

**Instructions for students**

- Write your name and roll no. at the top of the first pages of all problems.
- This examination paper consists of 34 pages of problems including answer boxes.
- You have 3 hours to complete all the problems.
- Request the supervisor to provide you with rough sheets for rough work.
- **Use only a pen to write the answers in the answer boxes. Anything written by a pencil will not be considered for assessment.**
- All answers must be written in the appropriate boxes. Anything written elsewhere will not be considered for assessment.
- For calculations, you must show the main steps.
- Use only a non-programmable scientific calculator.
- For objective type questions: Mark **X** in the correct box. Some of the objective questions may have more than one correct choice.
- Values of fundamental constants required for calculations are provided on page 2.
- A copy of the Periodic Table of the Elements is provided at the end of the paper.
- Do not leave the examination room until you are directed to do so.
- The question paper will be uploaded on the HBCSE website by 4<sup>th</sup> February 2009.

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Tata Institute of Fundamental Research  
V.N. Purav Marg, Mankhurd, Mumbai 400 088.

**Fundamental Constants**

Avogadro constant	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
Electronic charge	$e = 1.602 \times 10^{-19} \text{ C}$
Molar gas constant	$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $= 8.314 \text{ K Pa} \cdot \text{dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ $= 0.082 \text{ L} \cdot \text{atm K}^{-1} \text{ mol}^{-1}$
1 atomic mass unit (1u)	$= 931.5 \text{ MeV}/c^2$
1 eV	$= 1.602 \times 10^{-19} \text{ J}$
Rydberg constant	$R_H = 2.179 \times 10^{-18} \text{ J}$
Mass of electron	$m_e = 9.109 \times 10^{-31} \text{ kg}$
Planck's constant	$h = 6.625 \times 10^{-34} \text{ Js}$
Speed of light	$c = 2.998 \times 10^8 \text{ ms}^{-1}$
Acceleration due to gravity	$g = 9.8 \text{ ms}^{-2}$
Density of mercury	$= 13.6 \times 10^3 \text{ kgm}^{-3}$

Name of Student

Roll no.

**Hydrogen atom**

The electronic ground state of a hydrogen atom contains one electron in the first orbit. If sufficient energy is provided, this electron can be promoted to higher energy levels. The electronic energy of a hydrogen-like species (any atom/ions with nuclear charge  $Z$  and one electron) can be given as

$$E_n = -\frac{R_H Z^2}{n^2} \quad \text{where } R_H = \text{Rydberg constant, } n = \text{principal quantum number}$$

- 1.1 The energy in Joule of an electron in the second orbit of H atom is

(0.5 mark)

- 1.2 The energy required to promote the ground state electron of H atom to the first excited state is

 eV

(1 mark)

When an electron returns from a higher energy level to a lower energy level, energy is given out in the form of UV/Visible radiation.

- 1.3 Calculate the wavelength of light (nm) for the electronic transition of H atom from the first excited state to ground state.

In the model of hydrogen-like atom put forward by Niels Bohr (1913), the electron orbits around the central nucleus. The Bohr radius of  $n^{\text{th}}$  orbit of a hydrogen-like species is given by

$$r = k \frac{n^2}{Z} \quad \text{where, } k \text{ is constant}$$

- 1.4 What is the principal quantum number,  $n'$  of the orbit of  $\text{Be}^{3+}$  that has the same Bohr radius as that of ground state hydrogen atom?

$n' =$

(1 mark)

- 1.5 The ratio of energy of an electron in the **ground state**  $\text{Be}^{3+}$  ion to that of ground state H atom is

(A) 16

(B) 4

(C) 1

(D) 8

(1 mark)

The kinetic and potential energies of an electron in the H atom are given as

$$K.E. = \frac{1}{2} m v^2 \quad \text{and} \quad P.E. = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

- 1.6 Calculate the following:

- the kinetic energy (in eV) of an electron in the ground state of hydrogen atom
- the potential energy (in eV) of an electron in the ground state of hydrogen atom

(2.5 marks)

1.7 A gaseous excited hydrogen-like species with nuclear charge  $Z$  can emit radiations of six different photon energies.

a) The principal quantum number of the excited state is

(A) 6

(B) 5

(C) 4

(D) 3

(0.5 mark)

b) It was observed that when this excited species emits photons of energy = 2.64 eV when it comes to next lower energy state. Calculate the nuclear charge of the species.

(1 mark)

The least energy required to remove an electron from a species is known as the ionization energy (I.E.) of the species. The experimental I.E. of He atom is 24.58 eV.

1.8 Total energy required to remove two electrons from He is

(1.5 marks)

Name of Student

Roll no.

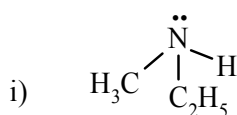
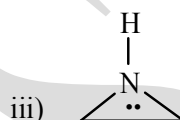
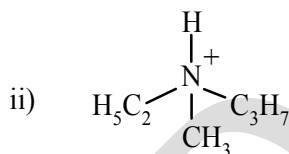
## Problem 2

19 Marks

## Nitrogen containing compounds

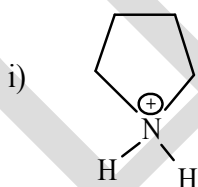
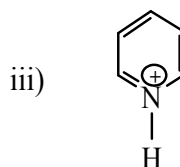
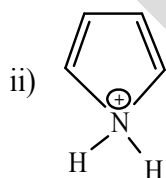
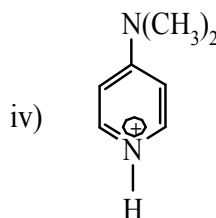
Several naturally occurring important compounds such as alkaloids, amino acids, proteins and peptides contain nitrogen. Nitrogen heterocycles in the form of pyrimidine and purine bases, are essential features of nucleic acids, which are responsible for storage of genetic information in an organism and for transmitting the same to its progeny.

2.1 Which of the following amine/s is/are resolvable?

☐☐☐☐

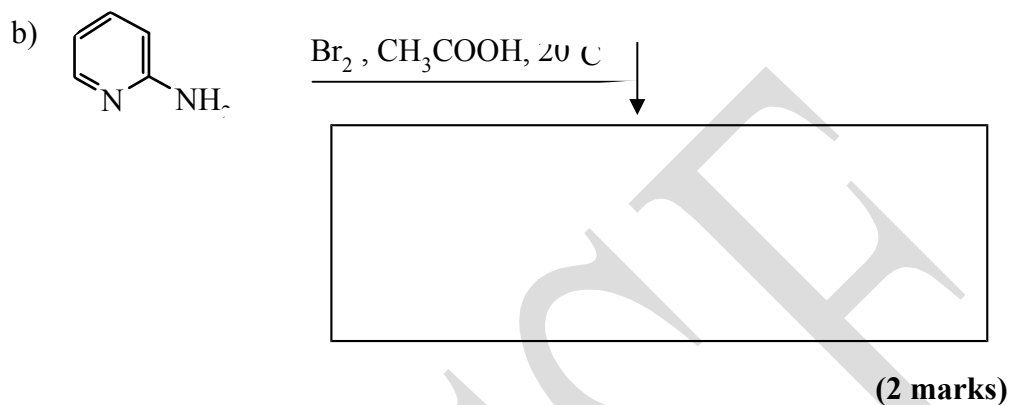
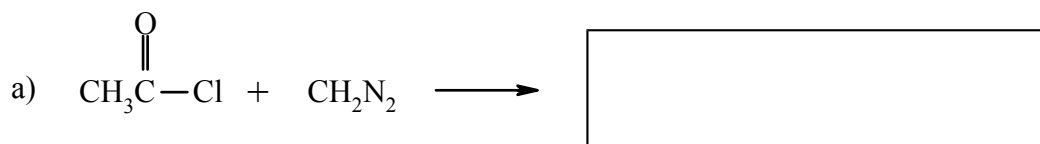
(1 mark)

