

THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

DECEMBER 18th 1998

Time: 3 Hours

READ ALL THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER ON **BOTH** YOUR EXAM 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, eg 4 out of 5. These will be graded by taking the first answers, 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 on the paper provided. A periodic table with atomic numbers and atomic weights, and tables of 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**.

20 PART 1 RELATIVE PROPERTIES

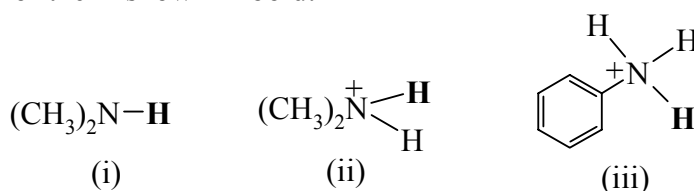
ANSWER ANY TEN (10) of Questions 1 to 14.

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

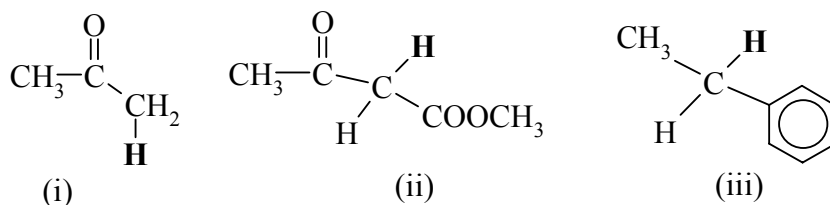
Use the following code to indicate your answers.

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

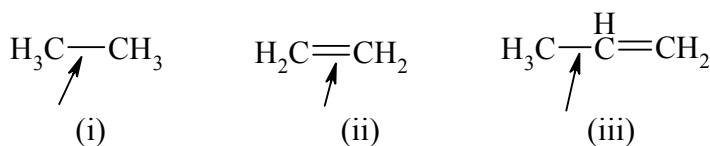
1. Acidity of the H shown in bold:



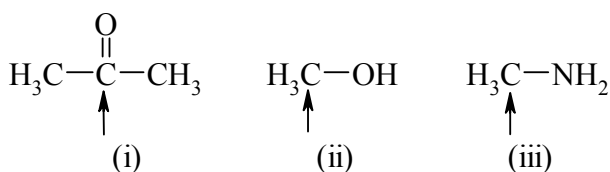
2. Acidity of the H shown in bold:



3. The bond length in the following bonds:



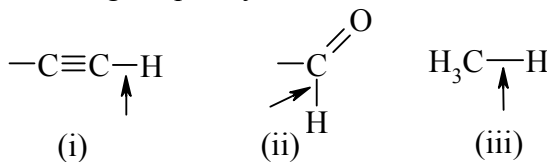
4. The ^{13}C chemical shift (δ) of the designated carbon in ppm (largest first):



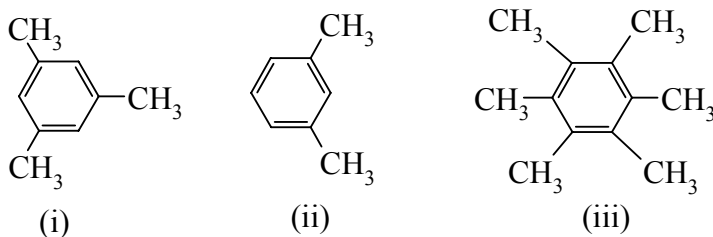
Use the following code to indicate your answers.

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

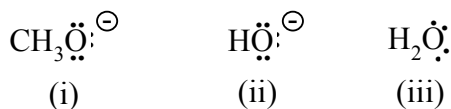
5. The IR stretching frequency in cm^{-1} of the indicated bond in:



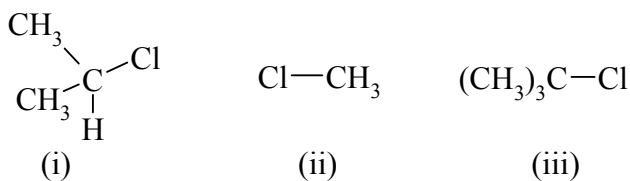
6. The number of *different* ^1H NMR chemical shifts expected for the following molecules:



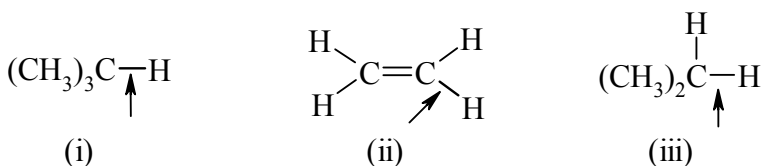
7. Nucleophilicity in an $\text{S}_{\text{N}}2$ reaction of:



8. Rate of $\text{S}_{\text{N}}2$ reaction of the following, with an iodide (I^-) nucleophile:



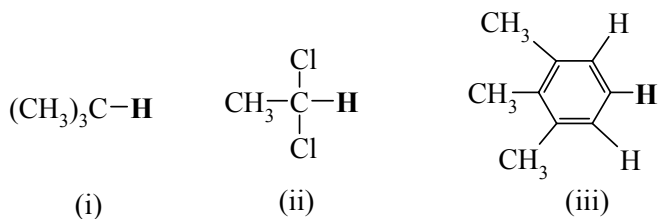
9. Homolytic bond energy of the following bonds:



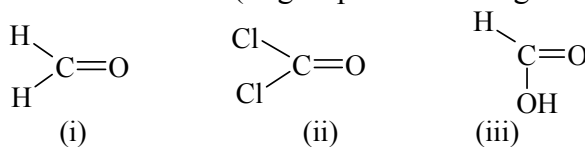
Use the following code to indicate your answers.

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

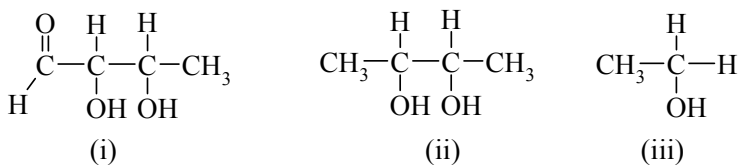
10. The multiplicity of the signal expected for the ^1H atom shown in bold (largest number first):



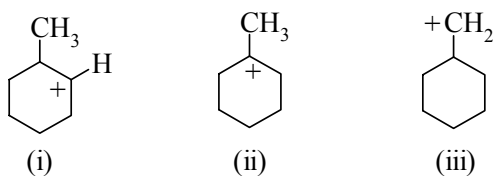
11. Oxidation state of the carbon atom in (largest positive to largest negative):



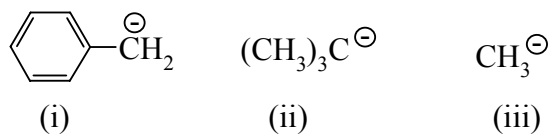
12. Number of stereoisomers of:



13. Stability of the following isomeric carbocations:



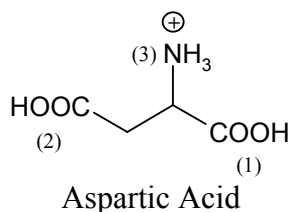
14. Stability of the following carbanions:



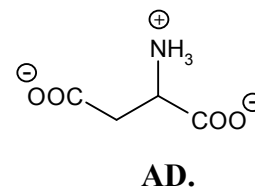
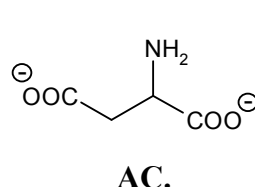
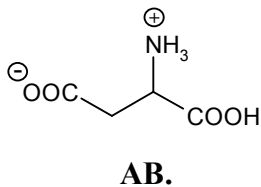
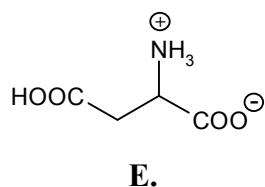
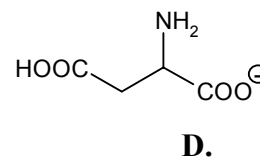
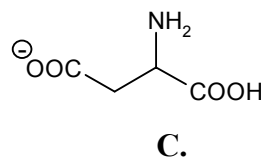
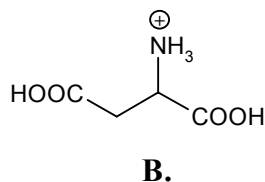
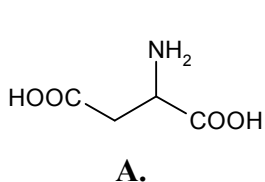
12 PART 2 ACIDS AND BASES

ANSWER ALL of questions 15 to 22.

