Value

THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

OCTOBER 20th 2000 Time: 2 Hours

READ THE INSTRUCTIONS CAREFULLY

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

The examination consists of Parts 1 - 8, each of which should be attempted. Note that some parts provide you with a choice of questions, *i.e*. answer 4 out of 5. These will be graded in numerical order until the required number have been completed, regardless of whether they are right or wrong. Parts 1 - 5 will be computer graded, and only Parts 6, 7, and 8 are to be answered in the booklet provided. A periodic table with atomic numbers and atomic weights is appended to the end of the exam.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 39 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***.

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14 PART 1 RELATIVE PROPERTIES

ANSWER ANY SEVEN (7) of Questions 1-8**.**

Arrange the items in Questions 1-8 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**

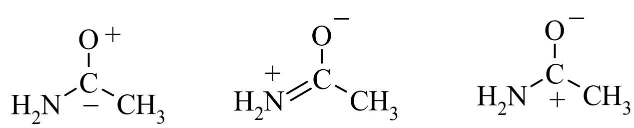
1. The oxidation state for the **carbon** atoms in each of the following :

$HC{\equiv}\mathbf{C}H$	$\mathbf{C}Cl_4$	$Cl\text{-}C{\equiv}\mathbf{C}Cl$
i	**ii**	**iii**

2. The length of the **CH** bonds indicated in each of the following

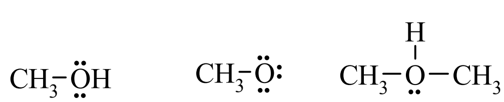
$CH_3C{\equiv}\mathbf{CH}$	$CH_3CH{=}\mathbf{CH_2}$	$H_3C{-}\mathbf{CH_3}$
i	ii	iii

3. The relative importance of the following resonance contributors to ethanamide



i **ii** **iii**

4. The formal charge on the **oxygen** atom in each of the following molecules:



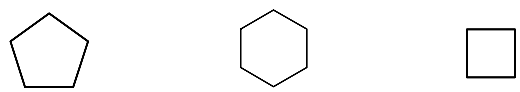
i **ii** **iii**

Value

Use the following code to indicate your answers.

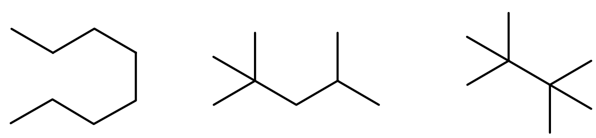
A.	**i** > **ii** > **iii**	D.	**ii** > **iii** > **i**
B.	**i** > **iii** > **ii**	E.	**iii** > **i** > **ii**
C.	**ii** > **i** > **iii**	AB.	**iii** > **ii** > **i**

5. The heat of combustion, ΔH_c^o, per methylene ($-CH_2-$) for each of the following molecules: (most endothermic to most exothermic)



i **ii** **iii**

6. The heat of formation, ΔH_f^o for each of the following molecules: (most endothermic to most exothermic)



i **ii** **iii**

7. The number of constitutional isomers for the following molecular formulae:

C_3H_6 C_3H_8 C_3H_8O

i **ii** **iii**

8. The H-C-X bond angle in each of the following molecules:

CH_3CH_3	CH_2O	HCN
(X = C)	(X = O)	(X = N)
i	**ii**	**iii**

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10 PART 2: LABORATORY

ANSWER ALL of the questions 9-18.

For **questions 9-14**, select the **most efficient** method for carrying out the required task from the list provided.

9. Purify a contaminated solid
10. Check the purity of a solid sample
11. Separate a mixture of miscible liquids with boiling points that differ by 5 ^{o}C
12. Remove an insoluble impurity from a solution
13. Remove an organic compound from an aqueous mixture
14. Collect crystals from the mother liquor

List of possible answers:

A filtration

B fractional distillation

C extraction

D recrystallisation

E simple distillation

AB melting point determination

AC boiling point determination

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The following **questions 15-18** are based on the extraction experiment you performed and the principles behind it.

Suppose you are extracting a sample of an organic compound **X** of molecular weight = 100g/mol, from an aqueous solution using dichloromethane where the distribution coefficient for **X**, K_D = 1 (recall that K_D = [concentration in solvent 1] / [concentration in solvent 2]).

