LAST NAME: ______________________________

FIRST NAME: ______________________________

Student Number: ______________________________

CHM 1311 D
Prof. Goto
Midterm #2
Fall 2018

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 35 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) What is the catalyst in the 2-step reaction mechanism given below?

$$\underline{Cl^{\bullet}} + O_3 \rightarrow ClO^{\bullet} + O_2$$

$$ClO^{\bullet} + O^{\cdot} \rightarrow \underline{Cl^{\bullet}} + O_2$$

$Cl^{\bullet}$
(SINCE IT IS REGENERATED IN RXN)

b) Suppose that for the elementary reaction A + B → P, a product is formed every time that A + B collide. What is the activation energy of this reaction?

$E_a \approx 0 \frac{kJ}{mol}$

c) Suppose that under a given set of conditions the reaction proceeds towards the reactants. Is *Q* greater than or less than *K* for this reaction?

∵ TOWARDS REACTANTS
∴ MORE PRODUCTS INITIALLY THAN @ EQUILIBRIUM
∴ $Q>K$

d) What is the conjugate base that will be produced by the reaction of HPO_4^- with NH_3?

$PO_4^{2-}(aq)$

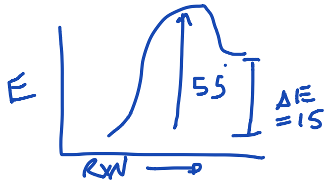
e) What is the rate of the reaction:

$$CH_2O\ (g) \rightarrow CO\ (g) + H_2\ (g),$$

if the rate constant for the reaction is 1.1 x 10^{-3} M^{-1} s^{-1} and the concentration of the reactant is 0.020 M.

$RATE = k\,[CH_2O]^2$
$= (1.1\times10^{-3} M^{-1} s^{-1})(0.020 M)^2$
$= 4.4\times10^{-7} M\, s^{-1}$

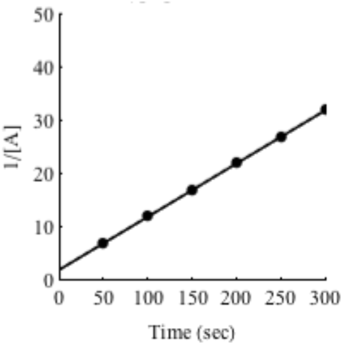
f) For a one step reaction, the activation energy for the forward reaction is 55.0 kJ mol^{-1}, and the enthalpy of reaction is 15.0 kJ mol^{-1}. What is the activation energy for the reverse reaction?



$\Delta E = E_{a,FWD} - E_{a,REV}$
$E_{a,REV} = 55.0\ kJ - 15\ kJ$
$= 40.0\ kJ$

g) What is the order of the reaction plotted on the right?

2^{nd} ORDER



Question 2. Short questions (2 marks each)

a) If a solution of $HONH_3NO_3$ is dissolved in water, will the solution be acidic, basic or neutral? Write the balanced chemical equation that explains your answer.

$$HONH_3NO_{3(aq)} \rightarrow HONH^+_{3(aq)} + NO^-_{3(aq)}$$

$$HONH^+_{3(aq)} + H_2O_{(l)} \rightleftharpoons HONH_{2(aq)} + \underbrace{H_3O^+_{(aq)}}_{\therefore \text{ ACIDIC}}$$

b) Given that:

$$Ni(OH)_2\,(s) \rightleftharpoons Ni^{2+}\,(aq) + 2\,OH^-\,(aq) \quad K_{sp} = 6.0 \text{ x } 10^{-16}$$
$$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq) \quad K_w = 1.0 \text{ x } 10^{-14}$$

– NEED 2 X'S REVERSE REACTION

Calculate the equilibrium constant for:

$$Ni(OH)_2\,(s) + 2\,H^+\,(aq) \rightleftharpoons Ni^{2+}\,(aq) + 2\,H_2O\,(l)$$

$$K = \frac{K_{sp}}{K_w^2} = \frac{6.0 \times 10^{-16}}{(1 \times 10^{-14})^2}$$
$$= 6.0 \times 10^{12}$$

c) What is the pH of water at 50 °C, given that Kw at this temperature is 5.48x 10^{-14}?

