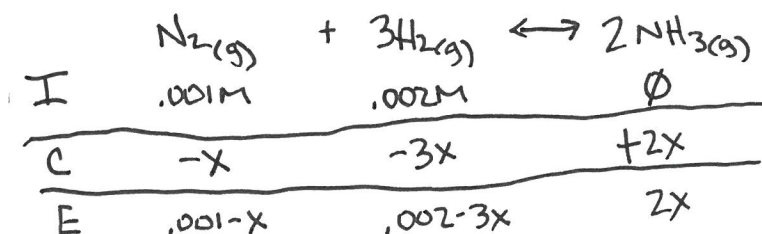
The initial amounts of reactants are $\text{N}_2 = 0.50$ moles and $\text{O}_2 = 0.86$ moles and it reacts in a 2-liter container.

EX 2: A reaction in a 1-liter container had the following amounts: 0.298 moles PCl_3 and 0.00870 moles of PCl_5 . It followed this equation:



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} .



VERY TINY! ANY CHANGE FROM X IS NEGLIGIBLE IF YOU ARE ADDING/SUBTRACTING. YAY!

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

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

$$\begin{aligned} [\text{N}_2] &= 0.001 - x = 0.001 \text{ M} \\ [\text{H}_2] &= 0.002 - 3x = 0.002 \text{ M} \\ [\text{NH}_3] &= 2x = 2.22 \times 10^{-12} \text{ M} \end{aligned}$$

NOW PLUG INTO EQUILIBRIUM VALUES!

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

K_c is related to pressure

K_c = concentrations []

K_p = pressures P_{gas}

T = Kelvin ($^{\circ}\text{C} + 273$)

R = 0.08206

Δn = 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°C

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

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

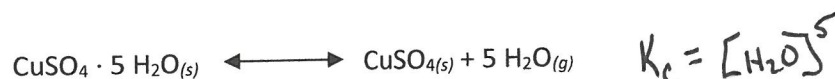
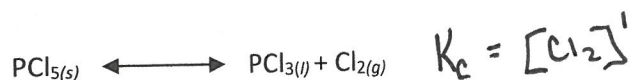
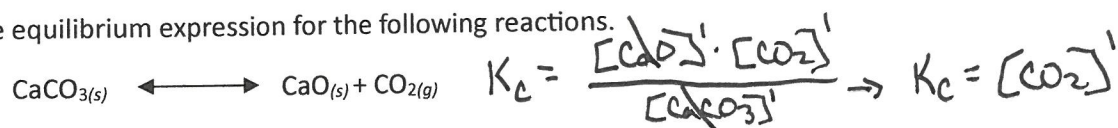
$$1.9 \times 10^{-3} = K_c \cdot (0.04089)$$

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

$$\begin{aligned} \Delta n &= (2 \text{ PRODUCTS} - 3 \text{ REACTANTS}) \\ * \Delta n &= -1 * \\ K &= 298 + 273 \\ * K &= 298 * \end{aligned}$$

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 reactants

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

EX 6: From the following reaction:

	#1	#2	#3
$\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$			
[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

$$K_c = 0.06 \text{ L}^2/\text{mol}^2$$

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

Which direction will the equilibrium shift in the three trials?

#1) $Q = \frac{[0.001]^2}{[0.00001] \cdot [0.002]^3} = \frac{0.000001}{(0.00001)(8 \times 10^{-9})} = 1.3 \times 10^7$ $Q > K_c$, so ←

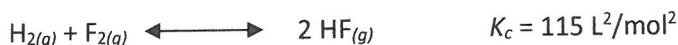
#2) $Q = \frac{[0.0002]^2}{[5.0 \times 10^{-5}] \cdot [0.354]^3} = \frac{4 \times 10^{-8}}{(6.7 \times 10^{-7})} = .06$

$Q = K_c$, so it is at EQUILIBRIUM

#3) $Q = \frac{[0.0001]^2}{[5.0] \cdot [0.01]^3} = \frac{1 \times 10^{-8}}{5 \times 10^{-6}} = .002$

$Q < K_c$, so →

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. * $\frac{3.0 \text{ mol}}{1.5 \text{ L}} = 2.0 \text{ M}$ For EACH! * * WHICH DIRECTION SINCE WE HAVE BEGINNING VALUES FOR ALL? *

	H_2	F_2	2HF
I	2.0M	2.0M	2.0M
C	-X	-X	+2X
E	2-X	2-X	2+2X

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

$$Q = \frac{[2.0]^2}{[2.0] \cdot [2.0]} = 1$$

$Q < K$, so $\rightarrow$

$$10.7 = \frac{2+2x}{2-x}$$

$$(21.4 - 10.7x) = 2 + 2x \rightarrow 19.4 = 12x \rightarrow x = 1.53$$

$$[\text{H}_2] + [\text{F}_2] = 2 - x \rightarrow .47 \text{ M } \text{H}_2, \text{F}_2$$

