THE UNIVERSITY OF CALGARY

FACULTY OF CONTINUING EDUCATION

MIDTERM EXAMINATION

CHEMISTRY 351

JUNE 6th 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. 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***.

14 PART 1 RELATIVE PROPERTIES

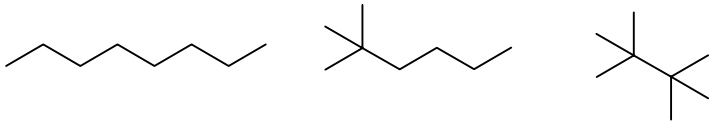
ANSWER ANY SEVEN (7) of Questions 1-8**.**

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.

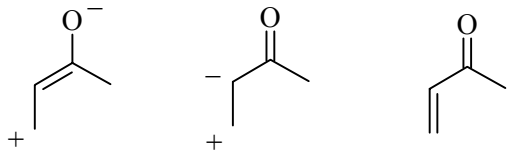
A.	i > ii > iii	D.	ii > iii > i
B.	i > iii > ii	E.	iii > i> ii
C.	ii > i > iii	AB.	iii > ii > i

1. The relative stability of the following molecules:



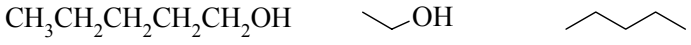
i **ii** **ii**

2. The relative importance of the following resonance structures of 3-buten-2-one:



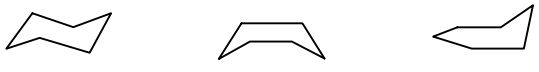
i **ii** **iii**

3. The solubility of each of the following in water:



i **ii** **iii**

4. The relative energies of the following conformations of cyclohexane::

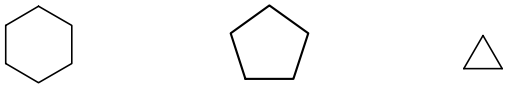


i **ii** **iii**

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 formation, ΔH_f^o, per methylene ($-CH_2-$) for each of the following molecules: (most endothermic to most exothermic)



i **ii** **iii**

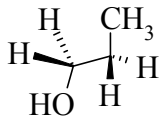
6. The relative acidity of the following systems:

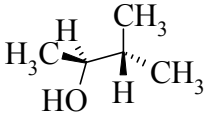
CH_3CO_2H $CH_3CH_2NH_2$ CH_3CH_2OH

i **ii** **iii**

7. The number of eclipsed conformations of different energies that are possible for the following molecules:

CH_3-CH_3





i **ii** **iii**

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

H_2O C_2H_4 CH_4

i **ii** **iii**

10 PART 2: LABORATORY

ANSWER ALL of the questions 9-18.

For questions 9-15, decide whether the whole statement is true or false.
If it is **TRUE**, then blacken **A**.
If it is **FALSE**, then blacken **B**.
(1 mark / question)

9. During the determination of a melting point, the sample should be heated rapidly to ensure that the sample melts in a short time frame.

10. In an extraction using a separatory funnel, the organic layer will always be the lower layer.

11. The boiling points of pure liquids increase with increasing pressure.

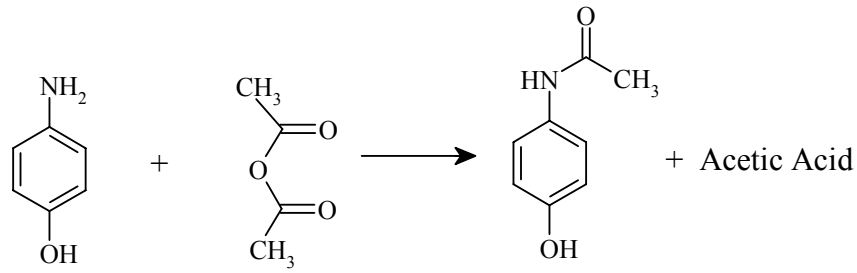
12. Recrystallisation is used to purify solids.

13. Recrystalisation is usually carried out using the minimum volume of hot solvent to ensure a saturated solution is formed.

14. Raoult's Law describes the ideal behaviour of a pair of miscible liquids.

15. The partition or distribution coefficient is given by the ratio of the concentrations of a solute dissolved in two miscible solvents.

Questions **16-18** (1 mark per question) refer to the following reaction scheme:



	Aminophenol	Acetic anhydride	Acetaminophen
MW	109	102	151
Density		1.08 g/ml	

A student used 2.18 g of aminophenol and 1.51 ml of acetic anhydride to prepare 1.81 g of crude acetaminophen, and 1.51 g of pure material after purification.

Note 1 mmol = 0.001 mol.