Starting off with 1g of **X** in 50ml of water….

15. What % of the initial amount of **X** will be extracted in an extraction with a 50ml portion of dichloromethane ?

    A 100 % **B** 75 % **C** 50 % **D** 25 % **E** 0 %

16. What % of the initial amount of **X** will then be extracted in an extraction with a second 50ml portion of dichloromethane ?

    A 100 % **B** 75 % **C** 50 % **D** 25 % **E** 0 %

17. What % of the initial amount of **X** in total has now been extracted after the two 50ml portions of dichloromethane have been used ?

    A 100 % **B** 75 % **C** 50 % **D** 25 % **E** 0 %

18. What % of the initial amount of **X** will be extracted if the sample is extracted with a single 100ml portion of dichloromethane ?

    A 100 % **B** 75 % **C** 67 % **D** 50 % **E** 33 %

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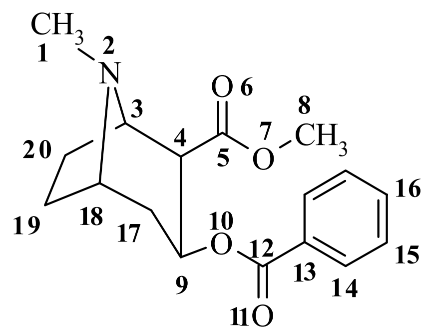
14 PART 3: MOLECULAR PROPERTIES

ANSWER ALL of the questions 19 - 25.

For each of the questions 19 - 25 about the drug COCAINE (below), select the answer from those provided.
In some case more than one answer may be correct and for full marks all correct answers must be selected.

COCAINE



19. What is the oxidation state of **C5** ?

A. +4 B. +3 C. +2 D. -3 E. -4

20. What is the oxidation state of **C18** ?

A. +2 B. +1 C. 0 D. -1 E. -2

21. Which atom(s) is (are) sp^2 hybridised ?

A. **C1** B. **C5** C. **O6** D. **C14** E. **C19**

22. What is the hybridisation of **N2** ?

A. sp B. sp^2 C. sp^3 D. sp^4 E. $1s^2 2s^2 2p^3$

23. Which carbon(s) is (are) secondary ?

A. **C1** B. **C3** C. **C4** D. **C13** E. **C20**

24. Which of the following functional groups are found in cocaine ?

A. amide B. amine C. ketone D. ether E. ester

25. Which carbon atom is located in a position *meta* to an ester substituted carbon ?

A. **C13** B. **C14** C. **C15** D. **C16** E. **C18**

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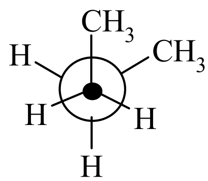
12 PART 4: CONFORMATIONAL ANALYSIS

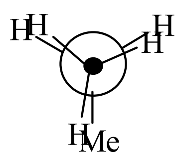
ANSWER ALL of the questions 26-31.

26. Which one of the following terms **best** describes the conformation of butane shown ?



A anti
B eclipsed
C gauche
D staggered
E syn

27. Which of the following terms **best** describes the conformation of propane shown ?



A anti
B eclipsed
C gauche
D staggered
E syn

28. Which term **best** describes the relationship between a pair of structures with the same molecular formulae, yet differing in the spatial arrangement of bonds, but can be interconverted by rotation about sigma bonds ?

A: canonicals **B**: constitutional **C**: configurational
D: conformational **E**: geometric **AB**: identical

29. Which term **best** describes the isomer relationship between isopropyl methyl ether and diethyl ether ?

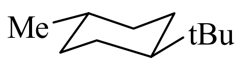
A: canonicals **B**: constitutional **C**: configurational
D: conformational **E**: geometric **AB**: identical

<u>*Value*</u>

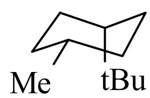
30. Which of the following is the **best** example of a steric interaction ?

A: the interaction between the lone pairs in a water molecule
B: the strain of cyclopropane compared to propane
C: the eclipsing interaction of two Cl atoms in 1,2-dichloroethane
D: the alignment of the C-C bonds in cyclopropane
E: the 1,3-diaxial interaction in the axial conformer of methylcyclohexane

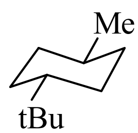
31. Which of the following represents the most stable conformation of *cis*-1-t-butyl-4-methylcyclohexane ?



