

THE UNIVERSITY OF BRITISH COLUMBIA

CHEMISTRY 123 EXAMINATION

17 April 2004

This examination consists of 15 numbered pages.

PLEASE CHECK THAT YOU HAVE A COMPLETE PAPER

TIME LIMIT:

2.5 HOURS

GIVEN NAME(S): _____
(IN INK)

SURNAME: _____
(CAPITALS) (IN INK)

STUDENT NUMBER: _____
(IN INK)

SIGNATURE: _____
(IN INK)

NO CALCULATORS ALLOWED PREPROGRAMMED WITH ANY CHEMISTRY OR PHYSICS FORMULAE OR TEXTUAL MATERIAL. MOLECULAR MODELS ARE ALLOWED.

Lecture Section (check \checkmark your section)

- ___ 201 (MWF 1:00) Drs. Lermer/Tanner
- ___ 202 (MWF 2:00) Drs. Patey/Tanner
- ___ 209 (MWF 9:00) Dr. Herring
- ___ 210 (MWF 10:00) Drs. Comisarow/Dolphin
- ___ 211 (MWF 11:00) Drs. Comisarow/Dolphin
- ___ 299 (T,Th 9:30) Dr. McIntosh
- ___ 222 (T,Th 2:00) Dr. Herring

Question	Maximum	Obtained	Initials
1	10		
2	10		
3	13		
4	12		
5	16		
6	18		
7	15		
8	15		
9	8		
10	4		
11	4		
12	5		
TOTAL	130		
MARK	65		

REGULATIONS FOR EXAMINATIONS

- Each candidate must be prepared to produce upon request, a Library/AMS card for identification.
- Candidates are not permitted to ask questions of the invigilators, except in cases of supposed errors or ambiguities in examination questions.
- No candidates shall be permitted to enter the examination room after the expiration of one-half hour from the scheduled starting time, or to leave during the first half hour of the examination.
- Candidates guilty of any of the following, or similar, dishonest practices shall be immediately dismissed from the examination and shall be liable to disciplinary action:
 - Making use of any books, papers or memoranda, calculators, audio or visual cassette players or other memory and devices, other than those authorized by the examiners.
 - Speaking or communicating with other candidates.
 - Purposely exposing written papers to the view of other candidates. The plea of accident or forgetfulness shall not be received.
- Candidates must not destroy or mutilate any examination material; must hand in all examination papers; and must not take any examination material from the examination room without permission of the invigilator.

ANSWER ALL QUESTIONS

*** ADDITIONAL DATA ***

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$1 \text{ L atm} = 101.3 \text{ J}$$

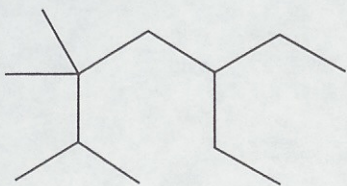
$$F = 96,500 \text{ coulombs mol}^{-1}$$

$$1 \text{ J} = 1 \text{ volt coulomb}$$

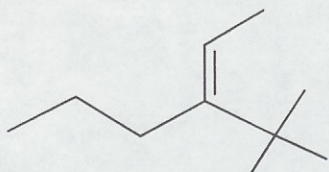
$$K_w = 1.00 \times 10^{-14} \text{ at } 25^\circ\text{C (298 K)}$$

1. Name the following compounds, including as necessary, any designation of stereochemistry.

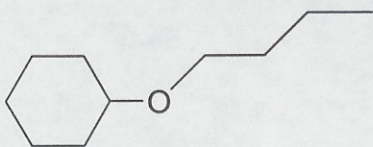
a)



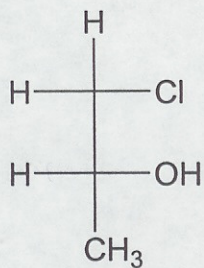
b)



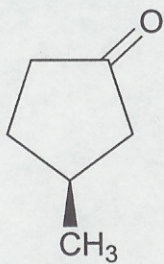
c)



