LAST NAME: ____

FIRST NAME: ____

Student Number: ____

CHM 1311 D
Prof. Goto
Midterm #2
Fall 2017

Please keep your work covered at all times and keep your eyes on your own paper! Cheating or any appearance of cheating will result in an F in the course and possible expulsion from the university.

There are 7 pages in this test, for a total of 40 marks. An equation sheet is provided at the end that may be removed from the exam and used to cover your work during the test. Any scratch work should be done on the back of the equation sheet.

Please show all work to receive partial credit.

Make sure that units are included in your final answer.

You have 90 minutes to complete the test.

Warning:
Cellular phones, unauthorized electronic devices or course notes are not allowed during this exam. Phones and devices must be turned off and stored in your bag. Do not keep them in your possession, such as in your pockets. If caught with such a device or document, academic fraud allegations will be filed which may result in your obtaining a **0** (zero) for the midterm.

Question 1. Short answer questions (7 marks)

a) If a plot of $[A]_t$ versus time gives a straight line, then the reaction order with respect to reagent A will be ZERO order.

b) If a reaction is run at a higher temperature, will its activation energy increase, decrease or remain the same?

REMAIN THE SAME

c) Which of the following changes will cause the equilibrium below to shift to the left?

$$Pb^{2+}(aq) + 2\,Cl^{-}(aq) \rightleftharpoons PbCl_2(s) \quad \Delta H° = -25.3 \text{ kJ mol}^{-1}$$

Circle all that apply:

i) add $PbCl_2$ [✓ ii) increase temperature] [✓ iii) add water]

d) What is the conjugate acid that will be produced by the reaction of HCO_3^- with HCN?

H_2CO_3

e) Write the rate law for the reaction A (g) + B (g) → 2 C(g), given that it is second order in A and zero order in B.

$\text{RATE} = k[A]^2$

f) Which of the following are acceptable units of rate for a gas phase chemical reaction? (Circle all that apply.)

[✓ i) atm s^{-1}] ii) $atm^{-1}\,s^{-1}$ iii) atm s [✓ iv) Torr s^{-1}] v) s $Torr^{-1}$

g) What is the pOH of water at 25°C? pOH = 7

Question 2. Short questions (2 mark each, unless otherwise indicated)

a) Calculate the activation energy for the reaction:

$$C_2H_4F_2\,(g) \rightarrow C_2H_3F\,(g) + HF\,(g)$$

given rate constants of $k = 5.59 \times 10^{-6}\ s^{-1}$ at 460 °C and $k = 6.31 \times 10^{-6}\ s^{-1}$ at 735 °C.

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = \frac{-R\ln\left(\frac{k_2}{k_1}\right)}{\frac{1}{T_2} - \frac{1}{T_1}}$$

$$= \frac{-(8.314\text{ J K}^{-1}\text{mol}^{-1})\ln\left(\frac{5.59\times10^{-6}}{6.31\times10^{-6}}\right)}{\left(\frac{1}{(460+273)\text{K}}\right) - \left(\frac{1}{735+273\text{K}}\right)} = 2.71\ \frac{\text{kJ}}{\text{mol}}$$

b) Determine K_{eq} for the reaction

$$H_2O(g) + CO(g) \rightleftharpoons CO_2(g) + H_2(g)$$

given that:

$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$ $K_c = 3.3 \times 10^{91}$ ← DIVIDE BY 2, REV

$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$ $K_c = 9.1 \times 10^{80}$ ← DIVIDE BY 2

$H_2O \rightleftharpoons 2 H_2(g) + \frac{1}{2}O_2(g)$ $K_1 = \frac{1}{(3.3 \times 10^{91})^{\frac{1}{2}}}$

$CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$ $K_2 = (9.1 \times 10^{80})^{\frac{1}{2}}$

$$K_{eq} = K_1 K_2 = \frac{\sqrt{9.1 \times 10^{80}}}{\sqrt{3.3 \times 10^{91}}}$$

$$= 5.3 \times 10^{-6}$$

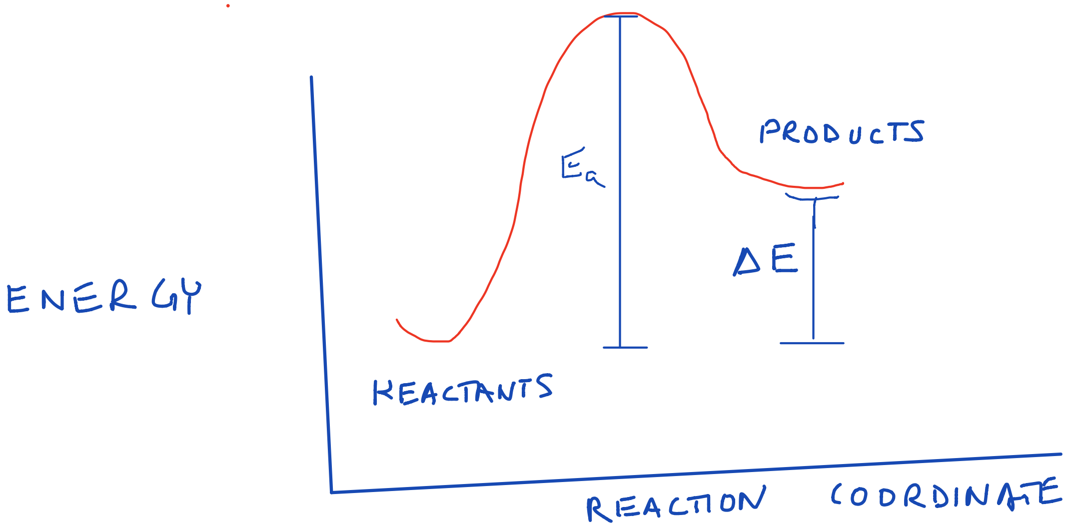
c ~~b~~) A pure gas C in a sealed reaction vessel at 400 K allowed to come to equilibrium in the reaction:

$$A(g) + B(g) \rightleftharpoons C(g)$$

If $K_{eq} = 4.3 \times 10^5$ at 400 K, can we assume that the initial pressure of C is approximately equal to the equilibrium pressure of C? Justify your answer in one sentence.

YES. ∵ K_{eq} IS LARGE ∴ MOSTLY PRODUCTS PRESENT @ EQUILIBRIUM. THIS IS VERY SIMILAR TO THE INITIAL CONDITIONS ∴ THERE WILL ONLY BE A SMALL AMOUNT OF GAS C THAT REACTS.

d ~~c~~) Draw a reaction energy profile for an uncatalyzed endothermic reaction that is very slow. Be sure to label your axes, reactants, products, ΔE and E_a for the forward reaction. (3 marks)



e ~~d~~) What is the pH of a 0.065 M solution of a weak acid that is 3.65 % hydrolyzed?

$$\% \text{ HYDROLYZED} = \frac{[H_3O^+]}{[HA]} \times 100\%$$

$$[H_3O^+] = \frac{[HA]\ \% \text{ HYDROLYZED}}{100\%}$$

$$= (0.0365)(0.065M)$$

$$= 2.37\times10^{-3} M$$

$$pH = 2.6$$

f) ~~e~~) Given that carbonic acid (H_2CO_3) has two ionizable protons, with pK_{a1} = 6.35 and pK_{a2} = 10.33, write the reaction with water that you would expect if sodium bicarbonate ($NaHCO_3$) is dissolved in water. Briefly justify your answer. $NaHCO_3 \longrightarrow Na^+ + HCO_3^-$

$HCO_3^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + OH^-$ $pK_b = 14 - 6.35 = 7.65$

OR $HCO_3^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons CO_3^{2-}{}_{(aq)} + H_3O$ $pK_a = 10.33$

1st REACTION HAS LARGER EQUILIBRIUM CONSTANT THAN 2nd RXN ∴ HCO_3^- WILL REACT WITH H_2O TO PRODUCE BASE (1st RXN)

f) Cyclopropane converts to propene by first-order kinetics with a rate constant at 500°C of 5.5×10^{-4} s^{-1}. Calculate how long it takes for 90% of the sample to react. ← $[A]_t = 0.1[A]_0$

$$\ln\frac{[A]_0}{[A]_t} = kt$$

$$t = \frac{1}{k}\ln\frac{[A]_0}{0.1[A]_0}$$

$$= \frac{1}{5.5\times10^{-4}\,s^{-1}}\ \ln 10$$

$$= 4.2\times10^{3}\,s$$

Question 5. (6 marks)

For the decomposition of carbon tetrachloride:

$$CCl_4\,(g) \rightleftharpoons C\,(s) + 2\,Cl_2\,(g)$$

At 850 K, if the initial pressure of CCl_4 is 3.65 bar, the total pressure at equilibrium is 4.53 bar.

a) What is K_{eq} at 850 K?