2.2 The most acidic species amongst the following is

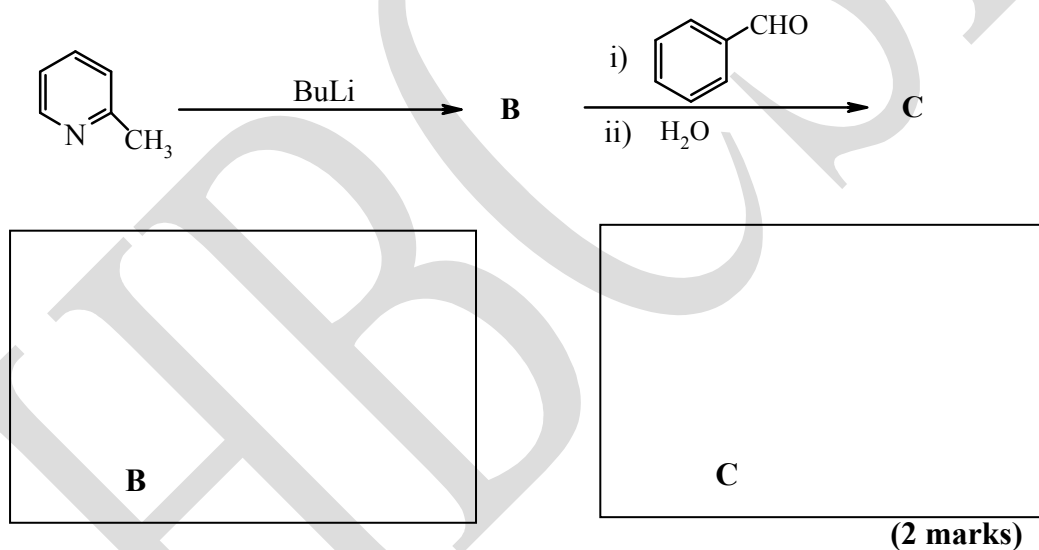
☐☐☐☐

(1 mark)

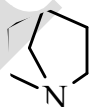
2.3 Draw the structures of the *isolable* products of the following reactions.



2.4 Identify **B** and **C** in the following reaction sequence.

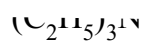


2.5 Which of the following statements is true with respect to the following pair of compounds?



**D**

and



**E**

- i) **D** is more basic than **E**
- ii) **E** is more basic than **D**
- iii) **D** and **E** are of comparable basicity

(1 mark)



Alkaloids are naturally occurring biologically active nitrogenous compounds, isolated from plants. Structure determination of alkaloids involves a few general steps, some of which are mentioned below.

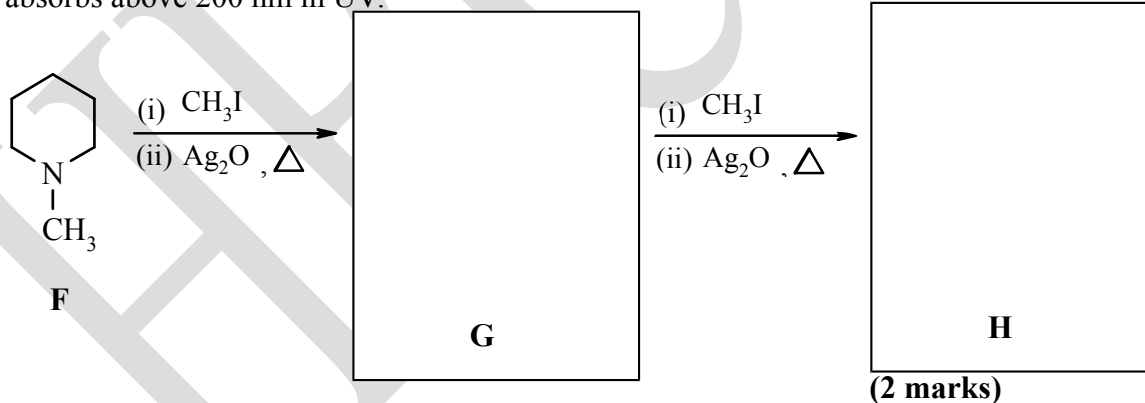
- (a) **Zeisel method:** It is used to determine the presence and number of methoxyl groups. Here an alkaloid is heated with HI at its boiling point (126°C) when methyl iodide is formed, which is absorbed in ethanolic AgNO<sub>3</sub> and the AgI formed is separated and weighed.
- (b) **Hoffmann exhaustive methylation method:** It is used to determine the skeleton of an alkaloid. It involves the exhaustive methylation of an amine with CH<sub>3</sub>I followed by heating the resulting quaternary ammonium salt with moist Ag<sub>2</sub>O when elimination takes place as represented below.



Note:

During this reaction, the less stable alkene is formed.

- 2.6 Identify the products 'G' and 'H' obtained in the Hoffmann exhaustive methylation and degradation of N-methylpiperidine (F) in the following sequence. Note: H absorbs above 200 nm in UV.



Papaverine (C<sub>20</sub>H<sub>21</sub>NO<sub>4</sub>) is an optically inactive alkaloid. Goldschmidt and co-workers established the structure of papaverine in 1888 and their work is a classic example of the application of oxidative degradation to structure determination.

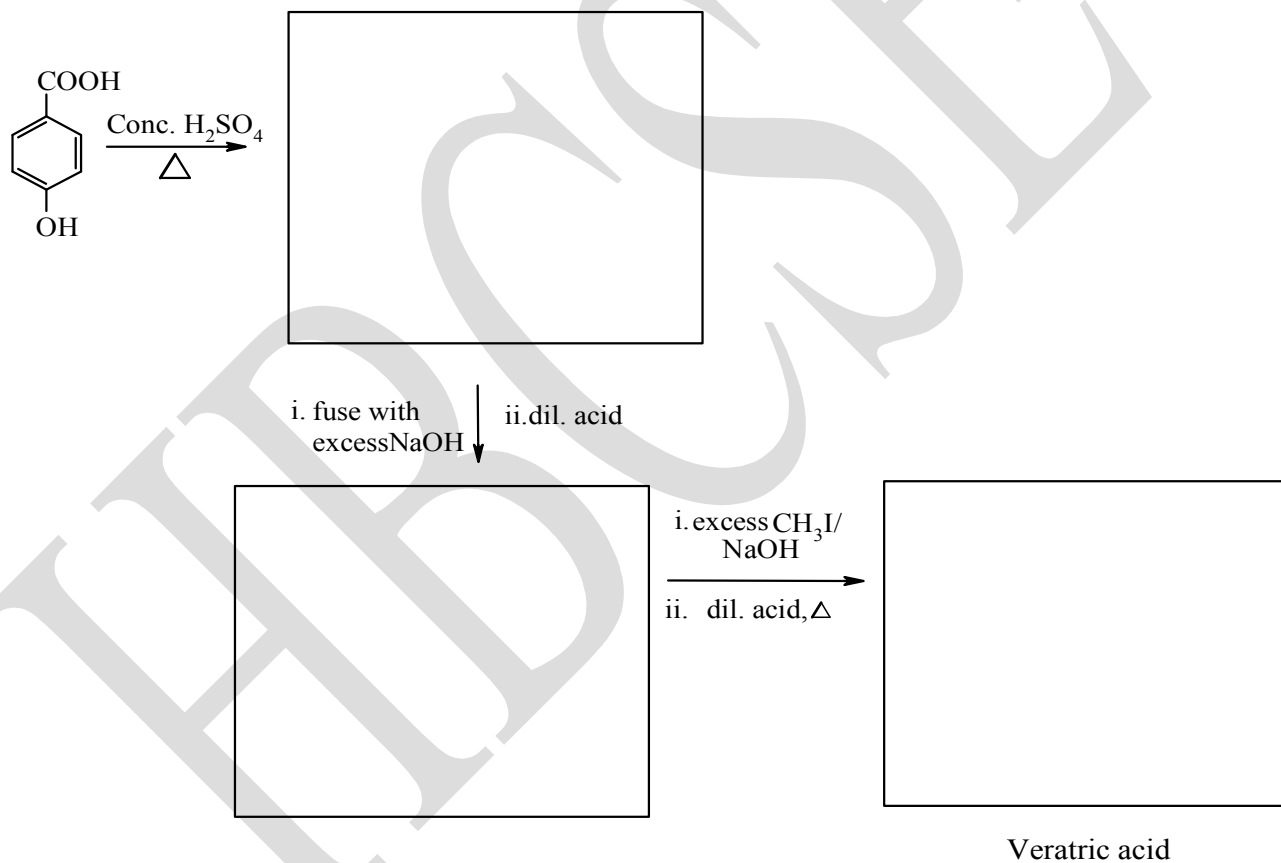
2.7 Papaverine reacts with four equivalents of HI at 126°C to give papaveroline as one of the products. The formula of papaveroline is

- |      |                    |                      |     |                    |                      |
|------|--------------------|----------------------|-----|--------------------|----------------------|
| i)   | $C_{16}H_{13}NO_4$ | <input type="text"/> | ii) | $C_{16}H_9NO_4$    | <input type="text"/> |
| iii) | $C_{16}H_{14}NO_4$ | <input type="text"/> | iv) | $C_{16}H_{15}NO_4$ | <input type="text"/> |

(1 mark)

Papaverine, when oxidized with hot conc.  $KMnO_4$  is decomposed into smaller fragments viz; veratric acid,  $C_9H_{10}O_4$  (**I**), metahemipinic acid (**J**), pyridine tricarboxylic acid (**K**) and 6,7-dimethoxyisoquinoline -1- carboxylic acid.

