2012

CHEMISTRY

(Major)

Paper : 1.1

Full Marks : 60

Time : 2½ hours

The figures in the margin indicate full marks for the questions

1. *(a)* What is the relationship between C_p and C_v for real gases? 1

(b) State the definition of work in thermodynamics. 1

(c) Give molecular interpretation of work and heat. 2

2. *(a)* Define the entropy change of a system to which heat has been transferred reversibly and isothermally. 1

(b) Slope of the line obtained by plotting ΔG against T is

(i) ΔH

(ii) ΔS

(iii) $-\Delta S$

(iv) 0

State the correct choice. 1

(c) What is meant by a state function? Give example of one state function and one that is not. 2

3. (a) What is 'turnover number' of an enzyme catalyst? 1

(b) The reaction $2A + B + C \rightarrow D + E$ is first order with respect to A, second order with respect to B and zeroth order with respect to C. Write the differential rate equation for the reaction. 1

(c) For the general reaction $0 \rightarrow \Sigma \nu_i A_i$, show that the rate of reaction is given by

$$r = \frac{1}{V}\frac{d\xi}{dt}$$

where ξ is the extent of reaction. 2

4. Answer any *two* : 3×2

(a) Explain the principle of liquefaction of gases by Joule-Thomson effect.

(b) For a system which can do only expansion work, show that $\Delta H = q_p$.

(c) What is the ΔH when 1 mole of H_2O at 101 kPa is heated from 353 K to 393 K? The following data are available :

C_p (l, H_2O) = 75·0 JK^{-1} mol^{-1}

ΔH (vaporization) = 47·3 kJ mol^{-1} at 373 K

C_p (g, H_2O) = 35·4 JK^{-1} mol^{-1}

5. Answer any *two* : 3×2

(a) Show how entropy will change for the following processes :

(i) Freezing of ethanol

(ii) Dissolving glucose in water

(iii) Cooling nitrogen gas from 373 K to 273 K

(b) For an ideal gas, show that $\mu = \mu_0 + RT \ln\left(\frac{p}{p^0}\right)$, where p^0 is the standard pressure.

(c) For the reaction equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, calculate the equilibrium constant at 500 K from its value at 298 K. ($K = 6 \times 10^5$ at 298 K, standard enthalpy of reaction is $-92 \cdot 2$ kJ mol^{-1})

6. Answer any *two* : 3×2

(a) For the set of reactions

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \text{ and } C + B \xrightarrow{k_2} D$$

find $-dC_A/dt$, $-dC_B/dt$, dC_A/dt and dC_D/dt.

(b) The reaction $2HI = H_2 + I_2$ is second order with a rate constant $k_2 = 1 \cdot 2 \times 10^{-3}$ mol^{-1} s^{-1} at 700 K. A sample of HI at a pressure of 100 kPa is maintained at 700 K. How long will it take to decompose 40% of the original HI?

(c) What is meant by Arrhenius plot? Write briefly, how this plot can be obtained for a particular reaction.

7. Answer any *two* : 5×2

(a) Derive an expression for the work done in a reversible isothermal expansion of n mol of an ideal gas from volume V_1 to volume V_2. Show that work obtained in isothermal reversible expansion of an ideal gas is more than that in an irreversible expansion.

(b) Draw the skeletal diagram for the experimental setup of Joule-Thomson effect, and show that Joule-Thomson expansion is an isoenthalpic process.

(c) Define internal energy and enthalpy of a system. The ΔH for the formation of NOCl (g) from the gaseous elements is $51 \cdot 71$ kJ mol^{-1} at 25 °C. If the gases are ideal, calculate ΔU.

8. Answer any *two* : 5×2

(a) Deduce all the forms of Gibbs-Helmholtz equation.

(b) Find an expression for the entropy change in an isothermal reversible expansion of n mol of an ideal gas from a volume V_1 to volume V_2. Volume of 1·00 mol of an ideal gas is doubled by a reversible isothermal expansion at 298 K. Calculate ΔS for the gas. What will be the entropy change of the gas when the same expansion is carried out irreversibly?

(c) Discuss the variation of the enthalpy function with temperature under various conditions of pressure and volume deriving the appropriate relations.

9. Answer any *two* : 5×2

(a) For the first-order reaction

$$A \rightarrow \text{products}$$

obtain the integrated rate law

$$[A] = [A]_0 e^{-kt}$$

Draw a graph to show the variation of concentration of the reactant with time. Show that first-order reaction can never be completed.

(b) What is rate determining step of a reaction? For the following pre-equilibrium mechanism

$$A + B \underset{k'_a}{\overset{k_a}{\rightleftharpoons}} C \xrightarrow{k_b} P$$

under what conditions the pre-equilibrium exists? Show that the overall order of the reaction is two.

