

2010

CHEMISTRY

( Major )

Paper : 1.1

( Physical Chemistry )

Time : 3 hours

The figures in the margin indicate full marks  
for the questions

Candidates **eligible** for Internal Assessment shall  
answer only one part each from Question Nos. 1 and  
2 along with the rest of the questions ( Marks : 65 )

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Candidates **not eligible** for Internal Assessment shall  
answer only two parts each from Question Nos. 1 and  
2 along with the rest of the questions ( Marks : 75 )

1. (a) State the most important postulates of the kinetic-molecular theory. Do they have any practical significance? Comment on the way the molecular speeds are distributed for (i) hydrogen, nitrogen and carbon dioxide at 300 K and for (ii) oxygen at 100 K, 500 K and 800 K.

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- (b) Define the compressibility factor of a gas. How can it be used to describe the deviation from ideal behaviour? 5
- (c) Obtain an expression for the collision frequency in a mixture of two ideal gases. 5
- (d) How does thermal conductivity of an ideal gas change with temperature? Obtain an expression for the thermal conductivity on the basis of the kinetic-molecular theory. 5
2. (a) Distinguish among closed, isolated and open thermodynamic systems. The enthalpy change for the formation of  $\text{NOCl(g)}$  from the gaseous elements is  $51.71 \text{ kJ/mol}$  at  $298 \text{ K}$ . If the gases are ideal, calculate internal energy change. 5
- (b) Derive general expressions for  $E(\text{thermal})$  of ideal monatomic, diatomic, linear polyatomic and non-linear polyatomic gases. 5
- (c) If a sample of gas is allowed to expand at constant temperature against atmospheric pressure, (i) does the gas do work on its surroundings; (ii) is there heat transfer between the system and the surroundings; (iii) what is  $\Delta E$  for the process? A non-ideal gas is heated slowly and the gas expands reversibly at a constant pressure of  $760 \text{ mm}$  from a volume of  $1385 \text{ cm}^3$  to  $1875 \text{ cm}^3$ . Find the work done in joules. 5

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( Continued )

- (d) For each of the following, state whether each of the  $\Delta U$  and  $\Delta H$  is positive, zero or negative. 5
- (i) Reversible melting at  $0^\circ \text{C}$
- (ii) Reversible adiabatic expansion of an ideal gas
- (iii) Adiabatic expansion into vacuum
3. Answer any five of the following. 5
- (a) Calculate the entropy change for  $1.00 \text{ mol}$  of water under reversible conditions for vaporization and fusion at  $0^\circ \text{C}$  respectively. Also calculate the enthalpy changes for the fusion of water and the vaporization of water at  $40.656 \text{ kJ/mol}$  and  $6.01 \text{ kJ/mol}$  respectively. 5
- (b) State how the entropy change, heat capacity, and internal energy change for the reversible expansion of  $1.00 \text{ mol}$  of ethane at  $1500 \text{ K}$  at constant pressure. Find that  $C_p = 5.351 + 177. \dots$  -6

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- (c) What are the characteristics of a spontaneous process? State how the entropy will change in case of (i) freezing of ethanol, (ii) dissolving glucose in water, (iii) evaporation of bromine from a bromine solution at room temperature and (iv) cooling nitrogen gas from 373 K to 273 K.
- (d) State and explain Nernst heat theorem. What is the most important application of the third law of thermodynamics?
- (e) In the relation  $\Delta G = \Delta H - T\Delta S$ , state the conditions when  $\Delta G$  can be positive or negative. Obtain the relation between the equilibrium constant and the standard Gibbs energy change.
- (f) Of the following pairs, which has higher chemical potential?
- (i)  $\text{H}_2\text{O}(\text{l})$  at 298 K, 1 atm and  $\text{H}_2\text{O}(\text{g})$  at 298 K, 1 atm
- (ii)  $\text{H}_2\text{O}(\text{s})$  at 273 K, 1 atm and  $\text{H}_2\text{O}(\text{l})$  at 273 K, 1 atm
- (iii)  $\text{H}_2\text{O}(\text{s})$  at 268 K, 1 atm and supercooled  $\text{H}_2\text{O}(\text{l})$  at 268 K, 1 atm
- (iv) Glucose (s) at 298 K, 1 atm and glucose (aq.) at 298 K, 1 atm
- Give brief reason in each case.