	CCl_4	$2Cl_2$
I	3.65	0
C	$-x$	$+2x$
E	$3.65-x$	$2x$

$P_T = 3.65 - x + 2x = 4.53$ bar

$x = (4.53 - 3.65)$ bar

$= 0.88$ bar

$$K_{eq} = \frac{P_{Cl_2}^2}{P_{CCl_4}} = \frac{(2x)^2}{3.65-x} = \frac{(2(0.88))^2}{3.65-0.88} = 1.1$$

b) What will happen to the partial pressure of CCl_4 in this equilibrium system if neon gas is introduced to increase the pressure inside the reaction vessel? Briefly explain your answer.

THERE WILL BE NO CHANGE IN EQUILIBRIUM ∵ NEON DOES NOT PARTICIPATE IN REACTION AND IS NOT IN EQULLIBRIUM EQUATION

Question 3.

a) Write the balanced chemical equation of the overall reaction for the reaction mechanism shown on the right. (1 mark)

$2\,A \rightleftharpoons \cancel{A_2}$	$k_1 = 3.38 \times 10^6$ $k_{-1} = 1.66 \times 10^6$
$\cancel{A_2} + B \rightarrow \cancel{C} + D$	$k_2 = 4.62 \times 10^2$
$\cancel{C} + B \rightarrow D + E$	$k_3 = 5.78 \times 10^5$

$2A + 2B \longrightarrow 2D + E$

b) Use the mechanism shown in (a) to derive the rate law for the overall reaction. (3 marks)

$$RATE = k_2[A_2][B]$$

$$k_1[A]^2 = k_{-1}[A_2]$$

$$[A_2] = \frac{k_1}{k_{-1}}[A]^2$$

$$\therefore RATE = \frac{k_1 k_2}{k_{-1}}[A]^2[B]$$

Question 4. (8 marks)

Sodium nitrite ($NaNO_2$) is a food additive used as a preservative. What is the pH of a 0.583 M solution of sodium nitrite given that the pKa of nitrous acid is 3.25. Don't forget to justify any assumption(s) made in this calculation!

	$NO_2^- + H_2O \rightleftharpoons$	HNO_2	$+OH^-$
I	0.583	0	$10^{-7} \approx 0$
C	$-x$	x	x
E	$0.583-x$	x	x

$pK_b = 14 - pK_a = 14 - 3.25$

$= 10.75$

VALID

$$\% \ ERROR = \frac{10^{-7}}{3.2\times10^{-6} + 10^{-7}} \times 100\%$$

$= 3.0\% \quad \therefore VALID$

$$K_b = \frac{[OH^-][HNO_2]}{[NO_2^-]} = \frac{x^2}{0.583-x} \approx \frac{x^2}{0.583}$$

VALID?

$$x = \sqrt{(0.583)\,10^{-10.75}}$$

$= 3.2\times10^{-6}\ M$

$$\% \ ERROR = \frac{x}{0.583-x} \times 100\%$$

$= 5.5\times10^{-4}\%$

$\therefore < 5\%$

$\therefore$ VALID ASSUMPTION

$pOH = 5.5$

$pH = 8.5$

Selected Constants and Conversion Factors

1 mmHg = 1 torr   760 mmHg = 1 atm   1 atm = 101.325 kPa   1 atm = 1.013125 bar

1 bar = 10^5 Pa   1 cm^3 = 1 mL   1 dm^3 = 1000 mL = 1 L   1 m^3 = 1000 L   1 cal = 4.184 J

Avogadro's Number	N_A	$6.022\text{x}10^{23}\ \text{mol}^{-1}$
Gas constant	R	$8.31451\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
	R	$0.08206\ \text{atm}\cdot\text{L}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
	R	$8.31451\ \text{L}\cdot\text{kPa}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
	R	$0.0831451\ \text{bar L}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

