

# **Past Exam and Other Questions, Including mid-terms and finals**

## **Chem. 14-B**

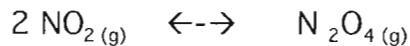
Dr. Eric Scerri

Please Note a couple of points about this book.

1. You may see some questions repeated from one year to the next, sometimes with altered numerical data.
  
2. Some questions may contain typographical errors. This happens because this book has been generated from the files on my computer. Typos are usually noticed during exams and the changes are not always made to the original computer files.

### Thermodynamics

1 Consider the reaction,



For each of the following reactants and products at 25°C, predict the direction in which the reaction will shift to reach equilibrium.

(i)  $p \text{NO}_2 = p \text{N}_2\text{O}_4 = 1.0 \text{ atm.}$

(ii)  $p \text{NO}_2 = 0.50 \text{ atm}, \quad p \text{N}_2\text{O}_4 = 0.21 \text{ atm.}$

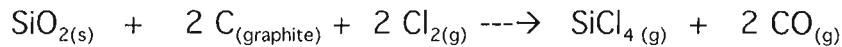
Use the thermodynamic data shown on the page of equations and data.

$$\Delta G^{\circ} \text{ formation for } \text{N}_2\text{O}_{4(g)} = 98 \text{ kJ / mol}$$

$$\Delta G^{\circ} \text{ formation for } \text{NO}_{2(g)} = 52 \text{ kJ / mol}$$

## 2 THERMO QUESTION WITH THE CYCLE FROM HELL.

Given the following data calculate the standard free energy for the given reaction at 25°C,



	$\text{SiO}_{2(s)}$	$\text{C}_{(\text{graphite})}$	$\text{Cl}_{2(g)}$	$\text{SiCl}_{4(g)}$	$\text{CO}_{(g)}$
$\Delta H_f^0$ (kJ/mol)	-910.0	0	0	-657.0	-110.5
$S^\circ$ (J/K.mol)	41.84	5.740	223.0	330.6	197.6

(b). Is the reaction spontaneous or not according to this calculation? Calculate the temperature for which the spontaneity or otherwise would be reversed.

(c) Calculate the equilibrium constant for the above reaction

3a. A balloon filled with 31.9 mol of helium has a volume of 876 L at 0.00 °C and 1.00 atm pressure. At constant pressure, the temperature of the balloon is suddenly increased to 38.0 °C, causing the balloon to expand to a volume of 998L. Calculate q, w and  $\Delta E$  for the helium balloon. (molar heat capacity for He is 20.8 J/°C mol. )

3b. Is enthalpy change alone a reliable guide to whether a reaction is spontaneous? Explain very briefly.

3c. Also discuss what makes a reaction spontaneous in general, including any relevant equation and a discussion on the magnitude and signs of any terms in this equation. Mention all possible combinations.

- 4 Consider an ideal gas which is allowed to expand slowly under constant temperature conditions. Derive an expression for the heat change for such a process, explaining any key stages in the derivation.



carried out at 25 °C and 1 atm. Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta G^\circ$  from the following data.

Substance	$\Delta H^\circ$	$S^\circ$
$\text{SO}_{2\text{(g)}}$	- 297 kJ/mol	248 J/mol.K
$\text{SO}_{3\text{(g)}}$	- 396 ...	257 ...
$\text{O}_{2\text{(g)}}$	0 ...	205 ...

5b. Above what temperature will the above reaction be non-spontaneous?

6     1.50 mol of helium gas is in a cylinder is held at a volume of 22.4 L by a piston at 273K and 1.00 atm. Heat is supplied to the system to double the volume and temperature of the gas while maintaining the internal pressure at 1.00 atm.

A     What is the change in internal energy?

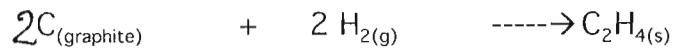
B     How much work is done ?

C     How much heat is added?

D     What is the enthalpy change?

7a State Hess' law. On what important property of enthalpy does this depend upon for its validity?

7b Calculate the enthalpy for the reaction,



given the following data,

reaction	$\Delta H$ in kJ
$C_{\text{(graphite)}} + O_{2(g)} \longrightarrow CO_{2(g)}$	- 393.5
$C_2H_{4(g)} + 3 O_{2(g)} \longrightarrow 2 CO_{2(g)} + 2 H_2O_{\text{l}}$	-1410.9
$H_{2(g)} + 1/2 O_{2(g)} \longrightarrow H_2O_{\text{l}}$	-285.8

- 8 Consider a reaction for which  $\Delta S$  is positive and  $\Delta H$  is negative. Discuss briefly the conditions under which this reaction will not be spontaneous.
- 9 The  $\Delta G^{\circ}$  value for the following reaction is -33.32 kJ.



Calculate  $\Delta G$  for a reaction mixture that contains 1.0 atm.  $\text{N}_2$ , 3.0 atm.  $\text{H}_2$  and 0.50 atm.  $\text{NH}_3$ .

10. The standard enthalpies of formation of methanol, methanal and water are -240, -118, and ~~-286~~ kJ/mol, respectively, and the standard enthalpies of combustion of methanol ( $\text{CH}_3\text{OH}$ ) and methanal ( $\text{HCOH}$ ) are -725 and -561 kJ/mol respectively. *You don't need to use all the data given.*

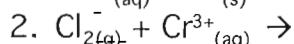
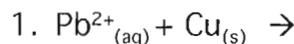
- (a) Define standard enthalpy of formation.
- (b) Define standard enthalpy of combustion
- (c) Calculate the enthalpy change for the oxidation of methanol to methanal.
- (d) Distinguish between bond enthalpy term and bond dissociation enthalpy.

- (e) The standard enthalpy of atomization of methanal is +1567 kJ/mol and the C-H bond enthalpy is + 412 kJ/mol. Calculate the C=O bond enthalpy term.

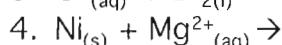
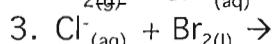


## Electrochemistry

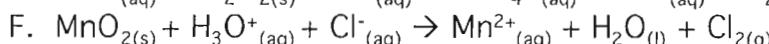
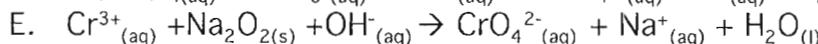
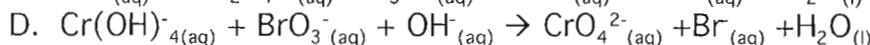
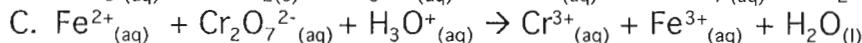
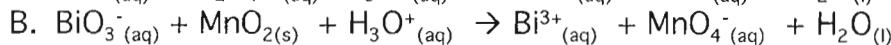
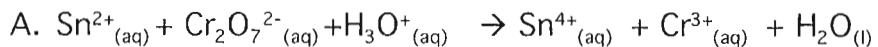
1. Making use of table of standard reduction potentials, predict (a) which of the following sets of reagents react spontaneously, and (b) what the products of each reaction are.



typo in 2. should be  $\text{Cl}^- + \text{Cr}^{3+}$



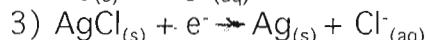
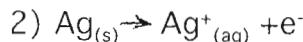
2. Balance the following equations



3. Calculate (a)  $E^\circ_{\text{cell}}$ , (b)  $K_{\text{eq}}$  and (c)  $\Delta G^\circ$  for the system



Using the half cell reactions



- (d) Is the reaction spontaneous? Why?

- (e) Calculate  $[\text{Ag}^+]$  and  $[\text{Cl}^-]$  in (1).

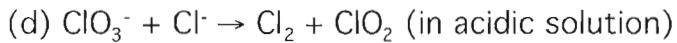
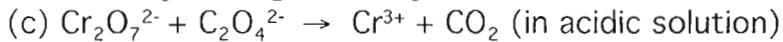
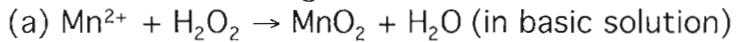
4. For the reaction



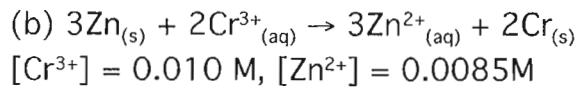
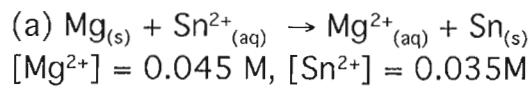
Calculate  $E^\circ$ ,  $\Delta G$  and  $K_{eq}$

What do the magnitude and sign of the above values suggest about the nature of this reaction?

6. Balance the following redox reactions.



7. Calculate  $E^\circ$ , E, and  $\Delta G$  for the following cell reactions.



# Redox.

15

Reaction	$E^\circ$ (volts)
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.34
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.80
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.36
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.87

1

Which of the following would be the best oxidizing agent?

- a)  $\text{Cl}_2$
- b) Fe
- c) Na
- d)  $\text{Na}^+$
- e)  $\text{F}^-$

2

Copper will spontaneously reduce which of the following?

- a)  $\text{Fe}^{2+}$  and  $\text{Ag}^+$
- b)  $\text{Fe}^{2+}$
- c)  $\text{Ag}^+$
- d)  $\text{Al}^{3+}$
- e)  $\text{Fe}^{2+}$  and  $\text{Al}^{3+}$

3

Determine the standard potential,  $E^\circ$ , of a cell that employs the reaction  
 $\text{Fe} + \text{Cu}^{2+} \rightarrow \text{Fe}^{2+} + \text{Cu}$ .

- a) -0.10 V
- b) 0.20 V
- c) 0.10 V
- d) 0.78 V
- e) -0.78 V

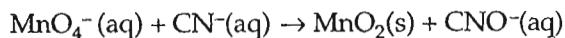
4

An excess of finely divided iron is stirred up with a solution that contains  $\text{Cu}^{2+}$  ion, and the system is allowed to come to equilibrium. The solid materials are then filtered off and electrodes of solid copper and solid iron are inserted into the remaining solution. What is the value of the ratio  $[\text{Fe}^{2+}]/[\text{Cu}^{2+}]$  at 25°C?

- a) 1
- b) 0
- c)  $2.2 \times 10^{26}$
- d)  $4.4 \times 10^{-27}$
- e) none of these

5

When the equation for the following reaction in basic solution is balanced, what is the sum of the coefficients?



- a) 13
- b) 8
- c) 10
- d) 20
- e) 11

6

The following two half-reactions are involved in a galvanic cell. At standard conditions, what species are produced at each electrode?

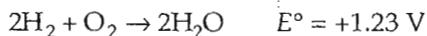
Stand. Reduction Potential

$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.80 V
$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.23 V

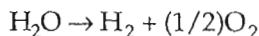
- a) Ag is produced at the cathode and Ni at the anode.
- b) Ag is produced at the cathode and  $\text{Ni}^{2+}$  at the anode.
- c)  $\text{Ag}^+$  is produced at the anode and Ni at the cathode.
- d)  $\text{Ag}^+$  is produced at the anode and  $\text{Ni}^{2+}$  at the cathode.
- e) None of these is correct.

7

Given the standard potential for the reaction of hydrogen and oxygen:



calculate the standard potential for the following reaction:



- a) 1.23 V
- b) 0.625 V
- c) -0.625 V
- d) -1.23 V
- e) -2.46 V

8

How many electrons are transferred in the balanced reaction (i.e., what will be the value of  $n$  in the Nernst equation)?

- a) 5
- b) 6
- c) 30
- d) 22
- e) 2

9

What is the cell potential at 25°C as read on the digital voltmeter?