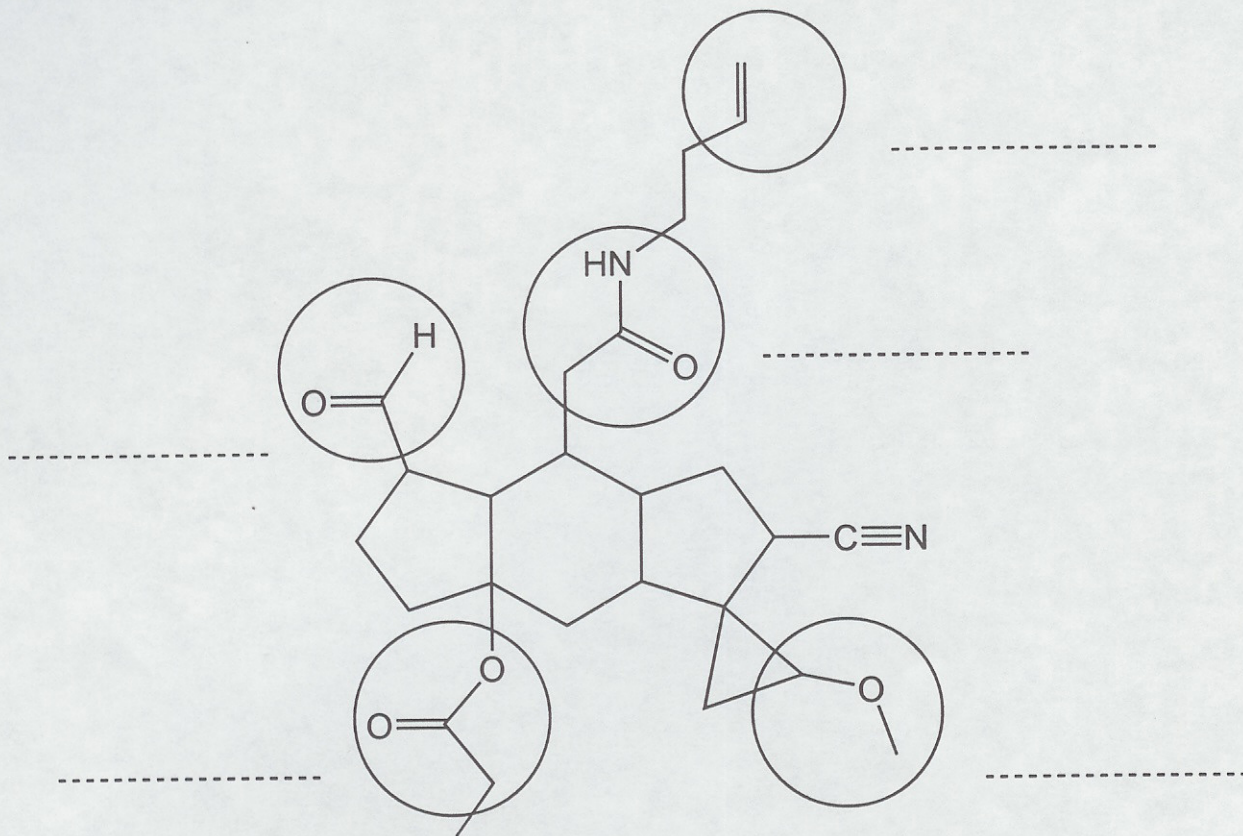
d)



