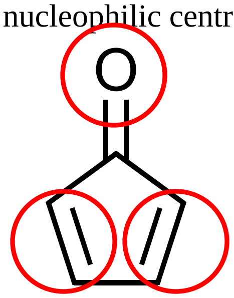
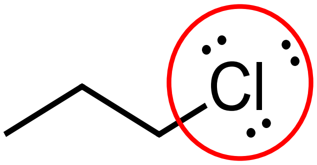
Name:____ Student Number:_______________

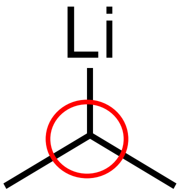
CHEM 1002 A, V Midterm Test #1
February 7, 2014
Calculators Allowed
Make sure this test has 7 pages. You may tear off the last page.

Part A. Answer each of the six questions with a few sentences or equations where necessary. (5 Marks each)

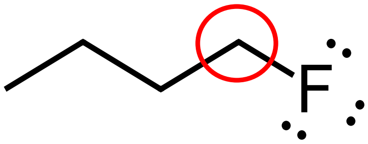
1. (a) Circle the nucleophilic centre(s) in each molecule:

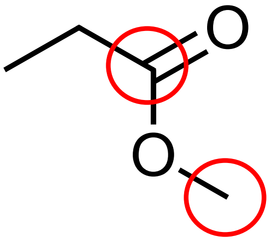






(b) Circle the electrophilic centre(s) in each molecule:





2. For each process, indicate whether ΔH^o and ΔS^o are positive (+), negative (–) or approximately zero (0), and at what temperatures (**high, low, all, or none**) ΔG^o is negative

Process	**ΔH^o**	**ΔS^o**	**ΔG^o**
$2\ C_2H_{2(g)} + 5\ O_{2(g)} \rightarrow 4\ CO_{2(g)} + 2\ H_2O_{(g)}$	–	–	low
$Cl^-_{(g)} + H_2O_{(l)} \rightarrow Cl^-_{(aq)}$	–	–	low
$H_2O_{(s)} \rightarrow H_2O_{(g)}$	+	+	high
$H_2O_{(l)} \rightarrow H_{2(g)} + \frac{1}{2}\ O_{2(g)}$	+	+	high
$CO_{2(g)} + 2\ H_2O_{(g)} \rightarrow CH_{4(g)} + 2\ O_{2(g)}$	+	0	none

3. A reaction has a rate constant k = $6.02 \times 10^5\ m^3\ kg^{-1}\ h^{-1}$. What is the overall order of this reaction?

   Two.

4. For the combustion reaction $C_3H_{8(g)} + 5\ O_{2(g)} \rightleftharpoons 3\ CO_{2(g)} + 4\ H_2O_{(l)}$, which direction will the equilibrium shift (left, right or no change) if:

(a) The container volume is decreased. **Right.** (The pressure will increase, and there are fewer moles of gas on the left)

(b) The temperature is increased. **Left.** (Increasing the temperature moves the reaction in the endothermic direction, and this reaction is exothermic because it is a combustion)

(c) The partial pressure of $O_{2(g)}$ is decreased. **Left.** (According to le Chatelier's principle.)

(d) Some liquid water is added. **No change.** (Liquid water is not involved in the reaction quotient.)

(e) Some $N_{2(g)}$ is added, with the volume kept constant. **No change.** ($N_{2(g)}$ is not involved in the reaction quotient.)

5. Why are S_N1 reactions of tertiary substrates faster than those of primary substrates?

   In an S_N1 reaction, the intermediate is a carbocation. Primary carbocations are less stable than tertiary carbocations, and decompose before the nucleophile attacks them. Thus their concentration is lower, and less of the product is formed per unit time.

6. Reaction A has $\Delta G^o = -34.0$ kJ mol^{-1}. Reaction B has $\Delta G = +34.0$ kJ mol^{-1}. From this information, what can be said about the rates of these two reactions?

   Nothing. G is a state function and does not depend on the reaction rate.