- a) 0.18 V
- b) 2.58 V
- c) 0.10 V
- d) 0.59 V
- e) 0.26 V

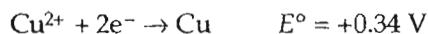
10

What is the value of the equilibrium constant at 25°C for the net spontaneous cell reaction?

- a)  $7.3 \times 10^{-11}$
- b)  $6.1 \times 10^{-92}$
- c) 91
- d)  $1.1 \times 10^3$
- e)  $1.6 \times 10^{91}$

11

A cell is set up with copper and lead electrodes in contact with  $\text{CuSO}_4(\text{aq})$  and  $\text{Pb}(\text{NO}_3)_2(\text{aq})$ , respectively, at 25°C. The standard reduction potentials are:

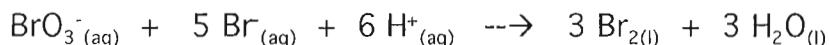


If the  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  are each 1 M, the potential of the cell, in volts, is:

- a) 0.47
- b) 0.92
- c) 0.22
- d) 0.58
- e) none of these

## Kinetics

1a The reaction between bromate ions and bromide ions in aqueous solution is given by the equation,



The table below gives the results of four experiments. Using these data, determine the orders for all three reactants

(b) the overall order and the value of the rate constant including units

Exp'	(Initial concentrations in mol/L)			initial rate in mol/L.s
	$\text{BrO}_3^-$	Br	$\text{H}^+$	
1	0.100	0.100	0.100	$8.0 \times 10^{-4}$
2	0.200	0.100	0.100	$1.6 \times 10^{-3}$
3	0.200	0.200	0.100	$3.2 \times 10^{-3}$
4	0.100	0.100	0.200	$3.2 \times 10^{-3}$

(c) Determine the rate if the concentrations of the three reactants as they appear in the equation are 1.0, 2.0 and 3.0 M respectively.

(d) Explain the term termolecular as it applies to some elementary steps.

(e). The rate constant, k, for the following first-order reaction is  $9.16 \times 10^{-3} \text{ s}^{-1}$  at  $0.0^\circ\text{C}$ . The activation energy of this reaction is 88.0 kJ/mol. Determine the value of k at  $2.0^\circ\text{C}$ .

(f) Determine the value of A.

2. The recombination of iodine atoms to form molecular iodine in the gas phase,



follows second-order kinetics and has the high rate constant of  $7.0 \times 10^9$  M.s at  $23^\circ\text{C}$ .

(a) If the initial concentration of I was 0.086 M, calculate the concentration after 2.0 minutes.

(b) Calculate the half-life of the reaction if the initial concentration of I is 0.60 M and if it is 0.42 M.

(c) Why can the rate law not be obtained from the stoichiometry of a reaction in general? How then can it be obtained?

- 3a Mercury(II) is eliminated from the body by a first order process with a 6 day half life. A farmer accidentally ingests Hg(II) by eating contaminated grain.

What percentage of the Hg(II) would remain in his body after 30 days if no therapeutic measures are taken?

- 3b  $\text{N}_2\text{O}_5$  decomposes with a first order rate constant of  $6.8 \times 10^{-3}$  at 343 K. Calculate the energy of activation given that  $k = 3.5 \times 10^{-5} \text{ s}^{-1}$  at 298 K.

4. A proposed mechanism for a reaction,



- (i) What is the molecularity of the first step?

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- (ii) What is the overall equation based on this mechanism?

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- (iii) What is the order of reaction according to this mechanism?

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- 4b. What three factors must be present for a successful reaction to occur?

- 4c.  $N_2O_5$  decomposes with a first order rate constant of  $6.8 \times 10^{-3} s^{-1}$  at  $70^\circ C$ . Calculate the energy of activation given that  $k = 3.5 \times 10^{-5}$  at  $25^\circ C$ .

- 5a. The dimerization of  $\text{C}_2\text{F}_4$  to  $\text{C}_4\text{F}_8$  is second order with respect to reactant. At  $450^\circ\text{C}$ ,  $k = 0.0448 \text{ L mol}^{-1} \text{ s}^{-1}$ . If the initial concentration of  $\text{C}_2\text{F}_4$  is  $0.100 \text{ mol/L}$  what will it be after 205 seconds?
- 5b. The decomposition of  $\text{N}_2\text{O}_5$  proceeds according to the following reaction,



If the rate of decomposition of  $\text{N}_2\text{O}_5$  at a particular instant in a reaction vessel is  $4.2 \times 10^{-7} \text{ M/s}$ , what is the rate of appearance of  $\text{NO}_2$  and  $\text{O}_2$ ?

6. Derive an expression for the integrated rate law for this 3<sup>rd</sup> order reaction,

$$\text{Rate} = -d[A]/dt = k [A]^3$$

7. Show what quantities would you plot of a graph in order to obtain the rate constant and how precisely would the slope of the graph be related to the rate constant?

## Questions for chem 14-B.

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- 2b. 1.50 mol of helium gas is in a cylinder is held at a volume of 22.4 L by a piston at 273K and 1.00 atm. Heat is supplied to the system to double the volume and temperature of the gas while maintaining the internal pressure at 1.00 atm.

What is the change in internal energy? (2)

- 2c. How much work is done ? (2)

- 2d. How much heat is added? (2)

- 2e. What is the enthalpy change? (2)

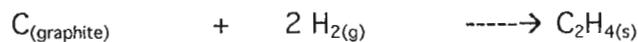
- 3a. State Hess' law. On what important property of enthalpy does this depend upon for its validity? (4 points)

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- 3b. Calculate the enthalpy for the reaction,



given the following data,  
reaction (6 points)  
 $\Delta H$  in kJ

$C_{(\text{graphite})}$	+	$2 O_{2(g)}$	$\longrightarrow$	$CO_{2(g)}$	- 393.5
$C_2H_{4(g)}$	+	$3 O_{2(g)}$	$\longrightarrow$	$CO_{2(g)}$ + $2 H_2O_{(l)}$	-1410.9
$H_{2(g)}$	+	$1/2 O_{2(g)}$	$\longrightarrow$	$H_2O_{(l)}$	-285.8

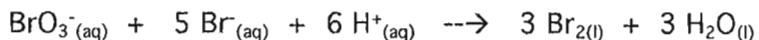
- 3c. Consider a reaction for which  $\Delta S$  is positive and  $\Delta H$  is negative.  
Discuss briefly the conditions under which this reaction will not be spontaneous. (5 points)

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1a The reaction between bromate ions and bromide ions in aqueous solution is given by the equation,



The table below gives the results of four experiments. Using these data, determine the orders for all three reactants

(3 pts),

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- (b) the overall order and the value of the rate constant including units  
(3 pts)

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	$\text{BrO}_3^-$	$\text{Br}^-$	$\text{H}^+$	
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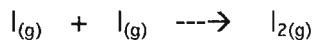
- (c) Determine the rate if the concentrations of the three reactants as they appear in the equation are 1.0, 2.0 and 3.0 M respectively. (2 points)

- (d) Explain the term termolecular as it applies to some elementary steps.  
(2 points)
- 

- (e). The rate constant,  $k$ , for the following first-order reaction is  $9.16 \times 10^{-3} \text{ s}^{-1}$  at  $0.0^\circ\text{C}$ . The activation energy of this reaction is 88.0 kJ/mol. Determine the value of  $k$  at  $2.0^\circ\text{C}$ . (2 points)

- (f) Determine the value of A. (2 points)

7. The recombination of iodine atoms to form molecular iodine in the gas phase,



follows second-order kinetics and has the high rate constant of  $7.0 \times 10^9 \text{ M.s}$  at  $23^\circ\text{C}$ .

(a) If the initial concentration of I was 0.086 M, calculate the concentration after 2.0 minutes. (3 pts)

(b) Calculate the half-life of the reaction if the initial concentration of I is 0.60 M and if it is 0.42 M. (2 pts)

(c) Why can the rate law not be obtained from the stoichiometry of a reaction in general? How then can it be obtained? (4 pts)

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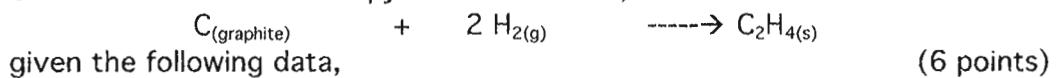
8a. State Hess' law. On what important property of enthalpy does this depend upon for its validity? (4 points)

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8b. Calculate the enthalpy for the reaction,



reaction	$\Delta H$ in kJ
$\text{C}_{(\text{graphite})} + 2 \text{O}_{2(\text{g})} \longrightarrow \text{CO}_{2(\text{g})}$	-393.5
$\text{C}_2\text{H}_{4(\text{g})} + 3 \text{O}_{2(\text{g})} \longrightarrow \text{CO}_{2(\text{g})} + 2 \text{H}_2\text{O}_{(\text{l})}$	-1410.9
$\text{H}_{2(\text{g})} + 1/2 \text{O}_{2(\text{g})} \longrightarrow \text{H}_2\text{O}_{(\text{l})}$	-285.8

The  $\Delta G^0$  value for the following reaction is -33.32 kJ.



Calculate  $\Delta G$  for a reaction mixture that contains 1.0 atm.  $\text{N}_2$ , 3.0 atm.  $\text{H}_2$  and 0.50 atm.  $\text{NH}_3$ . (4)

**Chemistry 14B-2**  
**Dr. Scerri**  
**mid term**  
**May 3rd, 2013**

45 minutes

PROBLEM	SCORE	POINTS
1		12
2		16
3		9
4		20
total		57

Name \_\_\_\_\_

**Last,** first

Signature \_\_\_\_\_

Discussion section or TA name \_\_\_\_\_

ID # \_\_\_\_\_

Please note:

Some questions carry more points than others.

Instructions: This exam has 4 questions and a periodic table at end of exam. Verify you have the right number of pages before you begin. Write your name on each page. Raise your hand if you don't understand a question. SHOW YOUR WORK! No credit will be given for an unsubstantiated or illegible answer. Write legibly, use proper units throughout and use significant figures in all answers. If you exceed the line limit any additional material will not be read by graders

Good luck!

$$P V = n R T, \quad R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}, = 0.0820578 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ L atm} = 101.325 \text{ J} \quad 1 \text{ calorie} = 4.184 \text{ Joules}$$

$$P_A = X_A P_T \quad \Delta E = (3/2) n R T$$

$$\Delta E = q + w, \quad \Delta G^0 = \Delta H^0 - T \Delta S^0$$

$$\Delta G = \Delta G^0 + RT \ln Q \quad \Delta S = q_{\text{rev}} / T$$

$$\Delta G^0 = -RT \ln K \quad \Delta G = -T \Delta S$$

$$S = k_B \ln W$$

$$\Delta H^0_{\text{reaction}} = \sum \Delta H^0_{\text{formation products}} - \sum \Delta H^0_{\text{formation reactants}}$$

$$\ln [A] = -kt + \ln [A]_0 \quad t_{1/2} = \ln(2) / k$$

$$1 / [A] = kt + 1 / [A]_0 \quad t_{1/2} = 1 / k [A]_0$$

$$\ln (k_1 / k_2) = E_A / RT (1 / T_2 - 1 / T_1)$$

$$k = A e^{-E_A/RT}$$

$$\Delta G = -n F E$$

$$E^0_{\text{cell}} = E^0_{\text{red}} + E^0_{\text{ox}}$$

$$\text{or } E^0_{\text{cell}} = (E^0_{\text{more+}}) - (E^0_{\text{more-}})$$

$$E = E^0 - (RT/nF) \ln Q$$

$$E = E^0 - (0.0592/n) \ln Q \quad \text{at 298 K}$$

$$\# \text{ of moles deposited} = (It)/nF$$

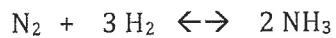
- 1(a) An equation for work done by gas expansion is  $w = -P \Delta V$ . Under what conditions is this true? Also explain how this equation can be used to obtain an equation for the heat accompanying the same process. Again explain any assumptions. (4)

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- 1(b) The  $\Delta G^{\circ}$  value for the following reaction is -33.32 kJ.