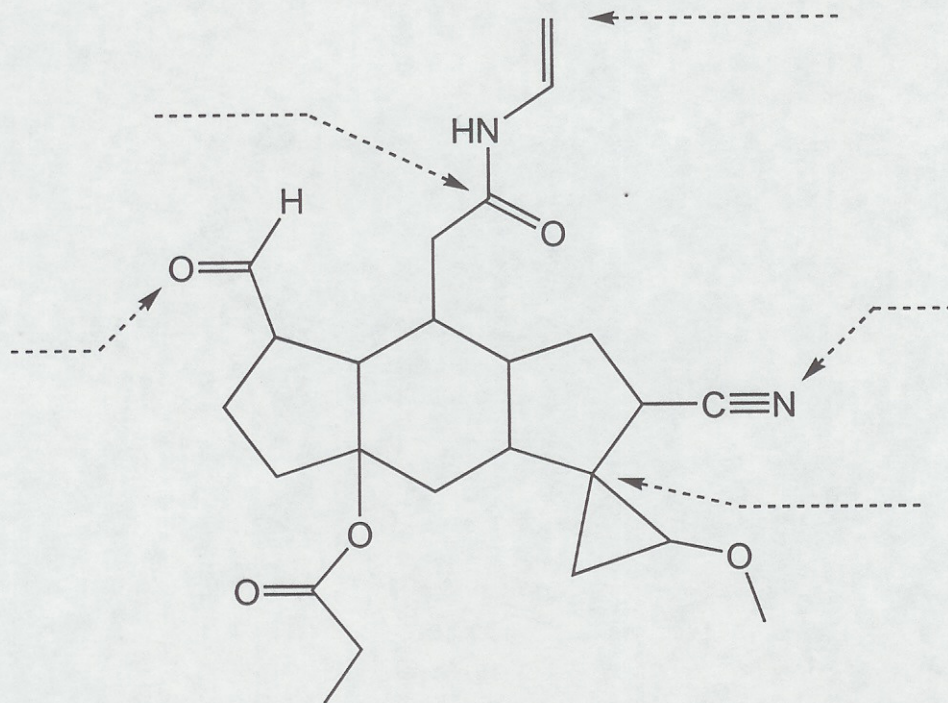
e)



2a) Name the functional groups that are circled.

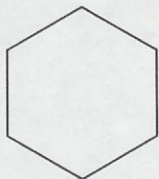


2b) What is the state of hybridization at the indicated atoms?



3a) Draw ALL possible isomers of C_5H_{10} clearly showing stereochemistry where appropriate (DRAW EACH ISOMER ONLY ONCE).

3b) Draw all the achiral (optically inactive) isomers of trichlorocyclohexane ($C_6H_9Cl_3$). Start with the template below and re-draw it as necessary. DRAW EACH ISOMER ONLY ONCE and show stereochemistry where appropriate using "wedges" and "dashes" for groups above or below the plane of the ring, respectively.



4. Shown below are six of pairs of structural formulas. In the box to the right of each pair, place the number (related to one of the terms listed below) that best describes the relationship between the two structures.

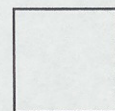
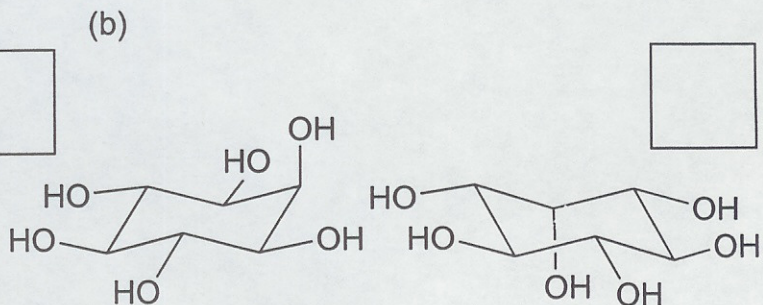
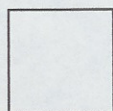
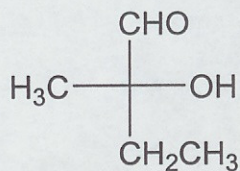
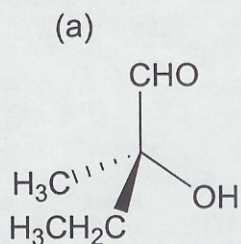
NOTE: Each term may be used more than once and not all of the terms need be used.