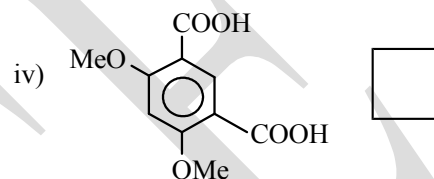
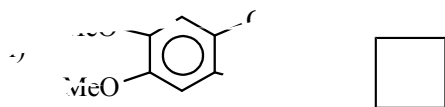
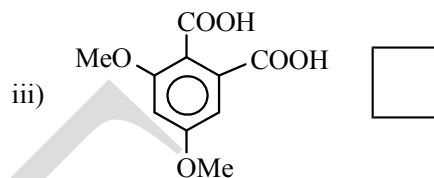
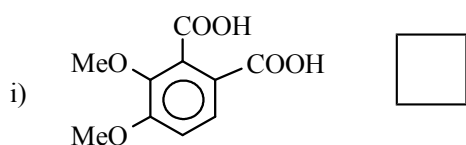
2.8 Veratric acid (**I**) is prepared from p-hydroxybenzoic acid by the following sequence. Identify the missing intermediates.



(3 marks)

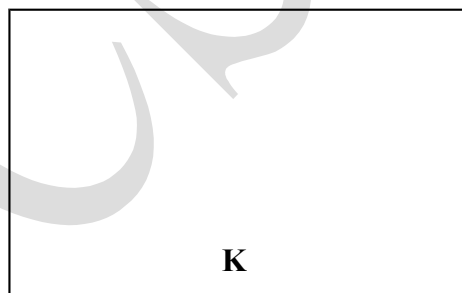
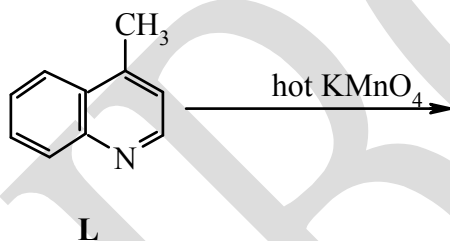
Metahemipinic acid **J**, ( $C_{10}H_{10}O_6$ ) on heating with  $CaO$ , gives veratrole, which is also formed by heating veratric acid (**I**) with  $CaO$ . **J** forms an anhydride on heating and forms only one monoester.

2.9 Structure of metahemipinic acid is



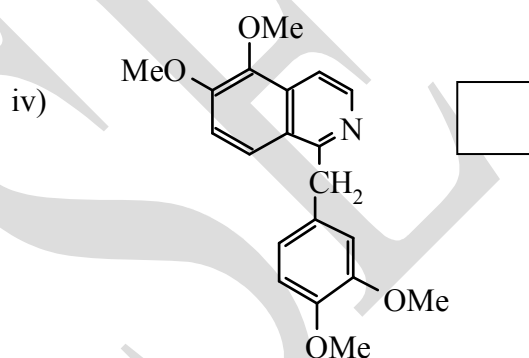
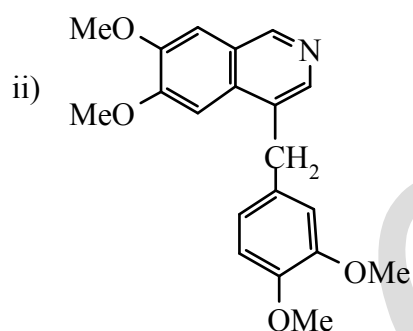
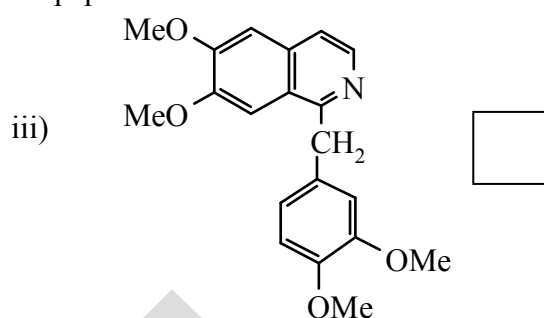
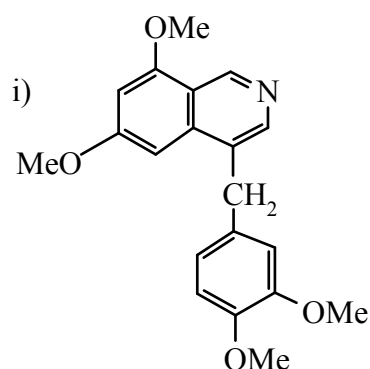
(1 mark)

2.10 The pyridine tricarboxylic acid **K** is produced when lepidine **L** (4-methylquinoline) is oxidized. Draw the structure of **K**.



(1 mark)

2.11 Based on the above observations, the structure of papaverine is



(2 marks)

Oxidation of papaverine with hot dilute  $\text{KMnO}_4$  gives papaverinic acid ( $\text{C}_{16}\text{H}_{13}\text{NO}_7$ ) which forms an oxime.

2.12 Structure of papaverinic acid is



(2 marks)

Name of Student

Roll no.

## Problem 3

17 marks

## Chemistry of silicon

Silicon is the second most abundant element (~27.2 %) in the earth's crust after oxygen (45.5 %). Carbon, silicon, germanium, tin and lead constitute the group 14 of the periodic table. Chemistry of silicon is distinctly different from that of carbon. For example, under standard conditions  $\text{CO}_2$  is a gas whereas  $\text{SiO}_2$  is a covalent solid.

3.1 Draw the structures of  $\text{CO}_2$  and  $\text{SiO}_2$ .



(1.5 marks)

3.2. The reason for the distinct difference in the properties of  $\text{CO}_2$  and  $\text{SiO}_2$  is

- |   |                          |
|---|--------------------------|
| a) carbon is more electronegative than O and in case of $\text{SiO}_2$ oxygen is more electronegative than silicon                              | <input type="checkbox"/> |
| b) carbon has small size and forms a $\pi$ bond with good overlap whereas silicon has larger size hence has a poor $\pi$ overlap                | <input type="checkbox"/> |
| c) carbon has only 'p' orbitals and lacks 'd' orbitals whereas silicon has 'd' orbitals   | <input type="checkbox"/> |
| d) first ionization potential of carbon is higher than that of silicon ( $1086 \text{ kJ mol}^{-1}$ for C and $786 \text{ kJ mol}^{-1}$ for Si) | <input type="checkbox"/> |

(1 mark)

3.3 Glass, made of  $\text{SiO}_2$ ,  $\text{Na}_2\text{SiO}_3$  and  $\text{CaSiO}_3$ , is attacked by hydrofluoric acid with formation of  $\text{SiF}_6^{2-}$  anion. The analogous  $\text{CF}_6^{2-}$  anion does not exist. The reason/s is/are

- a) carbon is more electronegative than silicon
- b) silicon has larger atomic size than carbon
- c) silicon has 3d orbitals which form an  $\text{sp}^3\text{d}^2$  hybrid orbitals
- d) carbon and fluorine have comparable atomic sizes

☐  
☐  
☐  
☐

(2 marks)

3.4 Group 14 elements have tendency to catenate. The first three members C, Si and Ge show significant catenation. Arrange these elements in decreasing order of their catenation tendency.

(0.5 mark)

3.5 The order in 3.4 can be explained on the basis of

- a) atomic size
- b) electronegativity
- c) bond strength
- d) non-metallic character

☐  
☐  
☐  
☐

(1 mark)

3.6 In a silicon manufacturing unit, silicon is obtained by heating 100 kg of pure sand with 45 kg of high grade coke in an electric furnace. Write the balanced equation of the reaction.

(1 mark)

- 3.7 Silicon can be purified by converting it into volatile  $\text{SiCl}_4$  (b.p.  $58^\circ\text{C}$ ) which is purified by fractional distillation.  $\text{SiCl}_4$  can then be converted into Si using molecular hydrogen. Write the balanced equations for the reactions involved.

