CHM1311 D: Principles of Chemistry (Prof. N. Goto)
Assignment #5
Due Nov 9th, at the beginning of class. Late assignments will not be accepted.

Assignments can be submitted individually, or by groups of up to 4 students.

1) Last Name: _____ **First Name:** _____ **Student ID:** _____

2) Last Name: _____ **First Name:** _____ **Student ID:** _____

3) Last Name: _____ **First Name:** _____ **Student ID:** _____

4) Last Name: _____ **First Name:** _____ **Student ID:** _____

Solutions must be written legibly, in the space provided. Adequate detail to the calculation (including units, appropriate sig figs) must be provided to make it possible for other students to understand how you arrived at the final solution. If more space is needed, use the back of the page. Do not add extra pages, as they will not be marked. Assignment pages must be stapled together.
NOTE: For each question a hint, or reference to an Office Hours video, or Interactive LearningWare (ILW) problem in WileyPLUS is given in brackets.

Question 1. (Video 14.3)
The reaction of Cl_2 gas with CO gas to give phosgene gas has been described this mechanism:

$$Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Cl$$

$$Cl + CO \xrightarrow{k_2} COCl$$

$$COCl + Cl_2 \xrightarrow{k_3} COCl_2 + Cl$$

a) What is the equilibrium constant expression for this reaction? (1 mark)

$$K_{eq} = \frac{p_{Cl}^2}{p_{Cl_2}} \times \frac{p_{COCl}}{p_{CO}\,p_{Cl}} \times \frac{p_{COCl_2}\,p_{Cl}}{p_{COCl}\,p_{Cl_2}} = \frac{p_{Cl}^2\,p_{COCl_2}}{p_{Cl_2}^2\,p_{CO}}$$

b) Express the equilibrium constant in terms of rate constants for the elementary reactions. (1 mark)

ALL ELEMENTARY REACTIONS CAN OCCUR IN REV DIRECTION, WITH CORRESPONDING RATE BEING DENOTED WITH A MINUS SIGN IN THE SUBSCRIPT ∴ FOR EACH ELEMENTARY REACTION:

$K_1 = \frac{k_1}{k_{-1}}$ $K_2 = \frac{k_2}{k_{-2}}$ $K_3 = \frac{k_3}{k_{-3}}$ $K_{OVERALL} = K_1 K_2 K_3 = \frac{k_1 k_2 k_3}{k_{-1} k_{-2} k_{-3}}$

Question 2. (Video 14.27)

The following exothermic gas-phase reaction is at equilibrium in a fixed volume reaction vessel:

$$PCl_5\,(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Predict what happens to the amount of PCl_5 in the system when each of the following changes is made. Provide justification for your answer. In some cases this may require a calculation.

a) The temperature is raised. (2 marks) NEED TO DETERMINE IF RXN IS EXOTHERMIC OR ENDOTHERMIC

$\Delta H_R^\circ = \Delta H_f^\circ(PCl_{3(g)}) + \Delta H_f^\circ(Cl_2) - \Delta H_f^\circ(PCl_5) = [-287.0 - (-374.9)]\,kJ\,mol^{-1} = 87.9\ kJ\,mol^{-1}$

∴ ENDOTHERMIC (HEAT IS ≈ A REACTANT)

∴ TEMPERATURE INCREASE WILL SHIFT REACTION TOWARDS PRODUCTS

∴ P_{PCl_5} WILL DECREASE

b) More Cl_2 gas is added to the vessel. (1 mark)

Cl_2 IS A PRODUCT ∴ REACTION WILL SHIFT TOWARDS REACTANTS

∴ P_{PCl_5} WILL INCREASE

c) Xenon gas is introduced to increase the pressure inside the reaction vessel. (1 mark)

Xe IS NOT A PRODUCT OR REACTANT IN THIS REACTION

∴ THERE WILL BE NO AFFECT ON EQUILIBRIUM

∴ P_{PCl_5} WILL NOT CHANGE

Question 3. (ILW 14.31)

When 0.313 mol of C_6H_5COOH is dissolved in 0.416 L of water, proton transfer occurs.

$$C_6H_5COOH\,(aq) + H_2O\,(l) \rightleftharpoons C_6H_5COO^-\,(aq) + H_3O^+\,(aq)$$

What is K_{eq}, given that the equilibrium concentration of H_3O^+ ions is 0.00686 M. (4 marks)

$$[C_6H_5COOH] = \frac{n}{V} = \frac{0.313\ mol}{0.416\ L} = 0.7524\ M$$

	C_6H_5COOH	$C_6H_5COO^-$	H_3O^+
INITIAL	0.7524	0	0
CHANGE	$-x$	$+x$	$+x$
EQUILIBRIUM	$0.7524 - x$	x	x

$$K_{eq} = \frac{[H_3O^+][C_6H_5COO^-]}{[C_6H_5COOH]} = \frac{x^2}{0.7524 - x}$$

$[H_3O^+]_{eq} = x = 0.00686\ M$

$$\therefore K_{eq} = \frac{(0.00686)^2}{(0.7524 - 0.00686)}$$

$$= 6.\times10^{-5}$$

Question 4. (ILW 14.35)

At 452°C, K_{eq} is 1.69×10^{-5} for the following reaction

$$A\ (s) + 2\ B\ (g) \rightleftharpoons 2\ C\ (g) + D\ (g)$$

If gas B at 0.483 bar is injected into a container at 452°C that contains excess A, what are the partial pressures of all the gases at equilibrium? (4 marks)