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



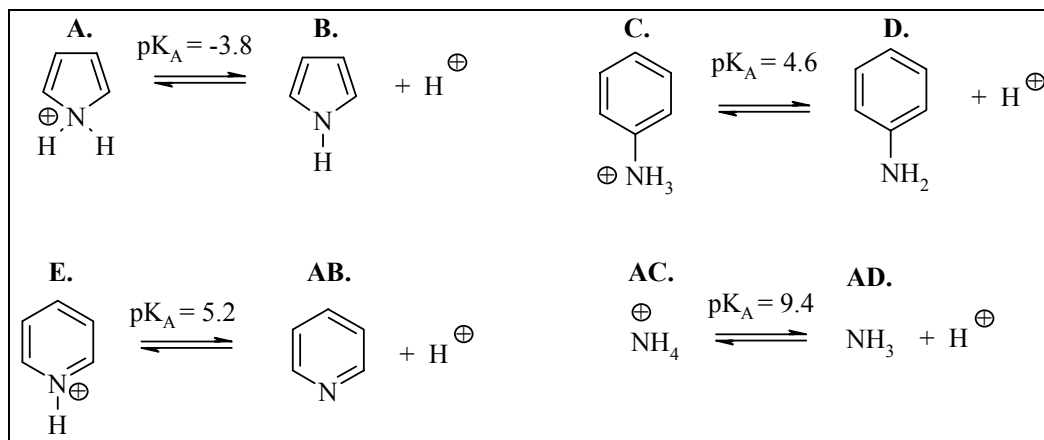
pK_A 1	2.1
pK_A 2	3.9
pK_A 3	9.8



AE: None of these !

15. At pH = 3.0, the predominant form of aspartic acid is ?
16. At pH = 6.0, the predominant form of aspartic acid is ?
17. At pH=11.0, the predominant form of aspartic acid is ?
18. Which species are electronically neutral AND can be observed experimentally ?

Answer questions 19 to 22 based on the following pK_a data:



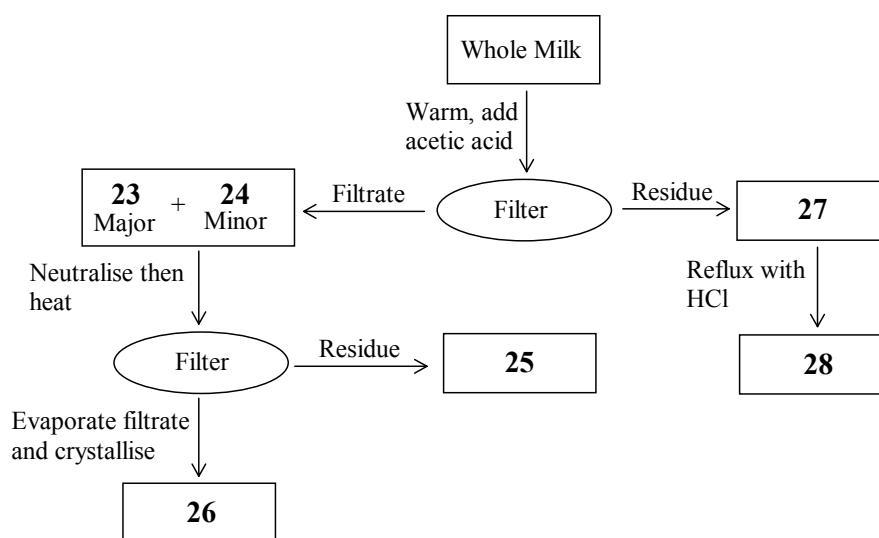
Henderson-Hasselbach equation: $pK_A = pH + \log \frac{[HA]}{[A^-]}$

19. Which species is the strongest acid ?
20. At pH = 4.2, what is the relative ratio of **E** to **AB** ?
- A. 1:100 B. 1:10 C. 1:1 D. 10:1 E. 100:1
21. Which is the better base pyridine (**AB**) or aniline (**D**) AND why ?
- A. Aniline because the lone pair is delocalised.
 B. Aniline because it is an 8π electron, anti-aromatic system.
 C. Pyridine because the lone pair is not delocalised.
 D. Pyridine because the lone pair is delocalised.
 E. Pyridine because it is a 6π electron, aromatic system
22. Pyrrole (**B**) is a weaker base than pyridine (**AB**) because:
- A. The ring in pyrrole only contains 5 atoms.
 B. Pyridine is a 6π electron, aromatic system.
 C. **A** is non-aromatic while **B** is aromatic, whereas **E** and **AB** are both aromatic.
 D. Protonating pyridine generates a cationic aromatic system.
 E. The N atom in pyrrole is sp² hybridised.

10 PART 3 LABORATORY

ANSWER ALL of the questions 23 to 32.

For each of the questions 23-28 indicated in the diagram about the MILK experiment, select the compound from the list below that best represents the material that should be obtained at each stage:



- | | | |
|------------|--------------|-----------------|
| A. Aspirin | E. Caffeine | AE. Lactose |
| B. Albumin | AB. Cumene | BC. Sucrose |
| C. Calcium | AC. Fructose | BD. Amino acids |
| D. Casein | AD. Glucose | BE. Starch |

