

Name: _____ Student Number: _____

CHEM 1002 A, N and V Midterm Test #1

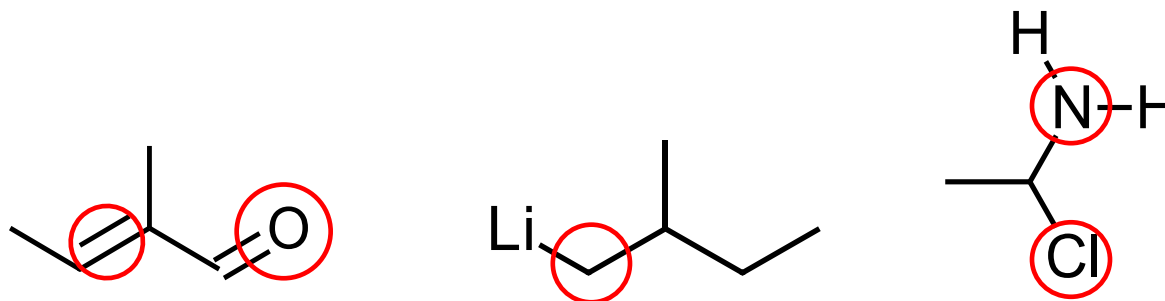
February 4, 2016

Calculators Allowed

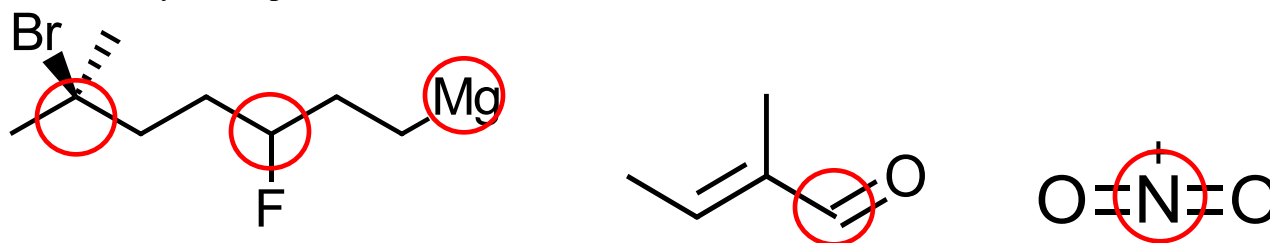
Make sure this test has 7 pages. You may tear off the last page.

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°
$\text{C}_6\text{H}_{12(\text{g})} + 9 \text{O}_{2(\text{g})} \rightarrow 6 \text{CO}_{2(\text{g})} + 6 \text{H}_2\text{O}_{(\text{g})}$	-	+	All
$\text{H}_{2(\text{g})} \rightarrow \text{H}_{2(\text{l})}$	-	-	Low
$\text{Hg}_{(\text{s})} \rightarrow \text{Hg}_{(\text{l})}$	+	+	High
$2 \text{CO}_{2(\text{g})} + 3 \text{H}_2\text{O}_{(\text{g})} \rightarrow \text{C}_2\text{H}_6_{(\text{g})} + 3.5 \text{O}_{2(\text{g})}$	+	-	None
1 mol $\text{H}_{2(\text{g})}$ in 1.00 L at 298 K \rightarrow 1 mol $\text{H}_{2(\text{g})}$ in 0.50 L at 298 K	0	-	None

3. What three factors related to collisions contribute to the value of a rate constant? (Answer with words, not with numbers or equations).

The number of collisions per unit time

The orientations of the collisions

The energies of the collisions

4. Why are S_N1 reactions involving a tertiary substrate faster than those involving a secondary substrate?

In an S_N1 reaction, the first step is loss of the leaving group, which results in a carbocation. Tertiary carbocations are more stable than secondary ones and thus exist for long enough times to be attacked by the nucleophile, resulting in a product. The secondary ones less stable, disappear faster, and so do not exist for long enough to be attacked by the nucleophile.

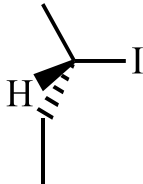
5. If a spontaneous process has $\Delta S_{\text{sys}} < 0$, what must be true about ΔS_{surr} ? Why?

ΔS_{surr} must be positive, and must be more positive than ΔS_{sys} is negative. This is because for spontaneity, $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ must be positive.

