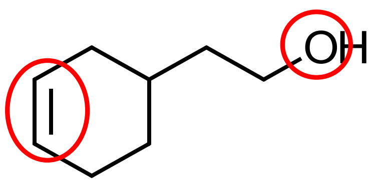
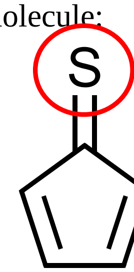
Name:____ Student Number:_______________

CHEM 1002 A, N and V Midterm Test #1
January 30, 2015
Calculators Allowed
Make sure this test has 7 pages. You may tear off the last page.

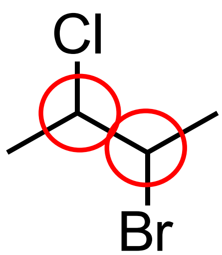
Part A. Answer each of the six questions with a few sentences or equations where necessary. (5 Marks each)

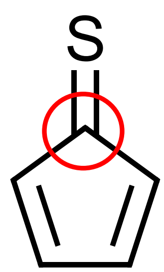
1. (a) Circle the nucleophilic centre(s) in each molecule:

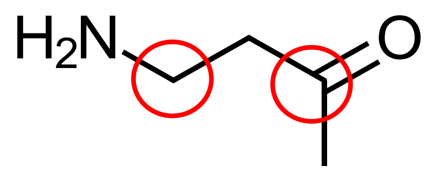




(b) Circle any electrophilic centre(s) in each molecule:







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**
$3\ CO_{2(g)} + 4\ H_2O_{(g)} \rightarrow C_3H_{8(g)} + 5\ O_{2(g)}$	+	–	Never
1 mol $PH_{3(g)}$ at 250°C is cooled to 150°C	–	–	low
$Sb_{(s)} \rightarrow Sb_{(l)}$	+	+	high
$CH_{4(g)} \rightarrow C_{(s)} + 2\ H_{2(g)}$	+	+	high
$C_4H_{10(g)} + 6.5\ O_{2(g)} \rightarrow 4\ CO_{2(g)} + 5\ H_2O_{(g)}$	–	+	all

3. A reaction has a rate constant $k = 4.9 \times 10^{-3}\ L^2\ kg^{-2}\ s^{-1}$. What is the overall order of this reaction? How do you know?

Three, because the units are $concentration^{-2}\ time^{-1}$.

4. Why are the *R* and *S* enantiomers of the product of an S_N1 reaction equally likely?

Once the carbocation is formed in the first step, it has a trigonal planar shape, which is flat. This ion can therefore be attacked by the nucleophile from either side with equal likelihood, and so the two products are equally likely.

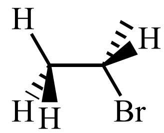
5. Define the terms "catalyst" and "intermediate."

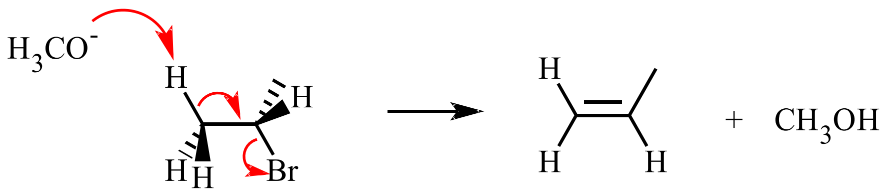
A catalyst is a chemical species that is consumed in an early step in the reaction mechanism and regenerated in a later one. An intermediate is generated in an early step and consumed in a later one.

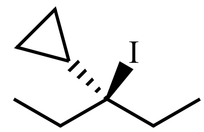
6. Suppose a reaction is not spontaneous under standard conditions. Using the equation $\Delta G = \Delta G^o + RT\ln(Q)$, describe what we can do in the lab to make the reaction become spontaneous.

The equation shows that ΔG, and therefore the spontaneity, of the reaction depends on the reaction quotient Q. If we remove products from the reaction, (or add more reactants), Q decreases, causing ΔG to become more negative, and eventually the reaction will become spontaneous.

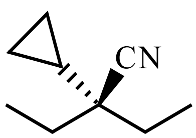
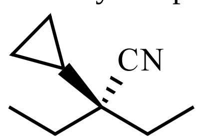
Part B. Answer any three of B1, B2, B3 and B4. (20 marks each)
If you answer all four questions, the best three will count.

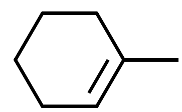
B1. (a) [5 marks] Show the E2 mechanism for the reaction of  with CH_3O^-
(Show the flow of electrons with arrows and draw the products)

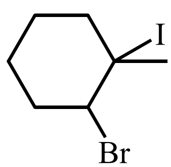


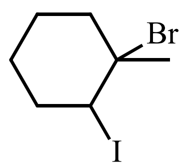
(b) [5 marks] Draw the two possible products of the S_N1 reaction of  with CN^-.