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

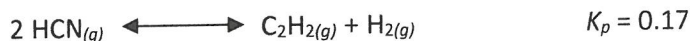
Intermediate values of K - 5% rule

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



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:



What are the partial pressures of all gases at equilibrium if initial partial pressures are $P_{\text{C}_2\text{H}_2} = 0.32 \text{ atm}$, $P_{\text{H}_2} = 0.32 \text{ atm}$, $P_{\text{HCN}} = 0.45 \text{ atm}$? * $K_p = K_c \cdot (.08206 \cdot 273)^0 \rightarrow K_p = K_c$

DIRECTION?

$$Q = \frac{(0.32)(0.32)}{(0.45)^2} = .50$$

$Q > K$, so $\leftarrow$



	HCN	C_2H_2	H_2
I	.45	.32	.32
C	+2X	-X	-X
E	.45+2X	.32-X	.32-X

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

$$.4123 = \frac{(0.32-x)}{(0.45+2x)} \rightarrow (.1855 + .8246x) = .32 - x$$

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

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

$$P_{\text{C}_2\text{H}_2}, P_{\text{H}_2} = .32 - x = .246$$

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:



$$\frac{3.0 \text{ mol}}{3.0 \text{ L}} = 1M \quad \frac{6.0 \text{ mol}}{3.0 \text{ L}} = 2M$$

$$K_c = 115 \rightarrow \text{LARGE } K, \text{ CAN'T IGNORE!}$$

Calculate the concentrations of all the species at equilibrium.

	H_2	F_2	$2HF$
I	1.0M	2.0M	0
C	-X	-X	+2X
E	1-X	2-X	+2X

$$K_c = 115 = \frac{[2X]^2}{[1-X][2-X]} \rightarrow 115 = \frac{4X^2}{2-3X+X^2} \rightarrow 230 - 345X + 115X^2 = 4X^2$$

$$111X^2 - 345X + 230 = 0$$

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \rightarrow \frac{-(-345) \pm \sqrt{(-345)^2 - [4(111 \cdot 230)]}}{2(111)}$$

$$= \frac{345 \pm \sqrt{16905}}{222} = \frac{.968 \text{ or } 2.19}{1} \rightarrow \text{Too big!}$$

$$[H_2] = 1-X \rightarrow .032$$

$$[F_2] = 2-X \rightarrow .032$$

$$[HF] = 2X \rightarrow 1.936$$

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:



$$K_c = 100$$

Calculate the partial pressures of all species when the reaction reaches equilibrium.

	H_2	I_2	$2HI$
I	.01	.005	.50
C	+X	+X	-2X
E	.01+X	.005+X	.50-2X

LARGEST, 30

$$K_p = 100 = \frac{(0.5-2x)^2}{(0.01+x)(0.005+x)} \rightarrow 100 = \frac{.25 - 2x + 4x^2}{.00005 + .015x + x^2}$$

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

$$96x^2 + 3.5x - .245 = 0$$

$$\frac{-3.5 \pm \sqrt{(3.5)^2 - [4(96 \cdot -.245)]}}{2(96)} \rightarrow \frac{-3.5 \pm \sqrt{44.2025}}{192}$$

$$X = \frac{.03232}{.0687} \leftarrow \text{CAN'T BE (-)}$$

* WHICH DIRECTION? *

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

$$= 100 \cdot [(0.08206)(298)]^0$$

$$K_p = 100 \quad Q = K$$

$(H_2) = .01 + X \rightarrow .04232$ $(I_2) = .005 + X \rightarrow .03732$ $(HI) = .50 - 2X \rightarrow .435 \text{ ATM}$

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:



$$K_c = 701$$

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:



$$K_c = 1100$$

LARGE! WILL RUSH TO ONE SIDE + BOUNCE BACK!

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	-.10	-.10	+.10
E	0	1.9	+.10
	+x	+x	-x
E2	x	1.9+x	.10-x

$$K_c = 1100 = \frac{[.10-x]}{[x] \cdot [1.9+x]} \rightarrow 1100 = \frac{[.10-x]}{[1.9x+x^2]} \rightarrow 2090x + 1100x^2 = .10 - x$$

$$1100x^2 + 2091x - .10 = 0 \rightarrow \frac{-2091 \pm \sqrt{(2091)^2 - 4(1100)(-.10)}}{2(1100)}$$

$$\frac{-2091 \pm \sqrt{4372281 - 440}}{2200} \rightarrow \frac{-2091 \pm 2091.054}{2200} \quad x = 4.8 \times 10^{-4} \text{ or same value}$$

$$[Fe^{3+}] = x \rightarrow 4.8 \times 10^{-4} \quad [SCN^-] = 1.9 + x \rightarrow 1.9 \quad [FeSCN^{2+}] = .10 - x \rightarrow .10M$$

END 7.3

BEGIN 7.4

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.