- Calculate  $\Delta G$  for a reaction mixture at 50°C that contains the following gases with the following partial pressures, 6.0 atm. N<sub>2</sub>, 3.0 atm. H<sub>2</sub> and 0.70 atm. NH<sub>3</sub>. (4)

- 1(c) Discuss the spontaneity of a reaction for which  $\Delta S$  is positive and  $\Delta H$  is positive. (2)

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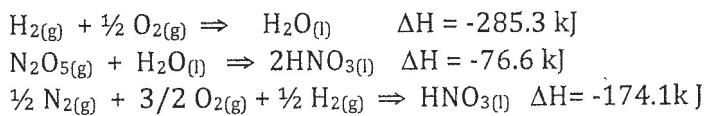
- 1(d) Discuss the spontaneity of a reaction for which  $\Delta S$  is negative and  $\Delta H$  is negative. (2)

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2(a) Given the following data,



calculate  $\Delta H$  for the reaction  $2\text{N}_2\text{(g)} + 5\text{O}_2\text{(g)} \Rightarrow 2\text{N}_2\text{O}_5\text{(g)}$  (6)

2b. How can the Arrhenius formula for the rate constant be used to obtain activation energy experimentally? (4)

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2c. Under what conditions does the following equation apply? What is the main assumption made in the derivation of this equation and how can this assumption be realized in practice? (6)

$$w = -P\Delta V$$

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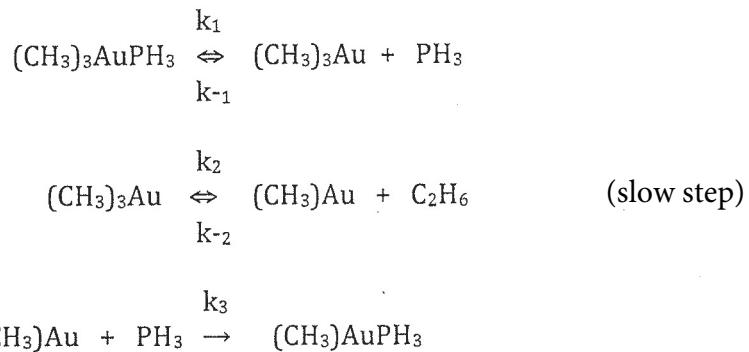


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3(a) In a hydrocarbon solution the gold compound  $(CH_3)_3AuPH_3$  into  $C_2H_6$  and  $(CH_3)AuPH_3$ . The following mechanism is proposed for the decomposition of the first gold compound,



Write the overall reaction (2)

Obtain a rate law based on this mechanism (4)

3(b) The following data were obtained at  $25^\circ C$  for the reaction,  
 $C_2H_5Br + OH^- = C_2H_5OH + Br^-$

Determine the rate law for the reaction from these data. (3)

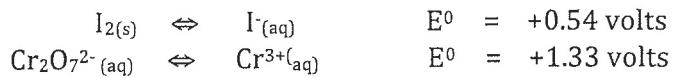
<u><math>[C_2H_5Br]</math></u>	<u><math>[OH^-]</math></u>	<u>Rate</u>
0.150	0.200	$4.8 \times 10^{-5}$
0.150	0.400	$4.8 \times 10^{-5}$
0.450	0.200	$4.32 \times 10^{-4}$

Choose one correct answer (a) Rate =  $k[C_2H_5Br]^2$  (b) Rate =  $k[OH^-]^2$

(c) Rate =  $k[C_2H_5Br][OH^-]$  (d) Rate =  $k[C_2H_5Br]^2[OH^-]$

(e) Rate =  $k[C_2H_5Br]^2[OH^-]$

4(a) Consider 2 half-cells one consisting of iodine and the other of the dichromate ion. Give balanced half-cell equations for each half-cell involving the following compounds of these metals. Assume basic conditions. (8)



4(b) Use the standard reduction potential data to predict the direction in which the reaction will occur and explain your reasoning. (3)

4(c) State what is being oxidized and what is being reduced in each half-cell and identify the anode and cathode. (4)

4(d) Explain briefly how standard half-cell reduction potentials are actually measured.

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(3)

4(e) Calculate the cell potential of the above iodine - dichromate cell. (2)

**Chemistry 14B**   
**Dr. Scerri**  
**mid term**  
**April 27<sup>th</sup>, 2011**

50 minutes

PROBLEM	SCORE	POINTS
1		12
2		12
3		12
4		18
total		54

Name \_\_\_\_\_

**Last,** first

Signature \_\_\_\_\_

ID # \_\_\_\_\_

**Please note:**

**Some questions carry more points than others.**

**Instructions:** This exam has 4 questions and a periodic table at end of exam. Verify you have the right number of pages before you begin. Write your name on each page. Raise your hand if you don't understand a question. **SHOW YOUR WORK!** No credit will be given for an unsubstantiated or illegible answer. Write legibly, use proper units throughout and use significant figures in all answers. **If you exceed the line limit any additional material will not be read by graders**

Good luck!

$$P V = n R T, \quad R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}, = 0.0820578 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

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$$1 \text{ calorie} = 4.184 \text{ Joules}$$

$$P_A = X_A P_T$$

$$\Delta E = (3/2) n R T$$

$$\Delta E = q + w,$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

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$$\Delta S = q_{\text{rev}} / T$$

$$\Delta G^0 = -RT \ln K$$

$$\Delta G = -T \Delta S$$

$$S = k_B \ln W$$

$$\ln [A] = -kt + \ln [A]_0$$

$$t_{1/2} = \ln(2) / k$$

$$1/[A] = kt + 1/[A]_0$$

$$t_{1/2} = 1/k [A]_0$$

$$\ln(k_1/k_2) = E_A / RT (1/T_2 - 1/T_1)$$

$$k = A e^{-E_A/RT}$$

$$\Delta G = -nFE$$

$$\begin{aligned} E_{\text{cell}}^0 &= E_{\text{red}}^0 + E_{\text{ox}}^0 \\ \text{or } E_{\text{cell}}^0 &= (E_{\text{more+}}^0) - (E_{\text{more-}}^0) \end{aligned}$$

$$E = E^0 - (RT/nF) \ln Q$$

$$E = E^0 - (0.0592/n) \ln Q \quad \text{at 298 K}$$

$$\# \text{ of moles deposited} = (It)/nF$$

1(a) Explain the sign convention used for work and heat (2 points)

1(b) State the second law of thermodynamics in words. (2)

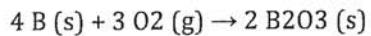
1(c) Using the following values for entropy determine if a reaction would be spontaneous for each case I, II and III. (6)

- I)  $\Delta S_{sys} = 30 \text{ J/K}$ ,  $\Delta S_{surr} = 50 \text{ J/K}$
- II)  $\Delta S_{sys} = 60 \text{ J/K}$ ,  $\Delta S_{surr} = -85 \text{ J/K}$
- III)  $\Delta S_{sys} = 140 \text{ J/K}$ ,  $\Delta S_{surr} = -85 \text{ J/K}$

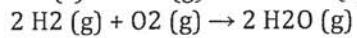
1(d) Discuss the spontaneity of a reaction for which  $\Delta S$  is negative and  $\Delta H$  is positive. (2)

1(e) Discuss the spontaneity of a reaction for which  $\Delta S$  is negative and  $\Delta H$  is negative. (2)

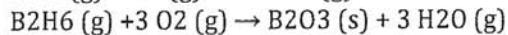
2(a) The standard molar enthalpy of formation,  $\Delta H_f^\circ$ , for diborane,  $B_2H_6$  (g), cannot be found directly because the compound cannot be prepared by the reaction of boron and hydrogen. It can be calculated, however, using the following reactions:



$$\Delta H_{rxn}^\circ = - 2543.8 \text{ kJ}$$



$$\Delta H_{rxn}^\circ = - 484. \text{ kJ}$$



$$\Delta H_{rxn}^\circ = - 2032.9 \text{ kJ}$$

Calculate  $\Delta H_f^\circ$  for  $\text{B}_2\text{H}_6$  (g).

(6)

Now do the calculation using the 'vector method'.

(6)

3(a) Nitrogen monoxide converts ozone into molecular oxygen, as follows,

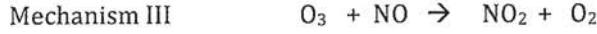
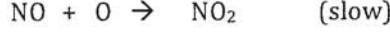
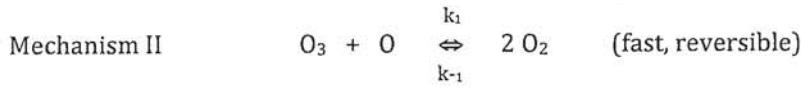
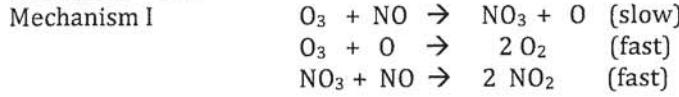


The experimental rate law is,                              Rate =  $k [\text{NO}] [\text{O}_3]$

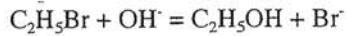
Which of the following mechanism are consistent with the experimental rate law?

Show your work.

(9)



3(b) The following data were obtained at 25° C for the reaction



Determine the rate law for the reaction from these data.

(3)

<u>[C<sub>2</sub>H<sub>5</sub>Br]</u>	<u>[OH<sup>-</sup>]</u>	<u>Rate</u>
0.150	0.200	$4.8 \times 10^{-5}$
0.300	0.200	$9.6 \times 10^{-5}$
0.450	0.200	$14.4 \times 10^{-5}$
0.300	0.600	$28.8 \times 10^{-5}$

Choose one correct answer

- (a) Rate =  $k[\text{C}_2\text{H}_5\text{Br}]$                               (b) Rate =  $k[\text{C}_2\text{H}_5\text{Br}]^2$   
 (c) Rate =  $k[\text{C}_2\text{H}_5\text{Br}][\text{OH}^-]$                       (d) Rate =  $k[\text{C}_2\text{H}_5\text{Br}]^2[\text{OH}^-]$   
 (e) Rate =  $k[\text{C}_2\text{H}_5\text{Br}]^2[\text{OH}^-]^3$

4(a) Consider 2 half cells one consisting of titanium compounds and the other of tantalum compounds. Give balanced half-cell equations for each half-cell involving the following compounds of these metals. Assume basic conditions.

(

8)



4(b) Use the standard reduction potential data to predict the direction in which the reaction will occur and explain your reasoning. Write an equation for the reaction that occurs. (3)

4(c) State what is being oxidized and what is being reduced in each half-cell. (2)

4(d) Explain briefly how standard half-cell reduction potentials are actually measured.

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(3)

4(e) Calculate the cell potential of the above titanium – tantalum cell. (2)



**Chemistry 14-B**  
**Dr. E. Scerri**  
**Final Exam**  
**June, 2011**  
**Three hours**

PROBLEM	SCORE	POINTS
1		22
2		22
3		18
4		24
5		14
6		19
7		22
8		24
total		165

Name \_\_\_\_\_  
Last \_\_\_\_\_ First \_\_\_\_\_

Student ID \_\_\_\_\_

Signature \_\_\_\_\_

Total of 8 questions with varying numbers of points.