16. How many moles of limiting reagent were used?

A. 1.5 mmol B. 1.6 mmol C. 15 mmol D. 16 mmol E. 160 mmol

17. How many mmoles of crude acetaminophen were obtained?

A. 1.0 B. 1.2 C. 10 D. 12 E. 120

18. What was the % yield of PURE acetaminophen?

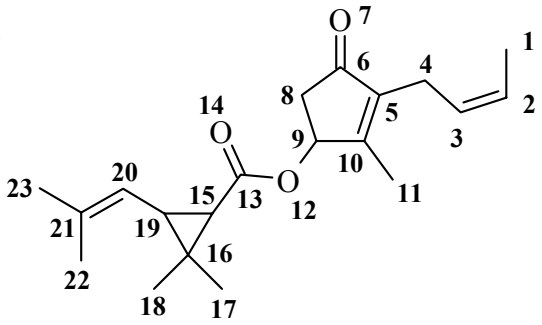
A. < 60% B. 60-70% C. 70-80% D. 80-90% E. > 90%

14 PART 3: MOLECULAR PROPERTIES

ANSWER ALL of the questions 19 - 25.

For each of the questions 19 - 25 about a naturally occurring insecticide, **CINERIN 1** (below), select the answer from those provided. In some case more than one answer may be correct.

CINERIN 1



19. What is the oxidation state of **C9** ?

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

20. What is the oxidation state of **C13** ?

A. +4 B. +3 C. +2 D. +1 E. 0

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

A. C1 B. C4 C. C6 D. C9 E. C20

22. What is the hybridisation of **O7** ?

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

23. What is the hybridisation of **O12** ?

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

24. Which of the following functional groups are found in **CINERIN 1** ?

A. alkene B. aldehyde C. ether D. ester E. ketone

25. How many units of unsaturation are there in **CINERIN 1** ?

A. 3 B. 4 C. 5 D. 6 E. 7

12 PART 4: CONFORMATIONAL ANALYSIS

ANSWER ALL of the questions 26-31.

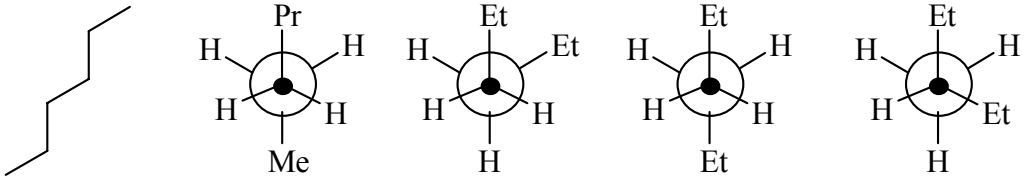
26. Which one of the following terms best describes the most stable conformation of butane ?

A anti **B** eclipsed **C** gauche **D** staggered **E** syn

27. Which of the following terms about strain best describe the repulsive interaction between a pair of atoms ?

A ankle **B** angle **C** ring **D** steric **E** torsional

28. Which of the following diagrams shows a Newman projection of the C3-C4 bond in the anti conformation of hexane ?



A **B** **C** **D** **E**

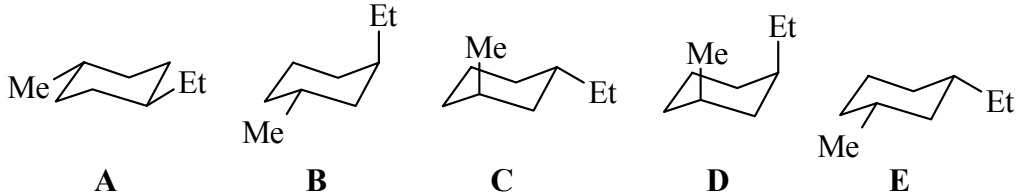
29. Which term best describes the boat and chair isomers of cyclohexane ?

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

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

A: the eclipsing interaction of two H atoms in ethane
B: the strain of cyclobutane compared to butane
C: the flagpole interaction in boat cyclohexane
D: the alignment of the C-C bonds in cyclopropane
E: the interaction between the lone pairs in a water molecule

31. Which of the following represents the most stable conformation of *trans*-1-ethyl-3-methylcyclohexane ?



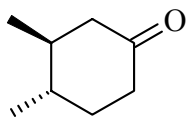
A **B** **C** **D** **E**

14 PART 5: NOMENCLATURE

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

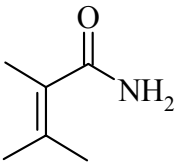
For each of questions 32 to 35, select the correct name for the compound shown:

32.



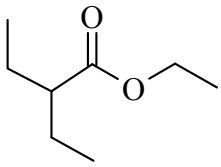
A. *trans*-3,4-dimethoxycyclohexanone
B. *cis*-3,4-dimethoxycyclohexanone
C. *trans*-4,5-dimethylcyclohexanone
D. *trans*-3,4-dimethylcyclohexanone
E. *cis*-3,4-dimethylcyclohexanone

33.



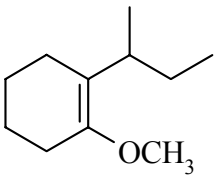
A. (Z)- 2,3-dimethyl-2-butenoic acid
B. 2,3-dimethyl-2-butenamine
C. 2,3-dimethyl-2-butenone amine
D. (Z)-2,3-dimethyl-2-hexenoic acid
E. 2,3-dimethyl-2-butenamide

34.



A. 2,3-diethylbutanoate
B. ethyl 2-ethylbutyl ether
C. ethyl 2-ethylbutanoate
D. ethyl 2,2-diethylethanoate
E. ethyl 2-ethylbutanoic acid

35.

