LAST NAME: ____________________

FIRST NAME: ____________________

Student Number: ____________________

CHM 1311 B
Midterm #2
Fall 2015

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 8 pages in this test. The last page includes equations covered in the course, and data that may be useful for some questions. You may rip this page off of the midterm and use it to cover your work during the test.

You must show all work to receive partial credit.

Make sure your final answer has appropriate units.

Marks may be deducted if an unreasonable number of sig figs are shown in your final answer.

You have 75 minutes to complete this test.

Question	**Points Possible**	**Points Earned**
1	**11**	
2	**8**	
3	**15**	
4	**11**	
TOTAL	**45**	

Question #1. Short Answer Questions

a) An ideal gas absorbs 500 J of heat and does 300 J of work. What is the change in internal energy of this gas? (1 mark)

ΔU =____________**200 J**___________

b) What is the enthalpy change for 1 g of water that increases in temperature by 1^{o}C? (1 mark)

ΔH =____________**4.184 J**_____________

c) What would be the value of ΔH for the reaction $2\ A \leftrightarrows 2\ B + 3\ C$, given that $\Delta H = 75$ kJ mol^{-1} for the reaction $9\ C + 6\ B \leftrightarrows 6\ A$ (1 mark)

ΔH =_____________**-25 kJ mol^{-1}**__________

d) Write the rate equation for a reaction that is second order in reactant A and has an order of -1 for reactant B. (2 marks)

Rate = _______**$k[A]^2[B]^{-1}$**______________

e) If reaction $2\ A \rightarrow B$ is zero order, then a plot of _____**[A]**_________ **versus** _____**time**_____ **will be linear. (1 mark)**

f) What is the rate constant for the radioactive decay of ^{40}K, which has a half-life of 1.25 billion (1 billion = 10^9) years? (2 marks)

k =_______**5.5×10^{-10} $year^{-1}$**_____________________

g) Suppose you start a reaction with $Q = 1.6 \times 10^{-3}$. If the equilibrium constant equals 1, will the reaction go forwards or backwards? (1 mark)

forwards

h) What is the $[H_3O^+]$ concentration for a solution with pOH = 3.65? (1 mark)

pH = 14 – 3.65 = 10.35

$[H_3O^+]$ = ________**4.47×10^{-11} M** _______________

i) If a reaction vessel containing the reaction

$A\ (s) + 2\ B\ (g) \leftrightarrows 2\ C\ (g)$, $\Delta H_{rxn} = -25$ kJ/mol

was compressed isothermally, would you expect the reaction yield to increase, decrease or stay the same? (1 mark)

Stay the same

Question #2. Balsamic vinegar typically contains 6.0 g of acetic acid (CH_3COOH, $M = 60.05$ g/mol) in a 100 mL solution. The pK_b of the conjugate base of acetic acid (CH_3COO-) is 9.25.

a) What is the *Ka* of acetic acid? (1 mark)

$$Ka = \frac{K_w}{K_b} = \frac{K_w}{10^{-pK_b}} = \frac{10^{-14}}{10^{-9.25}} = 1.78 \times 10^{-5}$$

b) Write the net ionic chemical equation for the reaction of acetic acid with water. Be sure to include the phases of reactants and products. (1 mark)

$$\mathbf{CH_3COOH\ (\mathit{aq}) + H_2O\ (\mathit{l}) \rightleftharpoons CH_3COO\text{-}\ (\mathit{aq}) + H_3O\text{+}\ (\mathit{aq})}$$

c) What is the pH of this vinegar? Be sure to show that any assumptions you make in the calculation are valid. (6 marks)

	CH_3COOH	CH_3COO-	H_3O+
Initial	$c_o = \dfrac{\frac{6.0g}{60.05\text{ g mol}^{-1}}}{0.100\text{ L}} = 1.0\text{ mol L}^{-1}$ ①	0	10^{-7} ②
Change	-x	x	x
Equilibrium	1 M - x	x	10^{-7}+x

$$K = \frac{[CH_3COO-][OH\text{-}]}{[CH_3COOH]}$$ ①

Assume that [OH-]eq = x (check later)

Can we assume [CH_3COOH]eq = [CH_3COO-]?

