

**THE UNIVERSITY OF CALGARY**  
**FACULTY OF SCIENCE**  
**FINAL EXAMINATION**  
**CHEMISTRY 351**

DECEMBER 17, 1997

Time: 3 Hours

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER ON **BOTH** YOUR EXAM BOOKLET AND COMPUTER ANSWER SHEET.

Read the instructions carefully. The examination consists of Parts 1 - 8, each of which should be attempted. Note that some Parts provide you with a choice of questions. Parts 1 - 5 will be computer graded, and only Parts 6, 7, and 8 are to be answered on the paper provided. A periodic table with atomic numbers and atomic weights, and tables of NMR spectroscopic data are appended to the exam.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 49 which are to be answered on your computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a pencil only and **not ink**. In some cases it is required that you indicate **multiple** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out **both** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased **cleanly**.

Molecular models are permitted during the exam; calculators are also permitted, **but NOT programmable calculators**.

Value20 PART 1 RELATIVE PROPERTIES

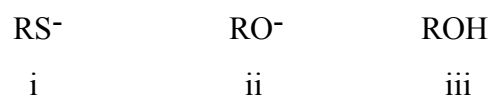
ANSWER ANY TEN (10) of Questions 1-14.

Arrange the items in Questions 1-14 in **DECREASING ORDER** (i.e. greatest, most etc. first) with respect to the indicated property.

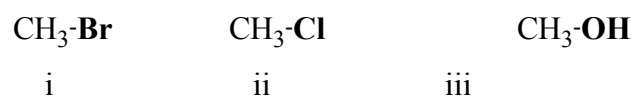
Use the following code to indicate your answers.

- |    |              |     |              |
|----|--------------|-----|--------------|
| A. | i > ii > iii | D.  | ii > iii > i |
| B. | i > iii > ii | E.  | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

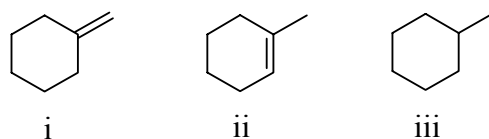
1. The relative nucleophilicity in polar solvent of:



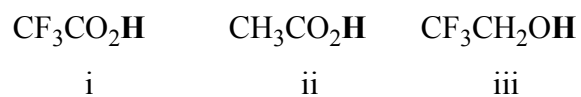
2. The leaving group ability of the group in bold:



3. The rate of reaction of HCl with:



4. The relative acidity of the bold H in:

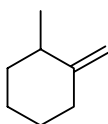


Value

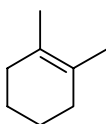
Use the following code to indicate your answers.

- |    |              |     |              |
|----|--------------|-----|--------------|
| A. | i > ii > iii | D.  | ii > iii > i |
| B. | i > iii > ii | E.  | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

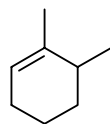
5. The heat of hydrogenation of:



i

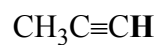


ii



iii

6. Acidity of the H shown in bold:



i

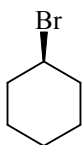


ii

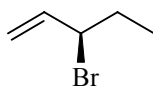


iii

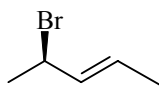
7. The number of stereoisomers of:



i

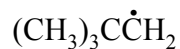


ii



iii

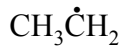
8. The stability of the following free radicals:



i

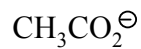


ii

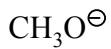


iii

9. Nucleophilicity in an  $\text{S}_{\text{N}}2$  reaction of:



i



ii



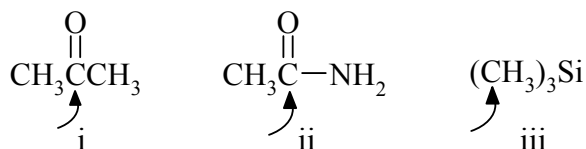
iii

Value

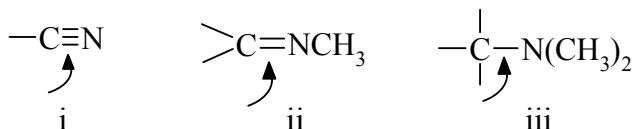
Use the following code to indicate your answers.