Part B. Answer any three of B1, B2, B3 and B4. (20 marks each)

If you answer all four questions, the best three will count.

B1. For the reaction $3\ BrO^{-}_{(aq)} \rightleftharpoons 2\ Br^{-}_{(aq)} + BrO_3{}^{-}_{(aq)}$, the following data are given:

	$BrO^{-}_{(aq)}$	$Br^{-}_{(aq)}$	$BrO_3{}^{-}_{(aq)}$
ΔH_f^o (kJ mol^{-1})	–94.1	–121.6	–83.68
S^o(J K^{-1}mol^{-1})	41.84	82.42	163.2

(a) [3 marks] Calculate ΔH^o for the reaction (kJ mol^{-1})

$\Delta H^o = 2\ \Delta H_f^o\ (Br^{-}_{(aq)})\ +\ \Delta H_f^o\ (BrO_3{}^{-}_{(aq)}) - 3\ \Delta H_f^o\ (BrO^{-}_{(aq)})$

$= 2(-121.6) + (-83.68) - 3(-94.1)$ kJ mol^{-1} $= -44.58$ kJ mol^{-1}

(b) [3 marks] Calculate ΔS^o for the reaction (J K^{-1} mol^{-1})

$\Delta S^o = 2\ S^o(Br^{-}_{(aq)})\ +\ S^o(BrO_3{}^{-}_{(aq)}) - 3\ S^o(BrO^{-}_{(aq)})$

$= 2(82.42) + 163.2 - 3(41.84)$ J K^{-1} mol^{-1} $= 202.52$ J K^{-1} mol^{-1}

(c) [3 marks] Calculate ΔG^o for the reaction at 25.0°C (kJ mol^{-1})

$\Delta G^o = \Delta H^o - T\Delta S^o$

$= -44580\ \text{J mol}^{-1} - (25.0+273.15)\text{K}\ (202.52\ \text{J K}^{-1}\text{mol}^{-1}) = -104961\ \text{J mol}^{-1} = -105.0\ \text{kJ mol}^{-1}$

(d) [5 marks] Calculate the equilibrium constant of the reaction at 25.0°C.

$$K = e^{\frac{-\Delta G^o}{RT}}$$

$$= e^{\frac{-105000\ \text{J mol}^{-1})}{8.314\text{J K}^{-1}\text{mol}^{-1}(25.0+273.15)\text{K}}}$$

$$= e^{42.3}$$

$$= 2.49\times10^{18}$$

(e) [6 marks] If at equilibrium $[Br^{-}_{(aq)}] = 1.5$ M and $[BrO_3{}^{-}_{(aq)}] = 0.75$ M, calculate $[BrO^{-}_{(aq)}]$.

$$\frac{[Br^{-}_{(aq)}]^2[BrO^{-}_{3(aq)}]}{[BrO^{-}_{(aq)}]^3} = K$$

$$[BrO^{-}_{(aq)}]^3 = \frac{[Br^{-}_{(aq)}]^2[BrO^{-}_{3(aq)}]}{K}$$

$$[BrO^{-}_{(aq)}] = \left(\frac{[Br^{-}_{(aq)}]^2[BrO^{-}_{3(aq)}]}{K}\right)^{1/3}$$

$$= \left(\frac{1.5^2(0.75)}{2.49\times10^{18}}\right)^{1/3}$$

$$= 8.78\times10^{-7}\ \text{M}$$

B2. The atmospheric reaction 2 $HO_{2(g)} \rightarrow H_2O_{2(g)} + O_{2(g)}$ has a rate constant $k = 1.02 \times 10^9$ L $mol^{-1}s^{-1}$ at 25°C.

(a) [4 marks] If at time zero $[HO_2]_o = 1.66 \times 10^{-14}$ M, calculate the half–life of the reaction (s).