Test: $\frac{[CH_3COOH]}{K_a} = \frac{1}{1.78 \times 10^{-5}} >> 400$, therefore this assumption is valid. ①

$K = \frac{x^2}{1\text{ M}}$, so $x = [H_3O^+] = \sqrt{1.78 \times 10^{-5}} = 0.00422$ M, and $\text{pH} = -\log(0.00422) = 2.4$ ①

Was it reasonable to assume $[H_3O+]_o$= 0 M?

$\%\text{ error} = \frac{[H_3O+]_o}{[H_3O+]_{eq}} \times 100\% = \frac{10^{-7}}{.00422} \times 100\% = 0.002\%$ Error << 5%, therefore valid assumption.

Question #3. For the decomposition of gaseous N_2O_5:

$$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$$

the rate constant is $k = 2.8 \times 10^{-3}\ s^{-1}$, and the equilibrium constant is $K_p = 1.30 \times 10^{26}$ at 60°C.

a) **What is the order of the reaction? Provide a brief justification of your answer. (1 mark)**

$$Rate\ \text{units} = k\ \text{units}*[A]^m$$

$$[A]^m = \frac{Rate\ \text{units}}{k\ \text{units}} = \frac{\text{mol L}^{-1}\text{s}^{-1}}{\text{s}^{-1}} = M$$

Therefore $m = 1$ and the reaction is first order.

b) **Suppose a reaction is started at 60°C with 1.58 mol/L of N_2O_5. What is $[N_2O_5]$ after the reaction has run for 5 minutes? (3 marks)**

$$\ln\frac{[A]_o}{[A]_t} = kt \quad ①$$

$$\frac{[A]_o}{[A]_t} = e^{kt}$$

① ①

$$[A]_t = \underline{[A]_o} e^{-kt} = (1.58\ \text{mol L}^{-1})\, e^{-(2.8\times10^{-3}\ \text{s}^{-1})(5\ \text{min})(60\ \text{s min}^{-1})} = 0.68\ \text{mol L}^{-1}$$

c) **Suppose it was proposed that this reaction proceeds through a one-step collision of reactants. Explain why this mechanism would not be valid for this reaction. (2 marks)**

If this was a one step reaction then the overall reaction would also be an elementary reaction, with an empirical rate equation: $Rate = k[N_2O_5]^2$. However, the experimentally determined rate equation was first order in N_2O_5. Therefore the proposed mechanism is not consistent with the experimental data and is not valid.

d) **How much faster will this reaction proceed at 60°C if a catalyst is provided that lowers E_a by 15 kJ/mol? (3 marks)**

RATIO ①

$$\left\{ \frac{k_{catalyzed}}{k_{uncatalyzed}} = \frac{Ae^{-\frac{Ea,cat}{RT}}}{Ae^{-\frac{Ea,uncat}{RT}}} \right. \leftarrow ①$$

$$= \exp\left(-\frac{(E_{a,cat} - E_{a,uncat})}{RT}\right) = \exp\left(-\frac{(-15000\ \text{J})}{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(273+60)K}\right) = 230$$

