THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 351

November 7th, 2007 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 graded, 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 located inside the back cover.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 42 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***.

Absolutely no other electronic devices are allowed.

16% **PART 1 RELATIVE PROPERTIES**

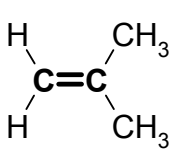
ANSWER ANY EIGHT (8) of questions 1-10 (2 marks per question)

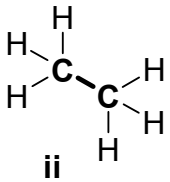
Arrange the items in **questions 1-10** in **DECREASING ORDER** (*i.e*. greatest, most etc. **first**) with respect to the indicated property.

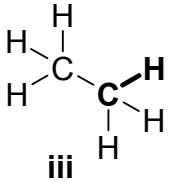
Use the following code to indicate your answers.

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

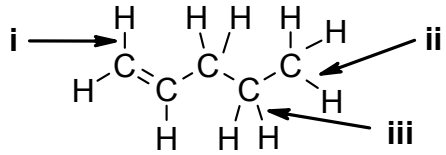
1. The relative lengths of the **BOLD** bonds in each of the following molecules:


i

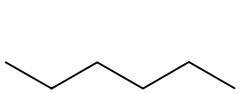

ii

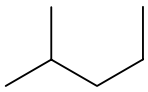

iii

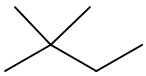
2. The relative strength of the CH bonds indicated in each of the following:



3. The boiling points of the following molecules:


i


ii


iii

4. The relative basicity of the following:

$CH_3CH_2CO_2^-$ $(CH_3)_2NH$ Br^-

i **ii** **iii**

5. The relative energies of the following molecular orbitals in ethene **:**

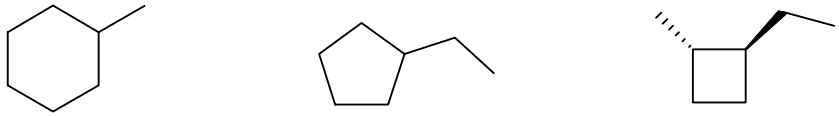
C C π C C π^* C C σ

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**

6. The relative stabilities of the following isomers :



i **ii** **iii**

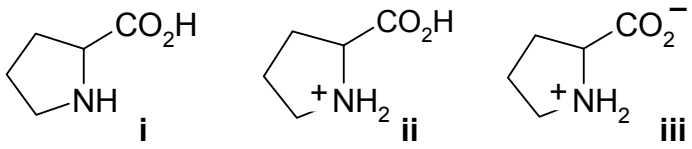
7. The relative energies of the most stable conformations of the following isomeric cyclohexanes:

i trans-1-isopropyl-3-methylcyclohexane

ii cis-1,3-diethylcyclohexane

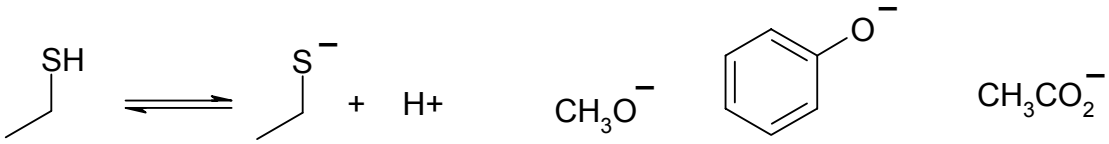
iii 1,1,2,2-tetramethylcyclohexane

8. The relative amounts of the following produced when an aqueous solution of the amino acid proline is reacted with 1 mole equivalent of HCl :



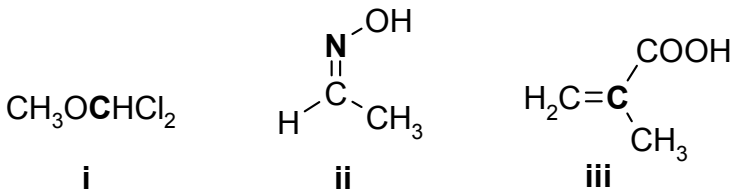
i **ii** **iii**

9. The relative amount of the conjugate base of ethylthiol formed by the reaction of ethylthiol with1 mole equivalent of each of the following:



i **ii** **iii**

10. Oxidation state of the **BOLD** atoms in each of the following molecules:



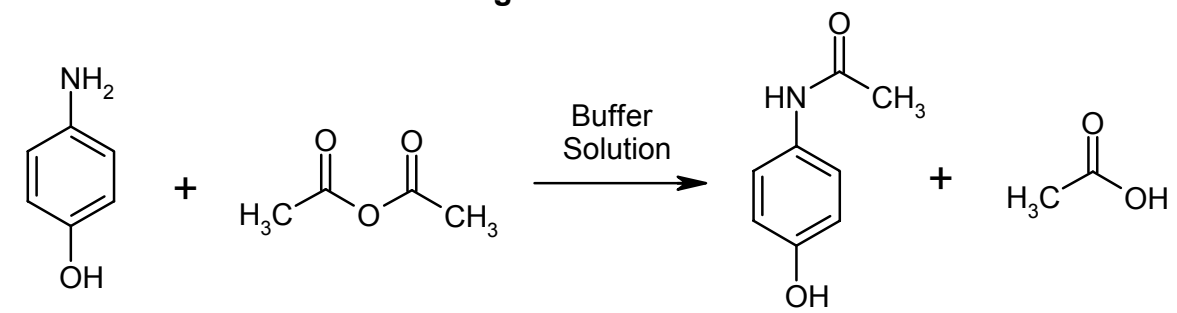
i **ii** **iii**

9% **PART 2: LABORATORY**

ANSWER ALL of the questions 11-16 (1.5 marks per question).

For questions 11-16, select the answer from those provided. **If in some cases more than one answer may be correct, then all correct answers must be selected for full marks.**

Questions 11-16 refer to the following reaction:



1.05g (M.W. 109)

1.00 mL (density = 1.08 g/ mL) (M.W. 102)

Experimental Yield 1.05g (M.W. 151)

11. Which of the following would affect the theoretical yield in grams for this experiment ?

A The solid product containing traces of solvent

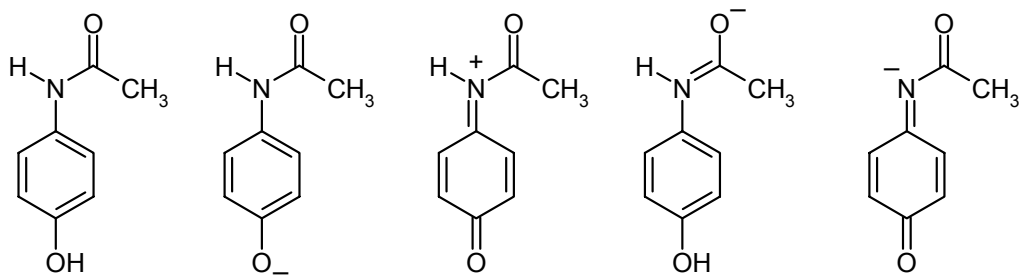
B The product containing impurities

C Using more than 1.05g of p-aminophenol

D Using less than 1.05g of p-aminophenol

E The reaction temperature

12. The measured melting point of the acetaminophen product was found to be 120-121°C. The melting point of a solid is the point at which it goes from the solid to the liquid phase. Which structure below best represents acetaminophen in the liquid phase ?



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

13. Calculate the percent yield of this synthesis.

A 49 % **B** 65 % **C** 72 % **D** 97 % **E** 100 %

14. How many types of hydrogen and carbon are there in acetaminophen ?

A 4H, 3C **B** 4H, 5C **C** 4H, 6C
D 5H, 5C **E** 5H, 6C **AB** 7H, 8C

15. Which experimental technique would be most efficient at purifying the acetaminophen product from any reaction impurities ?

A thin layer chromatography **B** vacuum filtration **C** simple distillation
D fractional distillation **E** recrystallisation **AB** separatory funnel
BC melting point analysis **CD** rotary evaporation