LET $[H_3O^+] = X$

$$K_w = [H_3O^+][OH^-] = x^2$$
$$X = \sqrt{K_w} = \sqrt{5.48 \times 10^{-14}}$$
$$= 2.3 \times 10^{-7}$$
$$pH = -\log [H_3O^+]$$
$$= 6.6$$

d) Write the reaction between hydroxylamine ($HONH_2$, pK_b = 8.06) and hydrocyanic acid (HCN, pK_a = 9.21). Will the equilibrium favor the reactants or products? Briefly justify your answer.

$$\begin{array}{ccccccc} HONH_{2(aq)} & + & HCN_{(aq)} & \rightleftharpoons & HONH^+_{3(aq)} & + & CN^-_{(aq)} \\ pK_b & & pK_a & & pK_a & & pK_b \\ = 8.06 & & = 4.21 & & = 14 - 8.06 & & = 14 - 9.21 \\ & & & & = 5.94 & & = 4.79 \end{array}$$

∴ EQUILIBRIUM WILL FAVOR SIDE WITH WEAKER ACID & BASE (HIGHER pK_a & pK_b)

∴ EQUILIBRIUM WILL FAVOR REACTANTS

Question 3 (7 marks)

What will be the pH of a 0.651 M solution of $(C_2H_5)_3NHCl$, given that the pK_b of triethylamine is 3.25? Show your justification for any assumption(s) that were made to solve this problem.

$$(C_2H_5)_3NHCl \rightarrow (C_2H_5)_3NH^+_{(aq)} + Cl^-_{(aq)}$$

$$(C_2H_5)_3NH^+_{(aq)} + H_2O_{(l)} \rightleftharpoons (C_2H_5)_3N_{(aq)} + H_3O^+_{(aq)}$$

I	0.651	0	$10^{-7} \approx 0$
C	$-x$	x	x
E	$0.651-x$	x	x

$$K_a = \frac{K_w}{K_b} = \frac{[H_3O^+][(C_2H_5)_3N]}{[(C_2H_5)_3NH^+]} = \frac{x^2}{\underbrace{0.651-x}_{\approx 0.651}} = \frac{x^2}{0.651}$$

$$= \frac{10^{-14}}{10^{-3.25}}$$

$$= 1.78\times10^{-11} = \frac{x^2}{0.651}$$

$$x = \sqrt{(1.78\times10^{-11})(0.651)}$$

$$= 3.40\times10^{-6}$$

$$= [H_3O^+]$$

$$\therefore pH = -\log[H_3O^+]$$

$$= 5.47$$

CHECK ASSUMPTIONS

$[(C_2H_5)_3N] \approx [(C_2H_5)_3N]_0$ VALID?

$$\%ERROR = \frac{x}{0.651-x}\times100\%$$

$$= \frac{3.40\times10^{-6}}{0.651-3.40\times10^{-6}}\times100\%$$

$$= 6\times10^{-5}\%$$ ∴ VALID

$[H_3O^+]_0 = 0$ VALID?

$$\%ERROR = \frac{10^{-7}}{x+10^{-7}}\times100\%$$

$$= 0.2\%$$

∴ VALID

Question 4.

For the first order reaction,

$$C_2H_5I\ (g) \rightarrow C_2H_4\ (g) + HI\ (g)$$

The half-life was found to be 29.0 min at 660 K and rate constant was found to be 0.158 s^{-1} at 775 K.