From the units of the rate constant, we see this is a second order reaction. For a second order reaction,

$$t_{1/2} = \frac{1}{k[HO_2]_o} = \frac{1}{1.02\times10^9 \text{ L mol}^{-1}\text{ s}^{-1}(1.66\times10^{-14}\text{mol L}^{-1})} = 55060 \text{ s}$$

(b) [6 marks] If at time zero $[HO_2]_o = 1.66 \times 10^{-14}$ M, find $[HO_2]$ after 20000 s.

For a second order reaction,

$$\frac{1}{[HO_2]} = \frac{1}{[HO_2]_o} + 2kt$$

$$= \frac{1}{1.66\times10^{-14}\text{mol L}^{-1}} + 2(1.02\times10^9 \text{L mol}^{-1}\text{s}^{-1})(20000 \text{ s})$$

$$= 6.02\times10^{13} \text{ L mol}^{-1} + 4.08\times10^{13} \text{ L mol}^{-1}$$

$$[HO_2] = \frac{1}{6.02\times10^{13} \text{ L mol}^{-1} + 4.08\times10^{13} \text{ L mol}^{-1}} = 9.90\times10^{-15}\text{mol L}^{-1}$$

(The answer is 1.24×10^{-14} M if you left out the ‘2’ in the integrated rate equation. I realize there is some confusion about the necessity of the ‘2’, so I will also accept this answer.)

(c) [10 marks] The same reaction has $k = 1.07 \times 10^9$ L $mol^{-1}s^{-1}$ at –25°C. Calculate the activation energy of the reaction (kJ mol^{-1}).

$$k_{25^o C} = Ae^{\frac{-E_a}{R(25+273)K}}$$

$$k_{-25^o C} = Ae^{\frac{-E_a}{R(-25+273)K}}$$

$$\frac{k_{25^o C}}{k_{-25^o C}} = \frac{1.02}{1.07} = \frac{Ae^{\frac{-E_a}{R(25+273)K}}}{Ae^{\frac{-E_a}{R(-25+273)K}}} = \frac{e^{\frac{-E_a}{R(25+273)K}}}{e^{\frac{-E_a}{R(-25+273)K}}}$$

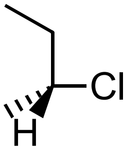
$$\ln\left(\frac{1.02}{1.07}\right) = \frac{-E_a}{R(25+273)K} - \frac{-E_a}{R(-25+273)K}$$

$$= E_a \frac{-1}{R(25+273)K} + \frac{1}{R(-25+273)K}$$

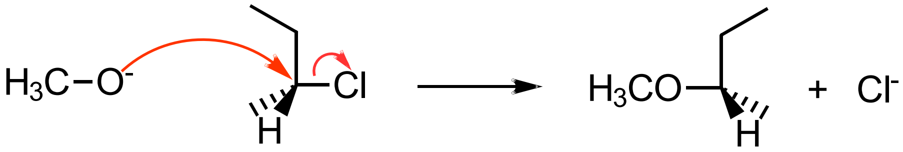
$$E_a = \frac{R \ln\left(\frac{1.02}{1.07}\right)}{\frac{-1}{(298)K} + \frac{1}{(248)K}} = -588 \text{ J mol}^{-1}$$

(Activation energies can be negative!)

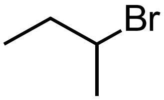
B3. (a) Show the S_N2 mechanism for the reaction of with H_3C-O^-



