

2017

CHEMISTRY

(Major)

Paper : 1.1

(Physical Chemistry)

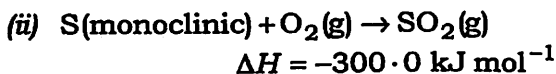
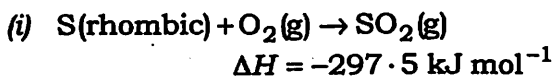
Full Marks : 60

Time : 3 hours

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

1. (a) How is it possible to find the value of Δu and not the value of u ? 1
- (b) Which of the following is correct expression for the first law of thermodynamics under adiabatic condition? 1
- (i) $\Delta u = q + W$
 - (ii) $\Delta u = q - W$
 - (iii) $q = -W$
 - (iv) $\Delta u = W$

(c) Given the following thermochemical equations :



Calculate ΔH for the transformation of one gram atom of rhombic sulphur into monoclinic sulphur.

2

2. (a) Give a statement which includes the main ideas of the first law and second law of thermodynamics.

1

(b) Why, for predicting the spontaneity of a reaction, free energy criteria is better than the entropy criteria?

1

(c) Calculate residual entropy for CO crystal at 0 K.

2

3. (a) Reactions of higher molecularity are less observed. Explain.

1

(b) The half-life for a given reaction was doubled when the initial concentration was doubled. Evaluate the order of the reaction.

1

(c) On the basis of Arrhenius equation, answer the following : 2

(i) What is the limiting value of rate constant k as temperature of reaction becomes infinitely large?

(ii) Which reaction will have the greater temperature dependence for the rate constant—one with a small value of E_a or one with a large value of E_a ?

4. Answer any *two* of the following : 3×2=6

(a) Define the following with example :

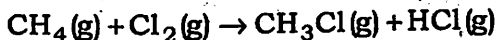
(i) An isolated system

(ii) State functions

(iii) Reversible process

(b) If a specified set of reactants can be converted to a specified set of products through more than one path, the enthalpy change in each case remains the same. Discuss the significance with an example.

(c) What is bond enthalpy? Determine the enthalpy change for the given reaction :



Bond energies are given as follows :

$$\text{C—H} = 412 \text{ kJ mol}^{-1}$$

$$\text{C—Cl} = 338 \text{ kJ mol}^{-1}$$

$$\text{Cl—Cl} = 242 \text{ kJ mol}^{-1}$$

$$\text{H—Cl} = 431 \text{ kJ mol}^{-1}$$

5. Answer any *two* of the following : 3×2=6

(a) Define Gibbs' energy. Enthalpy and entropy changes of a reaction are $40.63 \text{ kJ mol}^{-1}$ and $108.8 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively. Predict the feasibility of the reaction at 27°C .

(b) Discuss variation of free energy change with temperature and pressure.

(c) Show that for a mixture of two components, A and B at constant temperature and pressure

$$n_A d\mu_A + n_B d\mu_B = 0$$

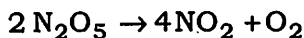
6. Answer any *two* of the following : 3×2=6

(a) For a reaction of n th order, show that

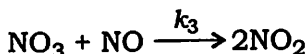
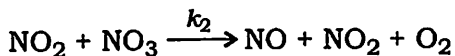
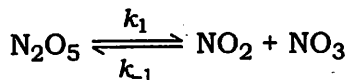
$$t_{1/2} = \frac{2^{n-1} - 1}{a^{n-1} k (n-1)}$$

where a , k and $t_{1/2}$ are the initial concentration of the reactant, rate constant and half-life period of the reaction.

(b) For the reaction



the proposed mechanism is



Applying steady state approximation, derive the rate law.

(c) Half-life of a first-order reaction is 69 hours at 300 K. Also, the rate of this reaction is doubled as temperature is increased from 300 K to 310 K. Determine activation energy and pre-exponential factor for this reaction.

7. Answer any *two* of the following : 5×2=10

(a) What is an adiabatic process? Obtain the P , V , T relation for adiabatic expansion of an ideal gas. How does it differ from that of an isothermal expansion? 1+3+1=5

(b) One mole of an ideal gas (monatomic) at 27 °C expands adiabatically against a constant external pressure of 1 atm

from a volume of 10 dm^3 to a volume of 20 dm^3 . Calculate (i) q , (ii) w , (iii) Δu and (iv) ΔH for this process. Also calculate the final temperature of the gas.

Assume that $C_v = \frac{3}{2}R$.

5

(c) (i) How do you relate reaction enthalpy to internal energy change?