Please note: Any activities that remotely resemble cheating will be treated very seriously!

Name \_\_\_\_\_

$$P V = n R T, \quad R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}, = 0.0820578 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

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$$k = A e^{-E_A/RT}$$

$$\Delta G = -n F E \quad E^0_{cell} = E^0_{red} + E^0_{ox}$$

$$\Delta G^0 = -n F E^0 \quad E^0_{cell} = (E^0_{more+}) - (E^0_{more-})$$

$$E = E^0 - (RT/nF) \ln Q$$

$$E = E^0 - (0.0592/n) \ln Q \quad \text{at } 298 \text{ K}$$

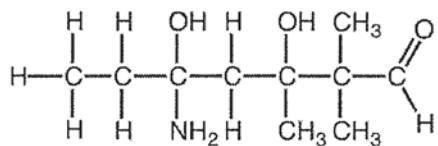
$$\# \text{ of moles deposited} = (It)/nF$$

**order of priority for naming:** carboxylic acid > ester > acyl halide > amide > nitrile > aldehyde > ketone > alcohol > amine > alkyl group > ether > halogen

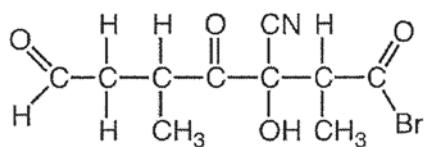
Name \_\_\_\_\_

- 1a. Consider the formula C<sub>5</sub>H<sub>12</sub>O<sub>1</sub> and find 8 structural isomers of this compound. Bear in mind that four of these should belong to one homologous series and the other four to an entirely different series. (There is no need to draw all the H atoms). (8)

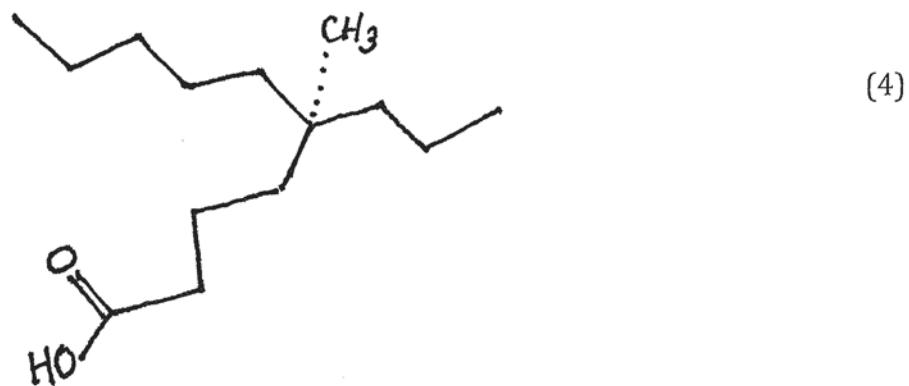
- 1b. Name the following compounds,



(5)

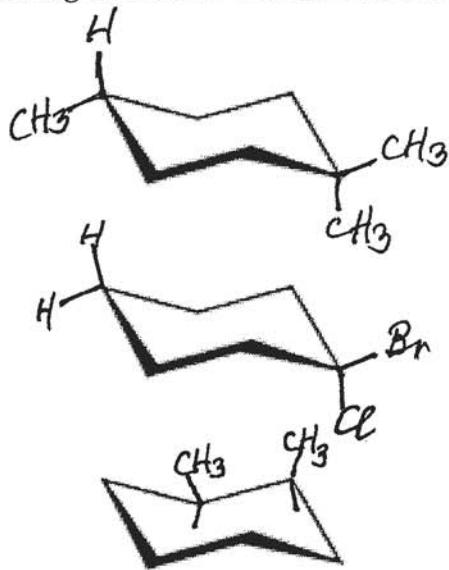


(5)



Name \_\_\_\_\_

2. In which of the following molecules will the two chair forms be equivalent in terms of stability? (3)



In each case explain your answer.

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- 2b. Assuming the gauche and anti conformers of 1,2 dibromoethane differ by 6.50 kJ/mole, calculate the relative proportion of the two forms at 150°C. (5)

- 2c. Draw the two forms using the Newman projections and also using sawhorse projections. A total of four diagrams is required. (8) total 22

Name \_\_\_\_\_

3a. Consider the monomer  $\text{CH}_2=\text{CBr}_2$  or 1,1 dibromoethene and draw the polymer former from it. Also suggest a name for the polymer. (2)

3b. Explain the term condensation reaction as it is used in organic chemistry and give an example of such a reaction that involves a carboxylic acid of your choice and an amine of your choice. (the full reaction equation is required). (4)

3c. How is condensation polymerization different from addition polymerization? (3)

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3d. Explain three factors, with examples of each, that make the element carbon the basis of organic chemistry. (6)

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3e. What was the significance of Wohler's synthesis of urea,  $\text{CO}(\text{NH}_2)_2$  ?

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Name \_\_\_\_\_

**18**

4a.

Redraw several versions of this molecule and modify it if necessary in order to explain the terms (i) chair flip, (ii) 1,3 di-axial interaction. (6)

4b. Explain the difference between geometrical isomerism and structural isomerism, including how each type arises and how properties differ among isomers. (6)

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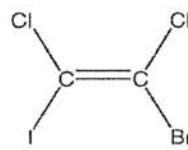
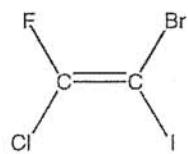


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4c. Name the following molecules, using systematic IUPAC names rather than common names, (4)



4d. Give and explain the detailed mechanism for the reaction of  $\text{CN}^-$  with the organic molecule,  $\text{CH}_2\text{BrC}(\text{CH}_3)_3$  and explain any terms you have used. (8)

X

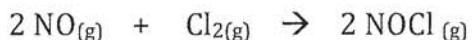
Name \_\_\_\_\_

5a. The following reaction of  $\text{NO}_2$  has been studied as a function of temperature. The rate constant was found to be  $2.7 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  at  $227^\circ\text{C}$  and  $2.4 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$  at  $277^\circ\text{C}$ .



Calculate the activation energy. (5)

5b. The following rates of reaction were obtained in three experiments with the reaction,



expt	initial $[\text{NO}]$ , M	Initial $[\text{Cl}_2]$ , M	Initial Rate, $\text{M s}^{-1}$
1	0.0125	0.0255	$2.27 \times 10^{-5}$
2	0.0125	0.0510	$4.45 \times 10^{-5}$
3	0.0250	0.0255	$9.08 \times 10^{-5}$

Determine the rate law. (4)

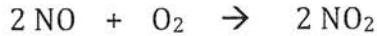
5c. In the first order reaction,  $\text{A} \rightarrow \text{products}$ , it is found that 99% of the original amount of reactant A decomposed in 137 minutes. What is the half-life of this decomposition reaction? (4)

Name \_\_\_\_\_

6a. Derive an expression for the work done by an isothermal gas expansion against a force. Assume that the gas is ideal and that the expansion is carried out in a reversible or controlled manner. (6)

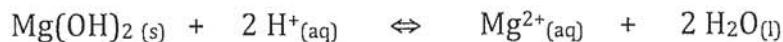
6b. What is the standard molar entropy of vaporization of water at 373K given that the standard molar enthalpy of vaporization is 40.7 kJ/mol? (3)

6c. Consider the following reaction and calculate the standard Gibbs Free Energy for it,



given that  $\Delta H^0 = -114.1 \text{ kJ}$  and  $\Delta S^0 = -146.5 \text{ J.K}^{-1}$ . Also comment on the spontaneity or otherwise of this reaction at 298K. Are there any conditions under which your answer might be different? If so state this condition. (6)

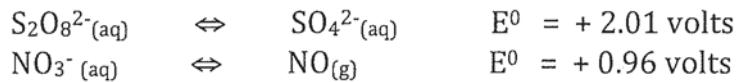
6d. Now consider a completely different reaction,



If  $\Delta G^0 = -95.5 \text{ kJ/mol}$ . calculate the equilibrium constant at  $50^\circ\text{C}$ . (4). Total 19

Name \_\_\_\_\_

- 7a. Here are a couple of half-cell equations (unbalanced)



Predict which element is oxidized and which is reduced and briefly explain your reasoning. (4)

- 7b. Write a balanced reaction for what actually happens spontaneously. (10)  
(Assume basic conditions)

- 7c. Calculate the cell emf. (3)

- 7d. Give a schematic representation for the cell using the accepted cell convention. (Not a diagram of actual glassware etc.) (5)

Name \_\_\_\_\_

8. Briefly explain the following terms or phrases, and any relevant points about them. This question is deliberately left somewhat open to see if you have understood the connections with the rest of the subject matter. You should choose what you think is relevant/important. (3 each) total **24**

(a) Racemic mixture

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(b) R and S notation

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(c) half-life

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(d) molecularity

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(e) the mechanical equivalence of heat

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(f) steric strain

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(g) cracking reaction

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(h) the sign convention for electrodes in a Galvanic cell

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<b>1</b> <b>H</b> 1.0080 Hydrogen	<b>2</b> <b>He</b> 4.003 Helium
<b>3</b> <b>Li</b> 6.941 Lithium	<b>4</b> <b>Be</b> 9.013 Beryllium
<b>11</b> <b>Na</b> 22.990 Sodium	<b>12</b> <b>Mg</b> 24.305 Magnesium
<b>19</b> <b>K</b> 39.098 Potassium	<b>20</b> <b>Ca</b> 40.08 Calcium
<b>37</b> <b>Rb</b> 85.468 Rubidium	<b>21</b> <b>Sc</b> 44.96 Scandium
<b>55</b> <b>Cs</b> 132.91 Cesium	<b>22</b> <b>Ti</b> 47.90 Titanium
<b>87</b> <b>Fr</b> (223) Francium	<b>23</b> <b>V</b> 50.94 Vanadium
<b>88</b> <b>Ra</b> 226.025 Radium	<b>24</b> <b>Cr</b> 51.996 Chromium
	<b>25</b> <b>Mn</b> 54.94 Manganese
	<b>26</b> <b>Fe</b> 55.85 Iron
	<b>27</b> <b>Co</b> 58.94 Cobalt
	<b>28</b> <b>Ni</b> 58.71 Nickel
	<b>29</b> <b>Cu</b> 63.55 Copper
	<b>30</b> <b>Zn</b> 65.38 Zinc
	<b>31</b> <b>Ga</b> 69.72 Gallium
	<b>32</b> <b>Ge</b> 72.60 Germanium
	<b>33</b> <b>As</b> 74.92 Arsenic
	<b>34</b> <b>Se</b> 78.96 Selenium
	<b>35</b> <b>Br</b> 79.904 Bromine
	<b>36</b> <b>Kr</b> 83.80 Krypton
	<b>5</b> <b>B</b> 10.81 Boron
	<b>6</b> <b>C</b> 12.011 Carbon
	<b>7</b> <b>N</b> 14.007 Nitrogen
	<b>8</b> <b>O</b> 15.999 Oxygen
	<b>9</b> <b>F</b> 18.998 Fluorine
	<b>10</b> <b>Ne</b> 20.179 Neon
	<b>13</b> <b>Al</b> 26.98 Aluminum
	<b>14</b> <b>Si</b> 28.09 Silicon
	<b>15</b> <b>P</b> 30.974 Phosphorus
	<b>16</b> <b>S</b> 32.066 Sulfur
	<b>17</b> <b>Cl</b> 35.453 Chlorine
	<b>18</b> <b>Ar</b> 39.948 Argon
	<b>31</b> <b>In</b> 114.82 Indium
	<b>32</b> <b>Sn</b> 118.70 Tin
	<b>33</b> <b>Sb</b> 121.75 Antimony
	<b>34</b> <b>Te</b> 127.60 Tellurium
	<b>35</b> <b>I</b> 126.905 Iodine
	<b>36</b> <b>Xe</b> 131.30 Xenon
	<b>5</b> <b>B</b> 10.81 Boron
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**Chemistry 14B  
Dr. Scerri  
mid term  
May 2nd, 2012**