- (g) Calculate  $\Delta G$  for compression of 30.0 g of gas from 1.0 atm to 100.0 atm. State the variations in  $V$  with  $p$ .
4. Answer any two of the following questions.
- (a) Clearly state Ostwald's law. Show how these laws are used to predict the behaviour of a real solution.
- (b) What are abnormal properties? Give examples. How do real solutions show positive deviations from ideal properties of mixing solvent?
- (c) The vapour pressure of water is 1074.6 mm. Find the vapour pressure of a sucrose solution in water. What approximation you have used?
- (d) Define 'activity coefficients'. State how they depend on (i) concentration, (ii) temperature and (iii) pressure.
- (e) Discuss qualitatively the properties of liquid water. Why are they important?

5. Answer any five of the following :  $3 \times 5 = 15$

- What do you mean by zero-order and pseudo-order reactions? Give examples.
- Obtain the integrated rate expression for a first-order reaction and draw a graph to show variation of the concentration of the reactant with time.
- For a homogeneous reaction  $aA + bB + cC + \dots = eE + fF + \dots$ , obtain the complete rate expression. Show that the rate is an intensive property that depends on  $T$ ,  $p$  and concentration.
- Show, indicating the principle involved, how an expression for the concentration of the final product can be obtained for a consecutive reaction of the type  $A \rightarrow B \rightarrow C$ . How do the concentrations of  $A$ ,  $B$  and  $C$  change with time?
- How does the reaction rate depend on temperature? Show how Arrhenius plot of a reaction can be obtained. What is the significance of the pre-exponential factor?
- Discuss the kinetics of thermal decomposition of ethanol.
- What are zeolites? Why are they important as catalysts? Give two examples where zeolites are used as catalysts.

6. Answer any five of the following :

- Define mobility of an ion. How do ions have different mobilities?
- State how the molar conductivity of a strong electrolyte solution varies with concentration according to the Hückel-Onsager equation. Explain qualitatively why the conductivity increases at higher concentrations.
- How many different types of electrodes exist? Describe the construction of a calomel electrode.
- Give an expression for the activity of an electrolyte solution. Calculate the ionic strength of 0.05 M  $KCl$  and  $Zn(NO_3)_2$ .
- Define  $pK$  of acids and bases. How do you arrange a number of acids in respect of their  $pK$  values? Give examples.
- Describe a concentration cell. What is transference.
- Write short notes on :
  - Dry cells
  - Corrosion and its prevention

2010

CHEMISTRY

( Major )

Paper : 1.2

( Organic Chemistry )

Time : 3 hours

The figures in the margin indicate full marks  
for the questions

Candidates **eligible** for Internal Assessment shall  
answer from PART—I only ( Marks : 65 )

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Candidates **not eligible** for Internal Assessment shall  
answer both from PART—I and PART—II ( Marks : 75 )

PART—I

( Marks : 65 )

1. Answer any four of the following :  $1 \times 4 = 4$ 

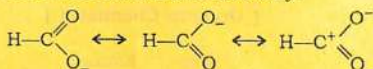
(a) Arrange the following bonds in the  
increasing order of bond lengths :

C—H ; O—H ; N—H

(b) Why does neopentane melt at a higher  
temperature ( $-16.8\text{ }^{\circ}\text{C}$ ) than pentane  
( $-129.8\text{ }^{\circ}\text{C}$ )?

(c) Of ethanol and dimethyl ether (functional group isomers), which one will have a higher boiling point and why?

(d) Amongst the following resonating structures for acetate ion, which one is the minor contributor and why?

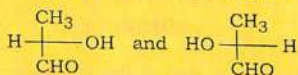


(e) Which one of the two, ethanol and ethane thiol is a stronger acid?

(f) Why is acetic acid a stronger acid than propanoic acid?

2. (a) Draw and label the *E,Z*-isomers of 1-chloro-2-methyl-pent-1-ene.

(b) Give the *R* and *S* designations to the following pair of optical isomers :



(c) Draw the Newman projection formula for the staggered conformation of the compound



with  $\text{C}_2-\text{C}_3$  bond as the projected bond.