(1 mark)

Silicon is widely used in semiconductor industry in which the purity required is of the order of 1 part per billion. This can be achieved using “zone refining technique”. The technique involves moving a heater coil across an impure Si rod.

- 3.8 In zone refining, silicon is purified as

- a) portions of Si rod are heated and cooled so that impurities are differentially evaporated  
b) impurities are more soluble in liquid phase than in solid  
c) impurities are less soluble in liquid phase than in solid  
d) impurities are insoluble in molten Si and can be separated

(1 mark)


The reactivities of  $\text{CCl}_4$  and  $\text{SiCl}_4$  are different. For example  $\text{SiCl}_4$  can be easily hydrolysed and is prone to substitution reactions, whereas  $\text{CCl}_4$  is inert.

- 3.9 The observed difference is because

- a) carbon atom has smaller size hence substitution is not possible  
b) carbon is more electronegative than silicon  
c) silicon has low lying unoccupied orbitals  
d) C-Cl bond is stronger than Si-Cl bond

(1 mark)

Silicon has high affinity for oxygen to form silicates having  $\text{SiO}_4$  units. Silicates can have chain or cyclic structures.

**3.10** Draw the structure of a cyclic silicate having structural formula of  $[\text{Si}_6\text{O}_{18}]^{n-}$ . Also determine the value of  $n$ . [Hint:   $\text{SiO}_4$  can be shown as unit]



(4 marks)

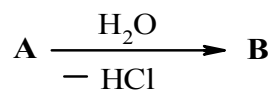
**3.11** Draw the structure of the anion present in pyroxene ( $\text{MgCaSi}_2\text{O}_6$ ).



(1 mark)



Silicones are important synthetic polymers which find extensive applications due to their chemical inertness and water repelling nature. They are produced via the following reactions.



3.12 Identify **A** and the corresponding linear polymer **B**.



(2 marks)

Name of Student

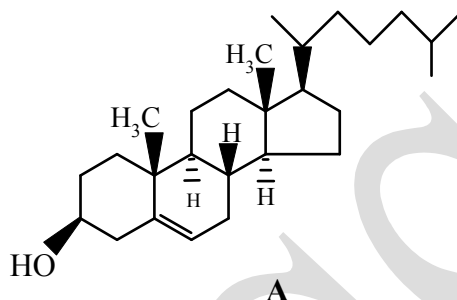
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## Problem 4

17 Marks

## Natural compounds and intermediates

Cholesterol (A) is the most abundant compound from steroids in animals. It is the precursor of all other steroids. It is an important component of the cell membrane.



[Note: Thick solid wedge indicates a bond coming above the plane, while broken wedge indicates a bond below the plane]

4.1 The total number of stereoisomers possible for A is

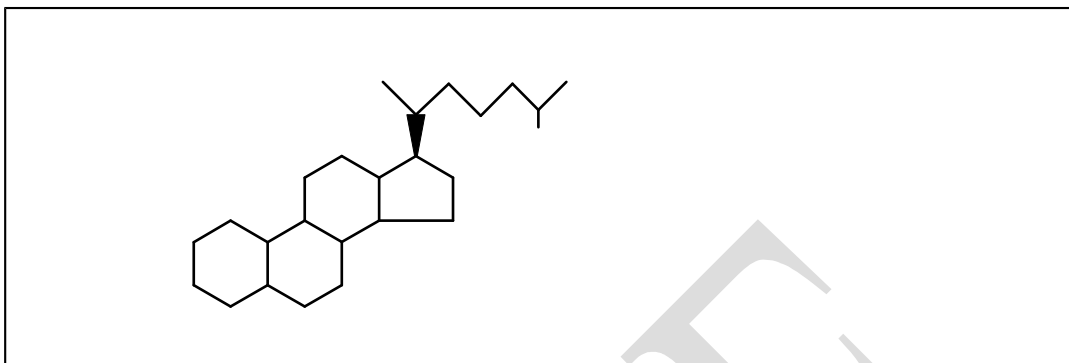
- a) 32 ☐      b) 256 ☐      c) 128 ☐      d) 64 ☐
- (0.5 mark)

4.2 Draw the structure of the ester of cholesterol with a fatty acid containing 16 carbon atoms with a double bond at the C<sub>4</sub> in E configuration.



(1 mark)

- 4.3 a) Complete the structure of the product, with stereochemistry, of the reaction of  $B_2H_6$  with cholesterol in tetrahydrofuran, followed by  $H_2O_2$  in an alkaline medium.



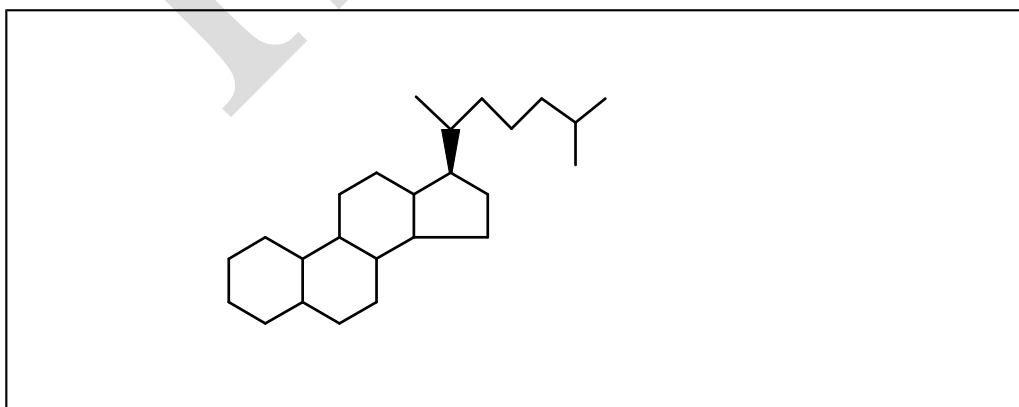
(1 mark)

- b) The 3D perspective formula of the skeleton of the steroid obtained in **a** is given below. Complete the structure of the product obtained in **a**, by placing the substituents at the appropriate places with the correct stereochemistry.



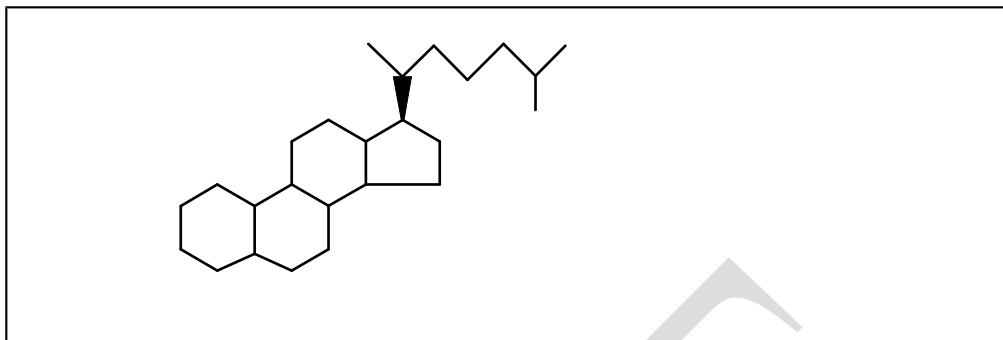
(2 marks)

- c) Complete the structures of the products (with stereochemistry) of the reaction of **A** with
- i)  $H_3O^+$  (room temperature)