This substrate is not chiral, so in fact there is only one possible product:

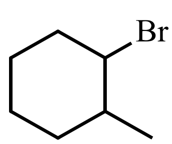
 or  (same

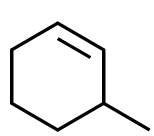
(c) [5 marks] Draw the two possible products in the addition reaction of IBr with  and predict which is major and which is minor.

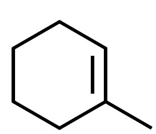

Minor


Major

(The less electronegative I atom attaches preferentially to the carbon having the greater number of H atoms)

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


Minor


Major

(The major product is the more highly substituted alkene)

B2. For the reaction $CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3\ H_{2(g)}$, the following data are given:

	$CH_{4(g)}$	$H_2O_{(g)}$	$CO_{(g)}$	$H_{2(g)}$
ΔH_f^o (kJ mol^{-1})	– 74.6	– 241.8	– 110.5	
S^o(J K^{-1}mol^{-1})	186.3	188.8	197.7	130.7

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

$\Delta H^o = \Delta H_f^o(CO_{(g)}) + 3\ \Delta H_f^o\ (H_{2(g)}) - \Delta H_f^o\ (CH_{4(g)}) - \Delta H_f^o\ (H_2O_{(g)})$

$= -110.5 + 3(0) - (-74.6) - (-241.8)$

$= 205.9$ kJ mol^{-1}

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

$\Delta S^o = S^o(CO_{(g)}) + 3\ S^o\ (H_{2(g)}) - S^o\ (CH_{4(g)}) - S^o\ (H_2O_{(g)})$

$= 197.7 + 3(130.7) - 186.3 - 188.8$ J K^{-1}mol^{-1}

$= 214.7$ J K^{-1}mol^{-1}

(c) [8 marks] Calculate ΔG^o for the reaction at 25.0°C and at 1000°C (kJ mol^{-1})

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

$$\Delta G^o_{25^o C} = 205.9 \text{ kJ} - (25 + 273)\text{K}(0.2147 \text{ kJ K}^{-1}\text{mol}^{-1})$$

$$= 141.9 \text{ kJ mol}^{-1}$$

$$\Delta G^o_{1000^o C} = 205.9 \text{ kJ} - (1000 + 273)\text{K}(0.2147 \text{ kJ K}^{-1}\text{mol}^{-1})$$

$$= -67.4 \text{ kJ mol}^{-1}$$

(d) [6 marks] Find the temperature (°C) at which $\Delta G^o = 0$ for this reaction.

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

$$\text{If } \Delta G^o = 0, \text{ then } \Delta H^o = T\Delta S^o$$

$$\text{or, } T = \frac{H^o}{\Delta S^o}$$

$$= \frac{205.9 \text{ kJ mol}^{-1}}{0.2147 \text{ kJ K}^{-1}\text{mol}^{-1}}$$

$$= 959 \text{ K}$$

$$= 686^o \text{C}$$

B3. The reaction $SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$ has a rate constant $k = 1.02 \times 10^{-6}\ s^{-1}$ at 552 K.

(a) [2 marks] Calculate the half–life of the reaction (s).

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

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.02\times10^{-6}s^{-1}} = 6.79\times10^{5}s$$

(b) [4 marks] If at time zero $[SO_2Cl_2] = 3.4 \times 10^{-4}$ M, find $[SO_2Cl_2]$ after 200 hours.

For a first order reaction, $[A] = [A]_0 e^{-kt}$

$$[SO_2Cl_2] = [SO_2Cl_2]_0\, e^{-kt}$$
$$= 3.4\times10^{-4}M\left(e^{-1.02\times10^{-6}s^{-1}(200\,h)\left(\frac{3600\,s}{h}\right)}\right)$$
$$= 1.63\times10^{-4}M$$

(c) [8 marks] The same reaction has $k = 4.54 \times 10^{-6}\ s^{-1}$ at 572.5 K. Calculate the activation energy (kJ mol^{-1})

$$k_{552K} = Ae^{\frac{-E_a}{R(552\,K)}}$$

$$k_{573\,K} = Ae^{\frac{-E_a}{R(573\,K)}}$$

$$\frac{k_{552\,K}}{k_{573\,K}} = \frac{1.02\times10^{-6}s^{-1}}{4.54\times10^{-6}s^{-1}} = \frac{Ae^{\frac{-E_a}{R(552\,K)}}}{Ae^{\frac{-E_a}{R(573\,K)}}} = \frac{e^{\frac{-E_a}{R(552\,K)}}}{e^{\frac{-E_a}{R(573\,K)}}}$$

$$\ln\left(\frac{1.02\times10^{-6}}{4.54\times10^{-6}}\right) = \frac{-E_a}{R(552\,K)} - \frac{-E_a}{R(573)K} = E_a\left(\frac{-1}{R(552\,K)} + \frac{1}{R(573\,K)}\right)$$

$$E_a = \frac{R\ln\left(\frac{1.02\times10^{-6}}{4.54\times10^{-6}}\right)}{\frac{-1}{552\,K} + \frac{1}{573\,K}} = 1.87\times10^{5}\ J\ mol^{-1} = 187\ kJ\ mol^{-1}$$