16. One option in the procedure for this experiment involves adding Norit (charcoal) to the reaction. Why ?

A Carbon can act as a general catalyst for this type of acylation reaction

B Carbon catalyses the acylation of the nitrogen of the aminophenol

C Carbon prevents the acylation of the oxygen of the aminophenol

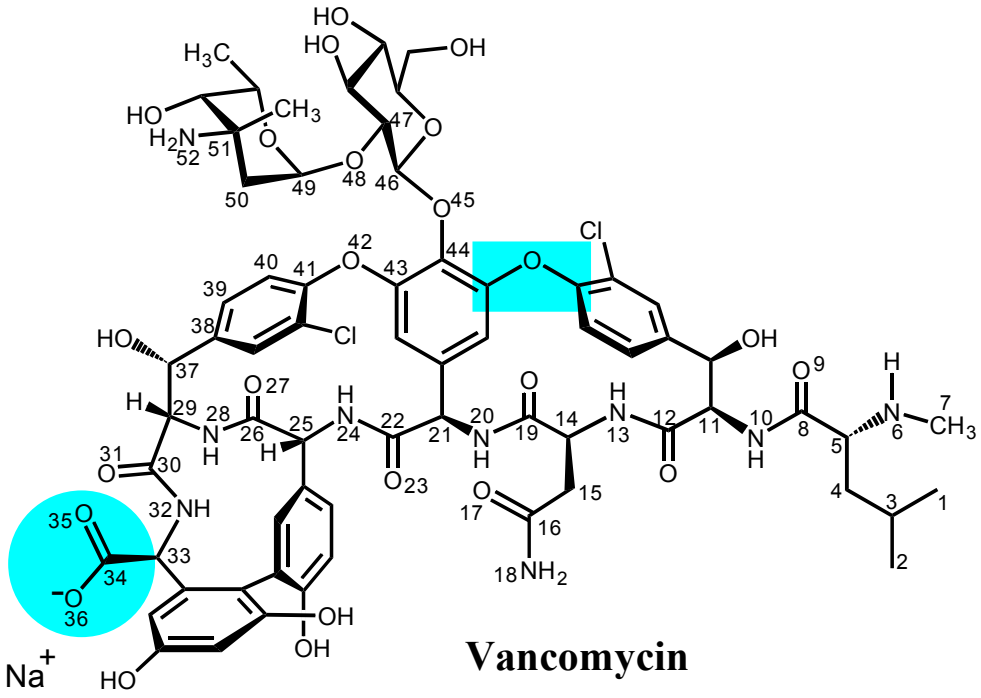
D Carbon can act as a drying agent

E Carbon removes impurities from the reaction

14% **PART 3: MOLECULAR PROPERTIES**

ANSWER ALL of the questions 17-27

For each of the questions 17- 27 about the drug Vancomycin salt (below), select the answer from those provided.



17. What is the oxidation state of **O36** ?

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

18. What is the oxidation state of **C41** ?

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

19. Which of the following is a primary amine ?

A. N6 **B**. N10 **C**. N18 **D**. N32 **E**. N52

20. Which of the following is the most basic ?

A. N6 **B**. N10 **C**. N18 **D**. N32 **E**. N52

21. The proton attached to which of the following atom has the **highest** pKa value ?

A. N6 **B**. N10 **C**. C25 **D**. C50 **E**. N52

22. For N18, what is the **H-N-H** bond angle ?

A. 90° **B**. 180° **C**. 109.5° **D**. 120° **E**. 112°

23. What are the hybridizations of **O36 / N52** ?
A. sp^3 / sp^3 **B**. sp^3 / sp^2 C. sp^2 / sp^2 **D**. sp^2 / sp^3 **E**. sp / sp^3

24. What is the absolute configuration of **C25** ?
A. E **B**. Z C. R **D**. S **E**. cis

25. What is the absolute configuration of **C51** ?
A. E **B**. Z **C**. R **D**. S **E**. cis

26. What is the functional group in the shaded rectangle ?
A. Ester **B**. Phenol **C**. Epoxide **D**. Phenolate **E**. Ether

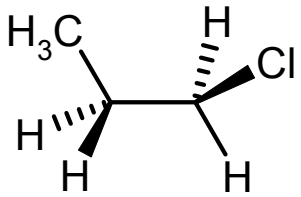
27. What is the functional group in the shaded circle ?
A. Aldehyde **B**. Alcohol **C**. Alkoxide **D**. Carboxylate **E**. Carboxylic acid

12% **PART 4: CONFORMATIONAL ANALYSIS**

ANSWER SIX of the questions 28-34 (2 marks per question).

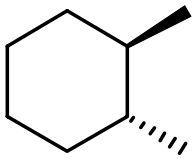
In some cases, more than one answer may be correct and for full marks all correct answers must be selected.

28. Which of the following terms best describes the relationship of the methyl group and the chloride in 1-chloropropane ?



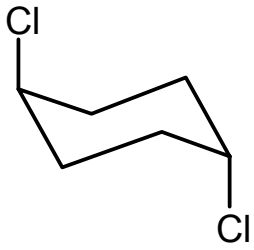
A. Staggered
B. Eclipsed
C. Gauche
D. Anti
E. Syn

29. What is the torsional angle between the two methyl groups in the *trans*-1,2-dimethylcyclohexane in its most stable conformation ?