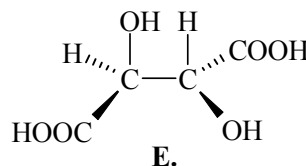
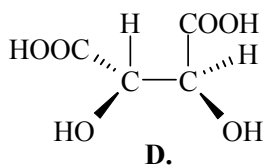
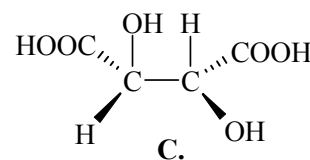
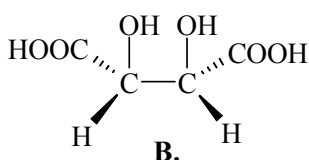
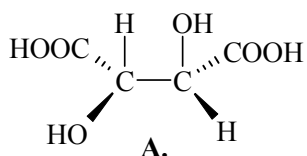
For each of the questions 29-32, decide whether the whole statement is true or false. If it is true, blacken A. If it is false, then blacken B.

29. The Rf value is (distance travelled by solvent front) / (distance travelled by sample).
30. Ninhydrin can be used to visualise amino acid chromatography plates.
31. During liquid-liquid extractions, higher yields will be obtained by using 3 x 50 ml portions rather than 1 x 150 ml portion.
32. Sublimation is the process by which a solid becomes a liquid at constant temperature.

16 PART 4 STEREOCHEMISTRY

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

Tartaric acid (2,3-dihydroxybutanedioic acid) exists in several different stereoisomeric forms. Use the following five structures A-E (not all are different) to answer questions 35-39.



35. Choose **TWO (2)** structures that are the same (but represented here in two different conformational forms).
36. Choose **ALL** structures which have a (2R, 3R) absolute stereochemistry.
37. Given that compound A has an $[\alpha]_D^{20} = -12.4^\circ$, what *single* compound would have an $[\alpha]_D^{20} = +12.4^\circ$?
38. Choose **ALL** structures which are achiral as shown, but which form a racemic mixture of mono-methyl esters on reaction with methanol.
39. Choose **TWO** structures which when mixed together in equal amounts would give a racemic mixture.

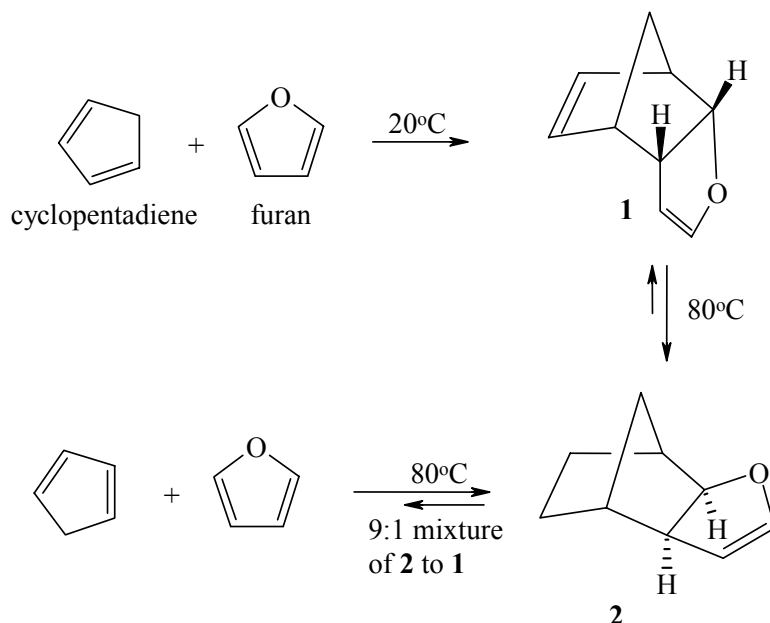
Suppose a sample of an initially pure single enantiomer of tartaric acid $[\alpha]_D^{20} = +12.4^\circ$ (H_2O) underwent a chemical isomerization reaction which yielded 10% of the other enantiomer and 20% of the meso isomer, in addition to 70% of the unchanged starting compound.

40. What is the enantiomeric excess (e.e.) of the major enantiomer relative to the minor enantiomer?
- A. 70% B. 700% C. 75% D. 87.5% E. 12.5%
41. If 1.0 g of the total mixture (including the *meso* isomer) was dissolved in 1 mL water and the rotation measured in a 1 dm cell, what value of α_D would one expect to observe?
- A. +9.92 B. +7.44 C. +12.4 D. +8.68 E. +6.20
42. From the total mixture, chromatographic separation on silica gel (a commonly used achiral solid adsorbent) might be expected to yield one of the three components in a pure state. Which one?
- A. the minor enantiomer
B. the meso isomer
C. the major enantiomer
D. the 1:1 racemic form of tartaric acid
E. only the enantiomeric excess of the major enantiomer would be obtained pure