1. constitutional isomers

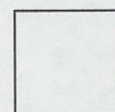
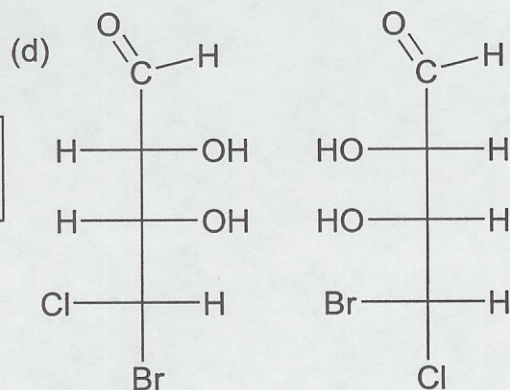
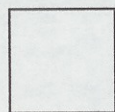
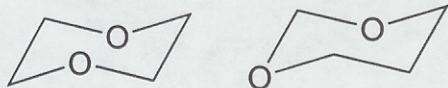
2. diastereomers

3. identical

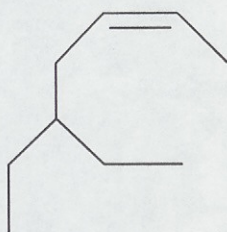
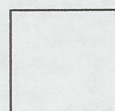
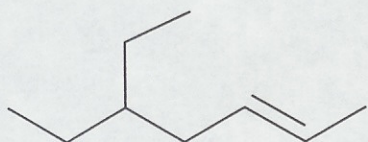
4. enantiomers



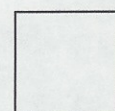
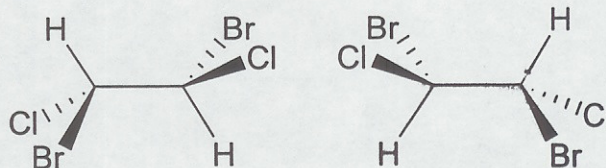
(c)



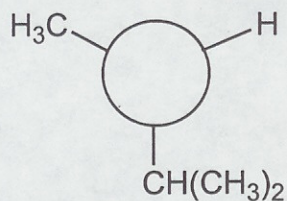
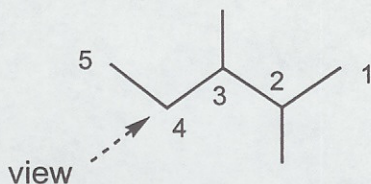
(e)



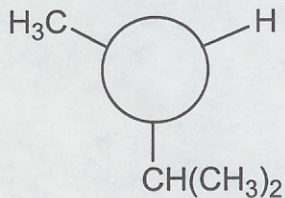
(f)



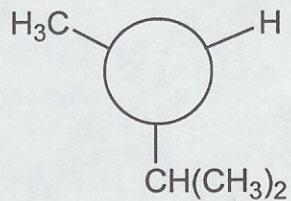
5a). Consider the conformations about the C4-C3 bond of the molecule shown below (view as indicated by the arrow). Complete the Newman projections below using only staggered and eclipsed conformations to indicate the order of stability of these conformations about this bond (starting with the **most stable** one and ending with the least stable one).