- |    |              |     |              |
|----|--------------|-----|--------------|
| A. | i > ii > iii | D.  | ii > iii > i |
| B. | i > iii > ii | E.  | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

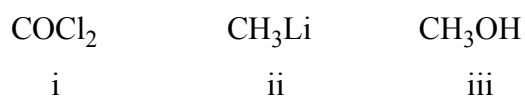
10. The  $^{13}\text{C}$  chemical shift ( $\delta$ ) of the designated carbon in ppm (largest first):



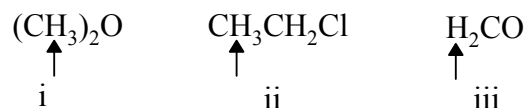
11. The IR stretching frequency in  $\text{cm}^{-1}$  of the indicated bond in:



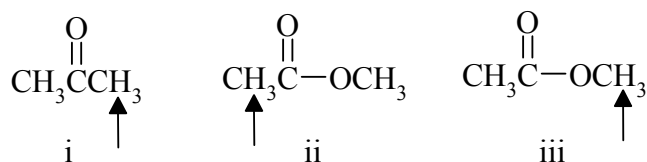
12. Oxidation state of the carbon atom in:



13.  $^1\text{H}$  nmr shifts of the indicated H atoms in:

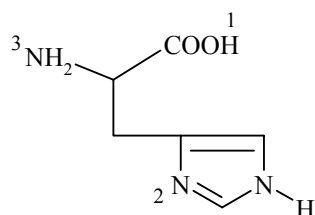


14. Acidity of indicated H in:



Value12 PART 2 ACIDS AND BASES**ANSWER ALL of questions 15-22.**

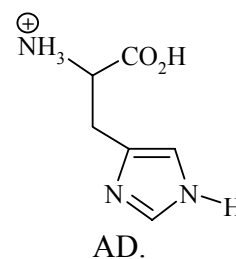
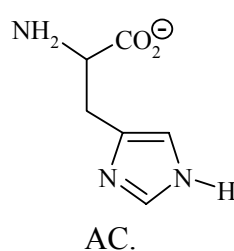
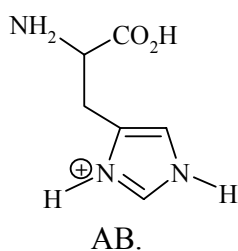
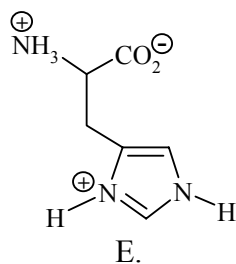
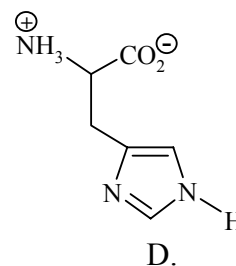
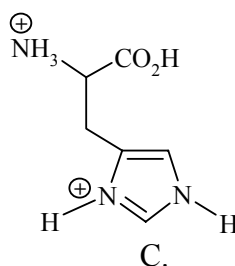
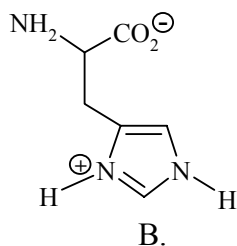
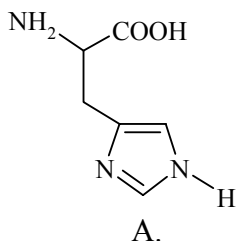
Shown below is the amino acid Histidine, and the  $pK_A$ 's of the acidic sites (1-3).  
Select your answer for questions 15-18 from the options A to AD given.