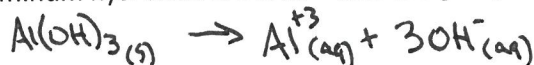
EX 15: What is the solubility of PbI_2 , $K_{sp} = 1.4 \times 10^{-8}$? $PbI_{2(s)} \rightarrow Pb^{2+}(aq) + 2 I^-(aq)$

	Pb^{2+}	I^-
I	0	0
C	x	2x
E	x	2x

$$K_{sp} = 1.4 \times 10^{-8} = \frac{[x] \cdot [2x]^2}{1(\text{Solid})} \rightarrow 1.48 \times 10^{-8} = 4x^3 \rightarrow x^3 = 3.5 \times 10^{-9}$$

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

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



$$K_{sp} = 2 \times 10^{-32} = \frac{[.5] \cdot [3x]^3}{1} \rightarrow 4 \times 10^{-32} = 27x^3 \rightarrow x^3 = 1.48 \times 10^{-33}$$

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

$$[OH^-] = 3x \rightarrow 3(1.14 \times 10^{-11}) = 3.42 \times 10^{-11} M$$

	Al^{3+}	OH^-
I	0	0
C	x	3x
E	x	3x



* SMALL! CAN DISREGARD *

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?

H₂O:

	Ag^+	SO_4^{2-}
I	0	0
C	$2x$	x
E	$2x$	x

$$K_{sp} = 1.2 \times 10^{-5} = [2x]^2 \cdot [x]$$

$$1.2 \times 10^{-5} = 4x^3$$

$$x = 1.44 \times 10^{-2} \frac{\text{mol}}{\text{L}}$$

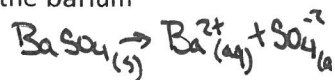
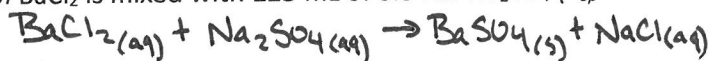
	Ag^+	SO_4^{2-}
I	.10	0
C	$2x$	x
E	$.10 + 2x$	x

$$1.2 \times 10^{-5} = [.1 + 2x]^2 \cdot [x]$$

$$1.2 \times 10^{-5} = [.1]^2 \cdot [x]$$

$$x = 1.2 \times 10^{-3}$$

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?



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

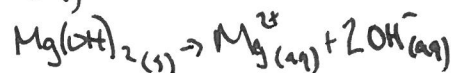
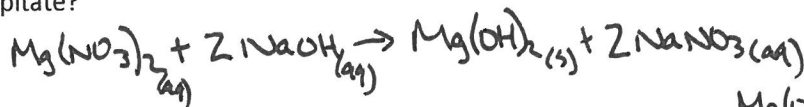
$$\text{SO}_4^{2-} \rightarrow \frac{.04 \text{ mol SO}_4^{2-}}{1 \text{ L sol'n}} \cdot \frac{.125 \text{ L SO}_4^{2-}}{.2 \text{ L TOTAL}} = \frac{.005 \text{ mol SO}_4^{2-}}{.2 \text{ L TOTAL}} = .025 \text{ M SO}_4^{2-}$$

$$Q = [\text{Ba}^{2+}]^1 \cdot [\text{SO}_4^{2-}]^1$$

$$= [.0075]^1 \cdot [.025]^1 \rightarrow 1.875 \times 10^{-4}$$

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

EX 19: 100 mL of 0.0004 M $\text{Mg}(\text{NO}_3)_2$ is mixed with 100 mL of 0.0002 M NaOH ($K_{sp} = 8.9 \times 10^{-12}$). Does the magnesium precipitate?



$$\text{Mg}^{2+} \rightarrow \frac{4 \times 10^{-4} \text{ mol Mg}^{2+}}{1 \text{ L sol'n}} \cdot \frac{.100 \text{ L}}{.2 \text{ L TOTAL}} = \frac{4.0 \times 10^{-5} \text{ mol Mg}^{2+}}{.2 \text{ L TOTAL}} = 2 \times 10^{-4} \text{ M Mg}^{2+}$$

$$\text{OH}^- \rightarrow \frac{2 \times 10^{-4} \text{ mol OH}^-}{1 \text{ L sol'n}} \cdot \frac{.100 \text{ L}}{.2 \text{ L TOTAL}} = \frac{2 \times 10^{-5} \text{ mol OH}^-}{.2 \text{ L TOTAL}} = 1 \times 10^{-4} \text{ M OH}^-$$

$$Q = [\text{Mg}^{2+}]^1 \cdot [\text{OH}^-]^2$$

$$= [2 \times 10^{-4}]^1 \cdot [1 \times 10^{-4}]^2$$

$$Q = 2 \times 10^{-12} < K_{sp} \therefore \text{PPT DOES NOT FORM}$$