14 PART 5 KINETICS & THERMODYNAMICS

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

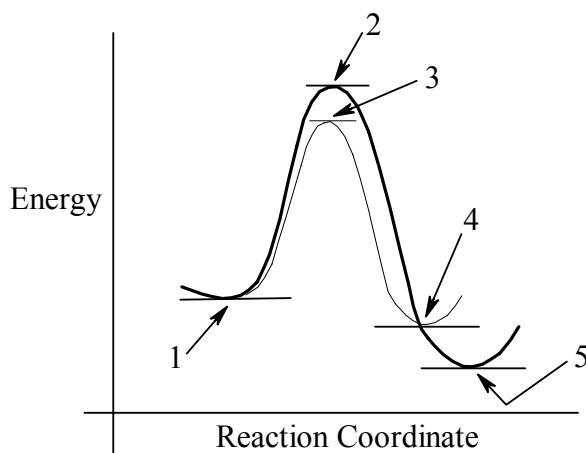
The Diels-Alder reaction of furan and cyclopentadiene at 20°C yields product **1**, as shown below. Heating a solution of **1** to 80°C for 1 hour gives a mixture containing a second product **2** (a stereoisomer of **1**) in a ratio of 9:1 (**2**:**1**). The reaction of cyclopentadiene and furan at 80°C gives the same 9:1 mixture of **2**:**1**.



43. The sole formation of **1** (and not **2**) at 20°C is an example of a reaction under:
- enthalpy control
 - thermodynamic control
 - kinetic control
 - bimolecular reaction control
 - heat of reaction control
44. At 80°C, the formation of a 9:1 mixture of **2**:**1**, starting from cyclopentadiene and furan, is an example of a reaction under:
- kinetic control
 - thermodynamic control
 - bimolecular reaction control
 - entropy control
 - transition-state control

45. Is the formation of 90% **2** from **1** (at 80°C) likely to be a *direct* isomerization of **1** into **2**?
- A. Yes B. No C. Not enough information to answer question
46. As previously stated, when **1** was heated to 80°C for 1 hour, 90% of the material was converted into **2**. Heating for a further 10 hours at 80°C produced no further change. Why can we not convert the remaining 10% of **1** into **2**?
- A. The heats of formation of **1** and **2** are very different.
B. The transition states for forming **1** and **2** are identical.
C. The free energy of **2** is about nine times that of **1**.
D. The free energy of **1** is about nine times that of **2**.
E. Compounds **1** and **2** reach equilibrium concentrations.
47. The bimolecular reaction of cyclopentadiene and furan at 20°C to produce **1** is an exothermic reaction. According to the “Hammond postulate” this implies that the transition-state for this reaction will:
- A. have a “structure” that will most resemble the two reactants
B. have a “structure” which only resembles cyclopentadiene
C. have a large negative entropy of activation
D. have a “structure” that will most resemble the reaction product **1**
E. have a “structure” which only resembles furan
48. The relationship between ΔG° for a reaction $A + B \rightleftharpoons C$, and the equilibrium constant $K = [C]/[B][A]$ is given by:
- A. $\Delta G^\circ = -TK \ln R$
B. $\Delta G^\circ = -RT \ln K$
C. $K = -RT \ln \Delta G^\circ$
D. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
E. $\Delta G^\circ = h\nu K$

49. Reaction coordinate diagrams are often used to illustrate the energy changes taking place during chemical reactions.



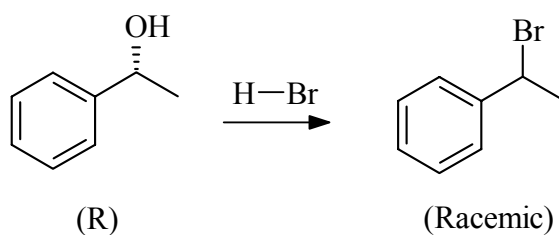
The Diels-Alder reactions shown at the start of **PART 5** can be represented by the reaction coordinate diagram shown above. The numbers 1-5 refer to:

- A. 1=reactants energy, 2=transition-state for forming **2**, 3=transition-state for forming **1**, 4=energy of **2**, 5=energy of **1**.
- B. 1=reactants energy, 2=transition-state for forming **1**, 3=transition-state for forming **2**, 4=energy of **1**, 5=energy of **2**.
- C. 1=products **1** and **2**, 2=transition-state for forming **2**, 3=transition-state for forming **1**, 4=cyclopentadiene energy, 5=furan energy.
- D. 1=reactants energy, 2=transition-state for forming **2**, 3=transition-state for forming **1**, 4=energy of **1**, 5=energy of **2**.
- E. 1=reactants energy, 2=transition-state for forming **1**, 3=transition-state for forming **2**, 4=energy of **2**, 5=energy of **1**.