Histidine

$pK_A$  1 1.8

$pK_A$  2 6.0

$pK_A$  3 9.2



15. At pH=1, the predominant form of histidine is?

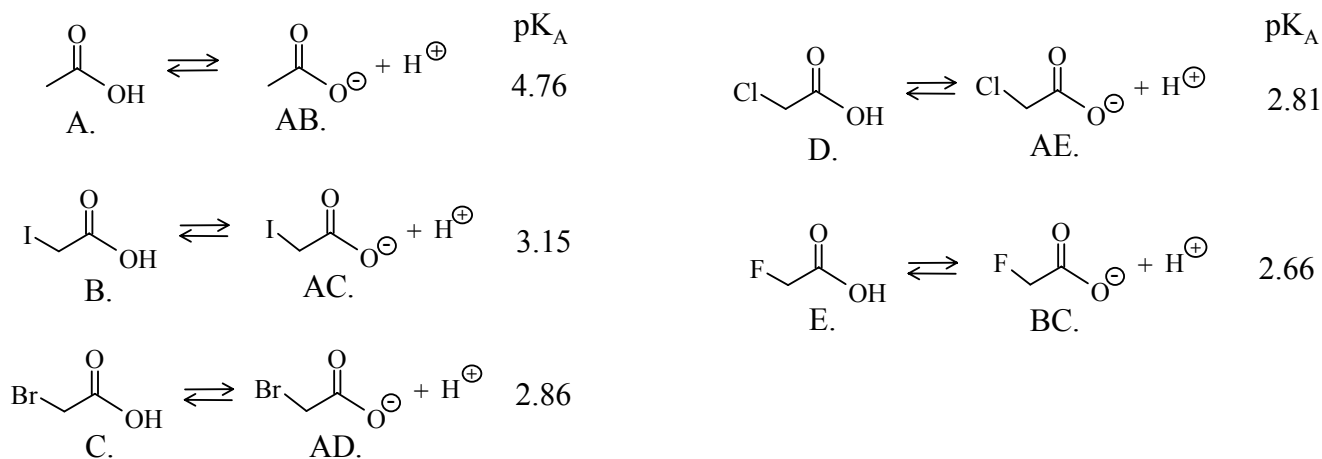
16. At pH=7, the predominant form of histidine is?

17. At pH=11, the predominant form of histidine is?

18. Which species are electronically neutral?

Value

Answer questions 19 to 22 based on the following data for a series of substituted acetic acids.



Henderson-Hasselbach equation:  $\text{pK}_A = \text{pH} + \log \frac{[\text{HA}]}{[\text{A}^-]}$

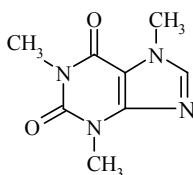
19. Which species is the weakest base?
20. At pH=2.86, what is the relative ratio of C to AD?
- A. 3.32    B. 5.72    C. 1.43    D. 1    E.  $1/2.86$
21. At pH=1.66, what is the relative ratio of E to BC?
- A.  $10^2$     B.  $10^1$     C. 1    D.  $10^{\Delta 1}$     E.  $10^{\Delta 2}$
22. The order of acidity can be explained by:
- A. The halogen atoms stabilize the acid by induction.
- B. The lone pairs on the halogen atoms increase the basicity.
- C. Acidity normally increases with decreasing molecular weight.
- D. Increased steric crowding forces the proton to dissociate from the acid.
- E. The halogen atoms stabilize the conjugate base by inductive electron withdrawal.

Value10 PART 3 LABORATORY**ANSWER ANY TEN (10) of questions 23 to 34.**

For questions 23-34, decide whether the whole statement is true or false. If it is true, blacken A. If it is false, then blacken B. (1 Mark each question.)

23. In a steam distillation, only water soluble materials can be separated.
24. The ratio of the quantities of solute per mL of solvent in two non-miscible solvents is given by the R<sub>f</sub> value.
25. Filtration of a hot solution during recrystallisation removes insoluble impurities.
26. Extractions are performed using miscible solvents.
27. Lactose is a carbohydrate containing glucose and fructose.
28. Casein in milk is a protein.
29. Heating casein in hydrochloric acid hydrolyses the ester bonds to produce the components sugars.
30. In Benedict's test for a reducing sugar,  $\text{Cu}^{2+} \rightarrow \text{Cu}^{1+}$ , so copper is oxidised.
31. When visualising the amino acids after TLC, iodine was used as the developing agent.

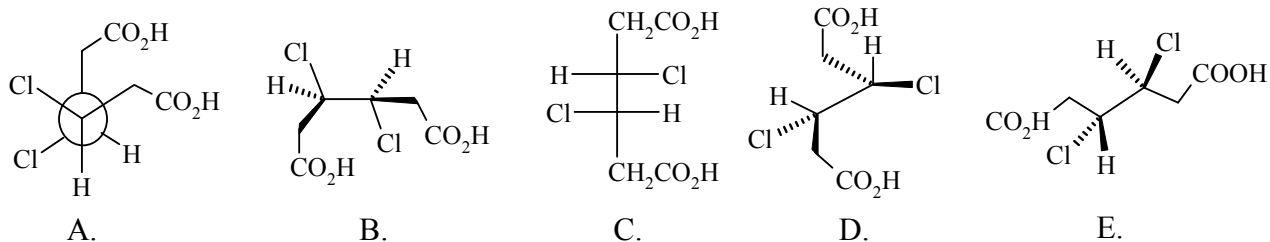
32. The structure of caffeine is



33. If you wanted to evaporate a flammable organic solvent to promote crystallisation, it should be safe to use a Bunsen burner.
34. When carrying out a vacuum filtration, the process will be more efficient if a fluted filter paper is used.