1st ORDER

a) Calculate the activation energy (in kJ/mol) for this reaction. (5 marks)

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} -$$

$$k = \frac{\ln 2}{t_{\frac{1}{2}}}$$

$$= \frac{\ln 2}{(29.0\,\text{min})}$$

$$= 0.023\overline{9}\ \text{min}^{-1} \times \frac{1\,\text{min}}{60\,\text{s}}$$

$$= 3.98 \times 10^{-4}\,\text{s}$$

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

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

$$= \frac{(8.314\ \text{J K}^{-1}\,\text{mol}^{-1}) \ln\left(\frac{3.48\times10^{-4}\,\text{s}^{-1}}{0.158\ \text{s}^{-1}}\right)}{-\left(\frac{1}{660\,\text{K}} - \frac{1}{775\,\text{K}}\right)}$$

$$= 220\ \frac{\text{kJ}}{\text{mol}}$$

b) How long will it take for 95% of 0.250 M C_2H_5I to react at 660 K? (2 marks)

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

$$[A]_t = 0.05[A]_0$$

$$t = \frac{1}{k} \ln \frac{[A]_0}{0.05[A]_0}$$

$$= \frac{1}{3.48\times10^{-4}\,\text{s}^{-1}} \ln \frac{1}{0.05}$$

$$= 7500\,\text{s}$$

Question 5.

2 molecules of acetic acid in the gas phase can hydrogen bond to form a dimer in the reaction:

$$2\ CH_3COOH\ (g) \rightleftharpoons C_4H_8O_4\ (g)$$

a) What is K_{eq} at 100.0°C if 1.000×10^{-3} mol of acetic acid gas is introduced to a 100.0 mL reaction flask, and the total pressure of gas in the flask at equilibrium at 100.0°C is 0.229 bar? (4 marks)

$$p = \frac{nRT}{V} = \frac{(1.000\times10^{-3}\ mol)(0.08314\ \frac{L \cdot bar}{K \cdot mol})(373.15\,K)}{0.1000\ L}$$

$$= 0.310\ bar$$

	$2\ CH_3COOH$	$\rightleftharpoons$	$C_4H_8O_4$
I	0.310		∅
C	$-2X$		X
E	$0.310-2X$		X

$$P_t = 0.310 - 2X + X$$
$$= 0.310 - X$$
$$X = 0.310 - 0.229$$
$$= 0.080$$

$$K_{eq} = \frac{X}{(0.310-2X)^2}$$

$$= \frac{0.080}{(0.310-2(0.080))^2}$$

$$= 3.7$$

b) Given that energy is required to break hydrogen bonds, will the equilibrium constant go up or go down if the temperature is raised? Justify your answer with one sentence. (1 mark)

HEAT IS A PRODUCT

∵ H-BONDS ARE BROKEN IN REVERSE RXN

∴ MORE REACTANTS FORM AS TEMP ↑

∴ K ↓

c) What will happen to the yield of the reaction if it is run in a smaller reaction vessel? Justify your answer with one sentence. (1 mark)

IF V↓, EQUILIBRIUM WILL FAVOR SIDE WITH SMALLER # OF MOLES OF GAS ∴ YIELD OF PRODUCT WILL ↑

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

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

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

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

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

$$\text{pH} = -\log\left[\text{H}_3\text{O}^+\right] \qquad \text{pOH} = -\log\left[\text{OH}^-\right] \qquad \text{pH} + \text{pOH} = 14 \qquad K_a \times K_b = K_w = 10^{-14} = \left[\text{H}_3\text{O}^+\right]\left[\text{OH}^-\right]$$

$$pK_b = -\log K_b \qquad pK_a = -\log K_a \qquad ax^2 + bx + c = 0 \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\%\ \text{error} = 100\% \times \frac{\text{difference from assumed value}}{\text{actual value}} \qquad \%\ \text{HA hydrolyzed} = 100\% \times \frac{\left[\text{H}_3\text{O}^+\right]_{eq}}{[\text{HA}]_{initial}}$$

Midterm 1 Equations

$$T(\text{in K}) = T(\text{in }^\text{o}\text{C}) + 273.15\ \text{K} \qquad n = \frac{m}{M} = \frac{N}{N_A} \qquad \%\ \text{Yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \qquad c(\text{mol/L}) = \frac{n}{V}$$

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

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

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

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

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