40 minutes

PROBLEM	SCORE	POINTS
1		13
2		15
3		14
4		12
total		54

Name \_\_\_\_\_

**Last,**

first

Discussion Section \_\_\_\_\_

Signature \_\_\_\_\_

ID # \_\_\_\_\_

**Please note:**

**Some questions carry more points than others.**

**Instructions:** This exam has 4 questions and a periodic table at end of exam. Verify you have the right number of pages before you begin. Write your name on each page. Raise your hand if you don't understand a question. **SHOW YOUR WORK!** No credit will be given for an unsubstantiated or illegible answer. Write legibly, use proper units throughout and use significant figures in all answers. **If you exceed the line limit any additional material will not be read by graders**

Good luck!

$$P V = n R T, \quad R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}, = 0.0820578 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ L atm} = 101.325 \text{ J} \quad 1 \text{ calorie} = 4.184 \text{ Joules}$$

$$P_A = X_A P_T \quad \Delta E = (3/2) n R T$$

$$\Delta E = q + w, \quad \Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\Delta G = \Delta G^0 + RT \ln Q \quad \Delta S = q_{rev} / T$$

$$\Delta G^0 = -RT \ln K$$

$$S = k_B \ln W$$

$$\ln [A] = -kt + \ln [A]_0 \quad t_{1/2} = \ln(2) / k$$

$$1 / [A] = kt + 1 / [A]_0 \quad t_{1/2} = 1 / k [A]_0$$

$$\ln (k_1 / k_2) = E_A / R (1 / T_2 - 1 / T_1)$$

$$k = A e^{-E_A/RT}$$

$$\Delta G = -n F E \quad E^0_{cell} = E^0_{red} + E^0_{ox}$$

$$\Delta G^0 = -n F E^0 \quad \text{or } E^0_{cell} = (E^0_{more+}) - (E^0_{more-})$$

$$E = E^0 - (RT/nF) \ln Q$$

$$E = E^0 - (0.0592/n) \log Q \quad \text{at 298 K}$$

$$\# \text{ of moles deposited} = (It)/nF \quad F = 96,485 \text{ Coulombs}$$

- 1 (a) State the first law of thermodynamics in words.  
Merely stating the equation in words does not count. (2points).
- (b) Under what conditions is the work done by the system equal to heat absorbed by the same system.  
Also state relevant equations (3)
- (c) Explain briefly the terms state function and path function as they apply to thermodynamic quantities and give one example of each. 3 lines maximum. (4).

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- (d) Given the following data,
- |   |                                  |
|---|----------------------------------|
| $C_6H_6(l) + 15/2 O_2(g) \rightarrow 6 CO_2(g) + 3 H_2O(l)$ | $\Delta G^0 = - 6399 \text{ kJ}$ |
| $C(s) + O_2(g) \rightarrow CO_2(g)$                         | $\Delta G^0 = - 394 \text{ kJ}$  |
| $H_2(g) + 1/2 O_2(g) \rightarrow H_2O(l)$                   | $\Delta G^0 = - 237 \text{ kJ}$  |

Calculate  $\Delta G^0$  for the reaction,  $6 C(s) + 3 H_2(g) \rightarrow C_6H_6(l)$  (4)

2(a) Consider 2 half-cells, one consisting of an oxide of copper and another of an oxyanion of sulfur. Write balanced half-cell equations for each redox reaction given below. Assume basic conditions.

(6)



2(b) Use the standard reduction potential data to predict the direction in which the reaction will occur when these half-cells are connected and explain your reasoning. Also give the net equation for the reaction and the cell potential.

(6)

2(c) Explain briefly how standard half-cell reduction potentials are actually measured.

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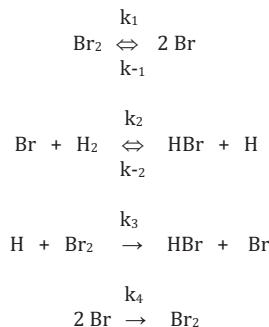
(3)

3(a). Consider the following table displaying the results of 5 experiments in which propanone, bromine and H<sup>+</sup> ions were reacted together,

expt	[CH <sub>3</sub> COCH <sub>3</sub> ]	[Br <sub>2</sub> ]	[H <sup>+</sup> ]	Rate of disappearance of Br <sub>2</sub> (M/s)
1	0.30	0.050	0.050	5.7 X 10 <sup>-5</sup>
2	0.30	0.10	0.050	5.7 X 10 <sup>-5</sup>
3	0.30	0.050	0.10	1.2 X 10 <sup>-4</sup>
4	0.40	0.050	0.20	3.1 X 10 <sup>-4</sup>
5	0.40	0.050	0.050	7.6 X 10 <sup>-5</sup>

Use this information to calculate the rate of disappearance of bromine if the initial concentrations are 0.600 mol/L, 0.100 mol/L and 0.400 mol/L for propanone, bromine and H<sup>+</sup> respectively. (8)

3b. The gas phase reaction between Br<sub>2</sub> and H<sub>2</sub> to form HBr is assumed to proceed by the following mechanism,



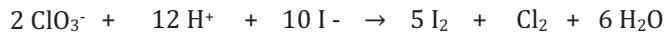
Under what conditions does the rate law have the form Rate = k'[Br<sub>2</sub>] ? (2)  
(show reasoning)

Under what conditions does the rate law have the form Rate = k'' [H<sub>2</sub>][Br<sub>2</sub>]<sup>1/2</sup> (4)  
(show reasoning)

**No 4. Multiple Choice****(3 points each)**

No partial credit.

- (i). How many electrons are transferred in the following reaction?



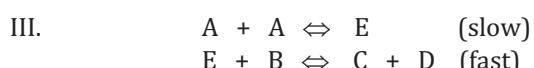
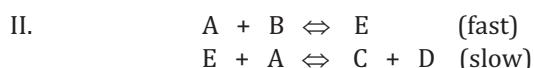
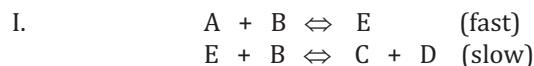
- (a) 12      (b) 5      (c) 2      (d) 30      (e) 10

- (ii). The rate constant for any reaction is dependent on,

- I. concentration of the reactants  
 II. activation energy  
 III. temperature  
 IV. the order of the reaction

- (a) none of these      (b) one of these  
 (c) two of these      (d) three of these      (e) all of these

- (iii). The rate law for a reaction is found to be, Rate =
- $k[\text{A}]^2 [\text{B}]$
- . Which of the following mechanisms gives this rate law?



- (a) I      (b) II      (c) III      (d) two of these      (e) none of these

- (iv). Given the standard electrode potential for the reaction of hydrogen and oxygen,



Calculate the standard potential for the following reaction,



- (a) 1.23 V      (b) 0.625 V      (c) -0.625 V  
 (d) -1.23 V      (e) -2.46 V

**Chemistry 14B  
Dr. Scerri  
Final exam  
June 2015**

3 hours.

PROBLEM	SCORE	POINTS
1		26
2		14
3		22
4		21
5		24
6		22
7		18
8		24
total		171

Name \_\_\_\_\_

Signature \_\_\_\_\_

ID # \_\_\_\_\_

Discussion Section \_\_\_\_\_

**Please note:**

**Some questions carry more points than others.**

**Instructions:** This exam has 8 questions plus a periodic table at end of exam. Verify you have the right number of pages before you begin. Write your name on each page. Raise your hand if you don't understand a question. **SHOW YOUR WORK!** No credit will be given for an unsubstantiated or illegible answer. Write legibly, use proper units throughout and use significant figures in all answers. **If you exceed the line limit any additional material will not be read by graders.** Any suspicious activity during the exam will result in your being reported to the Dean of Science

Good luck!

Possibly useful information:

$$P V = n R T \quad R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} = 0.0820578 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ L atm} = 101.325 \text{ J} \quad 1 \text{ calorie} = 4.184 \text{ Joules}$$

$$P_A = X_A P_T \quad \Delta E = (3/2) n R T$$

$$\Delta E = q + w, \quad \Delta G^0 = \Delta H^0 - T \Delta S^0$$

$$\Delta G = \Delta G^0 + RT \ln Q \quad \Delta S = q_{\text{rev}} / T$$

$$\Delta G^0 = -RT \ln K$$

$$S = k_B \ln W$$

$$[A] = -kt + [A]_0 \quad t_{1/2} = [A]_0 / 2k$$

$$\ln[A] = -kt + \ln[A]_0 \quad t_{1/2} = \ln(2) / k$$

$$1/[A] = kt + 1/[A]_0 \quad t_{1/2} = 1/k [A]_0$$

$$\ln(k_1 / k_2) = E_A / RT (1/T_2 - 1/T_1)$$

$$k = A e^{-EA/RT}$$

$$\Delta G = -nFE \quad E_{\text{cell}}^0 = E_{\text{red}}^0 + E_{\text{ox}}^0$$

$$\Delta G^0 = -nFE^0 \quad E_{\text{cell}}^0 = (E_{\text{more+}}^0) - (E_{\text{more-}}^0)$$

$$E = E^0 - (RT/nF) \ln Q$$

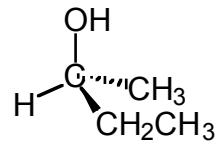
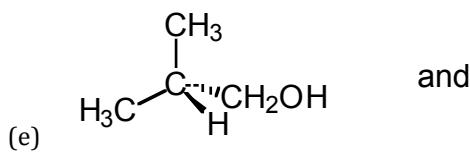
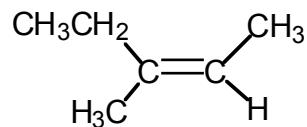
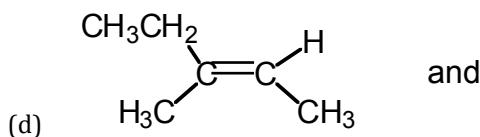
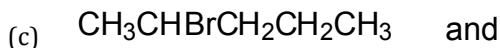
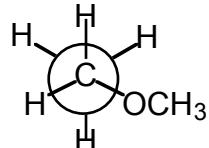
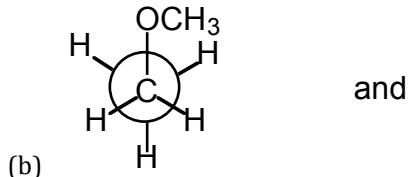
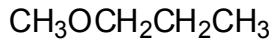
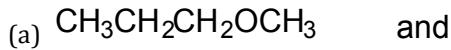
$$E = E^0 - (0.0592/n) \log Q \quad \text{at } 298 \text{ K}$$

$$\# \text{ of moles deposited} = (It)/nF \quad 1 F = 96,485 \text{ C mol}^{-1}$$

**order of priority for naming:** carboxylic acid > ester > acyl halide > amide > nitrile > aldehyde > ketone > alcohol > amine > alkyl group > ether > halogen

1(i). For each pair of examples which follow state whether they represent isomers of the same compound. For those that do identify the kind of isomerism involved

(10)



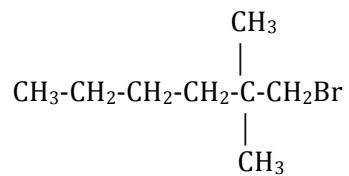
(ii) For whichever case(s) above where it is relevant, state whether chemical and physical properties differ and explain your answers.