Value16 PART 4 STEREOCHEMISTRY

ANSWER ALL EIGHT (8) of the questions 35 to 42.



35. Choose **TWO** compounds that are identical.
36. Choose **TWO** structures that are enantiomers.
37. Choose **TWO** structures that are diastereoisomers.
38. Choose **ALL** structures that are meso compounds.
39. Which structure is the most stable conformation of meso 3,4-dichloro-1,6-hexandioic acid?

A solution containing 1.0 g D and 0.25 g B in 10 ml of ethanol was placed in a 1 dm cell and the optical rotation measured in a polarimeter. The observed rotation was  $+2.625^\circ$ .

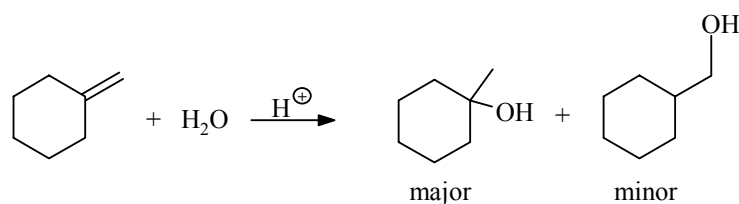
40. What is the specific rotation of the mixture?
- A.  $+26.25^\circ$     B.  $-2.1^\circ$     C.  $+2.1^\circ$     D.  $-21^\circ$     E.  $+21^\circ$
41. What is the specific rotation of (R,R)-3,4-dichloro-1,6-hexandioic acid?
- A.  $+12.6^\circ$     B.  $-12.6^\circ$     C.  $+35^\circ$     D.  $-35^\circ$     E.  $+33.6^\circ$     AB.  $\bar{A}33.6^\circ$
42. What is the % optical purity or enantiomeric excess (ee) of this mixture of D and B?
- A. 20    B. 40    C. 60    D. 80    E. 100



Value12 PART 5 KINETICS & THERMODYNAMICS

**ANSWER ALL SEVEN (7) of the questions 43 to 49.**

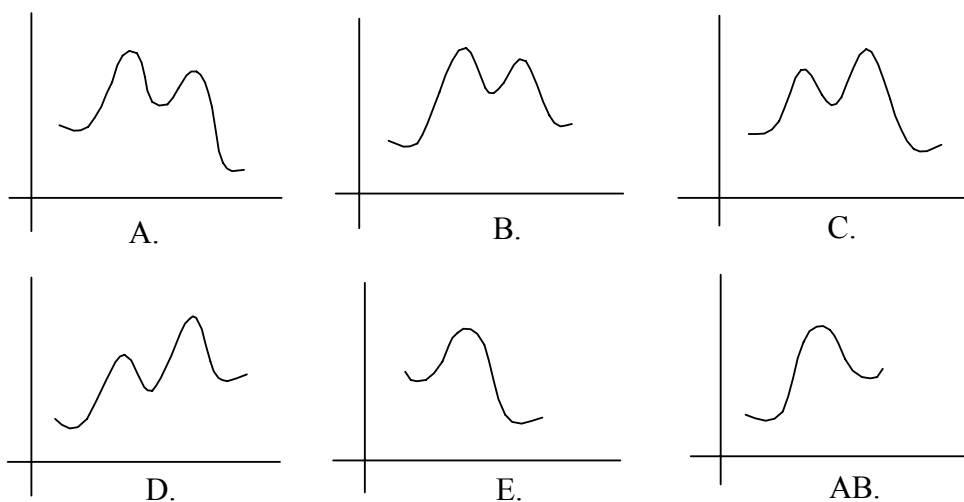
A student was trying to rationalise the selectivity of a reaction using average bond dissociation energies:



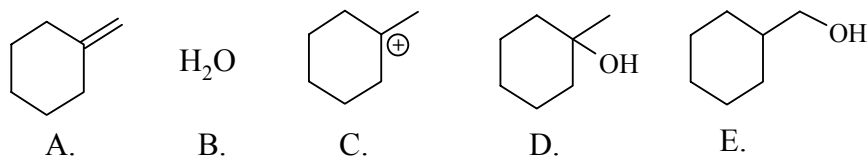
43. What is the calculated heat of reaction,  $\Delta H_r$  in  $\text{kcal mol}^{-1}$ , for the formation of 1-methylcyclohexanol?
- A. +122      B. +11      C. 0      D. -11      E. -94
44. Is this reaction (1 mark)
- A. Exothermic      B. Thermoneutral      C. Endothermic
45. What is the calculated heat of reaction,  $\Delta H_r$  in  $\text{kcal mol}^{-1}$  for the formation of the carbocation intermediate from which 1-methylcyclohexanol is produced?
- A. -36      B. +36      C. -75      D. +75      E. +174