(c) Derive the rate law for the formation of HBr in hydrogen-bromine reaction.

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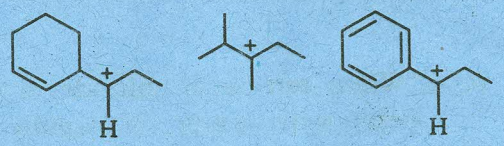
(e) What are carbocations? How can you generate carbocations? Arrange the following carbocations in decreasing order of stability and explain the reasons :



What are carbenes? Give the structures of the two types of carbenes. Give an example of a reaction which involves carbene as an intermediate. 1+2+3+1+2+1

(f) How do the following factors affect elimination versus substitution?

(i) Basicity versus nucleophilicity

(ii) Substrate structure

What are pyrolytic eliminations? Give an example. Propose a mechanism for the pyrolytic elimination reaction.

2½+2½+1+1+3

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1. Answer the following questions (any *seven*) : 1×7=7

(a) Draw the structural formula of 5,5-dimethyl-3-oxohexanoic acid.

(b) What is the hybridisation of each of the carbon atoms in an allene?

(c) In which of the two compounds OF_2 and NF_3, the bond angle is greater?

(d) Give one example of a compound which is optically active but does not contain a chiral centre.

(e) Name and give the structure of a free-radical inhibitor.

(f) Tropylium bromide is an ionic compound. Explain.

(g) Arrange the following in order of decreasing nucleophilicity :

$NH_3, NH_2^-, R_2NH, R_2N^-$

(h) In the reaction of 1-bromobutane with a base, which of the two bases EtO^- and $(CH_3)_3CO^-$ would lead to greater amount of the elimination product?

(i) Explain whether BF_4^- is a nucleophile or not.

2. Answer the following questions (any *four*) :

(a) Name a technique by which you can separate *ortho*-nitrophenol and *para*-nitrophenol. Which among the two has higher boiling point and why? ½+1½

(b) Classify the following as either aromatic, nonaromatic or antiaromatic. Give reasons : 1+1

(i) 

(ii) 

(c) Account for the fact that cyclopentadiene has $pK_a \approx 16$. 2

(d) Among pyridine and piperidine, which one is a stronger base and why? 1+1

(e) Draw the enantiomers of lactic acid and assign *R*, *S* designation. 1+1

3. Answer the following questions (any *three*) :

(a) Taking naphthalene as an example, explain what is partial bond fixation. Which bond phenanthrene is readily attacked by reagents and why? 3+2

(b) How many stereoisomers are observed for 2,3-diphenylbutane? Use Fischer formulas to draw all the stereoisomers and assign *R* or *S* designation to the asymmetric carbon atoms. Indicate the structures which are optically active. 1+3+1

(c) How is a racemic mixture different from a mesocompound? Give examples to illustrate the differences. What do you mean by percent optical purity and optical purity? 2+1+2

(d) With the help of an example, explain what you mean by optical pumping. Draw structural formulas of 1-bromo-2-chloropropene and assign *E* or *Z* designation to the geometrical isomers. 3+2

(e) Why is the chair form of cyclohexane more stable than the boat form? Draw the various chair forms of methylcyclohexane. Identify the stable one and give reasons for your answer. 2+1+2

4. Answer the following questions (any *three*) :

(a) What are configurational and conformational isomers? Draw the possible conformers of *n*-butane. Designate each of the conformers. Arrange the conformers in order of decreasing stability. Identify the least stable conformer and assign reason for it being least stable. Draw the potential energy diagram to show the variation of energy for the various conformers. 2+2+1+1+2+2

(b) Which one is more reactive towards nucleophiles—acetaldehyde or acetone? Explain. What happens when acetaldehyde is allowed to react with

aq. NaOH? Propose a mechanism. What is the driving force for this reaction? Complete the following :

$$CH_3CHO + C_6H_5CHO \xrightarrow{NaOH\ (aq.)} ?$$

1+3+1+3+1+1

(c) "When *tert*-butyl chloride is allowed to react with water, it rapidly produces *tert*-butyl alcohol. The product is the result of a substitution of chloride by hydroxy group." Propose a mechanism and write the steps involved. Draw the energy-profile diagram. What would happen to the rate of the reaction if instead of *tert*-butyl chloride, *tert*-butyl iodide is taken and why? What would be the effect on the rate of the reaction if a small amount of NaCl is added from outside and why? Would you expect any change in the rate of the reaction if water is replaced by some other nucleophile? 3+2+2+2+1

(d) Discuss the mechanistic steps involved in an elimination reaction, proceeding by the E2 mechanism. Discuss the stereochemical evidence to support the E2 mechanism. With the help of examples, explain what is Hofmann elimination and Saytzeff elimination. 3+3+4