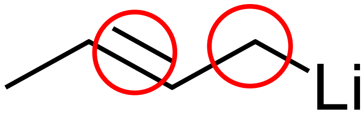
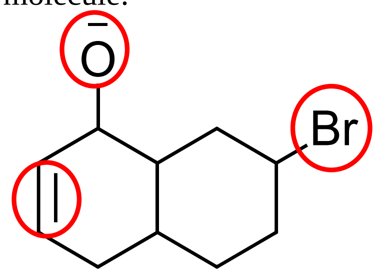
Name:____ Student Number:_______________

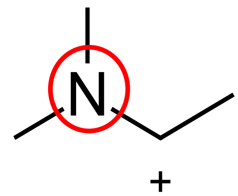
CHEM 1002 A and V Midterm Test #1
February 3, 2017
Calculators Allowed
Make sure this test has 7 pages. You may tear off the last page.

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

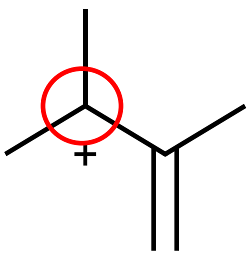
1. (a) Circle any nucleophilic centre(s) in each molecule:

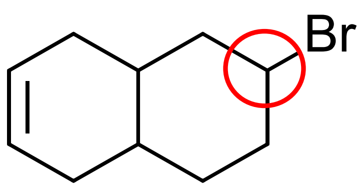


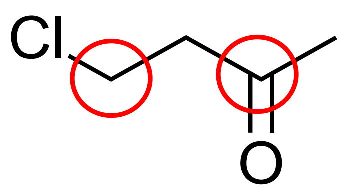




(b) Circle any electrophilic centre(s) in each molecule:







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

Process	**ΔH°**	**ΔS°**	**ΔG°**
$H_2O_{(s)}$ (-25°C) → $H_2O_{(s)}$ (-50°C)	–	–	Low
$H_2O_{(g)}$ → $H_2O_{(s)}$	–	–	Low
2 $Fe_{(s)}$ + 3/2 $O_{2(g)}$ → $Fe_2O_{3(s)}$	–	–	Low
$CO_{2(g)}$ + 2 $H_2O_{(l)}$ → $CH_{4(g)}$ + 3 $O_{2(g)}$	+	+	High
$N_{2(g)}$ + $O_{2(g)}$ → 2 $NO_{(g)}$	–	0	All

3. What does the “2” in “S_N2” signify and why is it a 2?

The”2” signifies that the rate of reaction is proportional to the concentrations of two reactants (the substrate and the nucleophile). It is 2 because these two reagents react together in the first step of the S_N2 mechanism and thus increasing the concentration of either one will cause the rate of reaction to increase.

4. Why are the products of an S_N1 reaction usually a 50:50 mixture of *R* and *S* enantiomers?

In an S_N1 reaction, the first step is loss of the leaving group, which results in a carbocation which has sp^2 hybridization, hence a trigonal planar shape. The nucleophile then attacks from either side with equal probability, resulting in both enantiomers.

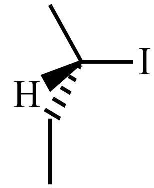
5. Freezing water ice at -25°C is a spontaneous process even though it has $\Delta S < 0$. Why is it spontaneous?

This is an exothermic process, i.e. $\Delta H < 0$, i.e. heat is released to the surroundings. This increases the entropy of the surroundings more than the entropy of the system has decreased. Thus $\Delta S_{universe} > 0$, and so the process is spontaneous.

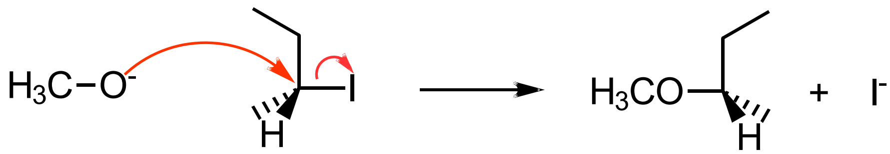
6. The rate law for the reaction $C_2H_5OH_{(g)} + HCl_{(g)} \xrightarrow{H_2SO_4} C_2H_5Cl + H_2O_{(l)}$ is Rate = $k[C_2H_5OH_{(g)}][HCl_{(g)}]$. Why is the H_2SO_4 not included in this rate law?

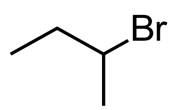
Apparently the H_2SO_4 is catalyst in this process.

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.

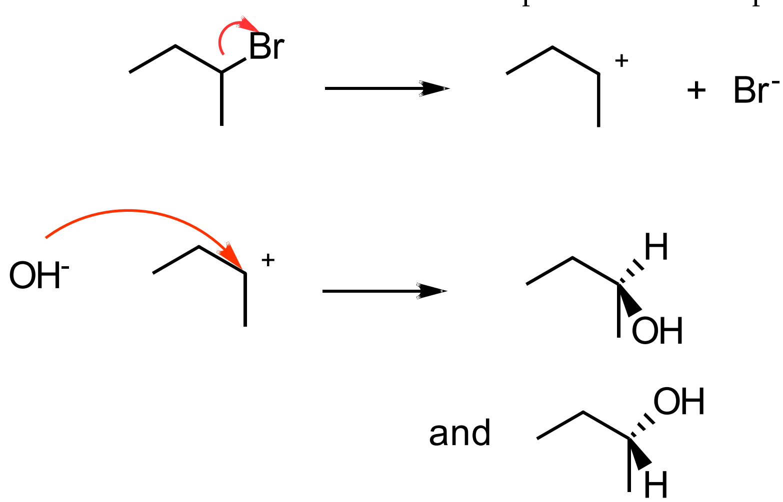
B1. (a) [5 marks] Show the S_N2 mechanism for the reaction of  with H_3C-O^-

(Show the flow of electrons with arrows and draw the product with the proper stereochemistry.)