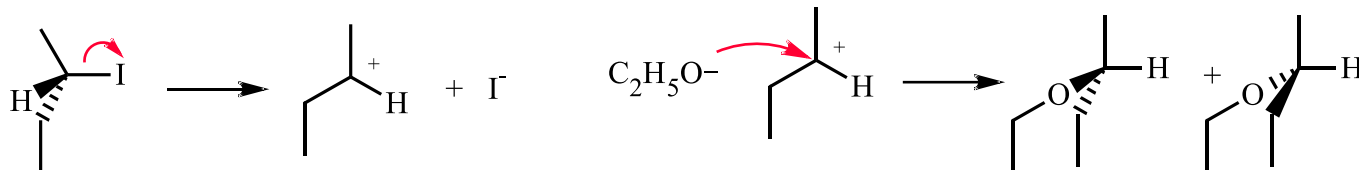
6. Why does a catalyst increase the rate of a reaction?

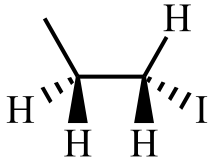
A catalyst provides a different mechanism which has a lower activation energy than the uncatalyzed process.

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.**

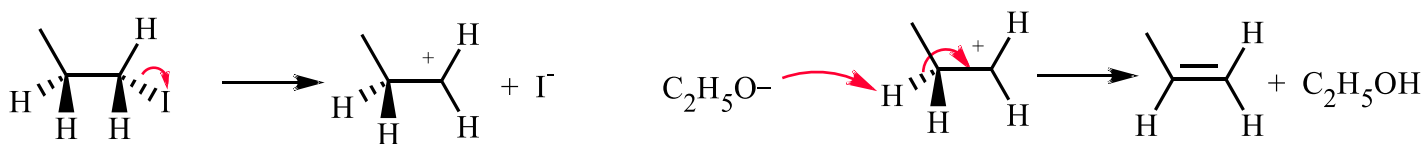
- B1. (a) [5 marks] Show the S_N1 mechanism for the reaction of  with C₂H₅O⁻.

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

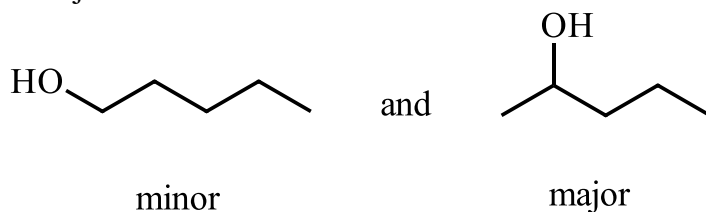


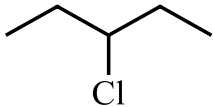
- (b) [5 marks] Show the E₁ mechanism for the reaction of  with C₂H₅O⁻.

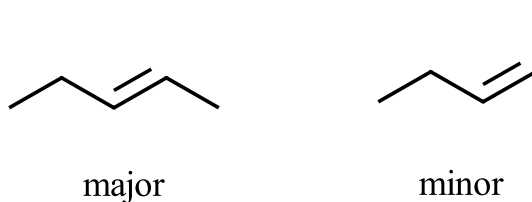
(Show the flow of electrons with arrows and draw the product with the correct stereochemistry)



- (c) [5 marks] Draw the two possible products in the addition reaction of H₂O with 1-pentene and indicate which is major and which is minor.



- (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.



B2. For the reaction $2 \text{ClO}_3^- (\text{aq}) \rightarrow \text{ClO}_2^- (\text{aq}) + \text{ClO}_4^- (\text{aq})$ the following data are given:

	$\text{ClO}_3^- (\text{aq})$	$\text{ClO}_2^- (\text{aq})$	$\text{ClO}_4^- (\text{aq})$
$\Delta H_f^\circ (\text{kJ mol}^{-1})$	-104	-67	-128
$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$	162	101	184

(a) [4 marks] Calculate ΔH° for the reaction (kJ mol^{-1}).