(d) Draw the chair conformation of methyl-4-*t*-butyl cyclohexane and identify the more stable isomer.

Or

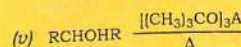
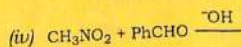
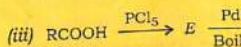
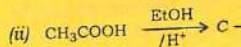
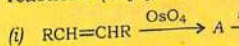
Draw the chair conformation of *cis*-1,3-dimethyl cyclohexane and comment on its optical activity.

(e) What is a racemic mixture? Give a method for the resolution of a racemic mixture with a suitable example.

Or

What are diastereomers? Give an answer with suitable examples.

3. (a) Give the products in the following reactions (any four) :



- (b) Why is acetylenic hydrogen acidic in nature? Give one reaction showing the acidic nature of acetylenic hydrogen. 2
- (c) Describe how starting from Ag-carboxylate, an alkyl bromide can be synthesised. 2

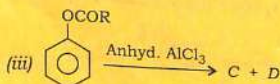
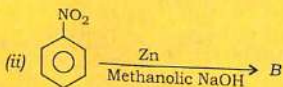
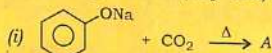
Or

What happens when—

- (i) glycerol is heated with  $\text{KHSO}_4$ ;
- (ii) propanoic acid is treated with  $\text{P}/\text{Br}_2$ ?
- (d) Describe how you can distinguish among  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  amines. 2

4. Answer any four of the following :  $2 \times 4 = 8$

(a) Give the products (any two) :



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( Continued )

- (b) What is *ortho*-effect? On this basis, why nearly all benzoic acids are stronger than benzoic acid.
- (c) Explain why electrophilic substitution in naphthalene prefers the 1 position over the 2 position.
- (d) Amongst phenol and benzene, identify the stronger acid. Give reason for that.
- (e) Write short note on (any two) :  
 (i) Friedel-Crafts alkylation  
 (ii) Benzoin condensation

5. Answer any five of the following :

- (a) What is allylic bromination? Illustrate the allylic bromination of propyl bromide with  $\text{NBS}$  in  $\text{CCl}_4$  solution. Discuss the support of the free radical mechanism.
- (b) What is Walden inversion? Give evidence in support of the inversion.

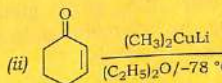
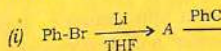
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- (c) What is an epoxidation reaction? Give its mechanism. Illustrate with a suitable example, how a *trans*-diol could be synthesised from an alkene through epoxidation.
- (d) Write the two empirical rules which govern the orientation in the elimination reactions of an unsymmetrical substrate. Provide explanations for these rules.
- (e) What is *syn*-elimination? Discuss a pyrolytic *syn*-elimination reaction with the mechanism.
- (f) Write short notes on (any two) :
- Aldol condensation
  - Reformatsky reaction
  - Knoevenagel reaction

6. Answer any three of the following :  $5 \times 3 = 15$

- (a) What are  $\sigma$ - and  $\pi$ -complexes in the context of electrophilic aromatic substitution? Illustrate your answer with suitable examples. Draw an energy profile diagram for electrophilic aromatic substitution on benzene ignoring the formation of the  $\pi$ -complex.

- (b) What is the intermediate mechanism in aromatic substitution? Illustrate with a suitable example.
- (c) What do you understand by intermediates? How does the establishment of benzyl aromatic nucleophilic substitution occur?
- (d) What is an organolithium reagent? Give a general method of preparation of an organolithium reagent. Complete the following reactions showing the intermediates and products.





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PART—II

( Marks : 10 )

( In lieu of Internal Assessment )

7. Answer any five of the following :  $2 \times 5 = 10$

- (a) Draw the tautomers of acetoacetic ester. Identify the stable form and explain why it is more stable than the other form.
- (b) Define enantiotopic and diastereotopic hydrogens. Give examples.
- (c) What happens when benzaldehyde is treated with a strong base?
- (d) Starting from nitrobenzene, how can you synthesise *p*-dinitrobenzene?
- (e) Explain why the nitro group is *m*-directing in aromatic electrophilic substitution.
- (f) Explain why *N*-ethylamine is more basic than *N*-methylamine.

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