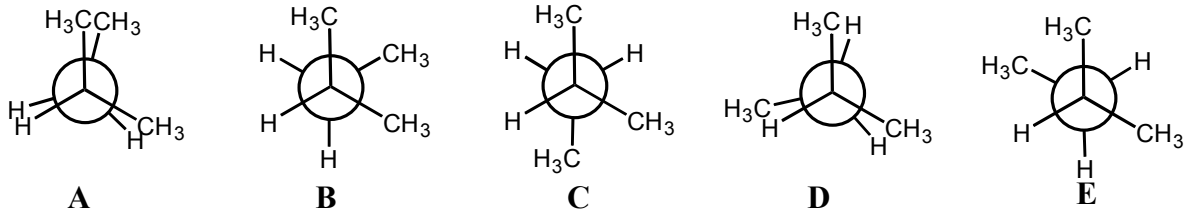
A. 0°
B. 60°
C. 109.5°
D. 120°
E. 180°

30. Which of the following terms best describes the relative position of the two chlorine substituents relative to each other?

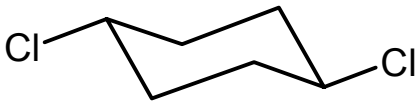


A. Anti
B. Trans
C. Chair
D. Axial
E. Gauche
AB. Equatorial

31. Among the conformations of 2-methylbutane, which one has the highest energy ?

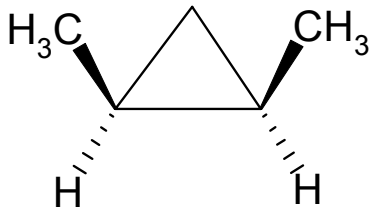


32. What kinds of strain exist in the following conformer ?



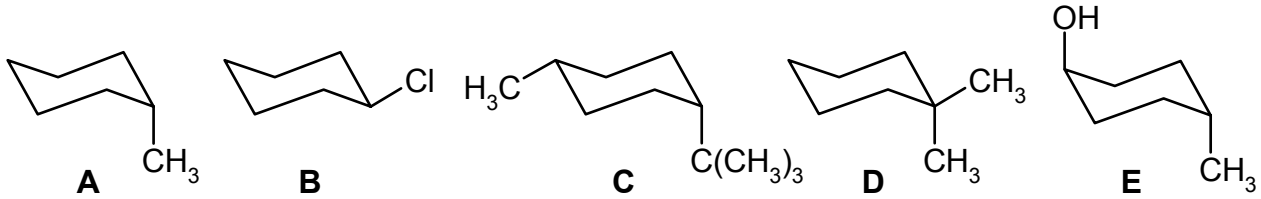
A. Torsional strain
B. Angle strain
C. Ring strain
D. Van der Waals strain
E. None of the above

33. What kinds of strains exist in the following molecule ?



A. Torsional strain
B. Angle strain
C. 1,3-Diaxial repulsion
D. Van der Waals strain
E. None of the above

34. Which of the following molecules has an equilibrium constant closest to 1 for its chair-to-chair ring flipping ?

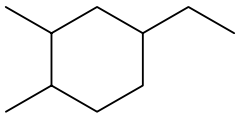


14% **PART 5: NOMENCLATURE**

ANSWER ANY SEVEN (7) of the questions 35-42 (2 marks per question).

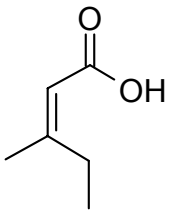
For each of questions 35 to 38, select the correct name for the compound shown:

35



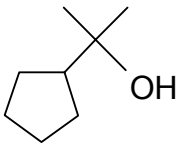
A. 4-ethyl-1,2-dimethylcyclohexane
B. 1,2-dimethyl-4-ethylcyclohexane
C. 1-ethyl-3,4-dimethylcyclohexane
D. 3,4-dimethyl-1-ethylcyclohexane
E. 1,2-dimethyl-5-ethylcyclohexane

36



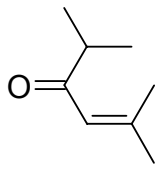
A. (Z)-3-methyl-2-pentenoic acid
B. (E)-3-methyl-2-pentenoic acid
C. (Z)-3-ethyl-2-butenoic acid
D. (E)-3-ethyl-2-butenoic acid
E. (Z)-3-methyl-3-pentenoic acid