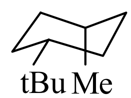
A



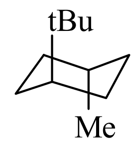
B



C



D



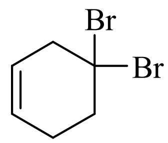
E

<u>*Value*</u>
14 PART 5: NOMENCLATURE

ANSWER ANY SEVEN (7) of the questions 32-39.

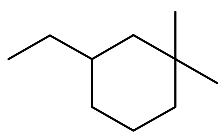
For each of questions 32 to 35, select the correct name for the compound shown:

32.



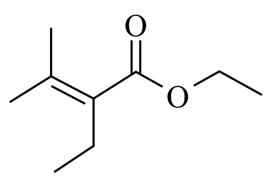
A. *trans*-1,1-dibromocyclohexene
B. 1,1-dibromocyclohex-3-ene
C. 3,3-dibromocyclohexene
D. 4,4-dibromohexane
E. 4,4-dibromocyclohexene

33.



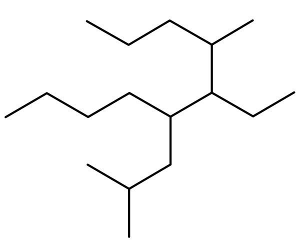
A. 1-ethyl-3,3-dimethylcyclohexane
B. 3,3-dimethyl-1-ethylcyclohexane
C. 3-ethyl-1,1-dimethylcyclohexane
D. 1,1-dimethyl-3-ethylcyclohexane
E. 1,1,3-dimethylethylcyclohexane

34.



A. ethyl 2-ethyl-3-methyl-2-butenoate
B. O,2-diethyl-3-methyl-2-butenaote
C. 1-ethoxy-2-ethyl-3-methyl-2-butenal
D. 2-methyl-2-pentenyl propanaote
E. ethyl heptenoate

35.



A. 4-isobutyl-3-pentyloctane
B. 5-ethyl-4-methyl-6-(2-methylpropyl)decane
C. 6-ethyl-7-methyl-5-(methylpropyl)decane
D. 4-butyl-5-ethyl-2,6-dimethylnonane
E. 4-isobutyl-3-*sec*-propyloctane

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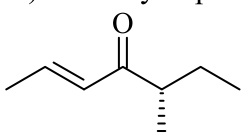
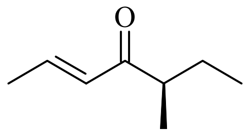
For each of questions 36 to 39, select the correct structure for the name shown:

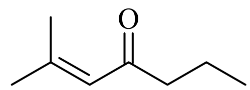
36. (2E, 5R)-5-methylhept-2-en-4-one:



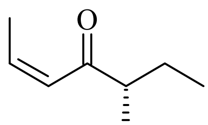
A



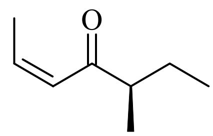
B



C

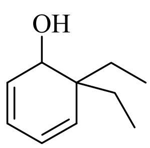


D

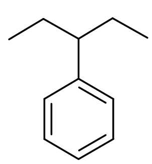


E

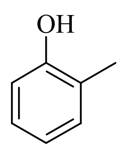
37. 2-ethylphenol:



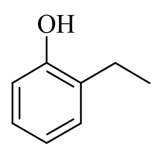
A



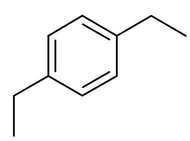
B



C



D



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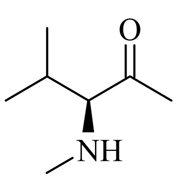
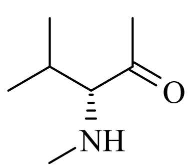
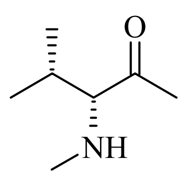
38. (S)-(N,4)-dimethyl-3-aminopentan-2-one:



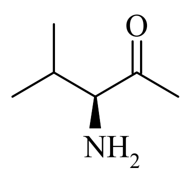
A.