(6)

(iii) Give the full IUPAC name for the compound on the right-hand side of the page for each pair above.

(10)

2 (i) Consider the reaction of,



with HCN.

Give the full mechanism for the reaction.

(6)

(ii) What is the full name given to this mechanism.

(1)

(iii) Explain any numbers and/or letters used

(3)

.....

(iv) Does the compound  $\text{C}(\text{CH}_3)_3\text{CH}_2\text{Br}$  react with  $\text{CN}^-$  via the same mechanism? Explain your answer.

(4)

.....

.....

.....

3. (i) Give the formula of a compound that includes an ester group an ether group and an amide group and that shows optical isomerism. The functional groups should be shown in full and not in abbreviated form. Also show the other optical isomer of the same compound. (7)

(ii) How, if at all, would you expect these isomers to differ from each other? (4)

.....  
.....  
.....

(iii) Give a schematic diagram and explain briefly how the optical activity of this compound can be experimentally observed. (5)

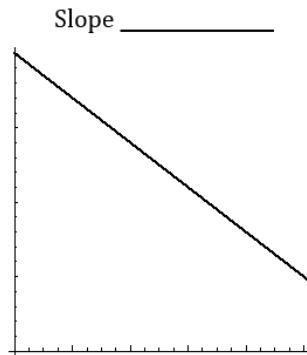
.....  
.....  
.....  
.....  
(iv) How does an addition reaction differ from a substitution reaction? Give equations to illustrate examples of each kind. (6)

(4 lines available altogether. Continue on back of page if necessary)

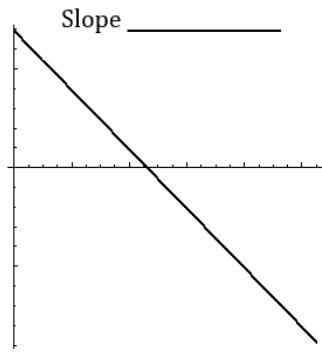
- 4(i) Draw a cyclohexane molecule in its chair conformer, and show all hydrogen atoms and how they are bonded to the six carbon atoms. (4)
- (ii) What happens to each hydrogen atom following a 'ring flip'? (2)
- (iii) Consider the di-substituted cyclohexane called E 1, 2 dibromo cyclohexane. State which of the two chair forms is the more stable and explain your answer. Give diagrams of both forms. (4)
- (iv) the di-substituted cyclohexane called Z 1, 2 dimethyl cyclohexane. State which of the two chair forms is the more stable and explain your answer. Give diagrams of both chair forms. (4)
- (v) Calculate the relative amounts of boat and chair isomer present at 250°C in a di-substituted cyclohexane for which the boat and chair conformers differ from in other by 26 kJ/mol. (3)
- (vi) By focusing on the C-C bond between C3 and C4 explain what kinds of strain are present in hexane. Also discuss the degree of strain present in the cyclohexane chair form and explain. (4)

5. (i) Label the axes for these reactions relating concentration to time. What is the slope of each graph? (6)

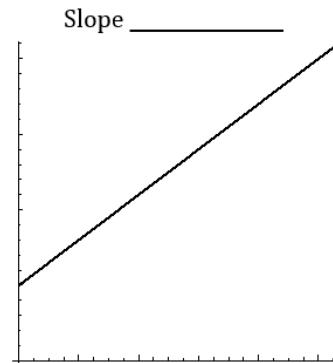
Zero Order



First Order



Second Order

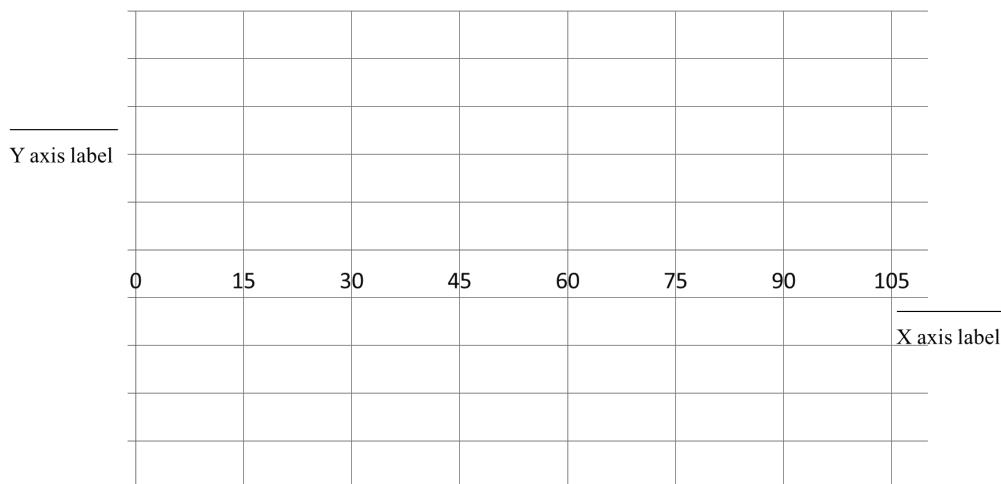


In the following section, reactant A decomposes into products. The concentration of A, [A], can be measured with respect to time. Use the table and graph to show that the reaction is first order with respect to A.

- ii) Complete the table (\*) with the needed information to make a linear plot. (3)

time (s)	[A] (mol/L)	*
0	3.00	*
15	2.19	*
45	1.17	*
105	0.33	*

- iii) Make a plot below to show that the reaction is first order. (5)



Use the following table and reaction to answer the parts iv) through vi).



Initial concentration			Initial reaction rate (mol/(L s))
[A] (mol/L)	[B] (mol/L)	[C] (mol/L)	
1.25	1.15	2.25	3.35
2.50	1.15	2.25	6.68
2.50	1.15	5.33	6.71
2.50	4.60	5.33	13.43

iv) What is the rate law of this reaction?

(3)

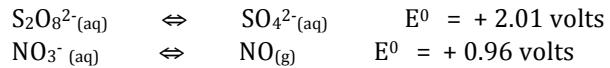
v) What is the rate constant for this reaction (including units)?

(4)

vi) What is the initial reaction rate of a mixture of 0.20 M A, 3.0 M B, and 2.50 M C?

(3)

6a(i) Here are a couple of half-cell equations (unbalanced)



Predict which element is oxidized and which is reduced and briefly explain your reasoning.  
(4)

(ii) Write a balanced reaction for what actually happens spontaneously.  
(Assume basic conditions) (10)

(iii) Calculate the cell emf. (3)

(iv) Give a schematic representation for the cell using the accepted cell convention. (Not a diagram of actual glassware etc.) (5)



Chemistry 14-B  
Dr. E. Scerri  
Final Exam  
June, 2016

Three hours

PROBLEM	SCORE	POINTS
1		16
2		21
3		15
4		27
5		30
6		15
7		25
8		33
total		<b>178</b>

Total of 8 questions with varying numbers of points.

Please note: Any activities that remotely resemble cheating will be treated very seriously!

Name \_\_\_\_\_  
**Last** \_\_\_\_\_ First \_\_\_\_\_

Student ID \_\_\_\_\_

Signature \_\_\_\_\_

**Instructions:** This exam has 8 questions and a periodic table at end of exam. Verify you have the right number of pages before you begin. Write your name on each page. Raise your hand if you don't understand a question. **SHOW YOUR WORK!** No credit will be given for an unsubstantiated or illegible answer. Write legibly, use proper units throughout and use significant figures in all answers. **If you exceed the line limit any additional material will not be read by graders. Use a pen except for diagrams for which you may use a pencil.**

Good luck!

$$P V = n R T,$$

$$R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}, = 0.0820578 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

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$$1 \text{ calorie} = 4.184 \text{ Joules}$$

$$P_A = X_A P_T$$

$$\Delta E = (3/2) n R T$$

$$\Delta E = q + w,$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$\Delta S = q_{\text{rev}} / T$$

$$\Delta G^0 = -RT \ln K$$

$$S = k_B \ln W$$

$$\ln [A] = -kt + \ln [A]_0$$

$$t_{1/2} = \ln(2) / k$$

$$1 / [A] = kt + 1 / [A]_0$$

$$t_{1/2} = 1 / k [A]_0$$

$$\ln (k_1 / k_2) = (E_A / R) (1/T_2 - 1/T_1)$$

$$k = A e^{-EA/RT}$$

$$\Delta G = -n F E$$

$$E^0_{\text{cell}} = E^0_{\text{red}} + E^0_{\text{ox}}$$

$$\Delta G^0 = -n F E^0$$

$$E^0_{\text{cell}} = (E^0_{\text{more +}}) - (E^0_{\text{more -}})$$

$$E = E^0 - (RT/nF) \ln Q$$

$$F = 96,500 \text{ Coulombs}$$

$$E = E^0 - (0.0592/n) \ln Q \quad \text{at } 298 \text{ K}$$

$$\# \text{ of moles deposited} = (It)/nF$$

**order of priority for naming:** COOH > COOR' > COCl > CONH<sub>2</sub> > CN > CHO > CO > OH > NH<sub>2</sub> > R > COC > X

- 1(a) The internal energy of a system increased by 982 J when it absorbed 492 kJ of heat. Was work done on the system or did the system do work on the surroundings? How much work was done? (4)

$$\Delta E = q + w$$

$$982 \text{ J} = 492,000 \text{ J} + w$$

$$w = 982 - 492,000 \text{ J} = -491 \text{ kJ}$$

**work is done on the surroundings (given – sign of w)**

- (b). A 245.7 g sample of a metal at 75.2 degrees Celsius was placed in 115.43 g of water at 22.6 degrees Celsius. The final temperature of the water was 34.6 Celsius. Assuming no heat was lost to the surroundings calculate the specific heat of the metal. (4)

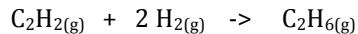
**heat lost by metal = heat gained by water**

$$\text{heat} = m c \Delta T$$

$$(245.7)(x)(40.6) = (115.43)(4.184)(12)$$

$$x = \frac{(115.43)(4.184)(12)}{(245.7)(40.6)} = 0.581 \text{ J/g}^{\circ}\text{C}$$

- (c) Determine the reaction enthalpy for the hydrogenation of ethyne to ethane, (4)

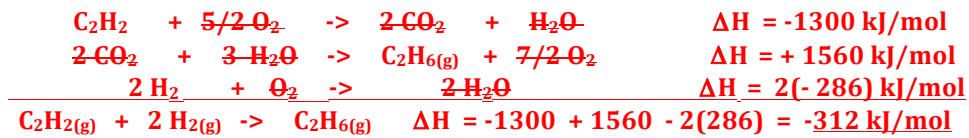


from the following data:

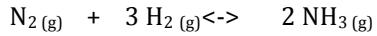
$$\Delta H_{\text{comb}}' (\text{C}_2\text{H}_{2(\text{g})}) = -1300 \text{ kJ/mol},$$

$$\Delta H_{\text{comb}}' (\text{C}_2\text{H}_{6(\text{g})}) = -1560 \text{ kJ/mol},$$

$$\Delta H_{\text{comb}}' (\text{H}_{2(\text{g})}) = -286 \text{ kJ/mol},$$



- (d) Consider the following reaction at 350 K,



Assuming the initial partial pressures are  $\text{N}_2$  1.50 atm',  $\text{H}_2$  3.60 atm',  $\text{NH}_3$  0.5 atm' and that  $\Delta G^0$  for the reaction is 33.32 kJ/mol, calculate  $\Delta G$  under these conditions. (4)