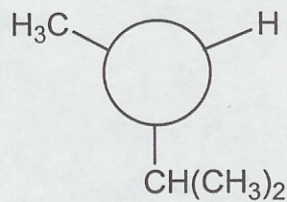
most stable



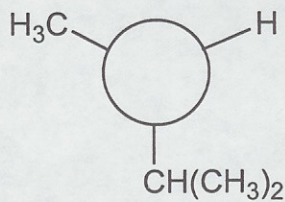
2nd



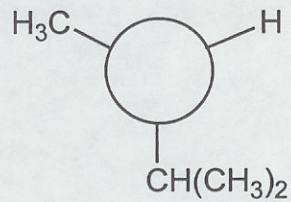
3rd



4th



5th

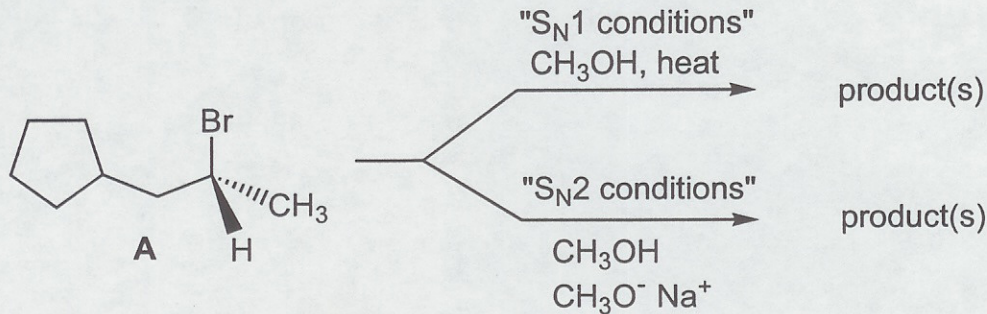


least stable

b) Draw the **most** stable stereoisomer of 4-isopropylcyclohexanol shown in its **most** stable conformation.

c) Draw the **least** stable stereoisomer of 4-isopropylcyclohexanol shown in its **most** stable conformation.

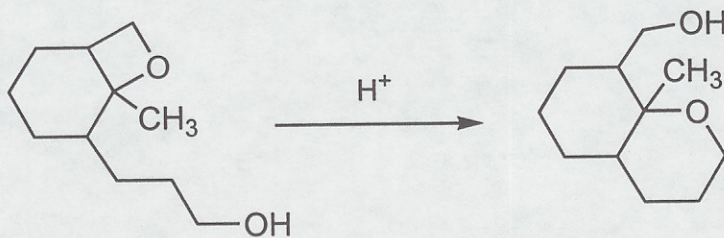
6. Secondary alkyl halides, such as compound A, may undergo either an S_N1 or S_N2 reaction depending upon the specific reaction conditions.



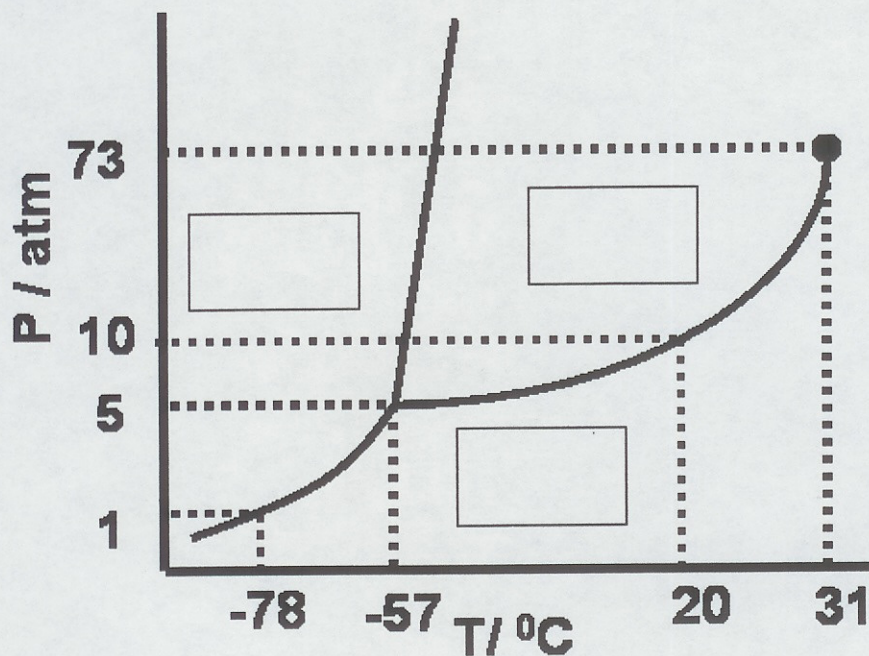
a) When optically active compound A was treated under carefully controlled " S_N1 conditions" it reacted solely via an S_N1 reaction. Write the product(s) and mechanism for this reaction, being careful to show any intermediates and transition states and state if the product(s) is/are optically pure or racemic. For all products clearly show the appropriate stereochemistry.

b) When optically active compound A was treated under carefully controlled " S_N2 conditions" it reacted solely via an S_N2 reaction. Write the product(s) and mechanism for this reaction, being careful to show any intermediates and transition states and state if the product(s) is/are optically pure or racemic. For all products clearly show the appropriate stereochemistry.

c) Propose a mechanism for the following reaction showing all steps and intermediates (no indication of stereochemistry is required).