	2 B	2 C	D
INITIAL	0.483	Ø	Ø
CHANGE	-2x	+2x	x
EQUILIBRIUM	0.483-2x	2x	x

$$K_{eq} = \frac{p_C^2 p_D}{p_B^2} = \frac{(2x)^2 x}{(0.483-2x)^2}$$

∴ K_{eq} IS VERY SMALL, WE CAN PROBABLY ASSUME

$0.483 - 2x \approx 0.483$

$$K_{eq} = 1.69 \times 10^{-5} = \frac{4x^3}{(0.483)^2}$$

$$x = \sqrt[3]{\frac{(1.69 \times 10^{-5})(0.483)^2}{4}}$$

$$= 9.95 \times 10^{-3}$$

∴ $p_D = 9.95 \times 10^{-3}$ bar

$p_C = 0.0199$ bar

$p_B = 0.463$ bar

WAS ASSUMPTION VALID?

$$\frac{p_{B,0} - p_B}{p_B} \times 100\% = \frac{0.468 - 0.463}{0.463} \times 100\%$$

$$= 4.12\%$$

∵ ERROR IS < 5% ∴ VALID

Question 5. (ILW 14.51)

The equilibrium constant for the association of NO_2 to form N_2O_4 gas at 515 K is 2.1×10^{-4}. If NO_2 gas at 298 K, 0.657 bar is placed in a sealed container and heated to 515 K, what is the equilibrium pressure of N_2O_4? (5 marks)

$$p_2 = \frac{p_1 T_2}{T_1} = \frac{(0.657\ bar)(515\ K)}{298\ K}$$

$$= 1.135\ bar$$

	$2\ NO_2$	$\rightleftharpoons$	N_2O_4
INITIAL	1.135		Ø
CHANGE	-2x		x
EQUILIBRIUM	1.135-2x		x

$$K = \frac{x}{(1.135-2x)^2} = 2.1 \times 10^{-4}$$

ASSUME $1.135 - 2x \approx 1.135$

$$K = \frac{x}{1.135^2} = 2.1 \times 10^{-4}$$

$$x = 2.71 \times 10^{-4}$$

∴ THE EQUILIBRIUM PRESSURE OF N_2O_4 IS 2.71×10^{-4} bar.

WAS ASSUMPTION VALID?

$$\frac{p_{NO_2,0} - p_{NO_2,EQ'N}}{p_{NO_2,EQ'N}} \times 100\%$$

$$= \frac{2(2.38 \times 10^{-4})}{1.135 - 2(2.71 \times 10^{-4})} \times 100\%$$

$$= 6.04\%$$ ∴ VALID ASSUMPTION

Question 6. (Additional Interactive LearnWare Problem 1)

Consider the following chemical equilibrium:

$$A\,(g) + B\,(s) \rightleftharpoons 2\,C\,(g) + D\,(s)$$

If the initial pressure of B is 3.01 bar, the total pressure at equilibrium is 5.67 bar. Use these pressures to calculate K_{eq}. (4 marks)

$A_{(g)} + B_{(s)} \rightleftharpoons 2C_{(g)} + D_{(s)}$

INITAL	3.01	∅	
CHANGE	$-x$	$+2x$	
EQUILIBRIUM	$3.01 - x$	$2x$	

$3.01 - x + 2x = 5.67$ bar

$\therefore x = 5.67 - 3.01$

$= 2.66$

$$K = \frac{(2x)^2}{3.01 - x} = \frac{[2(2.66)]^2}{(3.01 - 2.66)}$$

$= 80.9$

Question 7. (See Chapter 14 lecture slide 30, 31)

Lead chloride precipitates from solution when lead acetate is mixed with sodium chloride with an equilibrium constant of 5.88×10^4 at 298 K. Suppose 2.65 g of lead acetate was added to 500.0 mL of 0.500 M sodium chloride. Calculate the concentration of $Pb^{2+}(aq)$ that would remain in solution at equilibrium at 298K. (4 marks)

$Pb(OAc)_2 + 2NaCl \rightleftharpoons PbCl_2 + 2Na(OAc)_{(aq)}$

NET IONIC RXN:

$Pb^{2+}_{(aq)} + 2Cl_{(aq)} \rightleftharpoons PbCl_{2(s)}$

K_{eq} IS LARGE $\therefore$ ASSUME THAT EQUILIBRIUM WILL LIE CLOSE TO COMPLETE RXN:

$Pb^{2+}_{(aq)} + 2Cl^-_{(aq)} \rightleftharpoons PbCl_{2(s)}$

INITAL	0.01624	0.500
REACT	-0.01624	$-2(0.01624)$
NEW INITIAL	∅	0.4674
CHANGE	$+x$	$-2x$
FINAL	x	$0.4674 - 2x$

$$K = \frac{1}{x(0.4674 - 2x)^2}$$

ASSUME $[Cl^-] \approx [Cl^-]_0$ ← VALID?

$$K = \frac{1}{x(0.4674)^2}$$

$$x = \frac{1}{K(0.4674)^2} = \frac{1}{(5.88 \times 10^4)(0.4674)^2}$$

$= 7.78 \times 10^{-5}$

$\therefore [Pb^{2+}]_{eq} = 7.78 \times 10^{-5}$ mol/L

$$\frac{[Cl^-]_0 - [Cl^-]_{eq}}{[Cl^-]_{eq}} \times 100\% = \frac{2(7.78 \times 10^{-5})}{0.4674} \times 100\%$$

$= 3.3 \times 10^{-2}\%$

$\therefore$ ERROR $<< 5\%$

$\therefore$ ASSUMPTION IS VALID

$M_{Pb(OAc)_2} = 325.29$ g/mol

$$C_{Pb^{2+},0} = \frac{n}{V} = \frac{m}{MV} = \frac{2.65\text{ g}}{(325.29\text{ g/mol})(0.500\text{ L})}$$

$= 0.01624$ mol/L