Equations Covered Since Midterm 1

$$\text{Rate} = \frac{1}{v_\text{X}}\frac{\Delta[\text{X}]}{\Delta t} \qquad \text{Rate} = k[\text{A}]^y[\text{B}]^z \ldots \qquad \frac{\text{Initial Rate 1}}{\text{Initial Rate 2}} = \frac{k[\text{A}]_1^y[\text{B}]_2^z\ldots}{k[\text{A}]_2^y[\text{B}]_2^z\ldots} \qquad k = Ae^{-\frac{E_a}{RT}}$$

$$[\text{A}]_t = [\text{A}]_o - akt \qquad \ln\frac{[\text{A}]_o}{[\text{A}]_t} = akt \qquad \frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_o} = 2kt \qquad \ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$t_{\frac{1}{2}} = \frac{[\text{A}]_o}{2ak} \qquad t_{\frac{1}{2}} = \frac{\ln 2}{a\text{k}} \qquad t_{\frac{1}{2}} = \frac{1}{2k[\text{A}]_o} \qquad K_{eq} = \frac{[\text{C}]_{eq}^c[\text{D}]_{eq}^d}{[\text{A}]_{eq}^a[\text{B}]_{eq}^b} \qquad K_{eq} = \frac{p_{C,eq}^c p_{D,eq}^d}{p_{A,eq}^a p_{B,eq}^b}$$

$$Q = \frac{p_C^c p_D^d}{p_A^a p_B^b} \qquad Q = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \qquad K_{eq} = K_1 \times K_2 \times K_3 \times \ldots \qquad K_{eq,reverse} = \frac{1}{K_{eq,forward}} \qquad K_{eq,new} = \left(K_{eq,old}\right)^n$$

$$ax^2 + bx + c = 0 \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad \text{pH} = -\log\left[\text{H}_3\text{O}^+\right] \qquad \text{pOH} = -\log\left[\text{OH}^-\right] \qquad \text{pH} + \text{pOH} = 14$$

$$pK_a = -\log K_a \qquad \%\ \text{error} = 100\% \times \frac{\text{difference from assumed value}}{\text{actual value}} \qquad K_a \times K_b = K_w = 10^{-14} \qquad pK_b = -\log K_b$$

Midterm 1 Equations

$$T(\text{in K}) = T(\text{in }^\circ\text{C}) + 273.15\ \text{K} \qquad n = \frac{m}{M} = \frac{N}{N_A} \qquad \%\ \text{Yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \qquad c(\text{mol/L}) = \frac{n}{V}$$

$$c_1V_1 = c_2V_2 = n \qquad p = \frac{mg}{A} \qquad p = dgh \qquad pV = nRT \qquad \frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \qquad p_T = p_1 + p_2 + p_3 + \ldots$$

$$p_A = X_A \times p_T \qquad X_A = \frac{n_A}{n_T} \qquad d = \frac{m}{V} = \frac{p \cdot M}{RT} \qquad E_K = \frac{1}{2}m\text{v}^2 \qquad \bar{E} = \frac{3RT}{2N_A} \qquad \bar{v} = \sqrt{\frac{3RT}{M}}$$

$$\frac{Rate\ A}{Rate\ B} = \sqrt{\frac{M_B}{M_A}} \qquad p = \frac{nRT}{(V - nb)} - a\frac{n^2}{V^2} \qquad \Delta E = w + q \qquad w = F \times d = -p\Delta V$$

$$q_\text{calorimeter} = C_{cal}\Delta T \qquad q = mC\Delta T \qquad \Delta E_\text{reaction} = \Sigma BE_\text{reactant bonds broken} - \Sigma BE_\text{product bonds formed} \qquad \Delta E_\text{molar} = \frac{\Delta E}{n}$$

$$\Delta H^o_\text{reaction} = \Sigma v_p \Delta H^o_{f,p} - \Sigma v_r \Delta H^o_{f,r} \qquad \Delta H_\text{reaction} = \Delta E_\text{reaction} + RT\Delta n_{gas} \qquad H = E + pV$$