7. PART I The phase diagram for carbon dioxide is shown below.



a) Label the phase diagram (in the boxes provided) with the most stable phase in the region in which each box resides.

b) At which temperature and pressure do all three phases co-exist in equilibrium?

Temperature = _____ Pressure = _____

c) Can gaseous carbon dioxide be liquefied by pressure alone at 40 °C?

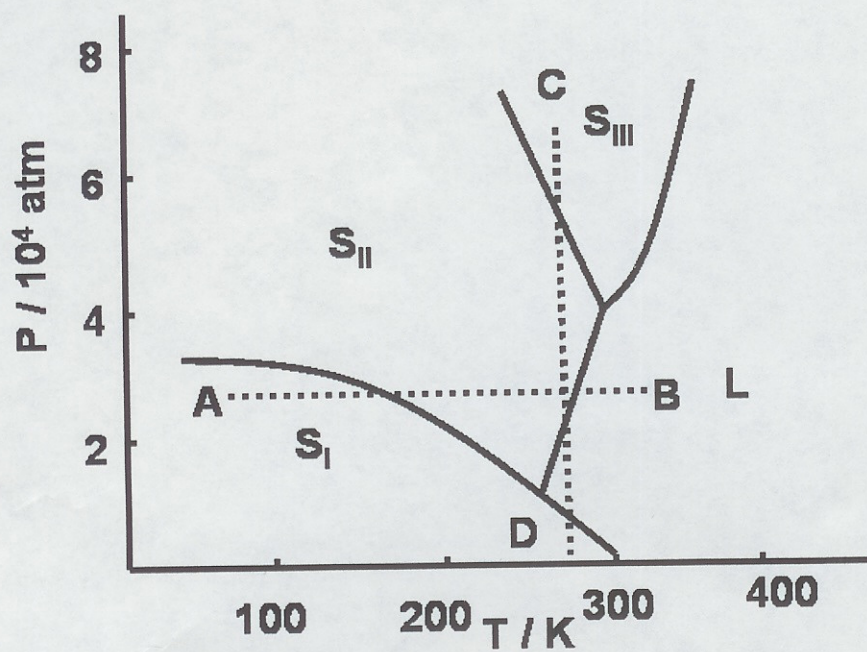
YES _____ or NO _____

d) Will solid carbon dioxide float on liquid carbon dioxide?

YES _____ or NO _____

e) Solid carbon dioxide is placed in an evacuated (empty) container in a temperature bath at 20 °C. When the system reaches equilibrium the pressure in the container is 10 atm. Describe carefully the phase changes that occur in the container as the system approaches equilibrium.

7. PART II. The phase diagram for the liquid (L) and solid (S_I , S_{II} , and S_{III}) phases of Gallium at high pressures is shown below. The liquid vapour line is not visible on this diagram.

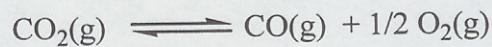


- f) Describe the phases and phase changes that occur when the temperature is increased according to the isobar from A to B.
- g) Describe the phases and phase changes that occur when the pressure is decreased according to the isotherm from C to D.
- h) What are the signs of ΔH and ΔS for the transition of S_I to S_{II} ?