37



A. 1-cyclopropylisopentanol
B. 2-cyclopentyl-2-propanol
C. 1-cyclopentyl-2-propanal
D. 1-cyclopentyl-2-propanol
E. 2-cyclopropyl-2-pentanol

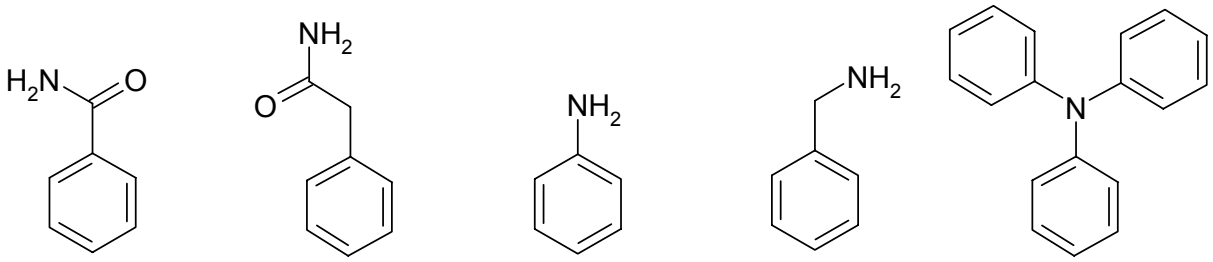
38



A. 2,5-dimethyl-4-hexene-3-one
B. (E)-2,5-dimethyl-2-hexene-4-one
C. (Z)-2,5-dimethyl-2-hexene-4-one
D. (E)-2,5-dimethyl-4-hexene-3-one
E. (Z)-2,5-dimethyl-4-hexene-3-one

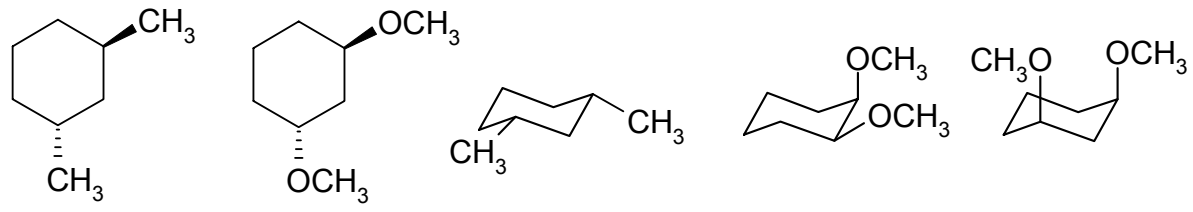
For each of questions 39 to 42, select the correct structure for the name provided:

39. Benzylamine



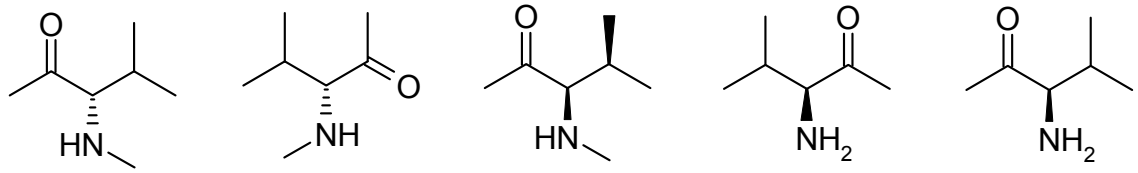
A **B** **C** **D** **E**

40. *cis* 1,3-dimethoxycyclohexane :



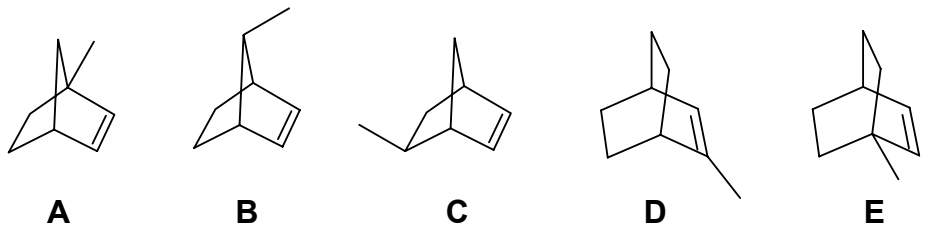
A **B** **C** **D** **E**

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



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

42. 1-methylbicyclo[2.2.1]hept-2-ene:



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

11% **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.

