THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

OCTOBER 20th 1998. 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 - 41 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***.

Value

14 PART 1 RELATIVE PROPERTIES

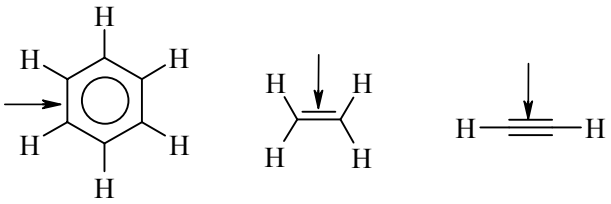
ANSWER ANY SEVEN (7) of Questions 1-8**.**

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 bond lengths of the indicated bonds in each of the following:



i ii iii

2. The C-C-C bond angle in each of the following:

$CH_3CH_2CH_3$ $CH_3CH{=}CH_2$ $CH_3C{\equiv}CH$

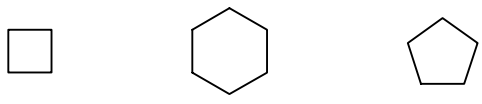
i ii iii

3. The boiling point of the following molecules:

$CH_3CH_2CH_2CH_3$ $H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-H$ $CH_3CH_2CH_2OH$

i **ii** **iii**

4. The ring strain energy of the following molecules:



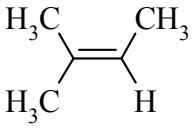
i **ii** **iii**

Value

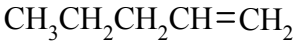
Use the following code to indicate your answers.

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

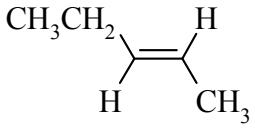
5. The heat of formation, ΔH_f^o, for each of the following molecules: (most +ve to most -ve)



i

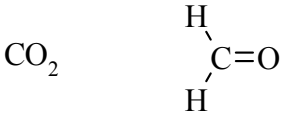


ii



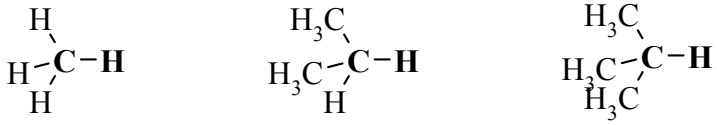
iii

6. The oxidation level for the carbon atom in each of the following:



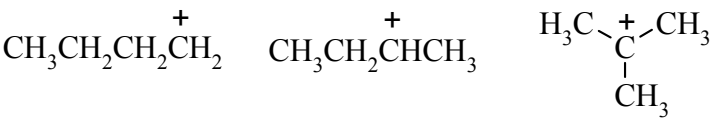
i ii iii

7. The bond energy of the **C-H** bonds indicated in each of the following:



i ii iii

8. The stability of the following carbocations:



i ii iii

Value

13 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, blacken A. If it is FALSE, then blacken B. (1 mark / question)

9. When recording the melting point of a solid it is important to correct to the sea level value for literature comparisons since melting point decreases with decreasing pressure.

10. When measuring a melting point it is important to heat vigorously to ensure that the sample melts in as short a time as possible.

11. The boiling point of water on a typical day in Calgary should be 100 ^{o}C.

12. The ideal behaviour of mixtures of liquids is described by Murphy's Law

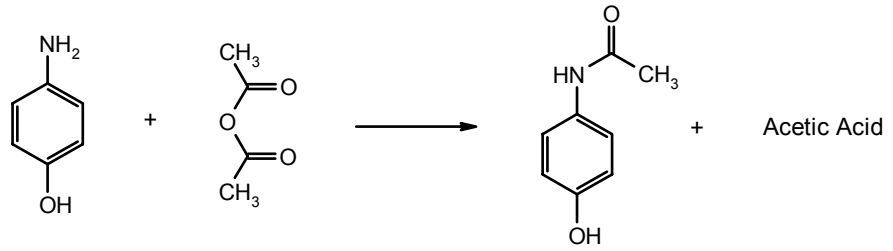
13. During distillation, the fractionating column should be cooled by a gentle flow of water.