8 PART 6 MECHANISM

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

- (a) Draw a double headed curly arrow mechanism (i.e. using \curvearrowright) to account for the following experimental observation:



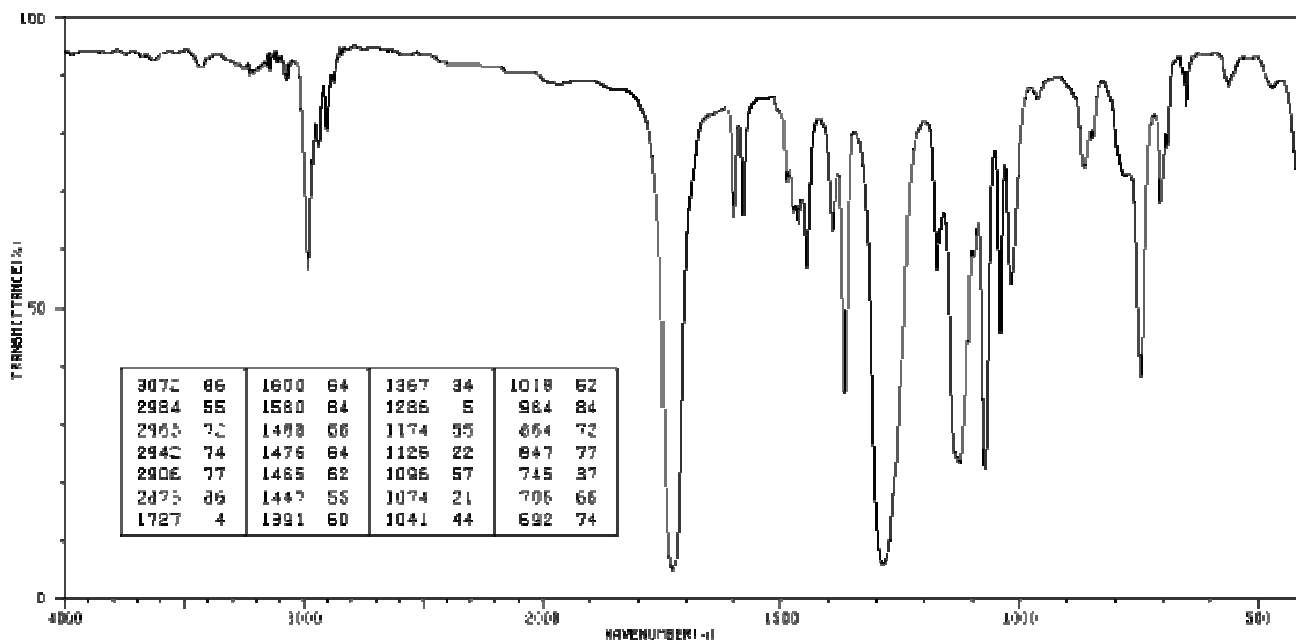
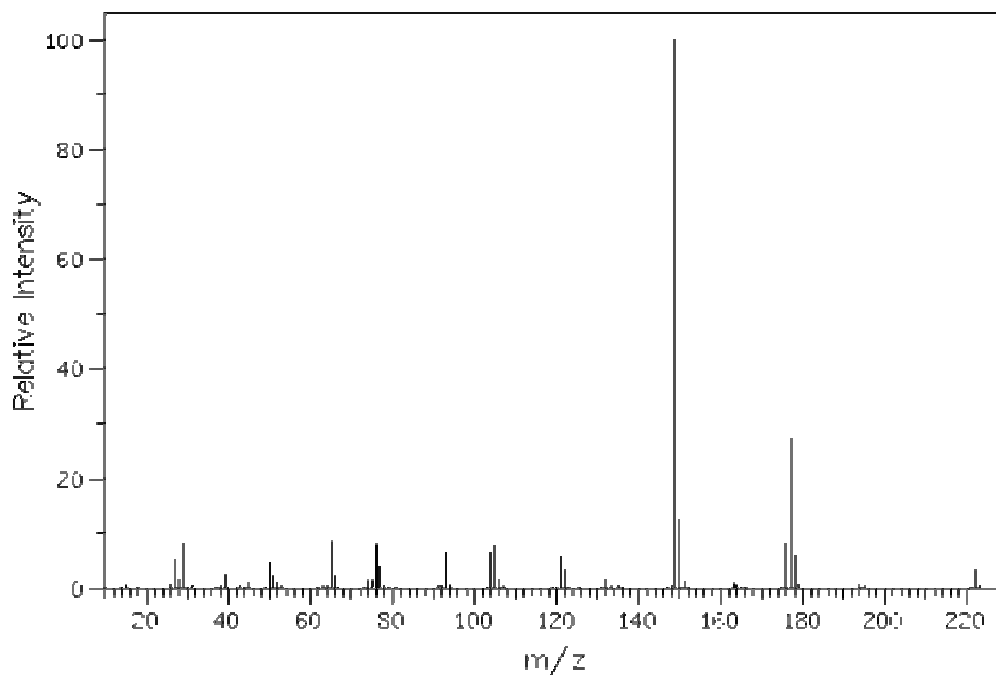
- (b) For each of the following compounds, identify **WHICH** proton the pKa data relates to, **AND EXPLAIN** using a short paragraph **AND / OR** diagrams the observed order of acidity.