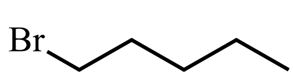


(b) [5 marks] Show an S_N1 mechanism for the reaction of  with OH^-

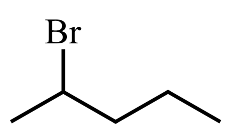
(Show the flow of electrons with arrows and draw the two products with the proper stereochemistries.)



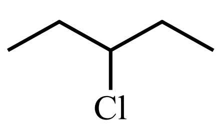
(c) [5 marks] Draw the two possible products in the addition reaction of HBr with 1-pentene and indicate which is major and which is minor.

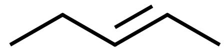


and

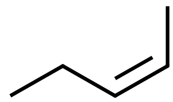


minor major

(d) [5 marks] In the E2 reaction of  using a strong base, draw the two possible products and indicate which is major and which is minor.



major



minor

B2. 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) [4 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) [4 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) [4 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 J mol^{-1} – (25.0+273.15)K (202.52 J K^{-1}mol^{-1}) = –104961 J mol^{-1} = – 105.0 kJ mol^{-1}

(d) [8 marks] Calculate ΔG for the reaction at 50.0°C (kJ mol^{-1}) if $[BrO^-_{(aq)}]$ = 0.5 M, $[BrO_3^-{}_{(aq)}]$ = 0.25 M and $[Br^-_{(aq)}]$ = 0.1 M.

$$\Delta G = \Delta G^o + RT\ln Q$$

$$= \Delta G^o + RT\ln\left(\frac{[Br^-_{(aq)}]^2[BrO_3^-]}{[BrO^-]^3}\right)$$

$$= -105000\ J\,mol^{-1} + 8.314\,J\,K^{-1}mol^{-1}(50+273)K\ln\left(\frac{(0.1)^2(0.25)}{(0.5)^3}\right)$$

$$= -105000\ J\,mol^{-1} + (-10505\,J\,mol^{-1})$$

$$= -115505\ J\,mol^{-1}$$

$$= -115.5\,kJ\,mol^{-1}$$

B3. The atmospheric reaction 2 $HO_{2(g)} \rightarrow H_2O_{2(g)} + O_{2(g)}$ has a rate constant k = 1.02 × 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 with a stoichiometric coefficient of 2,

$$t_{1/2} = \frac{1}{2k[HO_2]_o} = \frac{1}{1.02\times10^9\ \text{L mol}^{-1}\,\text{s}^{-1}(1.66\times10^{-14}\text{mol L}^{-1})} = 29500\ \text{s}$$

(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,

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

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

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

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

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

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

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

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

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

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

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

(Activation energies can be negative!)

B4. (a) Phosgene is a toxic gas prepared by the reaction of chlorine with carbon monoxide: $CO_{(g)} + Cl_{2(g)} \rightarrow COCl_{2(g)}$ The following data were obtained in a kinetic study of its formation:

Trial	**Initial [CO], mol L^{-1}**	**Initial [Cl_2], mol L^{-1}**	**Initial Rate, mol L^{-1} s^{-1}**
1	1.00	0.100	1.29
2	0.100	0.100	0.129
3	0.100	1.00	1.29
4	0.100	0.0100	0.0129

(i) Write the rate law for the formation of phosgene, including the correct orders for the two reactants.

Comparing experiments 1 and 2, we see that decreasing [CO] by a factor of 10 decreases the rate by a factor of 10. The reaction is therefore first order in [CO].
Comparing experiments 2 and 3, we see that increasing [Cl_2] by a factor of 10 increases the rate by a factor of 10. The reaction is therefore first order in [Cl_2] also.
The rate equation is therefore rate = k[CO][Cl_2]

(ii) Calculate the value and units of the rate constant.

Rearranging the rate equation, $k = \dfrac{\text{rate}}{[CO][Cl_2]}$

Using experiment 1 for data (we could use any of the four experiments),

$k = \dfrac{1.29\,\text{mol L}^{-1}\text{s}^{-1}}{1.00\,\text{mol L}^{-1} \times 0.100\,\text{mol L}^{-1}} = 12.9\,\text{L mol}^{-1}\,\text{s}^{-1}$, which has the appropriate units for a second order reaction.

(b) Calculate ΔS_{sys}, ΔS_{surr} and ΔS_{univ} (all in J K^{-1}) when 1.00 mol of $CO_{2(s)}$ at -78.0^{o}C sublimes to $CO_{2(g)}$ in an open beaker at 25.0^{o}C using the following data. Explain why the $CO_{2(s)}$ spontaneously sublimes.

	$CO_{2(s)}$	$CO_{2(g)}$
ΔH_f^o (kJ mol^{-1})	-418.7	–393.5

$$\Delta S_{sys} = \frac{q_{sys}}{T_{sys}} = \frac{25200\text{ J mol}^{-1}}{(-78.0 + 273.15)\text{K}} = +129\text{ J K}^{-1}$$

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-25200\text{ J mol}^{-1}}{(25.0 + 273.15)\text{K}} = -84.5\text{ J K}^{-1}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 129\text{ J K}^{-1} - 84.5\text{ J K}^{-1} = +44.5\text{ J K}^{-1}$$

The dry ice sublimes spontaneously because $\Delta S_{univ} > 0$.

Part A	B1	B2	B3	B4	Total / 90