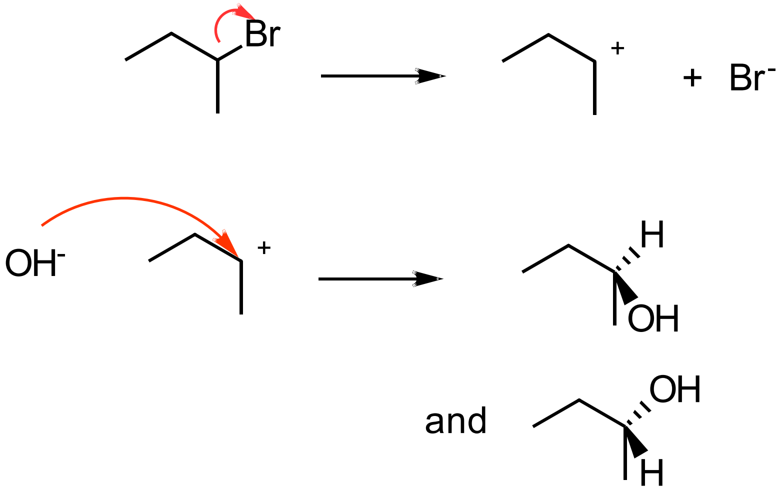
[5 marks] **(**Show the flow of electrons with arrows and draw the product with the proper stereochemistry.)



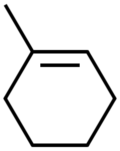
(b) Show an S_N1 mechanism for the reaction of with OH^-



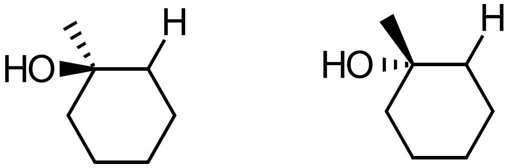
(Show the flow of electrons with arrows and draw the two products with the proper stereochemistries.)



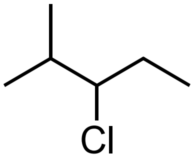
(c) Predict the two <u>major</u> products (with stereochemistries) for the addition reaction of H_2O with



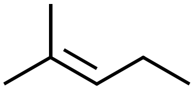
by Markonvikov's rule:



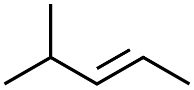
(d) In the elimination reaction of using H_3C-O^- as the base, draw the two



products and indicate which is major and which is minor.



major



minor

(The major product is the more highly substituted alkene)

B4. At 1000°C, the equilibrium constant for the reaction $H_{2(g)} + Br_{2(g)} \rightleftharpoons 2\,HBr_{(g)}$ is 155. $H_{2(g)}$ and $Br_{2(g)}$ are placed in a closed container at 1000°C and initially $p_{H_2} = 0.550\text{ bar}$ and $p_{Br_2} = 0.250\text{ bar}$. Calculate the equilibrium partial pressures of all three gases (bar).

	$H_{2(g)}$	**$Br_{2(g)}$**	**$HBr_{(g)}$**
Initial, bar	0.550	0.250	0
Change, bar	–x	–x	+2x
Equilibrium, bar	0.550–x	0.250–x	2x

At equilibrium,

$$\frac{p_{HBr}^2}{p_{H_2}p_{Br_2}} = K$$

$$\frac{(2x)^2}{(0.55-x)(0.25-x)} = 155$$

$$4x^2 = 155((0.55-x)(0.25-x))$$

$$4x^2 = 155(0.1375 - 0.55x - 0.25x + x^2)$$

$$4x^2 = 21.31 - 124x + 155x^2$$

$$0 = 151x^2 - 124x + 21.31$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$$

$$= \frac{-(-124) \pm \sqrt{(-124)^2 - 4(151)(21.31)}}{2(151)}$$

$$= \frac{124 \pm 50.0}{302}$$

$$= 0.576 \text{ or } 0.245$$

x = 0.576 would result in negative partial pressures of both H_2 and Br_2, thus we choose x = 0.245.

$$
\begin{aligned}
p_{H_2} &= 0.550 - x \\
&= 0.550 - 0.245 \\
&= 0.305 \text{ bar} \\
p_{H_2} &= 0.250 - x \\
&= 0.250 - 0.245 \\
&= 0.005 \text{ bar} \\
p_{HBr} &= 2x = 2(0.245) = 0.490 \text{ bar}
\end{aligned}
$$

$$\text{Check}: \frac{p_{HBr}^2}{p_{H_2} p_{Br_2}} = \frac{(0.490)^2}{(0.305)(0.005)} = 157 = K \ (\pm \text{ roundoff error})$$