14. When carrying out a fractional distillation it is important to heat the distilling flask slowly to ensure that equilibrium between the solution and the vapour is obtained.

15. Solutions can be decolourised by adding charcoal, warming and then filtering.

Value

Questions **16-18** (2 marks / question) refer to the following reaction scheme:



	Aminophenol	Acetic anhydride	Acetaminophen	
MW	109	102	151	60
Density		1.08g/ml		1.049g/ml

In the acetaminophen experiment, Stu Dent used 0.72g of aminophenol and 0.45 ml of acetic anhydride, and obtained 0.50g of crude acetaminophen and 0.29g of acetic acid. After recrystallisation Stu had only 0.25g of pure acetaminophen.

Note 1 mmol = 0.001 mol

16. How many moles of the limiting reagent were used ?

A. 4.1 mmol B. 4.8 mmol C. 6.6 mmol D. 48 mmol E. 66 mmol

17. What was the % yield of crude acetaminophen ?

A. < 65% B. 65-75% C. 75-85% D. 85-95% E. >95%

18. How many mmoles of pure acetaminophen were obtained ?

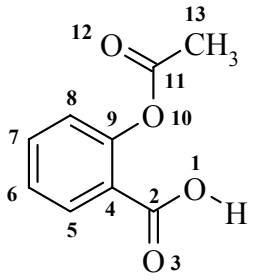
A. 1.7 B. 3.4 C. 17 D. 34 E. 604

Value

14 PART 3: MOLECULAR PROPERTIES

ANSWER ALL of the questions 19 - 25.

For each of the questions 19 - 25 about ASPIRIN (below), select the answer from those provided:



ASPIRIN

19. What is the oxidation level of **C11** ?

A. +3 B. +2 C. 0 D. -2 E. -3

20. What is the oxidation level of **O10** ?

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

21. Which carbon is sp^3 hybridised ?:

A. C4 B. C6 C. C9 D. C11 E. C13

22. Which oxygen is part of an ester carbonyl ?

A. O1 B. O3 C. O10 D. O12

23. What is the index of hydrogen deficiency (IHD) of Aspirin ?

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

24. Which hydrogen is the most acidic ? Designate this by selecting the atom to which the H is bonded.

A. 1 B. 4 C. 5 D. 6 E. 13

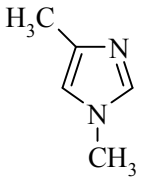
25. Which carbon atom is located in a position *para* to the carboxylic acid group ?

A. 4 B. 5 C. 6 D. 7 E. 9

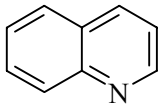
Value

14 PART 4: AROMATICITY AND RESONANCE

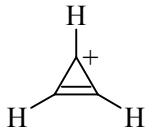
ANSWER ANY SEVEN (7) of the questions 26-33.



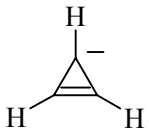
A



B



C

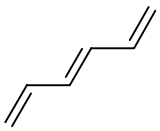


D

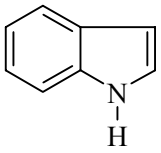
E

AB

AC



AD



AE

BC

For each of the questions 26-33 select a compound from the list above that is **best** described as:

26. A 4π-electron, anti-aromatic cationic system.

27. Non-aromatic as drawn, but has an aromatic conjugate base.

28. A non -conjugated hydrocarbon.

29. An aromatic system because n=0 in the Huckel 4n+2 rule

30. A 10π-electron, aromatic system with a moderately basic nitrogen.

31. An anti-aromatic heterocycle.

32. A non-aromatic, conjugated 6π-electron system.

33. A 10π-electron, aromatic system which on protonation becomes a 6π-electron, aromatic system.

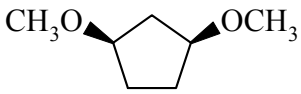
Value

14 PART 5: NOMENCLATURE

ANSWER ANY SEVEN (7) of the questions 34-41.