Value

46. Which of the following reaction coordinate diagrams best represents the complete reaction?



47. Based on the Hammond postulate, the transition state leading to the formation of the major product from the intermediate carbocation is most like:



48. For the complete reaction discussed the rate determining step is:

- A. formation of the carbocation.  
 B. dissociation of water to  $\text{HO}^-$  and  $\text{H}^+$   
 C. attack of  $\text{H}_2\text{O}$  on the  $\text{C}^+$   
 D. attack of  $\text{HO}^-$  on the  $\text{C}^+$   
 E. formation of product from the intermediate

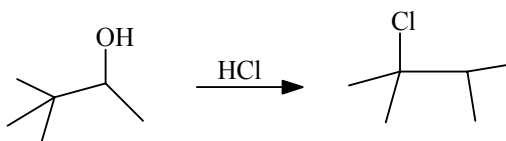
49. The reaction is an example of: (1 mark)

- A. An  $\text{S}_{\text{N}}1$  reaction.  
 B. An  $\text{S}_{\text{N}}2$  reaction.  
 C. An elimination reaction.  
 D. An addition reaction.  
 E. A rearrangement.

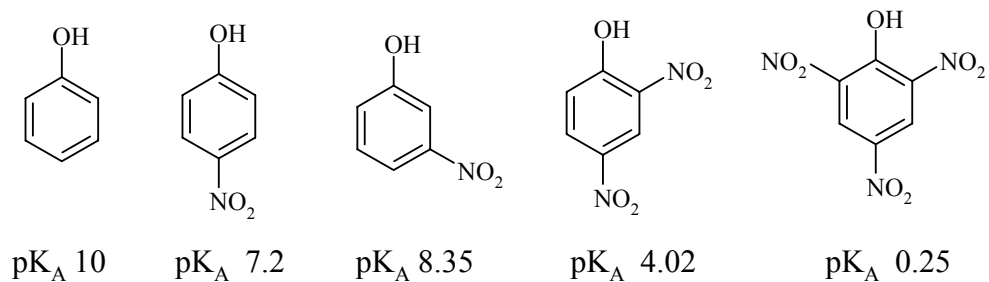
Value10 PART 6 MECHANISM

Write your answer in the booklet provided. Show your workings as **PARTIAL** marks will be given.

- (a) Draw a double headed curly arrow ( $\curvearrowright$ ) mechanism to account for the following experimental observations:



- (b) Explain, using resonance structures and/or a short paragraph, the following  $pK_A$  data for the following nitrophenols.



Value10 PART 7 SPECTROSCOPY

**Write your answer in the booklet provided. Show your workings as PARTIAL marks will be given.**

The combustion analysis of an unknown molecule is as follows:

53.09% C, 6.24% H, and 12.38% N

From this data and the I.R., M.S.,  $^{13}\text{C}$  and  $^1\text{H}$  NMR shown below, identify the structure of the molecule.

DIAGRAMS WILL BE ADDED AS SOON AS TIME ALLOWS

IN THE ORIGINAL EXAM THEY WERE PHOTOCOPIED IN TO PLACE

CONVERTING TO PDF REQUIRES A DIGITAL VERSION

Value10 PART 8 STRUCTURE DETERMINATION

**Write your answer in the booklet provided. Show your workings as PARTIAL marks will be given.**

4 constitutional isomers, **A**, **B**, **C**, and **D** each with the molecular formula  $C_4H_9Cl$ , are obtained from the reaction of the appropriate alcohols with  $ZnCl_2/HCl$ , better known as the Lucas test.

**A** was the product of a very fast reaction, **B** of an intermediately fast reaction, and **C** and **D** are the products of an extremely slow reaction. Identify and name (IUPAC) structures **A**, **B**, **C**, and **D**. Match each compound with the appropriate  $^1H$  NMR spectrum I-IV shown on the following page.

Value

DIAGRAMS WILL BE ADDED AS SOON AS TIME ALLOWS  
IN THE ORIGINAL EXAM THEY WERE PHOTOCOPIED IN TO PLACE  
CONVERTING TO PDF REQUIRES A DIGITAL VERSION

Value

**\*\*\*THE END\*\*\***