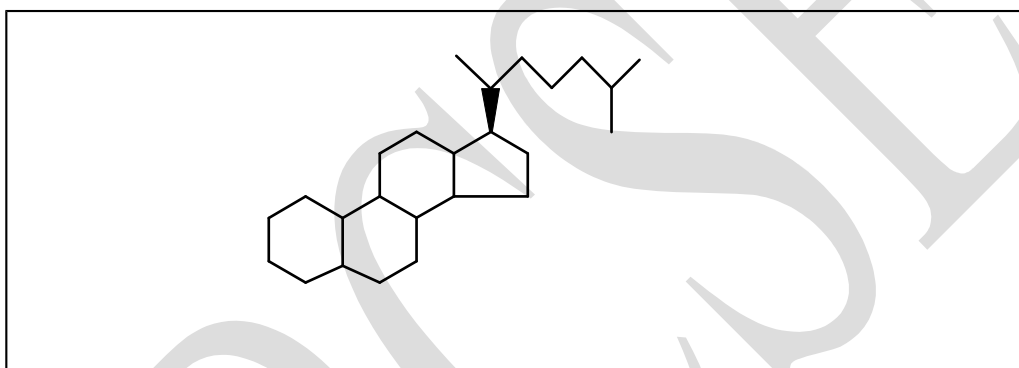
(0.5 mark)

ii) peroxyacetic acid,  $\text{CH}_3\text{COOOH}$



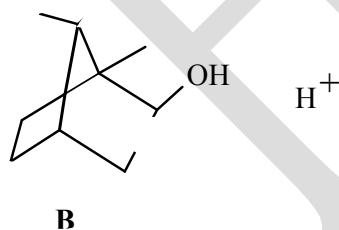
(0.5 mark)

iii)  $\text{Br}_2 / \text{H}_2\text{O}$

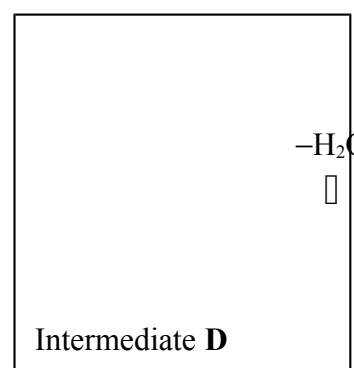
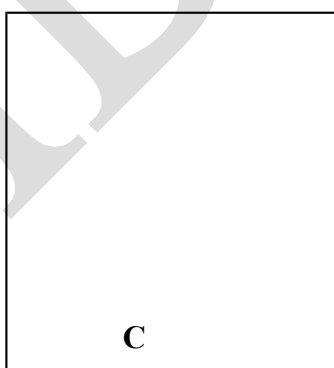


(1 mark)

4.4 Among the natural products, terpenes are interesting due to a variety of reactions they undergo. Borneol (**B**)  $\text{C}_{10}\text{H}_{18}\text{O}$ , a terpene, on treatment with a Brønsted acid undergoes a reaction to form **F**, ( $\text{C}_{10}\text{H}_{16}$ ). Identify the structures of **C**  $\rightarrow$  **F**.



$\text{H}^+$



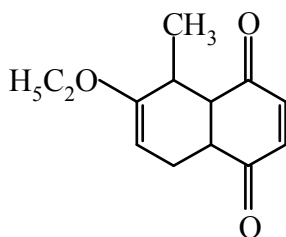
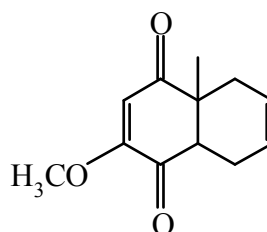
(1 mark)

Intermediate **D**Intermediate **E**[Note: Conversion of **D**→**E** involves formation of a more stable species]**(1 mark)****F****(1 mark)**

Diels-Alder reaction is an important reaction useful in the synthesis of cyclohexene derivatives. It involves the reaction of an electron rich “diene” with an electron deficient olefin referred to as “dienophile”.



Two different approaches have been designed to synthesize cortisone, a steroid. These require intermediates **G** and **H**.

**G****H**

- 4.5 Draw the starting compounds required for the synthesis of **G** and **H** through Diels-Alder reaction.

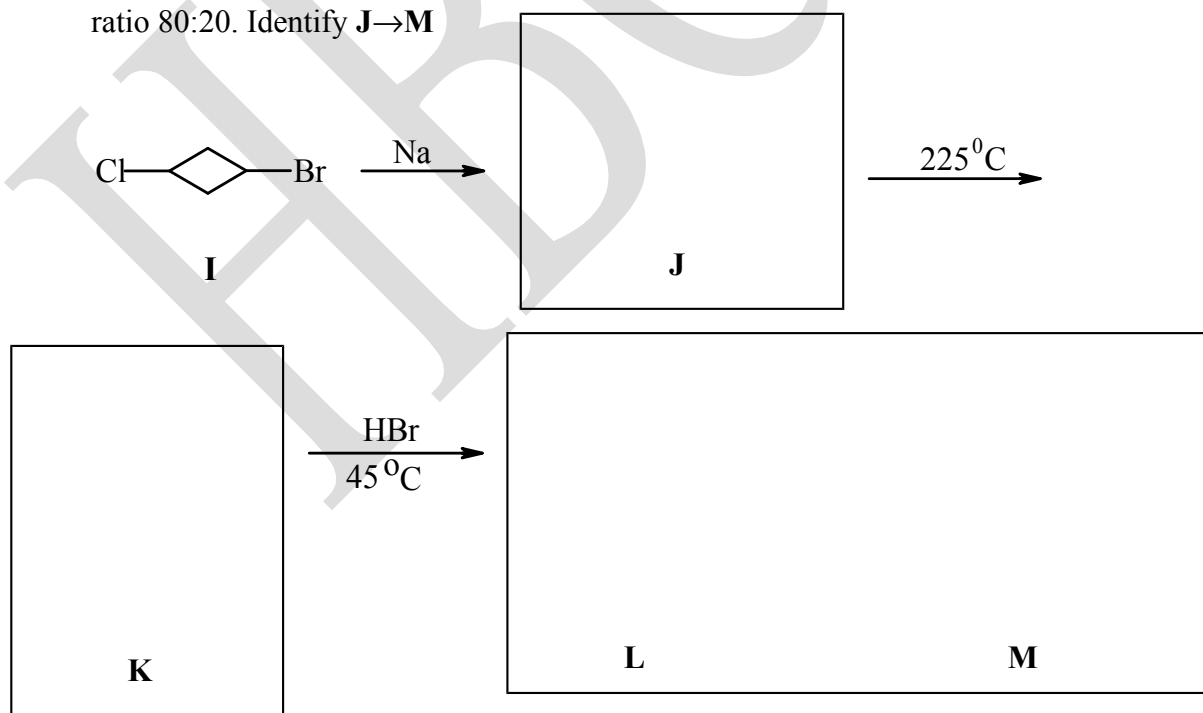
Starting compounds for synthesis of **G**

(1.5 marks)

Starting compounds for synthesis of **H**

(0.5 mark)

- 4.6 **I** is an interesting compound. It reacts with metallic sodium to form compound **J**, which is stable and on heating to 225°C forms **K** ( $C_4H_6$ ; UV -  $\lambda_{max}$  215nm). One mole of hydrogen bromide reacts with **K** at 45°C to give **L** ( $C_4H_7Br$ ) and **M** ( $C_4H_7Br$ ) in the ratio 80:20. Identify **J**→**M**

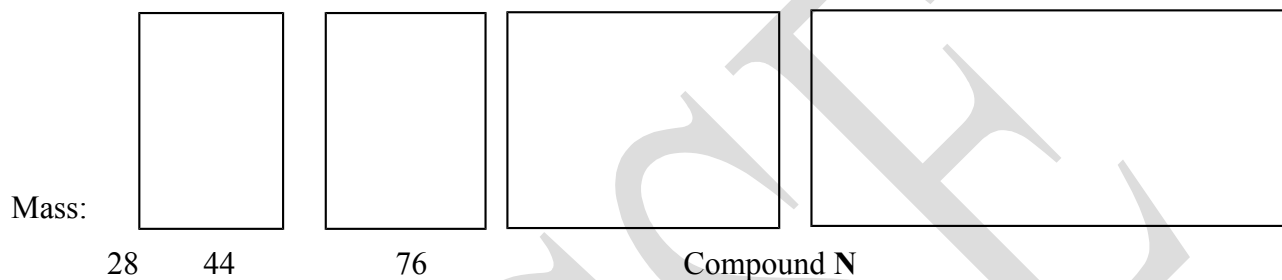


(3 marks)

2-Aminobenzoic acid on reaction with  $\text{NaNO}_2/\text{HCl}$  gives a compound **N**. In mass spectrometry, a compound is heated to a high temperature under vacuum and irradiated with a high energy electron beam to ionize it to form a cation. The cation undergoes fragmentation. The masses of the fragments are recorded in the spectra.

Alkaline solution of **N** is subjected to a flash discharge and a specially adapted mass spectrometer scans the spectrum of the products at rapid intervals. Mass spectrometric analysis of **N** gives peaks at masses 28, 44 and 76.