The laboratory of a retired professor has an unlabeled bottle of liquid. A sample was taken to be analyzed by GC-MS to show a single peak and has a molecular weight of 74.08. pH titration experiment shows that its pKa is in the ~ 4.5-5.0 range. The sample was further analyzed by elemental analysis to reveal that it contains 48.64% C and 8.16% H.

(a). Determine the molecular formula.

(b). What is the IHD of the molecule ?

(c). Propose a valid structure that match the chemical properties.

(d). Draw three molecules that fit the molecular formula, each molecule must contain a different functional group.

(e). Draw two molecules that fit the molecular formula and are diastereomers of each other.

(f). Draw a stereoisomer that contains two chiral centers but shows no optical properties.

(g). Give the IUPAC name of the molecule drawn in (f)

12% **PART 7: MECHANISM**

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

(a) Draw a mechanistic 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 alkene, 1-methylcyclohexene, reacts with aqueous sulfuric acid to give 1-methylcyclohexanol.

Step 1. Protonation of the alkene π-bond in 1-methylcyclohexene by sulfuric acid to create the more stable tertiary carbocation (i.e. the positive charge is on a tertiary carbon atom) and the bisulfate ion.

Step 2. Attack on the electrophilic carbocation by a molecule of water acting as a nucleophile to generate an oxonium ion.

Step 3. Deprotonation of the oxonium ion by the bisulfate ion acting as a base to give the alcohol, 1-methylcyclohexanol, and regenerating the catalyst, sulfuric acid.

(b) Based on the sequence described in part **a**, predict the product of the reaction if anhydrous hydrogen chloride was used instead of aqueous sulfuric acid.

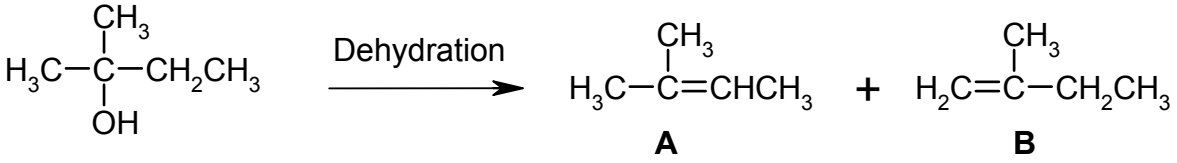
(c) Briefly explain why using aqueous hydrogen chloride (*i.e.* hydrochloric acid) instead of aqueous sulfuric acid would be a poor choice for preparing 1-methylcyclohexanol.

(d) Based on the sequence described in part **a**, predict the product of the reaction of 1-phenylpropene with aqueous sulfuric acid.

12% **PART 8: THERMODYNAMICS**

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

The following dehydration reaction can result in both products **A** & **B**



(a) Name the products **A** & **B**

(b) What is the empirical formula of **A** ?

(c) What would be the mass of 0.5 moles of **A** ?

A, **B**, and another alkene **C** can all react with hydrogen gas to give the same alkane product

(d) Propose the structure of alkene **C**.

(e) Calculate ΔH_f^o, for isomer **C**, given the following heats of combustion:

ΔH_C^o, alkene **C** = -3345 kJ mol^{-1} (-796 kcal mol^{-1})
ΔH_C^o, C (graphite) = -394.4 kJ mol^{-1} (-93.9 kcal mol^{-1})
ΔH_C^o H_2 (gas) = -287.3 kJ mol^{-1} (-68.4 kcal mol^{-1})

(f) Given that $\Delta H_C°$ for the two products in the dehydration reaction above are -3329 kJ mol^{-1} (-792 kcal mol^{-1}) & -3336 kJ mol^{-1}(-794 kcal mol^{-1}). Given that product **A** is the most stable product in the above reaction, assign heats of combustion to **A**, **B** and **C**. Briefly explain your choice.

(g) Comment briefly on the relative stabilities of the double bonds in the alkenes **A**, **B**, and **C**.

(h) Suggest an alcohol that could be dehydrated to produce isomer **C** as the only product from the dehydration reaction.

**** THE END ****

PERIODIC TABLE

1 1A																	18 8A
1 **H** 1.008	**2** 2A											**13** 3A	**14** 4A	**15** 5A	**16** 6A	**17** 7A	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57* **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0	89** **Ac** (227)	104 **Rf** (261)	105 **Ha** (262)	106 **Sg** (263)	107 **Ns** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Uun** (269)	111 **Uuu** (272)							

Lanthanides *	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
Actinides **	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.0	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)