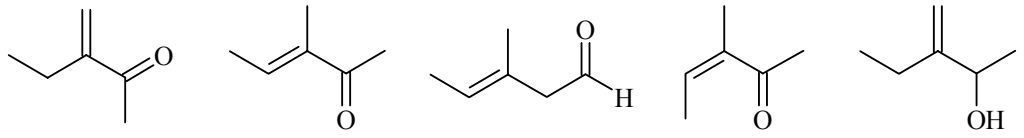


A. 1-methoxy-2-butylcyclohexene
B. 1-methoxy-2-(1-methylpropyl)cyclohexene
C. 1-(1-methylpropyl)-2-methoxycyclohexene
D. 1-(1-methylpropyl)-2-ethoxycyclohexane
E. 2-methoxy-1-(1-methylpropyl)cycloheptene

Value

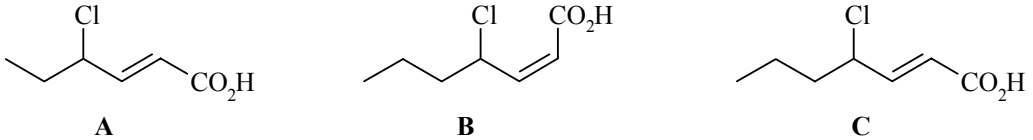
For each of questions 36 to 39, select the correct structure for the name shown:

36. (E)-3-methylpent-3-en-2-one



A **B** **C** **D** **E**

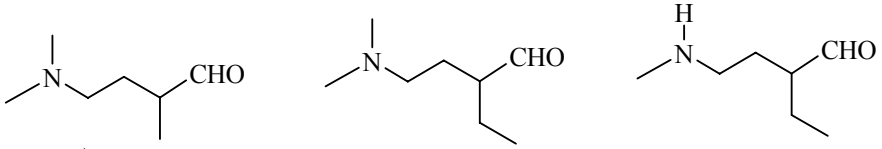
37. Z-4-chloro-2-hexenoic acid



A **B** **C**

D **E**

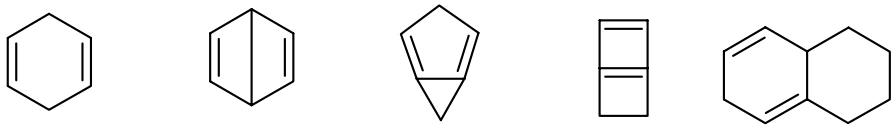
38. 4-(N,N-dimethylamino)-2-ethylbutanal:



A. **B.** **C.**

D. **E.**

39. 2,5-bicyclo[2.2.0]cyclohexadiene:



A **B** **C** **D** **E**

Value

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 refer to the following data:

A combustion analysis was performed on a sample taken from a illegal drug laboratory. The result indicated that the sample contained 66.62% C and 11.19% H. The sample was further analysed and found to be a mixture of isomers with a molecular weight = 72.115 g/mol.

Use the combustion analysis data to determine the empirical formula and the molecular formula

Draw a pair of constitutional isomers and provide the IUPAC names for them.

Draw a pair of geometrical isomers and provide the IUPAC names of them.

Draw an isomer that has resonance contributors, draw the resonance contributors and rank them as major or minor.

List 5 functional groups that are possible from this molecular formula.

Value

11 PART 7: MECHANISMS

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 phenylethanone is treated with aq. sulphuric acid to give the diol, 1-phenyl-1,1-ethandiol.

1. Protonation of phenylethanone (acetophenone) by sulphuric acid to give an oxonium ion.

2. A resonance structure of this species which is a carbocation.

3. Attack of water (as a nucleophile) on this carbocation to give a new oxonium ion.

4. Abstraction of a proton by water (as a base) to produce 1-phenyl-1,1-ethanediol.

Draw the other important resonance contributors to show the stability of the carbocation in 2.

Value

11 PART 8: THERMODYNAMICS

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

There are three possible configurational isomers of 1-t-butyl-2,3-dimethylcyclopropane. The calculated heats of formation, ΔH_f^o, of these three structures are listed below.

Draw the three possible structures

Match the heats of formation, ΔH_f^o, values to the appropriate structures

Justify your choice.

Using the available data, calculate **EITHER**:

i) the heat of combustion, ΔH_c^o, of the most stable structure, **OR**,

ii) the equilibrium constant, K, for the potential interconversion of the most stable and least stable forms at 25°C.

DATA:

Kcal/mol	kJ/mol
ΔH_f^o (**1**) = - 8.331	ΔH_f^o (**1**) = -34.857
ΔH_f^o (**2**) = -12.287	ΔH_f^o (**2**) = -51.409
ΔH_f^o (**3**) = -14.061	ΔH_f^o (**3**) = -58.831
ΔH_c^o (**H_2, gas**) = -68.0	ΔH_c^o (**H_2, gas**) = -284.51
ΔH_c^o (**C, graphite**) = -94.0	ΔH_c^o (**C, graphite**) = -393.3
R = 1.987 cal/molK	R = 8.314 J/molK

****THE END****