3

(ii) The enthalpy of combustion of glucose $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$ is $-2816 \text{ kJ mol}^{-1}$ at 25°C . Calculate ΔH_f° ($\text{C}_6\text{H}_{12}\text{O}_6$). The ΔH_f° values for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are $-393.5 \text{ kJ mol}^{-1}$ and $-285.9 \text{ kJ mol}^{-1}$ respectively.

2

8. Answer any *two* of the following : $5 \times 2 = 10$

(a) Using the combined form of the first law and second law of thermodynamics and appropriate Maxwell relations, derive the two thermodynamic equations of state.

(b) Starting from Clausius inequality, arrive at a condition of spontaneity for isothermal process involving Helmholtz free energy.

- (c) Give the physical interpretation of entropy. State the third law of thermodynamics and its usefulness in obtaining absolute entropies.

9. Answer any *two* of the following : 5×2=10

- (a) For the zero-order reaction



obtain the integrated rate law

$$[A] = [A]_0 - kt$$

Draw a graph to show the variation of concentration of the reactant with time. Determine the time required for the completion of the reaction. Under what conditions, a reaction is zero order?

- (b) What are chain reactions? Discuss the kinetics of branching chain reactions.

- (c) Give the mechanism of acid catalyzed reactions and obtain an expression for the rate of the reaction. Under what conditions are such reactions said to be subjected to general acid catalysis and specific hydrogen ion catalysis?

2017

CHEMISTRY

(Major)

Paper : 1.2

(Organic Chemistry)

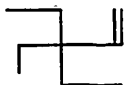
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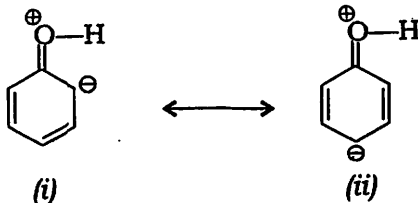
The figures in the margin indicate full marks for the questions

1. Answer/Choose the correct option for the following (any seven) : 1×7=7

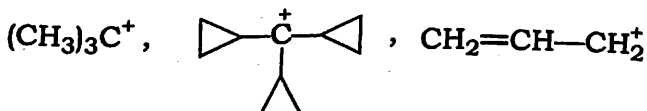
(a) Write the IUPAC name of the following compound :



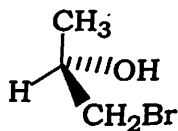
- (b) Which of the following structures contributes more to its resonance hybrid?



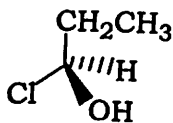
- (c) Why is the boiling point of ethyleneglycol much lower than that of glycerol?
- (d) Why is 1,3,5-cycloheptatrienyl cation aromatic but 1,3,5-cycloheptatriene is not?
- (e) Arrange the following carbocations in increasing order of their stability :



- (f) Between *o*-hydroxybenzoic acid and *p*-hydroxybenzoic acid, which is stronger acid and why?
- (g) Assign *R*- or *S*-configuration to each of the following compounds :



(i)



(ii)

- (h) The number of optically active isomers of $\text{HOCH}_2(\text{CHOH})_4\text{CHO}$ is

(i) 4

(ii) 8

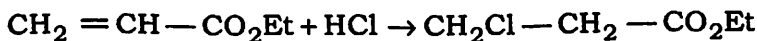
(iii) 16

(iv) 24

2. Answer the following questions (any four) :

2×4=8

- (a) Explain that cyclopentadiene is acidic ($pK_a = 16$).
- (b) The chair conformation of cyclohexane is more stable than the boat conformation. Explain.
- (c) Why does the addition of HCl to the following olefin take place in the opposite manner as predicted by Markonikov's rule?



- (d) Benzylchloride is more reactive than alkylchloride in nucleophilic substitution reaction. Why?
- (e) Account for the fact that naphthalene is less aromatic than benzene.

3. Answer the following questions (any three) :

5×3=15

- (a) What are kinetic and thermodynamic products? Justify these by taking naphthalene as an example at different temperatures (80 °C and 160 °C). 2+3=5
- (b) What is stereocentre? Justify with an example that enantiomer has stereocentre. Draw all the possible geometrical isomers of 2,5-heptadiene.