$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ(\text{ClO}_2^- (\text{aq})) + \Delta H_f^\circ(\text{ClO}_4^- (\text{aq})) - 2 \Delta H_f^\circ(\text{ClO}_3^- (\text{aq})) \\ &= -67 + (-128) - 2(-104) \\ &= 13 \text{ kJ mol}^{-1} \end{aligned}$$

(b) [4 marks] Calculate ΔS° for the reaction ($\text{J K}^{-1} \text{mol}^{-1}$).

$$\begin{aligned} \Delta S^\circ &= S^\circ(\text{ClO}_4^- (\text{aq})) + S^\circ(\text{ClO}_2^- (\text{aq})) - 2 S^\circ(\text{ClO}_3^- (\text{aq})) \\ &= 184 + 101 - 2(162) \\ &= -39 \text{ J K}^{-1} \text{mol}^{-1} \end{aligned}$$

(c) [4 marks] Calculate ΔG° for the reaction at 37.0°C (kJ mol^{-1}).

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 13000 \text{ J mol}^{-1} - ((37 + 273)\text{K})(-39 \text{ J K}^{-1} \text{mol}^{-1}) \\ &= 25090 \text{ J mol}^{-1} \\ &= 25.1 \text{ kJ mol}^{-1} \end{aligned}$$

(d) [8 marks] Calculate ΔG for the reaction at 37.0°C (kJ mol^{-1}) if $[\text{ClO}_3^- (\text{aq})] = 0.5 \text{ M}$, $[\text{ClO}_2^- (\text{aq})] = 0.25 \text{ M}$ and $[\text{ClO}_4^- (\text{aq})] = 0.1 \text{ M}$

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ &= \Delta G^\circ + RT \ln \left(\frac{[\text{ClO}_2^-][\text{ClO}_4^-]}{[\text{ClO}_3^-]^2} \right) \\ &= 25100 \text{ J mol}^{-1} + 8.314 \text{ J K}^{-1} \text{mol}^{-1} (37 + 273)\text{K} \ln \left(\frac{(0.25)(0.1)}{(0.5)^2} \right) \\ &= 25100 \text{ J mol}^{-1} + (-5934 \text{ J mol}^{-1}) \\ &= 19165 \text{ J mol}^{-1} \\ &= 19.2 \text{ kJ mol}^{-1} \end{aligned}$$

B3. (a) Assume the reaction $2 \text{HI} \rightarrow \text{H}_2 + \text{I}_2$ has a rate constant $k = 5.33 \text{ L mol}^{-1} \text{ min}^{-1}$.

(i) [2 marks] Calculate the half-life of the reaction (in min) when the initial concentration of HI is 1.5 mol L^{-1} .

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

$$t_{1/2} = \frac{1}{2k[\text{A}]_0} = \frac{1}{2(5.33 \text{ L mol}^{-1} \text{ min}^{-1})(1.5 \text{ mol L}^{-1})} = 0.0625 \text{ min}$$

(ii) [4 marks] If at time zero, $[\text{HI}] = 1.5 \text{ M}$, find $[\text{HI}]$ after 0.500 min.

For a second order reaction, with a stoichiometric coefficient of 2,

$$\begin{aligned} \frac{1}{[\text{A}]} &= \frac{1}{[\text{A}]_0} + 2kt \\ &= \frac{1}{1.5 \text{ mol L}^{-1}} + 2(5.33 \text{ L mol}^{-1} \text{ min}^{-1})(0.500 \text{ min}) \\ &= 0.666 \text{ L mol}^{-1} + 5.33 \text{ L mol}^{-1} \\ &= 5.996 \text{ L mol}^{-1} \end{aligned}$$

$$[\text{A}] = \frac{1}{5.996 \text{ L mol}^{-1}} = 0.167 \text{ mol L}^{-1}$$

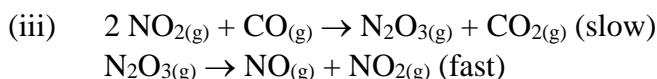
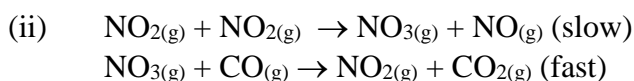
(iii) [8 marks] Calculate the rate of disappearance of HI (in $\text{mol L}^{-1} \text{ min}^{-1}$) when $[\text{HI}] = 1.5 \text{ mol L}^{-1}$.

$$\text{reaction rate} = \frac{-1}{2} \frac{d[\text{HI}]}{dt} = k[\text{HI}]^2$$

$$\begin{aligned} \text{thus, rate of disappearance of HI} &= \frac{d[\text{HI}]}{dt} = 2k[\text{HI}]^2 \\ &= 2(5.33 \text{ L mol}^{-1} \text{ min}^{-1})(1.5 \text{ mol L}^{-1})^2 \\ &= 24.0 \text{ mol L}^{-1} \text{ min}^{-1} \end{aligned}$$

(b) [6 marks] The reaction $\text{NO}_{2(g)} + \text{CO}_{(g)} \rightarrow \text{NO}_{(g)} + \text{CO}_{2(g)}$ has been found by experiment to have the rate law

$\text{rate} = k[\text{NO}_{2(g)}]^2$. Which of the following three mechanisms is consistent with this rate law? Why?