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$\Delta G = 33.32 + 8.3145 \times 350 \times \ln [(0.5)^2 / (1.50)(3.6)^3]$$

$$= 33.32 - 16.36 \text{ kJ} = \underline{16 \text{ kJ/mol}} \quad (2 \text{ sig figs})$$

- 2(a) Derive the integrated rate law for any first order reaction. (5)

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^1$$

$$\text{or } \frac{d[A]}{[A]} = -k dt$$

$$\int_{A_0}^A \frac{d[A]}{[A]} = -k \int_0^t dt$$

$$\ln A - \ln A_0 = -kt$$

$$\ln A = -kt + \ln A_0$$

**(1 point for each line. Final line not essential) + 1 more**

- (b) A substance A decomposes in a first order reaction and its half-life is 355 seconds. How much time must elapse for the concentration of A to reach  $1/8[A_0]$  and how much time to reach 15% of its initial concentration? (6)

$$t_{1/2} = \ln(2) / k$$

$$k = \ln(2) / 355 = 1.952 \times 10^{-3}$$

$$\begin{aligned} \ln [1/8 A_0 / A_0] &= -kt \\ -2.079 &= -1.952 \times 10^{-3} \times t \\ \underline{t &= 1065 \text{ sec.}} \end{aligned}$$

---


$$\ln [0.15 A_0 / A_0] = -kt$$

$$\begin{aligned} -1.897 &= -kt \\ \underline{t &= 971 \text{ sec}} \end{aligned}$$

- (c) The rate of the reaction :



(4)

was studied and the following information was obtained:

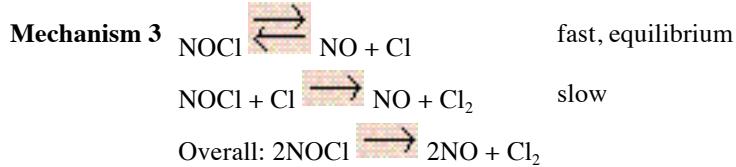
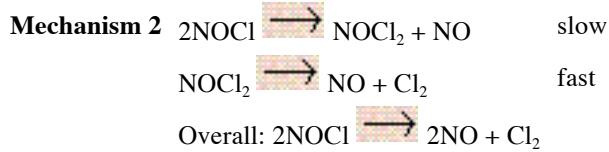
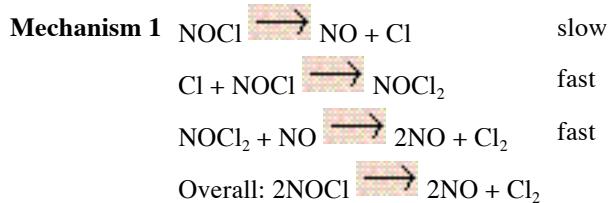
$[\text{BrO}_3^-]_0$	$[\text{Br}^-]_0$	$[\text{H}^+]_0$	Initial Rate {M/sec}
0.10	0.10	0.10	$8.0 \times 10^{-4}$
0.10	0.20	0.10	$3.2 \times 10^{-3}$
0.20	0.10	0.10	$1.6 \times 10^{-3}$
0.10	0.10	0.20	$3.2 \times 10^{-3}$

The rate law for this reaction is:  $\text{Rate} = k [\text{BrO}_3^-]^1 [\text{Br}^-]^2 [\text{H}^+]^2$

- (d) Consider the following reaction  $2\text{NOCl} \rightleftharpoons 2\text{NO} + \text{Cl}_2$

From the three postulated mechanisms given below show what rate law each of them gives.

(6)



Mech 1.  $\text{Rate} = k [\text{NOCl}]$  from slow step

Mech 2.  $\text{Rate} = k [\text{NOCl}]^2$  from slow step

Mech 3. From slow step  $\text{Rate} = [\text{NOCl}][\text{Cl}]$  (i)

Need to solve for [Cl]

From first step,  $k_1[\text{NOCl}] = k_2[\text{NO}][\text{Cl}]$

$$[\text{Cl}] = \frac{k_1[\text{NOCl}]}{k_2[\text{NO}]}$$

substitute into (i)  $\text{Rate} = [\text{NOCl}] \left\{ \frac{k_1[\text{NOCl}]}{k_2[\text{NO}]} \right\}$   
 $= k [\text{NOCl}]^2 [\text{NO}]^{-1}$

- 3(a) Explain how chemical reactions can lead to the creation of a direct electric current.  
You should use the examples of the following half-reactions, (5)

$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.771
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}$	-0.125

**Any  $\frac{1}{2}$  cell has an electric potential relative to H<sub>2</sub>  $\frac{1}{2}$  cell = 0 volts.**

---

**If two different half-cells are connected together, electric current flows from**

---

**the more – to the more +. In this case from Pb half-cell to the Fe half-cell.**

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- (b) How much time is required to electroplate 1.50 g of copper from a copper (II) nitrate solution by using a current of 13.6 mA? (3)

$$\text{moles deposited} = \frac{It}{nF}$$

$$\frac{1.50 \text{ g Cu}}{65.546 \text{ g Cu}} = \frac{13.6 \times 10^{-3} \text{ A} \times t}{2 \times 96,500 \text{ C}}$$

$$t = \frac{1.50 \times 2 \times 96,500}{65.546 \times 13.6 \times 10^{-3}} = 90.21 \text{ hrs.} = 3.76 \text{ days.}$$

**(if Cu = 65.55, answer is 93 hours).**

- (c) Write a balanced cell equation for the reaction that occurs when the following half-cells are connected together, (assume acidic conditions) (7)

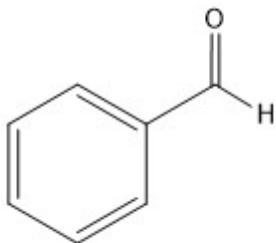


**from sep data, current flows from iodine into bromine half cell. So iodine undergoes reduction**

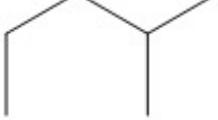


4(a) Name the following molecules using IUPAC rules.

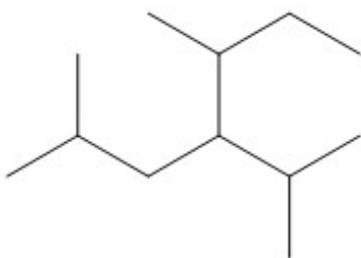
(6)



**benzaldehyde or benzene carbaldehyde or phenylmethanal**



**2 methyl pentane**



**4 isopropyl 2,5 dimethyl heptane or 4(1-methyl ethyl)**

Draw a molecule that contains a total of 6 C atoms and includes the following groups: aldehyde, carboxylic acid, nitrile and amide. Indicate any chiral centers with an \* (4) + (2)



Name the compound     **3 carbamoyl 2 cyano 4 formyl butanoic acid**

(2)

- (b) State the types of strain that are present in each of the following molecules, (6)
- (i) butane      (ii) cyclobutane      (iii) 1,ethyl 2,methyl cyclopentane

**Butane: Torsional & steric strain**

---

**Cyclobutane: Torsional and ring strain (or bond angle strain)**

---

**1 ethyl 2 methyl cyclopentane: Torsional, steric and ring strains**

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- (c) Consider the cyclopentane molecule. What bond angles would it have if it was a perfectly planar molecule? In fact the angles are about 105 degrees each.  
Give an explanation of why this happens. (3)

**When flat would have bond angles of  $108^\circ$ .**

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**$105^\circ$  actually found: This is less stable in terms of ring strain**

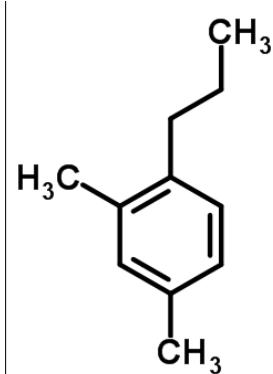
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**but more stable in terms of less torsional or eclipse strain.**

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5. (i) Give the name of the following molecules (3 each)



**1 propyl 2,4 dimethyl benzene**

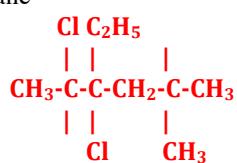
(ii)  $\text{Br}(\text{F})\text{C}=\text{CC}_2\text{H}_5(\text{CH}_3)$  depends on isomer drawn by student.

**Either E or Z 1 bromo 2 methyl butene**

(iii)

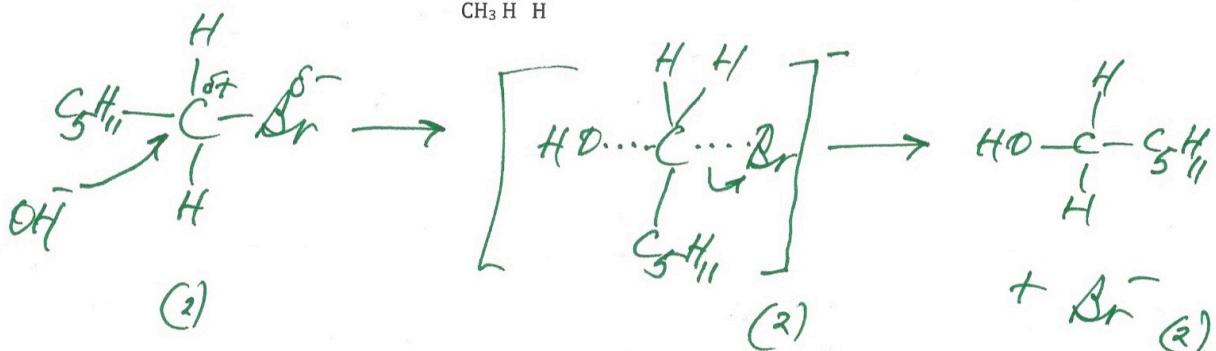
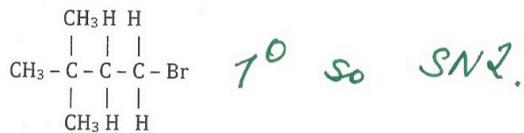
$\begin{array}{ccccc} \text{NH}_2 & \text{H} & \text{Cl} & \text{OH} \\   &   &   &   \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{CN} \\   &   &   &   \\ \text{Cl} & \text{Br} & \text{OH} & \text{H} \end{array}$	<b>5 amino 4 bromo 3,5 dichloro 2,3 dihydroxy pentan nitrile</b>
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(iv) Draw the structure of  
2,3-dichloro-3-ethyl-5-methyl-hexane

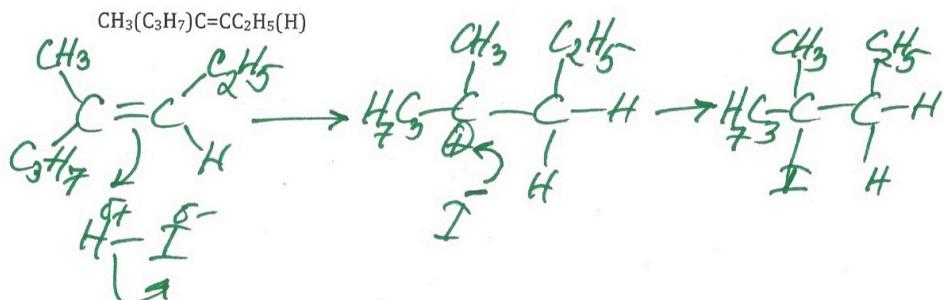


5(a) Give the full mechanism for the reaction of this compound with OH<sup>-</sup>

