

2018

CHEMISTRY

(Major)

Paper : 1.1

(**Physical Chemistry**)

Full Marks : 60

Time : 3 hours

*The figures in the margin indicate full marks
for the questions*

1. Answer the following as directed : 1×7=7

- (a) In a certain process, 600 J of work is done on a system which gives off 250 J of heat. Calculate the internal energy change for the process.
- (b) State zeroth law of thermodynamics.
- (c) Why is in some reactions heat evolved while some reactions take place only on absorption of heat?
- (d) The dissolution of ammonium chloride in water is endothermic still it dissolves in water. Give reasons.

(2)

(e) Which one of the following demonstrates a decrease in entropy?

(i) Dissolving a solid into solution

(ii) In expanding universe

(iii) Burning a log in a fireplace

(iv) Raking up leaves into a trash bag

(Choose the correct option)

(f) Oxygen is available in plenty in air yet fuels do not burn by themselves at room temperature. Explain.

(g) For a reaction $A + H_2O \rightarrow B$, rate $\propto [A]$, what are its molecularity and order of reaction?

2. Answer the following :

2×4=8

(a) Write two limitations of the first law of thermodynamics.

(b) Under what conditions enthalpy change (ΔH) becomes equal to internal energy change (ΔU) in a process?

(c) For the reaction $2Cl(g) \rightarrow Cl_2(g)$, what are the signs of ΔH and ΔS ?

(d) What are zeolites? Why are zeolites suitable for cracking of hydrocarbons?

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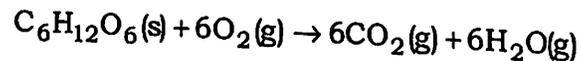
(3)

3. Answer any *three* of the following : 5×3=15

(a) Distinguish between isothermal and adiabatic processes. One mole of nitrogen gas contained in a cylinder at 300 K is allowed to expand isothermally against an external pressure of 5 atm from a volume of 1.0 dm³ to a volume of 3.0 dm³. Assuming ideality, calculate q , W , ΔU and ΔH .

2+3=5

(b) Derive Kirchhoff's equation relating the variation of enthalpy of a reaction with temperature. The heat evolved in the combustion of glucose is shown in the equation



$$\Delta_c H = -2840 \text{ kJ mol}^{-1}$$

What is the energy requirement for production of 0.36 g of glucose by the reverse reaction?

3+2=5

(c) State and explain Nernst heat theorem. How does it lead to the enunciation of the third law of thermodynamics? What do you mean by residual entropy of a substance?

2+2+1=5

A9/393

(Turn Over)

(d) Discuss van't Hoff's differential method for determination of order of a reaction. The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact contained wood that had only 80% of the ^{14}C found in living tree. Estimate the age of the sample. $3+2=5$

(e) Explain the terms 'frequency factor' and 'activation energy' of the Arrhenius equation. The rate of a particular reaction doubles when temperature changes from 27°C to 37°C . Calculate the activation energy of the reaction. $3+2=5$

4. Answer either (a), (b), (c) or (d), (e), (f) :

(a) What are state functions? Writing V as a function of T and P , show that for an ideal gas, dV is an exact differential.

(b) Define heat capacity of a system. Explain the molecular basis of the differences between heat capacity of a gas at constant pressure (C_p) and at constant volume (C_v).

(c) What is Joule-Thomson effect? Explain the principle of liquefaction of gases by Joule-Thomson effect. $3+4+3=10$

(d) What do you mean by internal energy? What are the possible contributions to the internal energy of a system? Which of these contributions will be present if the temperature of a system is reduced to $T = 0\text{ K}$?

(e) In what way is average bond energy different from bond energy of a diatomic molecule? Calculate the bond enthalpy of HCl . Given that the bond enthalpies of H_2 and Cl_2 are 430 kJ mol^{-1} and 242 kJ mol^{-1} respectively and $\Delta_f H^\circ$ for HCl is -91 kJ mol^{-1} .

(f) Prove that change in enthalpy of a system is equal to the heat supplied to the system at constant pressure. $5+2+3=10$

5. Answer either (a), (b), (c) or (d), (e), (f) :

(a) Define entropy. Why is it a state function? Discuss entropy changes in reversible and irreversible processes.