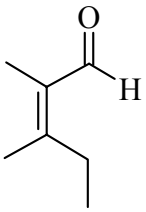
For each of questions 34 to 41, select the correct name for the compound shown:

34.



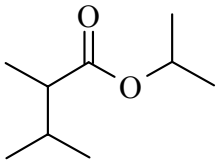
A. dimethyl *cis*-1,2-cyclopentanedicarboxylate
B. *cis*-1,4-dimethylcyclopentene
C. *cis*-1,3-dimethyoxycyclopentane
D. *trans*-1,3-dimethyoxycyclopentane
E. *cis*-1,3-dimethoxycyclohexane

35.



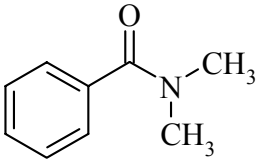
A. (Z)-2-methyl-3-ethyl-2-butenal
B. (Z)-2,3-dimethyl-2-pentenal
C. (E)-2,3-dimethyl-2-pentenone
D. (Z)-2,3-dimethyl-2-pentanol
E. (E)-2,3-dimethyl-2-pentenol

36.



A. 1,1,4,5,5-pentamethylpentanoate
B. propyl 2,3,3-trimethylpropanaote
C. propyl hexanoate
D. isopropyl 2,3-dimethylbutanoate
E. isopropyl-2-methylbutanoic acid

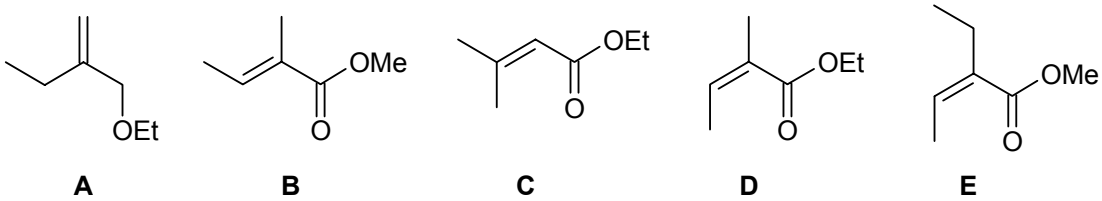
37.



A. N,N-dimethylaminobenzoic acid
B. N,N-dimethylbenzylamine
C. dimethylbenzamide
D. N,N-dimethylbenzamide
E. dimethylbenzonitrile

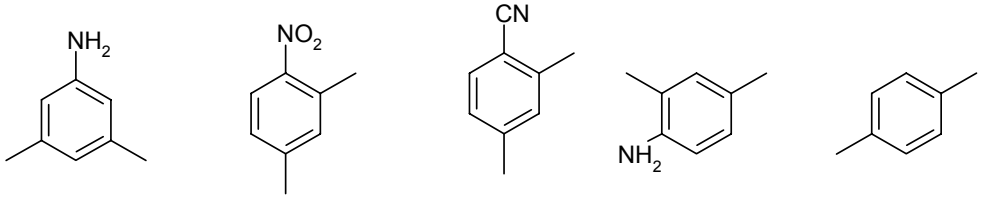
Value

38. Ethyl (Z)-2-methyl-2-butenoate



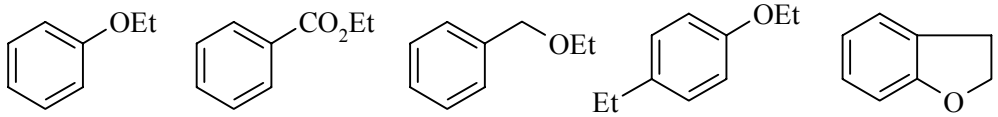
A **B** **C** **D** **E**

39. 2,4-dimethylaniline:



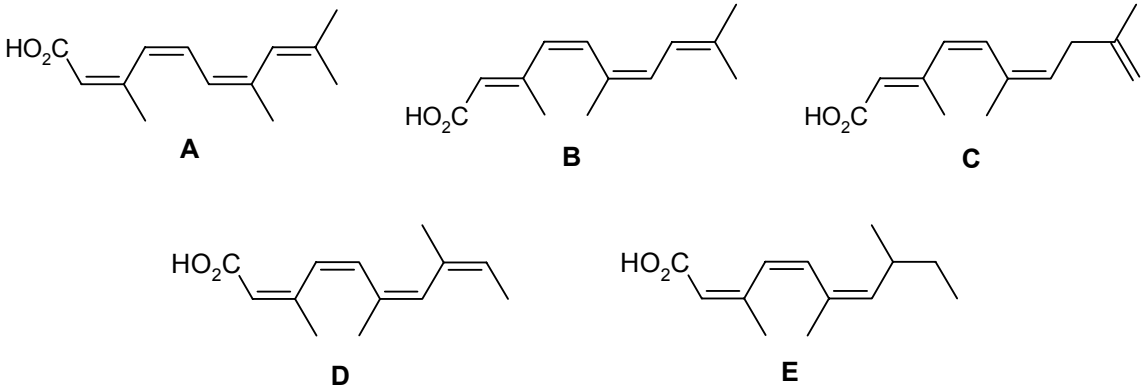
A **B** **C** **D** **E**

40. Benzyl ethyl ether:



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

41. (2Z,4Z,6Z,8Z)-3,6,8-trimethyl-2,4,6,8-decatetraenoic acid:



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

Value

10 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:

A combustion analysis was performed on a hydrocarbon sample from a railcar tanker spill. The result indicated that the sample contained 85.63% C and 14.37% H. The sample was further analysed and found to be a mixture of isomers with a molecular weight = 70.14 g/mol.

Use the combustion analysis data to determine the empirical formula.

What is the index of hydrogen deficiency (IHD) of the isomers ?

Draw the isomers (DO NOT INCLUDE CONFORMATIONAL ISOMERS)

Identify a pair of constitutional isomers, and name them.

Identify a pair of configurational isomers, and name them

Identify the most stable alkene and the most stable alkane.

Value

11 PART 7: MECHANISM and RESONANCE

Write your answer in the booklet provided.

Draw a sequence, using double headed (ie electron pair) curly arrows, that represents the events in the equilibrium between the starting material 2,4-cyclohexadienone and the product phenol. The processes involved are described by the following step-by-step points:

Step 1: Draw 2,4-cyclohexadienone and a resonance structure that shows that the oxygen is a good Lewis base.
Step 2: Add a proton to the base to give an oxonium ion.
Step 3: Draw two resonance structures that distribute the positive charge to two different carbon atoms.
Step 4: Show a generic base, B**:**, removing a proton from an sp^3 carbon atom to give phenol as the product.

Will the equilibrium favour the starting material or the product ?

Why ?

Value

10 PART 8: THERMODYNAMICS

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

Cyclopropane is unique among the cycloalkanes in that it can be hydrogenated with H_2 and Pt metal, giving propane. Similarly, propene can be hydrogenated to give propane.

The heats of formation (ΔH_f^o) for the hydrocarbons are:
propane = -24.8 kcal/mol, cyclopropane = +12.8 kcal/mol , and propene = +4.9 kacl/mol
You should recall that the ΔH_f^o for the elements (e.g. H_2) is defined to be zero.

(1.) From this data, calculate the heats of hydrogenation (ΔH_h^o) of cyclopropane and propene.

(2.) Show this data on an energy diagram in which the enthalpies of propene + H_2, cyclopropane + H_2 and propane are given in rough relative positions, with the more stable system at a lower position on the diagram (as shown in similar diagrams from Fox & Whitesell or in lectures).

(3.) The bond energy of a C-C single bond is about 83 kcal/mol, a C=C double bond is about 146 kcal/mol. Using this data, together with the data from part (1), calculate a "ring strain" for cyclopropane, and compare this with the "ring-strain" value of 28 kcal/mol found experimentally from combustion data.

****THE END****