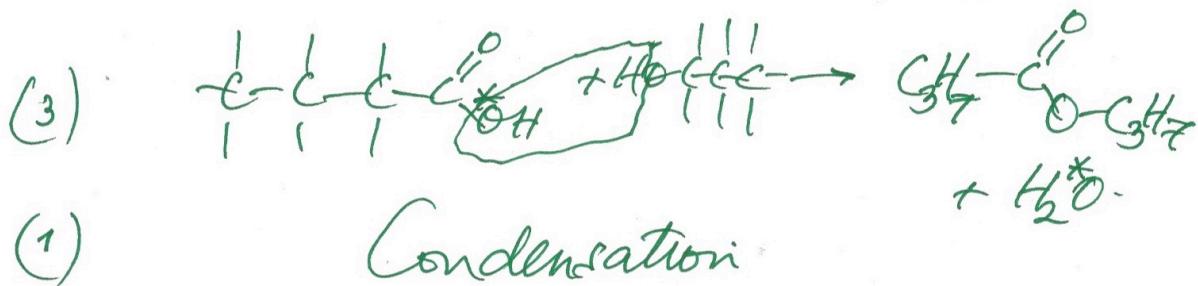
(6)



(b) Give the full mechanism for the reaction of this compound with hydrogen iodide (6)



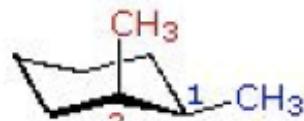
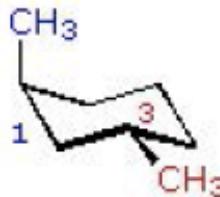
(c) Give the overall reaction (not the full mechanism) of the reaction of propanol with butanoic acid. What kind of reaction is this? (4)



(d) Using your response to part (c) show using \* what happens to a radioactively labeled oxygen atom that is originally introduced into the butanoic acid. (2)

Ends up in  $\text{H}_2\text{O}$ , not ester.

- 6(a) Name the following molecules. What kind of isomerism occurs in these cases and how does this kind of isomerism arise. (6 + 3)



**trans 1,3 dimethyl cyclohexane / cis 1,4 dimethyl cyclohexane / cis 1,4 dimethyl cyclohexane**

---

#### Structural isomerism due to different connectivity of CH<sub>3</sub> groups

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- 6(b) Two conformational isomers of a substituted cyclohexane compound differ in energy by 10.5 kJ/mol. Calculate the relative proportion of the two conformers at 300 K. (3)

$$\Delta G^0 = -RT \ln K$$

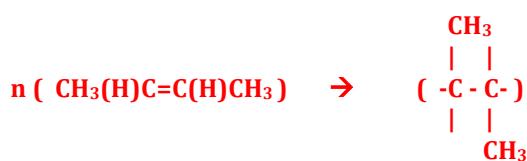
$$10,500 \text{ J} = -8.3145 \times 300 \times \ln K$$

$$\ln K = -4.209$$

$$K = 0.015$$

**or ratio of 1.5 to 100 for these two conformers or 1 to 67.3.**

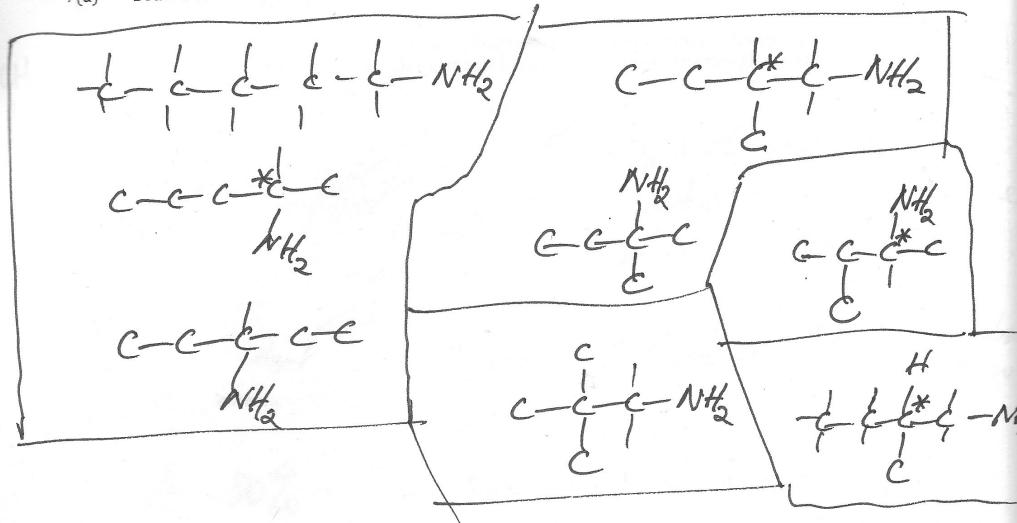
- 6(c) Show how the monomer but-2-ene molecule is expected to polymerize. (3)



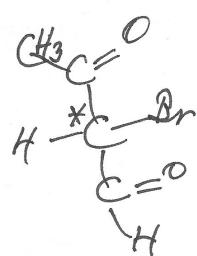
**(No significance to my drawing it 'trans')**

13

7(a) Draw 8 isomers of  $C_5H_{11}NH_2$ . Also show every chiral carbon atom with a \* (8)



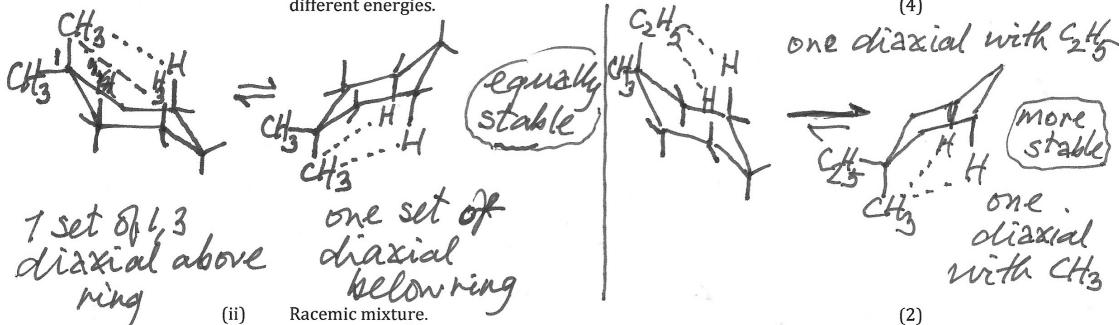
(b) Draw a molecule that contains just 4 carbon atoms, an aldehyde group, a ketone group, a bromine atom and that shows optical activity. (3)



13

(c) Explain the following terms

- (i) 1,3, diaxial interaction, using an example of a 1,1, di-substituent in which the two chairs have equal energies and another example in which the two chairs have different energies. (4)



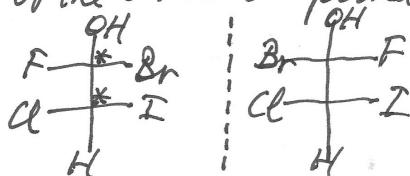
A 50% - 50% mixture of mirror image isomers. (or enantiomers).  
No net rotation of p.p.l. occurs.

- (iii) Diastereomers.

Give some examples to illustrate your answer

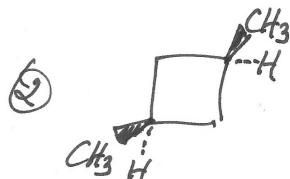
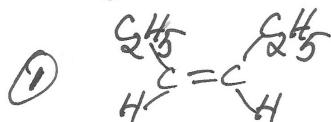
(4)

Not mirror images but both ~~stereo~~ optical isomers of the same compound



- (iv) Give two kinds of cases in organic molecules that produce geometrical isomerism.  
Also give actual examples of each kind. (4)

presence of hindered rotation around C=C  
② or " " " a ring.

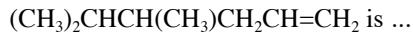


**8.** Circle one correct answer in each case. Show at least some working (3 points each)

a What is the IUPAC name for  $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)_2$ ?

- A) 3,3,5-trimethylhexane
  - B) 2,2,5-trimethylhexane
  - C) 2,4,4-trimethylhexane**
  - D) 1,1,3,3-tetramethylpentane
  - E) none of the above
- 

b. The IUPAC name for



- A) 4,5-dimethyl-1-hexene**
  - B) 4,5,5-trimethyl-1-pentene
  - C) 2,3-dimethyl-5-hexene
  - D) 4-methyl-4-isopropyl-1-butene
  - E) 3-methyl-3isopropyl-1-butene
- 

c How many cyclic isomeric alkenes ( $\text{C}_5\text{H}_{10}$ ) exist? (including structural, geometric and stereoisomers)

- A) 4
  - B) 5
  - C) 6
  - D) 7** including all geo and stereo isomers
  - E) 8
-

d The preferred conformation of *cis*-1,3-dimethylcyclohexane is ...

- A) chair--diaxial
  - B) chair--diequatorial**
  - C) chair--one axial / one equatorial
  - D) boat--mixed orientations
  - E) none of the above
- 

e A tertiary carbocation (carbonium ion) is more stable than either a secondary or primary carbocation because ...

- A) it carries three positive charges
  - B) it has a pyramidal configuration
  - C) it has a trigonal planar configuration
  - D) it possesses three electron-donating substituent groups**
  - E) it possesses three electron withdrawing groups
- 

f Which of the following is **not** an electrophile?

- A)  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
  - B)  $\text{BF}_3$
  - C)  $[\text{CH}_3]_3\text{C}^{(+)}$
  - D)  $\text{HOCl}$
  - E)  $\text{OH}^-$**
- 

g Which compound is a likely product from addition of  $\text{Cl}_2$  to 1-butene?

- A)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCl}_2$
  - B)  $\text{CH}_3\text{CH}_2\text{CHClCH}_2\text{Cl}$**
  - C)  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$
  - D)  $\text{CH}_3\text{CH}_2\text{CCl}_2\text{CH}_3$
  - E) none of the above
-

**h** Considering that the angles of a regular pentagon are  $108^\circ$ , why is cyclopentane not planar?

- A) all the carbons are  $sp^2$  hybridized, so there is considerable angle strain.
  - B) The C-C bonds are formed by overlap of p-orbitals, so the  $90^\circ$  angle results in large angle strain.
  - C) The cyclic overlap of bonding orbitals results in anti-aromaticity destabilization.
  - D) The five C-C bonds have eclipsing strain.**
  - E) Due to steric strain
- 

**i** A catalyst increases the rate of a reaction by:

- A) increasing the temperature.
  - B) decreasing the temperature.
  - C) increasing the activation energy.
  - D) decreasing the activation energy.**
  - E) decreasing  $\Delta H$ .
- 

**j** The half life for the first order decomposition of nitromethane,  $CH_3NO_2$ , at 500K is 650 seconds. If the initial concentration of  $CH_3NO_2$  is 0.500M, what will its concentration be after 1300 seconds have elapsed?

- A) 0.125**      B) 0.140      C) 0.250      D) 0.425      E) 0.81
- 

**k** Determine the rate law for the reaction,  $2ICl + H_2 \rightarrow I_2 + 2HCl$ , from the following initial rate data:

$[ICl]_0$	$[H_2]_0$	Initial Rate( $M s^{-1}$ )
0.250	0.500	$2.04 \times 10^{-2}$
0.500	0.500	$4.08 \times 10^{-2}$
0.125	0.125	$2.55 \times 10^{-3}$
0.125	0.250	$5.09 \times 10^{-3}$

 A)  $R = k[ICl]^2$ 
 B)  $R = k[H_2]^2$ 
 C)  $R = k[ICl][H_2]^2$ 
 D)  **$R = k[ICl][H_2]$** 
 E)  $R = k[ICl]^2[H_2]$