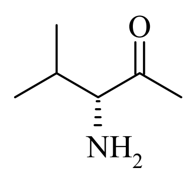
B.



C.

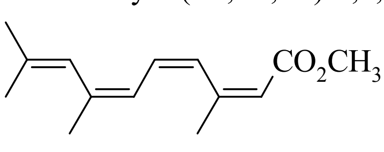


D.

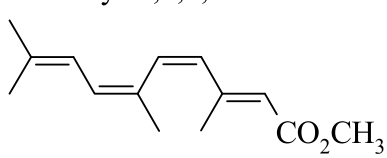


E.

39. Methyl (2Z,4Z,6Z)-3,6,9-trimethyl-2,4,6,8-decatetraenoate:



A



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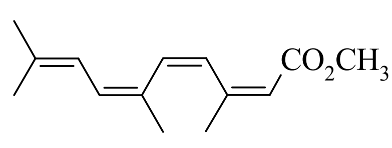
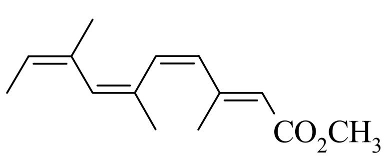
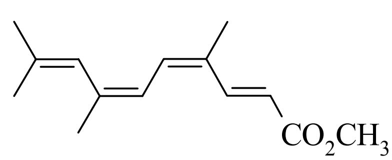


C



D



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12 PART 6: STRUCTURE DETERMINATION:

Write your answer in the booklet provided. For FULL marks you MUST show your working. PARTIAL marks will be awarded.

ALL THE QUESTIONS IN THIS SECTION SHOULD BE ANSWERED BASED ON THE FOLLOWING DATA:

An elemental analysis was performed on a sample taken from an unlabelled drum found in a landfill site. The result indicated that the sample contained 47.09% C, 6.59% H, and 46.33% of an unidentified element. The sample was further analysed and found to be a mixture of isomers with a molecular weight = 76.526 g/mol.

(a) Use the combustion analysis data to determine the empirical formula.

(b) Draw a pair of geometrical isomers

(c) Draw 3 compounds that are constitutional isomers of those in part (b)

(d) Provide the IUPAC name of for the 5 compounds from parts (b) and (c)

(e) For the 5 isomers above, draw diagrams to indicate any resonance contributors and label them as major or minor. If there are no other resonance contributors possible for a particular structure, indicate why.

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12 PART 7: MECHANISM

Write your answer in the booklet provided.

Draw a mechanism sequence using double headed (*i.e.* electron pair) curly arrows that represents the single reaction sequence described verbally by the following points in which an ester, ethyl ethanoate, is treated with aqueous sodium hydroxide to give the salt of the carboxylic acid, ethanoic acid and an alcohol, ethanol.

1. Draw a resonance structure of the ester that shows the electrophilic character of the carbonyl carbon.

2. Attack of the hydroxide (as a nucleophile) on this electrophilic carbon giving a tetrahedral intermediate with a negatively charged oxygen atom.

3. Reform the carbonyl group and simultaneously displacing an alkoxide and generating the carboxylic acid.

4. An acid base reaction that produces the alcohol, ethanol, and the carboxylate ion.

   Draw the resonance contributors to the structure of the carboxylate ion and rank them in order of importance.

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12 PART 8: THERMODYNAMICS

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

The heats of combustion for three simple alkanes are provided in the table below.

Use this data to answer the following questions:

(a) Calculate an *estimate* for the heat of combustion of a single methyl group, $-CH_3$

(b) Calculate an *estimate* for the heat of combustion of a single methylene group, $-CH_2-$

(c) Using these estimates, predict the heat of combustion of cyclobutane and cyclohexane.

(d) The actual value for cyclobutane is 656.3 kcal/mol (2746 kJ/mol). How does this compare to the value you calculated in part (c) ? Justify this result.

(e) The actual value for cyclohexane is 944.7 kcal/mol (3953 kJ/mol). How does this compare to the value you calculated in part (c) ? Justify this result.

Heats of Combustion, ΔH_c^o

Compound	**kcal/mol**	**kJ/mol**
Ethane	373.0	1561
Propane	530.4	2219
Butane	687.8	2878

THE END