Only the second mechanism predicts that the rate will be second order in $[\text{NO}_{2(g)}]$ and independent of $[\text{CO}_{(g)}]$. Remember that the rate of the overall reaction is that of the slow step, in this case the first, which has only 2 $\text{NO}_{2(g)}$ on the left hand side.

- B4.** (a) Calculate the enthalpy of vapourization of ammonia (kJ mol^{-1}) given the following vapour pressure data:

T, °C	P _{vap} , Pa
-91.9	1333
-45.4	53329

One form of the Clausius-Clapeyron equation is

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right), \text{ which can be rearranged to solve for } \Delta H_{\text{vap}}: \quad \Delta H_{\text{vap}} = \frac{R \ln\left(\frac{p_2}{p_1}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

Here,

$$p_1 = 1333 \text{ Pa at } T_1 = -91.9 + 273.15 = 181.25 \text{ K and } p_2 = 53329 \text{ Pa at } T_2 = -45.4 + 273.15 = 227.75 \text{ K}$$

$$\begin{aligned} \Delta H_{\text{vap}} &= \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \ln\left(\frac{53329 \text{ Pa}}{1333 \text{ Pa}}\right)}{\left(\frac{1}{181.25 \text{ K}} - \frac{1}{227.75 \text{ K}}\right)} = \frac{30.67 \text{ J K}^{-1} \text{ mol}^{-1}}{1.126 \times 10^{-3} \text{ K}^{-1}} = 27,227 \text{ J mol}^{-1} \\ &= 27.2 \text{ kJ mol}^{-1} \end{aligned}$$

- (b) The reaction $\text{Cl} + \text{O}_3 \xrightarrow{k} \text{ClO} + \text{O}_2$ has an activation energy of 260 J mol^{-1} , and at 298 K the rate constant is $7.22 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1}$. Calculate the rate constant at 220 K .

$$k = A e^{\left(\frac{-E_a}{RT}\right)}$$

$$A = \frac{k}{e^{\left(\frac{-E_a}{RT}\right)}} = \frac{7.22 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1}}{e^{\left(\frac{-260 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} (298 \text{ K})}\right)}} = 8.02 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\begin{aligned} k_{250 \text{ K}} &= A e^{\left(\frac{-E_a}{RT}\right)} = 8.02 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1} e^{\left(\frac{-260 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} (220 \text{ K})}\right)} \\ &= 6.96 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

OR

$$\frac{k_2}{k_1} = \frac{A e^{\left(\frac{-E_a}{RT_2}\right)}}{A e^{\left(\frac{-E_a}{RT_1}\right)}} = \frac{e^{\left(\frac{-E_a}{RT_2}\right)}}{e^{\left(\frac{-E_a}{RT_1}\right)}}$$

$$k_2 = k_1 \frac{e^{\left(\frac{-E_a}{RT_2}\right)}}{e^{\left(\frac{-E_a}{RT_1}\right)}} = k_1 e^{\left(\frac{-E_a}{RT_2} + \frac{E_a}{RT_1}\right)} = k_1 e^{\frac{-E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = 7.22 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1} e^{\frac{-260 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{220 \text{ K}} - \frac{1}{298 \text{ K}}\right)} = 6.96 \times 10^9 \text{ mol L}^{-1} \text{ s}^{-1}$$

Part A	B1	B2	B3	B4	Total / 90

Some Useful Constants

$$N_{Av} = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$0^\circ\text{C} = 273.15 \text{ K}$$

PERIODIC TABLE

IA (1)												VIIIA (18)					
1 H 1.008	2 He 4.003											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3 IIB (3)	4 IVB (4)	5 VB (5)	6 VIB (6)	7 VIIB (7)	VIII (8) (9) (10)			11 IB (11)	12 IIB (12)	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.70	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)	110 Ds (269)	111 Rg (280)	112 Cn (277)		114 Fl (289)		116 Lv (253)		

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)