SUBSTITUTIONS
①

e) What is K_c for this reaction at equilibrium at 60°C? (3 marks)

$$K = K_c (RT)^{\Delta n} \quad \text{①}$$

$$K_c = \frac{K}{(RT)^{\Delta n}} = \frac{1.30\times10^{26} \text{ — } 0.5}{\left[\underbrace{(0.08314\text{ L bar K}^{-1}\text{ mol}^{-1})(273+60)K}_{0.5}\right]^{\underbrace{(4+1-2)}_{\text{①}}}} = 6.12\times10^{21}$$

f) Suppose a new reaction was set up at 60°C so that at equilibrium there is 0.569 bar of O_2, and 2.65 bar of NO_2 present. What would be the partial pressure of N_2O_5 in this equilibrium system? (3 marks)

$$K = \frac{p_{NO_2}^4 p_{O_2}}{p_{N_2O_5}^2} \quad \text{①}$$

$$p_{N_2O_5} = \underbrace{\sqrt{\frac{p_{NO_2}^4 p_{O_2}}{K}}}_{0.5} = \underbrace{\sqrt{\frac{(2.65)^4(.569)}{1.3\times10^{26}}}}_{\text{CORRECT SUBSTITUTIONS, K, ①}} = 4.65\times10^{-13}\text{ bar}$$

Question #3. Ammonium perchlorate is a powerful oxidizing agent that is commonly used as a rocket propellant in the reaction:

$$\mathbf{6\ NH_4ClO_4\ (s) + 10\ Al\ (s) \rightarrow 5\ Al_2O_3\ (s) + 6\ HCl\ (g) + 3\ N_2\ (g) + 9\ H_2O\ (g)}$$

The standard reaction enthalpy at 298 K for this reaction is -9245 kJ mol^{-1}.

a) How much heat is produced by a reaction performed in an open vessel at 298 K that consumes 1.00 mol of aluminum? (1 mark)

$\Delta H_R^o = -9245$ kJ per mole of the reaction as it's written. This reaction consumes 10 equivalents of Al(s), so to create a balanced chemical equation that consumes only 1 molar equivalent of Al(s), we must divide it by 10:

$$0.6\ NH_4ClO_4\ (s) + Al\ (s) \rightarrow 0.5\ Al_2O_3\ (s) + 0.6\ HCl\ (g) + 0.3\ N_2\ (g) + 0.9\ H_2O\ (g)$$

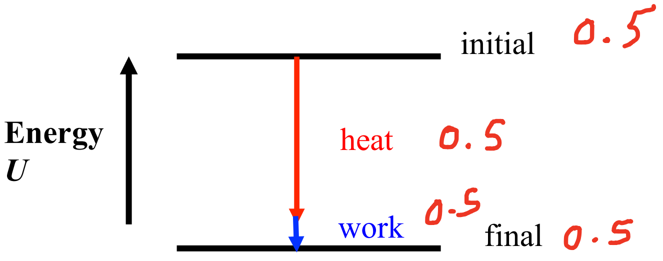
Since I had to divide the chemical equation by 10, I must do the same for the enthalpy. Therefore the heat of this reaction (that consumes 1 molar equivalent of Al(s)) is -924.5 kJ mol^{-1}.

b) How much work would be done in the reaction in part a)? (3 marks)

$$\text{①} \quad \underline{w = -p\Delta V} = -p\left(\frac{n_{final}RT}{p} - \frac{n_{initial}RT}{p}\right) = \underline{(n_{final} - n_{initial})}RT \quad \text{①}$$

$$= -\underbrace{(0.6+0.3+0.9)(8.314\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K})}_{\text{①}} = -4.46\text{ kJ mol}^{-1}$$

c) On the energy level diagram shown below, label the initial and final states, and draw arrows to indicate the work and heat of the process described in part a). (2 marks)



d) Suppose 1 mol of aluminum was reacted with ammonium perchlorate in a bomb calorimeter immersed in 2.55 L of water. If the calorimeter had a heat capacity of 403 J/K, how much would the temperature of the calorimeter increase? (5 marks)