(b) Derive an expression for the entropy of a mixture of ideal gases.

(6)

- (c) For the reaction $2A(g) + B(g) \rightarrow 2D(g)$, $\Delta U^\circ = 10.5 \text{ kJ}$ and $\Delta S^\circ = -44.10 \text{ J K}^{-1}$. Calculate ΔG° for the reaction and predict whether the reaction may occur spontaneously. 5+2+3=10

- (d) Show that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

- (e) Define chemical potential. Show how it varies with temperature.

- (f) What do you mean by standard Gibbs' energy of formation? Obtain the relation between the equilibrium constant and the standard Gibbs' energy change. Calculate Gibbs' energy change and standard Gibbs' energy change for the reaction $A + B \rightleftharpoons C + D$ at 27°C . Equilibrium constant (K) for the reaction = 10^2 . 2+3+5=10

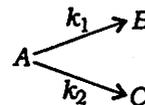
6. Answer either (a), (b), (c) or (d), (e) :

- (a) Define rate of reaction with respect to the reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$.

(7)

- (b) For a second-order reaction of the type $2A \rightarrow \text{products}$, find an expression for the rate constant. Show that for the second-order reaction, half-life is inversely proportional to the initial concentration of the reactant.

- (c) For the concurrent elementary reaction



show that $\frac{[B]}{[C]} = \frac{k_1}{k_2}$. 2+4+4=10

Or

- (d) What is steady state approximation? Applying steady state approximation, derive the rate expression for the $\text{H}_2\text{—Br}_2$ thermal reaction. Show that in the initial stage, the order of the reaction is 1.5.
- (e) Discuss Michaelis-Menten mechanism of enzyme catalyzed reaction. What type of potential energy diagram is expected for enzyme catalyzed reaction? How does the rate of enzyme catalyzed reaction depend on temperature? 6+4=10

2018

CHEMISTRY
(Major)

Paper : 1.2

(Organic Chemistry)

Full Marks : 60

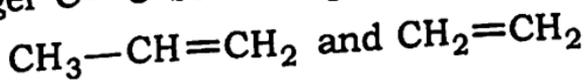
Time : 3 hours

*The figures in the margin indicate full marks
for the questions*

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

(a) Draw the structural formula of bicyclo-[2, 2·2]octane.

(b) Which of the following compounds has a longer C=C bond length?



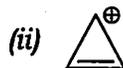
(c) Give one example by which benzyne can be trapped.

(d) Why is melting point of *p*-nitrophenol higher than *o*-nitrophenol?

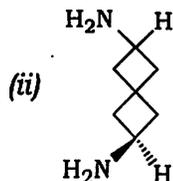
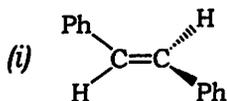
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(2)

- (e) Classify the following as either aromatic, non-aromatic or anti-aromatic :



- (f) Assign the absolute configuration *R/S* or *E/Z* to the following :



- (g) Between ethanol and ethanethiol, which is stronger acid?
- (h) Give one example of cross-conjugated compound.

2. Answer the following questions (any four) :

2×4=8

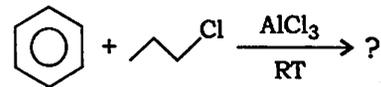
- (a) What is S_Ni reaction? Write with an example.
- (b) Write Fischer projection, staggered Sawhorse projection and Newman projection formulae of *threo*-2,3-dichloro-3-phenylpropanoic acid.
- (c) Why is triplet carbene more stable than singlet carbene? Explain.

A9/394

(Continued)

(3)

- (d) What is the major product of the following reaction? Justify your answer and give the name of the reaction :



- (e) Why does acid catalyzed dehydration of neopentyl alcohol yield 2-methyl-2-butene as the major product?

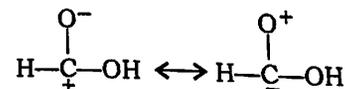
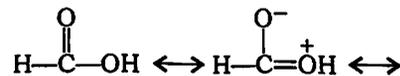
3. Answer the following questions (any three) :

5×3=15

- (a) Define dipole moment. How is it related to melting and boiling point? Why is dipole moment of nitrobenzene ($\mu = 3.95D$) higher than nitromethane ($\mu = 3.60D$) although both have same polar group? What is the μ -value of *p*-dinitrobenzene?