1+2+2=5

(c) What are different types of carbene? Distinguish between them. Give one method of formation of carbene. $1+2+2=5$

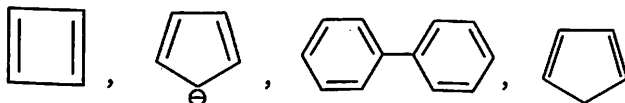
(d) What are electrophiles? Why does electrophilic substitution to naphthalene preferably take place at α -position rather than β -position? Write one alkylation of naphthalene with mechanism. $1+2+2=5$

(e) What is a *meso*-compound? How many different stereoisomers of tartaric acid are there? Give the *R*-, *S*-notations for the two chiral centres in *meso*-tartaric acid. $1+2+2=5$

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

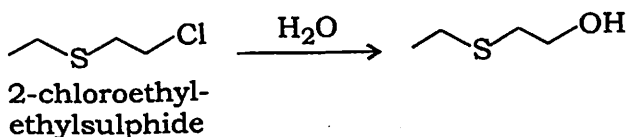
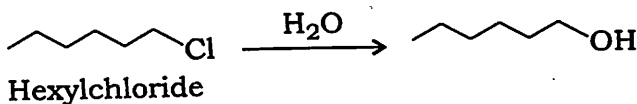
$10 \times 3 = 30$

(a) (i) What are aromatic compounds? Classify the following molecules as aromatic, anti-aromatic or non-aromatic. Why is 1,3,5,7-cyclo-octatetraene not aromatic?



$2+2+1=5$

- (ii) What is anchimeric assistance? How does it affect the rate of a reaction? Write the mechanism for the following transformation and comment on the rate of the reaction : 1+2+2=5

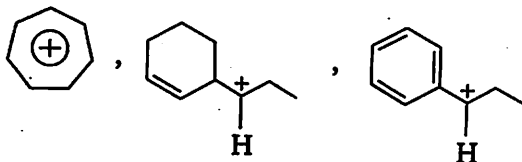


Or

- (b) (i) Why is maleic acid much stronger acid than fumaric acid even though they have same molecular formula, $C_4O_4H_4$? What kinds of stereomeric products are obtained when maleic and fumaric acids are treated with Br_2 in CCl_4 separately? Also mention the optical activity of the products. 2+3=5
- (ii) Explain why elimination reactions always compete with substitution reaction. How can you convert butanol-1 to butene-1 by pyrolytic elimination? 3+2=5

(6)

- (c) (i) What are carbocations? How can you generate carbocations? Arrange the following carbocations in decreasing order of stability and explain the reasons : 1+2+2=5

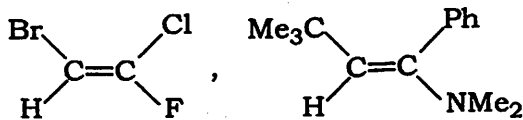


- (ii) Which one is more reactive towards nucleophiles—acetaldehyde or acetone? Explain. 3
- (iii) Addition of HCl to 1,3-butadiene gives both the 1,2- and 1,4-addition products. Using this example, explain kinetic and thermodynamic controls in reactions. 2

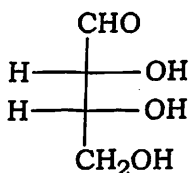
Or

- (d) (i) Between pyridine and piperidine, which one is a stronger base and why? 2
- (ii) Why does dibenzoyl methane not give addition compound with HCN even though there are two C=O groups? Explain. 2

- (iii) Explain with examples that addition of singlet carbene to alkene is stereospecific whereas with triplet carbene it is not stereospecific. 3
- (iv) Write all the possible chain isomers of the molecule having molecular formula, C_5H_{12} and give their IUPAC nomenclature. Arrange these isomers in decreasing order of their boiling point. $1+1+1=3$
- (e) (i) Acid-catalyzed dehydration of neopentyl alcohol yields 2-methyl-2-butene as the major product. Outline a mechanism showing all steps in its formation. 2
- (ii) Why does alkyl fluoride give Hofmann elimination whereas alkyl iodide gives Saytzeff elimination? 2
- (iii) Why is it difficult to resolve a racemic mixture? 2
- (iv) Assign *E*- or *Z*-nomenclature for the following molecules : $\frac{1}{2}+\frac{1}{2}=1$

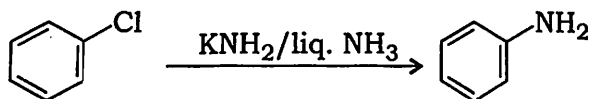


- (v) Convert the following molecule into sawhorse and Newman projections. Why is staggered form more stable than eclipsed form? 2+1=3



Or

- (f) (i) How is benzyne intermediate generated? Give the mechanism for the following transformation :



How can you trap benzyne intermediate? 1+2+1=4

- (ii) In the chair form of cyclohexylhalide, nucleophilic substitution by S_N2 process for axial substituent of halide is faster than that of an equatorial substituent of halide. Explain. 3
- (iii) Define enantiotopic and diastereotopic hydrogens and a prochirality centre. Illustrate your answer with suitable examples. 3