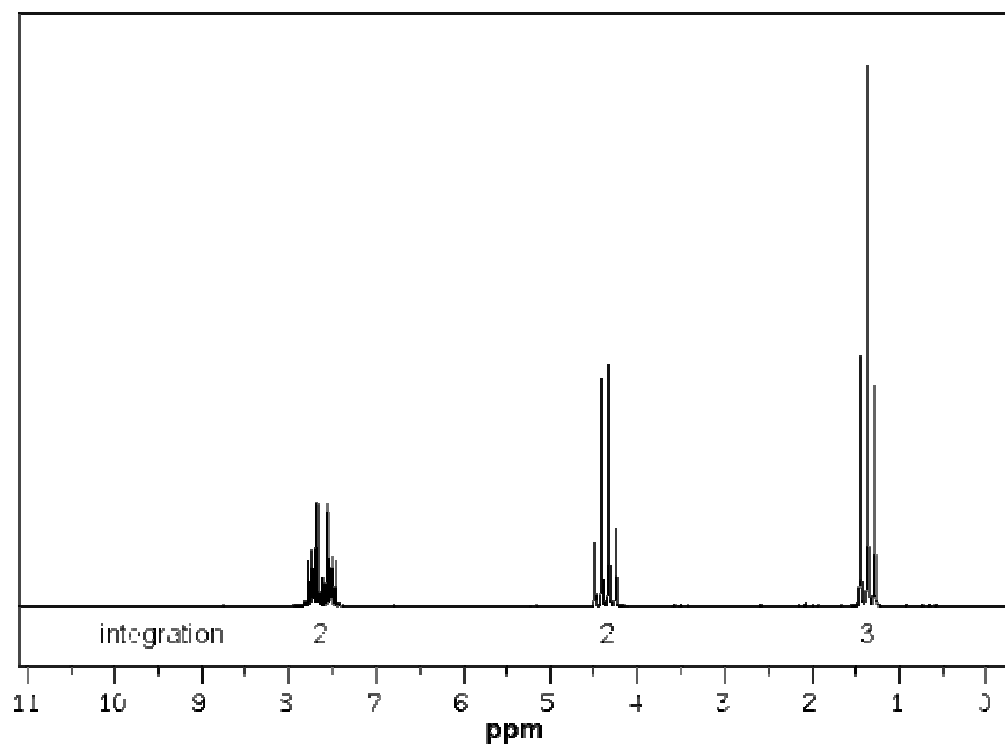
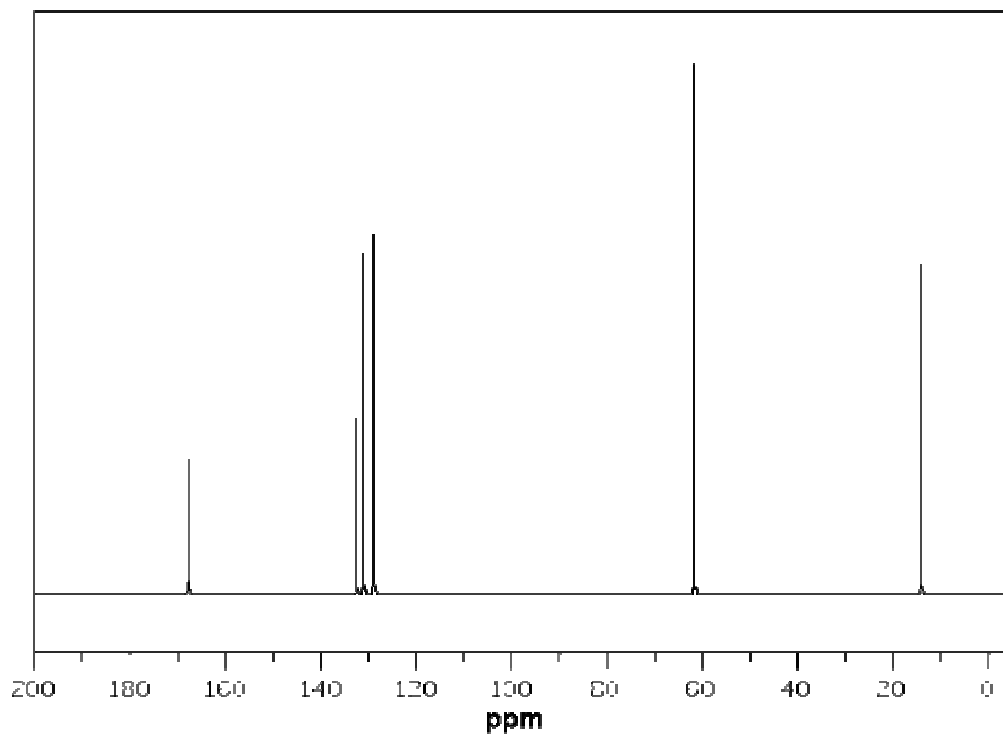
<chem>CH3CO2H</chem>	pKa = 4.8
<chem>(CH3)2CO</chem>	pKa = 19
<chem>CH3COOCH3</chem>	pKa = 25
<chem>CH3CON(CH3)2</chem>	pKa = 30
<chem>CH3CH3</chem>	pKa ~ 50