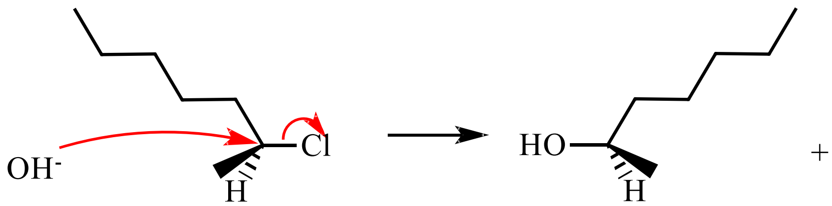
(d) [6 marks] Calculate the pre-exponetial factor (A) for this reaction (s^{-1}).

$$k = Ae^{\frac{-E_a}{RT}}$$

$$A = \frac{k}{e^{\frac{-E_a}{RT}}}$$

$$= \frac{1.02\times10^{-6}s^{-1}}{e^{\frac{-187000\,J\,mol^{-1}}{8.314\,J\,K^{-1}mol^{-1}(552\,K)}}} = 5.07\times10^{11}s^{-1}$$

B4. (a) [6 marks] For the S_N1 reaction of (*S*)–2–bromoheptane with OH^- , draw the reactants, show the flow of electrons with curved arrows and draw and name the product with the correct stereochemistry



The product shown is (*R*)–2–heptanol (or (*R*)–heptan–2–ol), but (*S*)–2–heptanol (or (*S*)–heptan–2–ol) is just as likely since this is an S_N1 mechanism.

(b) [6 marks] A 1 kg piece of dry ice ($CO_{2(s)}$) at –78.5°C is removed from the freezer and placed on a table at 21°C. Calculate the entropy changes in the system, the surroundings and the universe as this dry ice sublimes to $CO_{2(g)}$. The enthalpy of sublimation of CO_2 is 25.2 kJ mol^{-1}. Explain why the dry ice sublimes.

$$1 \text{ kg } CO_{2(s)} = \frac{1000 \text{ g}}{44.0 \text{ g mol}^{-1}} = 22.7 \text{ mol}$$

$$\Delta H = 22.7 \text{ mol}(25.2 \text{ kJ mol}^{-1}) = 573 \text{ kJ}$$

$$\Delta S_{sys} = \frac{+573\times10^3 \text{ J}}{(-78.5+273) \text{ K}} = 2946 \text{ J K}^{-1} \text{ mol}^{-1} \qquad \Delta S_{surr} = \frac{-573\times10^3 \text{ J}}{(21+273) \text{ K}} = -1949 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 2946 - 1949 = +997 \text{ J K}^{-1} \text{ mol}^{-1}$$

The dry ice sublimes because the entropy change in the universe is positive (or because the negative entropy change in the surroundings is more than offset by the positive entropy change when a solid becomes a gas in the system).

(c) [8 marks] For a particular reaction, the activation energy is 20.0 kJ mol^{-1} and this is decreased by 90% when using a catalyst. At 30°C, calculate how many times faster the catalyzed reaction will proceed than the uncatalyzed reaction.

Let k_1 and E_{a1} be the rate constant and activation energy for the uncatalyzed reaction and k_2 and E_{a2} those for the catalyzed reaction. Thus, $E_{a2} = 0.10\, E_{a1}$, and we want to find k_2/k_1.

$$\frac{k_2}{k_1} = \frac{Ae^{\frac{-0.10(E_{a1})}{RT}}}{Ae^{\frac{-E_{a1}}{RT}}} = \frac{e^{\frac{-0.10(E_{a1})}{RT}}}{e^{\frac{-E_{a1}}{RT}}}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-0.10(E_{a1})}{RT} + \frac{E_{a1}}{RT} = \frac{= 0.9E_{a1}}{RT} = \frac{0.9(20000 \text{ J mol}^{-1})}{8.314 \text{ J K}^{-1}\text{mol}^{-1}(30+273)\text{K}} = 7.15$$

$$\frac{k_2}{k_1} = e^{7.15} = 1268$$

In other words, at 30°C, the reaction is 1268 times as fast when using a catalyst.