4.7 Structures of the fragments at masses 28, 44 and 76 and **N** are



(2.5 marks)

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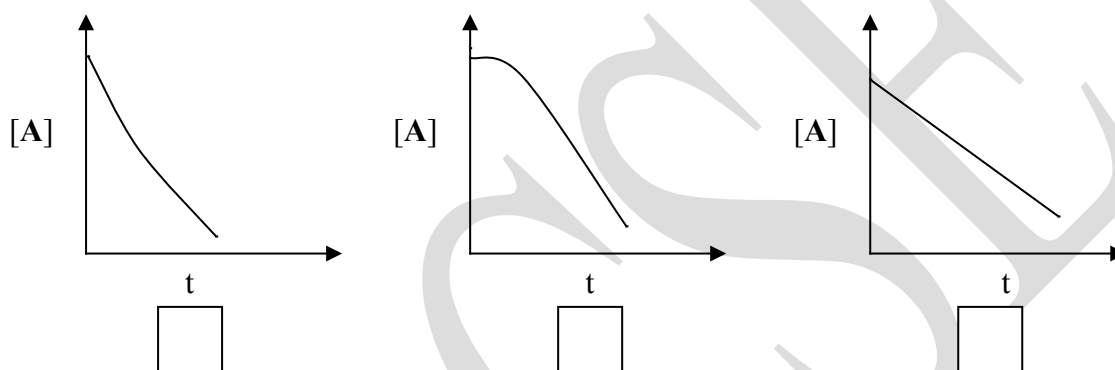
## Problem 5

11 Marks

## Chemical kinetics

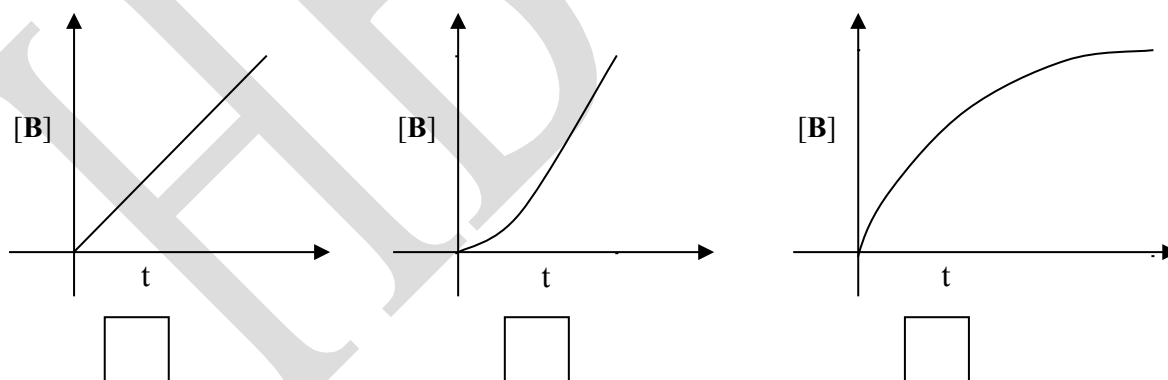
5.1 Consider a first order reaction  $A \rightarrow B$ , with initial concentration of  $A$  being  $[A]_0$  and that of  $B$  being zero.

Which of the following curves correctly describes the variation of  $[A]$  for small values of time ( $t$ )?



(0.5 mark)

5.2 Which of the following curves correctly describes the variation of  $[B]$  for small values of time ( $t$ )?



(0.5 mark)

5.3 Some chemical reactions are known to follow zero order kinetics. Consider such a reaction  $A \rightarrow B$  with a rate constant  $k$  in which concentration  $[A]$  reduces with time,  $t$ .

a) Write the differential equation for  $[A]$ .

(1 mark)



- b) Assuming the initial concentration of  $A = [A]_0$ , write the expression for  $[A]$  in terms of  $[A]_0$ ,  $t$  and  $k$  for a zero order reaction

(0.5 mark)

- c) Write the expression relating  $[A]_0$ ,  $k$  and the half life of this reaction.

(1 mark)

- 5.4 Ammonia decomposes on a tungsten wire at 1000 K. The following results have been obtained in a constant volume system. Find out the order of reaction and the corresponding rate constant of the reaction by approximate estimation.

P(torr)	310	321	332	355	377	421	476
t(sec)	0	100	200	400	600	1000	1500

- a) Order
- b) Rate constant with units


(2 marks)

- 5.5 Decomposition of  $SO_2Cl_2(g)$  is described by the reaction:



The initial concentration and the initial reaction rates are denoted as  $[SO_2Cl_2]_0$  and  $R_0$ , respectively. Determine by approximate calculation the order of the reaction with respect to the following data collected at 298 K.

$[SO_2Cl_2]_0$ (mol dm <sup>-3</sup> )	0.10	0.37	0.76	1.22
$R_0$ (mol dm <sup>-3</sup> s <sup>-1</sup> )	$2.24 \times 10^{-6}$	$8.29 \times 10^{-6}$	$1.71 \times 10^{-5}$	$2.75 \times 10^{-5}$

Determine the order of this reaction and the corresponding rate constant,  $k$  (report only 1 significant digit)

- a) Order:
- b)  $k$  (with units)


(1.5 marks)

- 5.6 Radioactive decay of an element follows first order kinetics. After how many years will 25% of the initial quantity of radium remain, if half life of radium is 1620 years?

(0.5 mark)

The Avogadro number can be calculated experimentally. In a classic experiment, Ernest Rutherford observed that a sample of 192 mg  $^{226}_{88}\text{Ra}$  left for 83 days produced 6.83 mm<sup>3</sup> of He gas measured at 273 K and 1 atm pressure.

- (i) Calculate the moles of He produced in the experiment.

(1 mark)

The number of disintegrations undergone by 1g of Ra in a second is  $4.6 \times 10^{10} \text{ g}^{-1}\text{s}^{-1}$

- ii) The number of disintegrations observed in the Rutherford's experiment is

(1 mark)

- iii)  $^{226}\text{Ra}$  emits  $\alpha$  particles to give  $^{214}\text{Pb}$ . Calculate the number of He atoms produced in the Rutherford experiment.

(1 mark)

- iv) Using the above data, calculate the Avogadro number.

(0.5 mark)

Name of Student

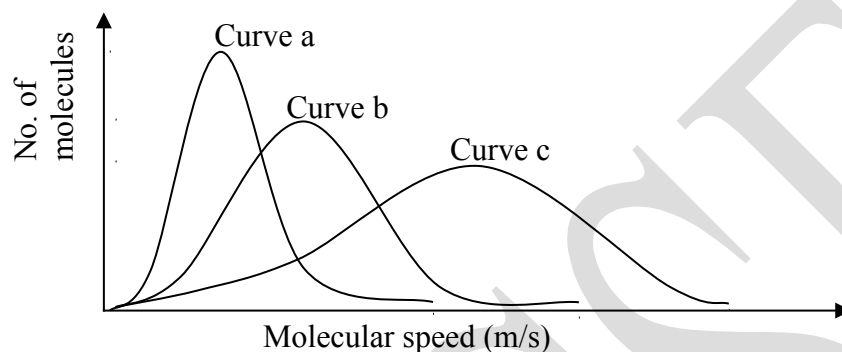
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## Problem 6

15 marks

## A. Kinetic theory of gases and Gas Laws

- 6.1. Typical Maxwell speed distribution curves for 1 mol of  $N_2$  gas at three different temperatures 100 K, 300 K and 700 K are shown below



- i. Match the curves with corresponding temperatures

Curve

Temperature

Curve a

Curve b

Curve c

(1 mark)

- ii. Theoretically area under the curves is same

True

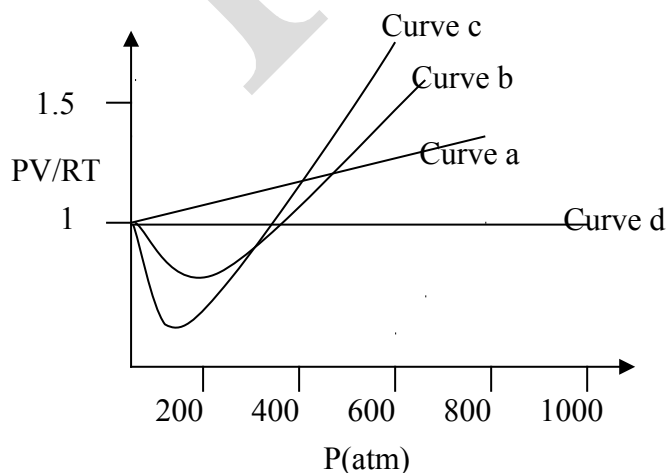
☐

False

☐

(0.5 mark)

- 6.2 Plots of  $PV/RT$  vs.  $P$  for 1 mol of  $H_2$ ,  $NH_3$ ,  $CH_4$  and Ar gases are given below.