1+1+2+1=5

- (b) (i) Arrange the following resonating structures in the order of decreasing stability and give reasonable explanation :



1+2=3

A9/394

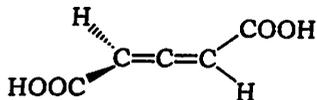
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(4)

(ii) Explain why 1,3,5-cyclohepta-trienyl cation is aromatic but 1,3,5-cycloheptatriene is not. 2

(c) Give the evidences for the formation of σ - and π -complexes in electrophilic aromatic substitution. Write the mechanism for the nitration of benzene. 3+2=5

(d) (i) The allene



is optically active although it has no chiral centre. Explain. 2

(ii) How is a racemic mixture different from *meso*-compound? Give examples to illustrate the differences. 2+1=3

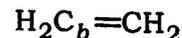
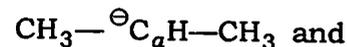
(e) (i) What happens when pyridine is treated with NaNH_2 ? Give the mechanism. 2½

(ii) Write the mechanism of cyclopropanation of alkene with singlet carbene. 2½

(5)

4. Answer the following questions [either (a) or (b), (c) or (d) and (e) or (f)] : 10×3=30

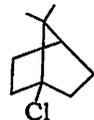
(a) (i) What is trigonal hybridization? Write its characteristics. Find the types of hybridization of C_a and C_b in the following by electron pair method : 1+2+2=5



(ii) What is *trans*-annular strain? The chair form of methylcyclohexane is less stable when methyl group is in axial position than it is in equatorial position. Explain. Draw the Newman projection for chair form of methyl cyclohexane when methyl group is (i) anti to C_3 and (ii) anti to C_5 . 1+2+2=5

Or

(b) (i) What is $\text{S}_{\text{N}}1$ reaction? What are the evidences for $\text{S}_{\text{N}}1$ reactions? Why does >C-Br give $\text{S}_{\text{N}}1$ reaction

whereas  does not give $\text{S}_{\text{N}}1$

reaction?

1+2+2=5

(6)

(ii) What do you mean by kinetically controlled and thermodynamically controlled reaction? Give two reactions to justify such reactions.

2+3=5

(c) (i) The addition of HBr to propene is regioselective. Explain this statement and illustrate the steps involved in the mechanism of the reaction.

4

(ii) What is pK_a ? Between 2-bromopentanoic acid and 3-bromopentanoic acid, which one has higher pK_a value and why?

1+2=3

(iii) What are carbanions? How are they different from carbene? Arrange the following carbocations in increasing order of their stabilities :

1+1+1=3



Or

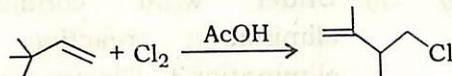
(d) (i) Why does ethoxymethylchloride react with nucleophiles 10^6 times faster than 1-chlorobutane even though both are primary alkyl chloride? Explain.

3

(7)

(ii) Write the mechanism for the following conversion :

2



(iii) 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.

2+3=5

(e) (i) Draw and label the *E,Z*-isomers of 1,2-dichloro-3-ethyl-4-methyl-2-pentene.

1

(ii) Write the structure of *meso*-tartaric acid. Is it optically active? Give the *R,S*-nomenclature for the two chiral centres in *meso*-tartaric acid.

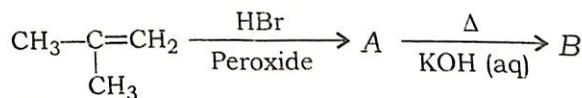
1+1+1=3

(iii) What are configurational and conformational isomers? Draw the possible conformations of *n*-butane. Arrange the conformations in order of decreasing stability.

2+2+1=5

(iv) What are the products A and B in the following?

1



Or

- (f) (i) Under what conditions E_2 -elimination reaction is syn-elimination? Discuss a pyrolytic syn-elimination reaction with one example. 2+2=4
- (ii) Define carbon-free radicals. How can carbon-free radical be generated? 1+2=3
- (iii) Distinguish S_N1 reaction from S_N2 reaction. 3