10 PART 7 SPECTROSCOPY

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

Elemental analysis of an unknown sample indicated that it contained 64.86% C and 6.31% H (by weight). Using this data along with the I.R., M.S., ¹³C, and ¹H NMR spectra provided below, determine structure of the unknown sample.



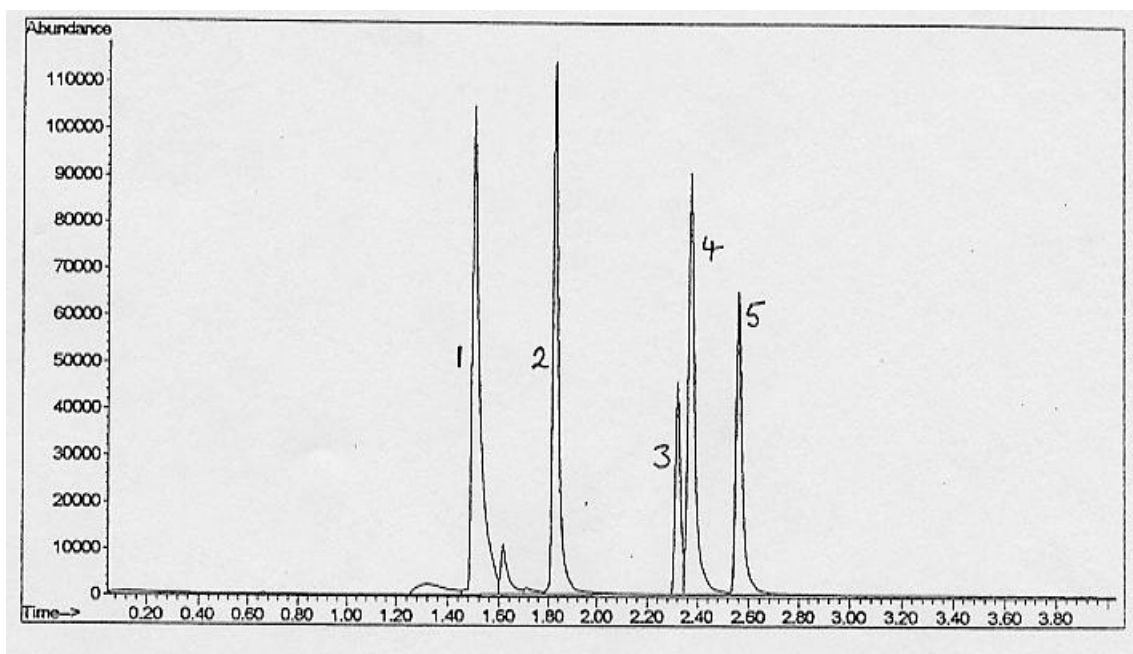


10 PART 8 STRUCTURE DETERMINATION

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

As part of an environmental analysis for a series of hydrocarbons in contaminated soil samples, the gas chromatograph (GC) shown below was obtained. Each peak was found to be a single compound, *except* peak 4, which on further analysis was found to be a mixture of two isomeric compounds, **D** and **E**. GC peak 5 was due to **F**, another isomer of **D** and **E**. The M^+ data from the mass spectrum (MS) and ^{13}C -nmr data for each of the six major components in the mixture is tabulated below.

Compound	M^+ data	^{13}C δ /ppm
A	78	128.5
B	92	21.3, 125.6, 128.4, 129.2, 137.8
C	106	15.8, 29.2, 125.9, 128, 128.5, 144.1
D	106	20.9, 129.0, 134.7
E	106	21.3, 126.1, 128.2, 129.9, 137.7
F	106	19.7, 125.8, 129.6, 136.4



Based on this data deduce the structures of the hydrocarbons **A - F**

Assign the compounds **A-C** to the GC peaks **1-3**. Explain your choice.

THE END