Match the curves with corresponding gases

Curve	Gas
Curve a	<input type="text"/>
Curve b	<input type="text"/>
Curve c	<input type="text"/>
Curve d	<input type="text"/>

(1.5 marks)

6.3 The van der Waals equation for one mol of a real gas is  $(P + a/V^2)(V - b) = RT$ . The correct order for the value of 'a' for  $H_2$ ,  $NH_3$ , and  $CH_4$  gases is

- |                          |                          |                         |                          |
|--------------------------|--------------------------|-------------------------|--------------------------|
| i) $H_2 < NH_3 < CH_4$   | <input type="checkbox"/> | ii) $H_2 > NH_3 > CH_4$ | <input type="checkbox"/> |
| iii) $H_2 < CH_4 < NH_3$ | <input type="checkbox"/> | iv) $H_2 > CH_4 > NH_3$ | <input type="checkbox"/> |

(0.5 mark)

6.4 A diver dives to 20 m depth of sea water ( $\rho = 1.03 \times 10^3 \text{ kg m}^{-3}$ ) and rises to the surface quickly without breathing. Change of pressure (in atmosphere) in coming to water surface from the depth is

(1 mark)

6.5 The total work done (Joule) on lungs if the same expansion is carried out at the sea surface at constant temperature is (Assume volume of air in the lungs is 2L under normal conditions).

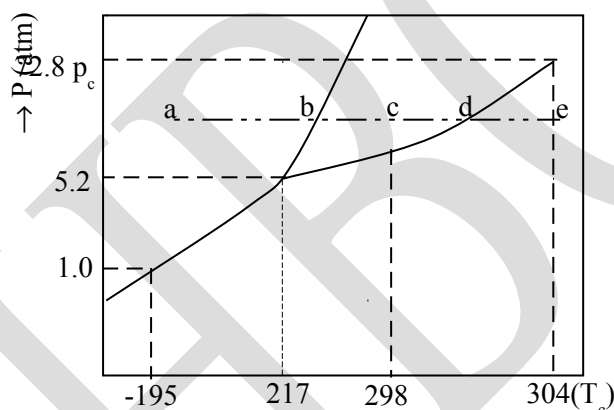
(1.5 marks)

- 6.6 Human body functions best when oxygen gas has a partial pressure of 0.2 atm. Calculate the percentage of oxygen by volume in air carried by the diver at the sea depth of 20 m for best body function.

(1 mark)

**B. Physical and chemical equilibrium**

A phase diagram summarizes the conditions at which a substance exists as a solid, liquid or gas. Each solid line between two phases specifies the conditions of temperature and pressure under which the two phases can exist in equilibrium. The phase diagram of a one component system **S** is shown below. Based on the diagram, answer the following questions.



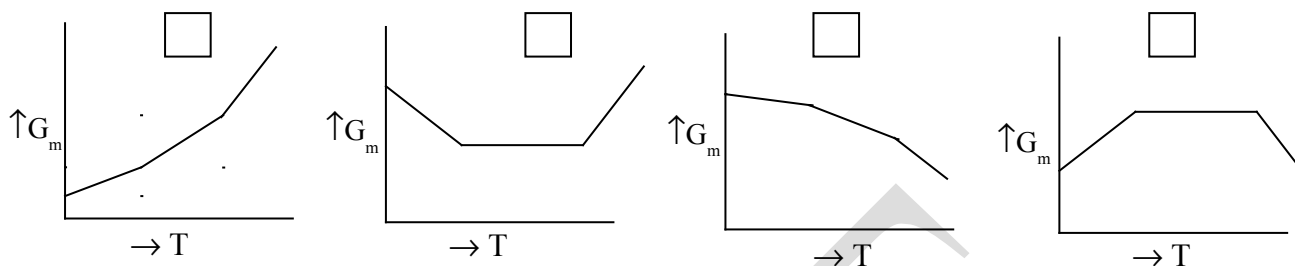
- 6.7 Which phases of **S** can coexist under atmospheric conditions?

(1 mark)

- 6.8 Under what conditions all the three phases of **S** can co-exist?

(0.5 mark)

- 6.9 Mark the correct graph showing the variation of molar Gibbs function ( $G_m$ ) vs. temperature ( $T$ ) along the line a-e of the phase diagram.



(1 mark)

- 6.10 Choose the correct option/s from the following statements for triple point of system S.

- a) All the three phases are in equilibrium ☐
- b) Molar Gibbs energy for the three phases is the same ☐
- c) Molar volume of the three phases is identical ☐
- d) Molar entropy of the three phases is the same ☐

(1 mark)

- 6.11 As a result of increase in external pressure, the melting point of solid S will

- a) increase ☐
- b) decrease ☐
- c) not change ☐

(1 mark)

- 6.12 How many phases exist at  $T > 304\text{ K}$  and  $P > 72.8\text{ atmosphere}$ ?

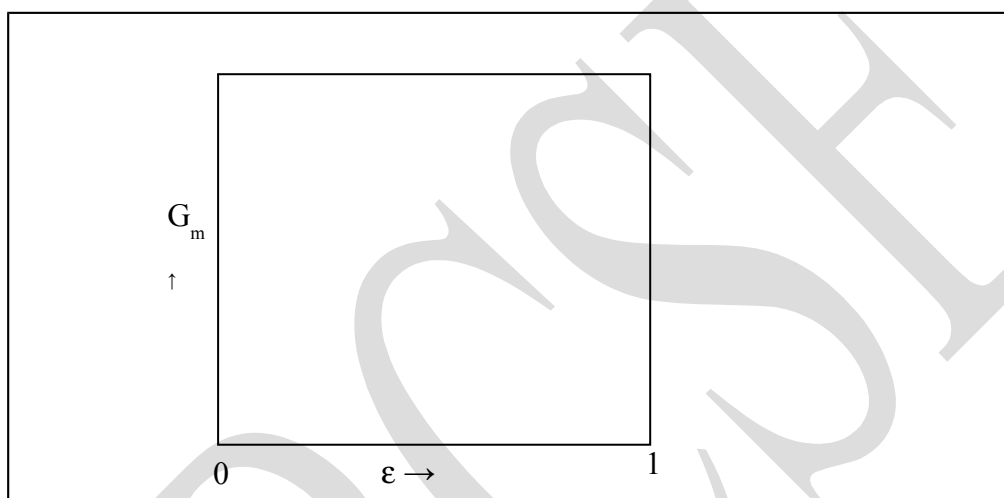
(0.5 mark)

- 6.13** For a chemical reaction  $A \rightarrow B$ , the extent of reaction expressed as  $\epsilon$  is a measure of progress of the reaction.  $\epsilon = 0$  corresponds to pure  $A$  and  $\epsilon = 1$  correspond to pure  $B$ .

Draw a graph showing the variation of Gibbs free energy ( $G_m$ ) vs.  $\epsilon$  for the spontaneous reaction  $A \rightarrow B$  as well as for  $B \rightarrow A$ .

Mark the following points on your graph i)  $P_1$  corresponding to  $\partial G_m / \partial \epsilon < 0$ ,

ii)  $P_2$  corresponding to  $\partial G_m / \partial \epsilon = 0$  and iii)  $P_3$  corresponding to  $\partial G_m / \partial \epsilon > 0$ .



(2 marks)

- 6.14** van't Hoff's equation for a chemical reaction under equilibrium is given by

$\frac{d \ln K}{dT} = \frac{\Delta_r H}{RT^2}$  where  $\Delta_r H$  is standard reaction enthalpy at temperature  $T$  and  $K$  is the equilibrium constant. Predict how  $K$  will vary with temperature for an exothermic reaction.

- a)  $K$  decreases as the temperature rises
- b)  $K$  increases as the temperature rise
- c)  $K$  remains unchanged.