Since it is a constant volume reaction, $\overset{0.5}{\underline{\Delta U_R}} = q_R = \overset{0.5}{\textcircled{-}}\left(q_{calorimeter} + \underset{0.5}{q_{H_2O}}\right)$

$$-q_R = \underbrace{c_{calorimeter}\Delta T}_{\textcircled{1}} + \underbrace{m_{H_2O}c_{H_2O}\Delta T}_{\textcircled{1}}$$

$$\Delta T = \frac{-\left(\Delta H_R + w\right)}{\left(c_{calorimeter} + d_{H_2O}V_{H_2O}c_{H_2O}\right)}$$

$$= \frac{-\left(-924.5\text{ kJ mol}^{-1} - 4.46\text{ kJ mol}^{-1}\right)\overbrace{\left(10^3\text{ J kJ}^{-1}\right)}^{0.5}}{\left(\left(403\text{ J K}^{-1}\right) + \underbrace{\left(1.000\text{ g mL}^{-1}\right)\left(2550\text{ mL}\right)}_{0.5}\left(4.184\text{ J g}^{-1}\text{ K}^{-1}\right)\right)}$$

$$= 84\text{ K}$$

OTHER SUBS
CORRECT:
0.5

Constants and Conversion Factors

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

1 cm^3 = 1 mL 1 dm^3 = 1000 mL = 1 1 m^3 = 1000 L 1 cal = 4.184 J

Avogadro's Number	N	$6.022\text{x}10^{23}$ mol^{-1}
Atomic mass unit	u	$1.66054\text{x}10^{-27}$ kg
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	$8.31451\ \text{m}^3\ \text{Pa}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
	R	$0.0831451\ \text{bar L}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

Data For Water

Density = 1.00 g/mL (at 25°C) c = 4.184 J g^{-1} K^{-1} (liquid) $K_w = 10^{-14}$

Equations Covered Since Midterm 1

$$w = -p\Delta V \qquad \Delta U = U_{final} - U_{initial} = q + w \qquad \Delta H = \Delta U + p\Delta V$$

$$\Delta_r H^o = \sum m\Delta_f H^o(\text{products}) - \sum n\Delta_f H^o(\text{reactants}) \qquad \Delta_r H^o = \sum m\text{BE}(\text{reactants}) - \sum n\text{BE}(\text{products})$$

$$q = c \times m \times \Delta T \qquad \text{Rate} = \frac{1}{v_\text{X}}\frac{\Delta[\text{X}]}{\Delta t} \qquad \text{Rate} = k[\text{A}]^m[\text{B}]^n\ldots \qquad k = Ae^{-\frac{E_a}{RT}}$$

$$[\text{A}]_t - [\text{A}]_o = -kt \qquad \ln\frac{[\text{A}]_o}{[\text{A}]_t} = kt \qquad \frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_o} = kt \qquad t_{\frac{1}{2}} = \frac{[\text{A}]_o}{2k} \qquad t_{\frac{1}{2}} = \frac{\ln 2}{\text{k}}$$

$$t_{\frac{1}{2}} = \frac{1}{k[\text{A}]_o} \qquad \ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad K = K_c(RT)^{\Delta n(\text{gas})} \qquad \ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta_r H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

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

$$K_a \times K_b = K_w \qquad pK_a = -\log K_a \qquad pK_b = -\log K_b$$

Midterm 1 Equations

$$T(\text{in K}) = T(\text{in }^\text{o}\text{C}) + 273.15\text{ K} \qquad n = \frac{m}{M} \qquad \%\text{ Yield} = \frac{\text{actual yield}}{\text{theoretical yield}}$$

$$c(\text{mol/L}) = \frac{n}{V} \qquad m(\text{mol}/kg) = \frac{n_{solute}}{m_{solvent}} \qquad c_1V_1 = c_2V_2 \qquad pV = nRT$$

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \qquad p_T = p_1 + p_2 + p_3 + \ldots \qquad p_A = X_A \times p_T \qquad d = \frac{m}{V} = \frac{p \cdot MM}{RT}$$

$$E_K = \frac{1}{2}m\text{v}^2 \qquad u_{rms} = \sqrt{\frac{3RT}{M}} \qquad \frac{Rate\ A}{Rate\ B} = \sqrt{\frac{M_B}{M_A}} \qquad \left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$