8. The following thermodynamic data have been measured at 25 °C:

Compound	ΔH_f° (kJ mol ⁻¹)	S° (J mol ⁻¹ K ⁻¹)	ΔG_f° (kJ mol ⁻¹)
CO(g)	-110.5	198	-137
CO ₂ (g)	-393.5	214	-394

Carbon monoxide, which is highly toxic, will be present whenever oxygen and carbon dioxide exist at equilibrium:



a) For this reaction, calculate the free energy change, ΔG , at 25 °C when:

(i) all three compounds are at 1 atm pressure. answer: _____

(ii) all three compounds are at 10⁻⁴ atm pressure. answer: _____

(iii) all three compounds are in equilibrium. answer: _____

b) For the reaction, also calculate:

(i) $\Delta H^\circ =$ _____

(ii) $\Delta S^\circ =$ _____

c) Provide a brief rationalization for the algebraic sign of ΔS° calculated in part (b) above.

d) Calculate the equilibrium constant for this reaction at 25 °C.

$K =$ _____

e) If this exam room is at 25 °C, the equilibrium partial pressures of O_2 and CO_2 are 0.2 atm and 0.003 atm, respectively. What is the equilibrium partial pressure of CO?

$P_{CO} =$ _____

f) If this room were warmed to 37 °C, will there be a higher or lower partial pressure of CO at equilibrium? Explain your answer in words (no calculation is required).

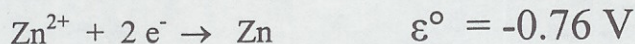
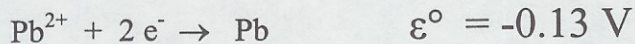
g) Assuming that the exam room is well sealed, state whether the equilibrium pressure of CO would **I** (increase), **D** (decrease), or **S** (stay the same) if:

(i) Nitrogen is introduced at a partial pressure of 2 atm. _____

(ii) Oxygen is introduced at a partial pressure of 2 atm. _____

(iii) The room is compressed to 1/2 of its initial volume. _____

9. Consider the cell, operating under standard conditions at 25 °C, based on the following half-reactions:



a) Write the chemical reaction for the overall cell reaction:

b) Which of the half cells is the anode? Briefly explain your selection.

For the cell reaction at 25 °C, calculate:

c) $\varepsilon^{\circ}_{\text{cell}} =$ _____

d) $\Delta G^{\circ} =$ _____

e) $K =$ _____

f) To the cell operating under standard conditions, NaOH is added to the zinc compartment causing precipitation of $\text{Zn}(\text{OH})_2(\text{s})$. After precipitation is complete, the equilibrium concentration of OH^{-} is 0.010 M and the measured cell potential is 1.05 V. Calculate the equilibrium constant for the reaction



10. A buffer has been made with a final concentration of 0.2 M propanoic acid ($pK_a = 4.89$) and 0.1 M sodium propionate. What is the pH of this buffer?

pH= _____

11. A 100 mL sample of the buffer described in Question 10 is treated with 10 mL of a 2 M solution of sodium hydroxide.

a) What is the resultant pH of the solution?

pH= _____

b) Briefly describe (two sentences maximum) whether or not the solution, after adding the sodium hydroxide, is still a buffer.

12. You are a summer student in a laboratory and your supervisor asks you to prepare a buffer at pH = 7.3. You find the following material in the laboratory stock room under the heading buffer supplies:

trimethylammonium chloride $[(\text{CH}_3)_3\text{NH}^+\text{Cl}^-]$ $\text{pK}_a=9.80$

triethylammonium chloride $[(\text{CH}_3\text{CH}_2)_3\text{NH}^+\text{Cl}^-]$ $\text{pK}_a=10.72$

triethanolammonium chloride $[(\text{HOCH}_2\text{CH}_2)_3\text{NH}^+\text{Cl}^-]$ $\text{pK}_a=7.76$

Two litres of 0.1 M HCl and two litres of 0.1 M NaOH

Answer the following:

- a) Which of the following compounds should you use to make the best buffer? Circle your answer.

trimethylammonium chloride

triethylammonium chloride

triethanolammonium chloride

- b) In order to achieve the desired pH of 7.3 what must be the ratio of the conjugate acid to base?

- c) Using only the chemical listed described above, describe how you would prepare this buffer. Provide balanced chemical equation(s) for any chemical reaction(s) involved in this procedure.