☐  
☐  
☐

(1 mark)

Name of Student

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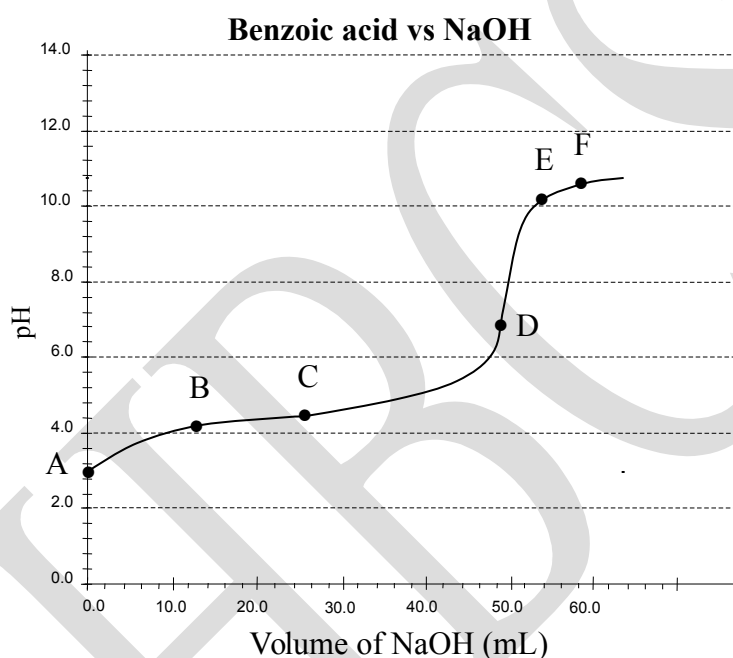
## Problem 7

11 marks

## Acid-Base chemistry

## Part A

- 7.1 Consider a pH titration of 50 mL 0.1 M benzoic acid vs 0.1M NaOH at 25°C. The experimentally observed curve is shown below, on which points A, B, C..... F are marked.

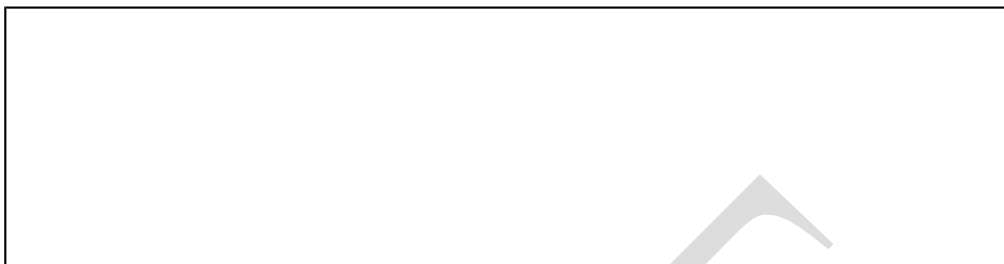


- a) Which point corresponds to approximately 0.07 M benzoic acid solution?
- b) At which point is the pH changing very rapidly?
- c) Which point represents the smallest concentration of  $[H^+]$ ?

(2 marks)



- 7.2 The pH at half equivalence point may be employed to estimate the  $pK_a$  value of a weak acid. Estimate the  $pK_a$  value from the graph.



(1 mark)

- 7.3 Suppose you are carrying out a conventional titration of benzoic acid and NaOH. Using the answer obtained in 7.2, choose an appropriate indicator from the table below.

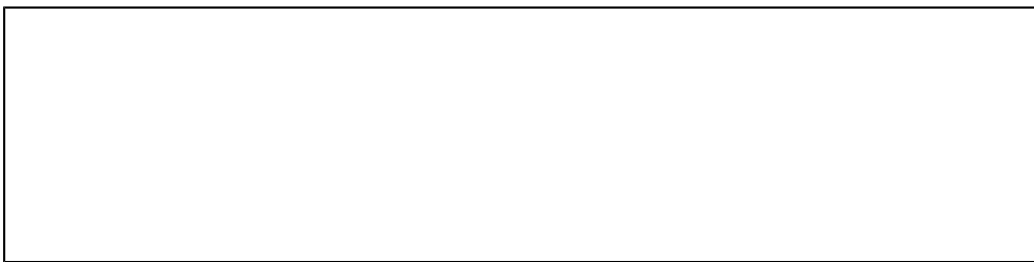
Indicator	pH range	Colour change
Methyl yellow	2.9 - 4.0	red-yellow
Methyl orange	3.1 - 4.4	red-orange
Phenolphthalein	8.0 - 9.8	colorless-red

(0.5 mark)

### Part B

The percentage of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  in a sample can be determined measuring the changes in pH during the titration of the sample with HCl. In a typical experiment, 0.500 g of the sample was dissolved in deionised water to make 50.0 mL solution. This solution was titrated with 0.115 M HCl. The pH titration curve showed two breaks at  $\text{pH} = 9.0$  and  $\text{pH} = 5.0$ .

7.4 Write the balanced equation corresponding to these breaks.



(1 mark)

7.5 Calculate the total number of moles of acid used

- a) to reach equivalence point at  $\text{pH} = 9.0$  if the volume of acid required is 9.6 mL.
- b) to reach equivalence point at  $\text{pH} = 5.0$  if the volume of acid required is 34.3 mL.



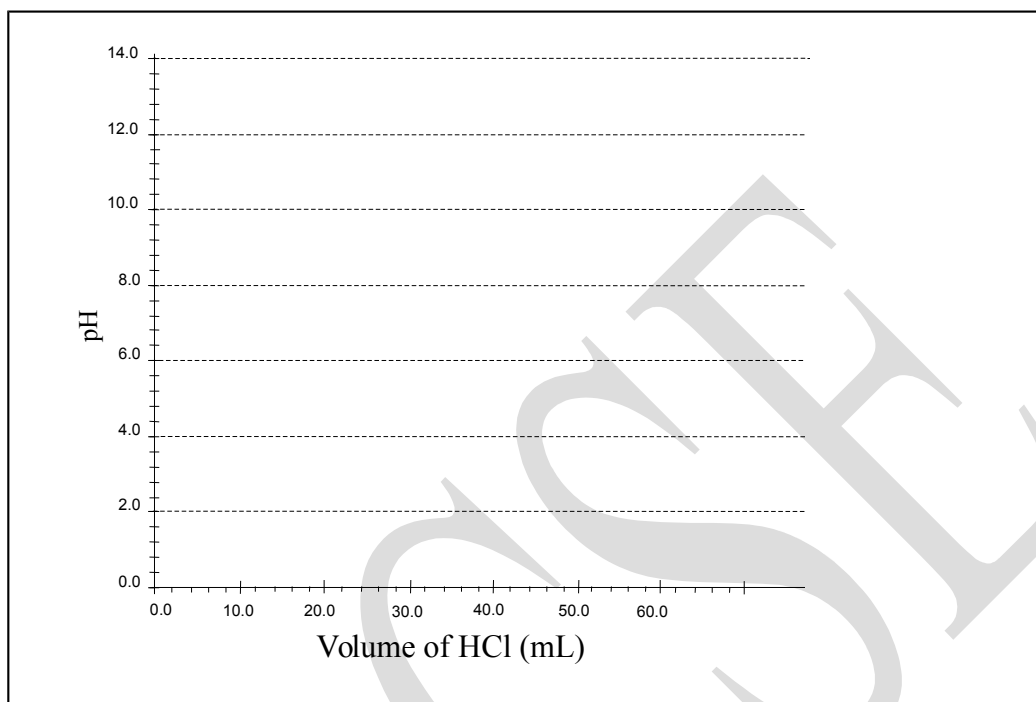
(1 mark)

7.6 Determine the number of grams of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  and their percentage in the mixture.



(2.5 marks)

- 7.7 30 mL of 0.1 M  $\text{Na}_2\text{CO}_3$  solution was titrated with 0.1 M HCl. (The initial pH of the  $\text{Na}_2\text{CO}_3$  solution is around 11.8). Qualitatively sketch the pH vs  $V_{\text{HCl}}$  curve for this titration.



(1 mark)

- 7.8 Choose the correct statement/s for the titration curve of pH vs  $V_{\text{HCl}}$  for  $\text{Na}_2\text{CO}_3$  drawn by you in 7.7

- i) The total volume of HCl required to reach the 2<sup>nd</sup> end point is twice that of the first one ☐
- ii) Number of moles of  $\text{CO}_3^{2-}$  is equal to the number of moles of  $\text{HCO}_3^-$  at some point on this curve ☐
- iii) Number of moles of  $\text{HCO}_3^-$  is equal to twice the number of moles of  $\text{CO}_3^{2-}$  at some point on this curve ☐
- iv) The total volume of HCl required to reach the 2<sup>nd</sup> end point is half that of the first one ☐

(2 marks)