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CHEMISTRY

(Major)

Paper : 1.2

(Organic Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions
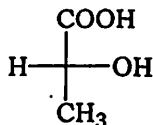
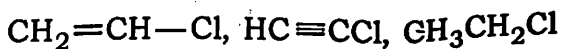1. Answer the following questions (any *seven*) :

    $1 \times 7 = 7$

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

    (b) Convert the following Fischer formula into flying-wedge formula :

    $$
    \begin{array}{c}
    \text{COOH} \\
    \text{H} \!-\!\!\!-\!\!\!-\! \text{OH} \\
    \text{CH}_3
    \end{array}
    $$

    (c) Arrange the following molecules in order of decreasing dipole moment :

    $CH_2{=}CH{-}Cl$, $HC{\equiv}CCl$, GH_3CH_2Cl

(Turn Over)

(d) Acetyl acetone is highly stable in enol form. Explain.

(e) Arrange the following compounds in order of their correct basicities :
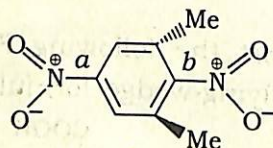
(i) $CH_3CH_2NH_2$

(ii) $CH_3-C\overset{NH}{\underset{NH_2}{\Vert}}$

(iii) $(CH_3)_2NH$

(iv) $CH_3-\overset{O}{\overset{\Vert}{C}}-NH_2$
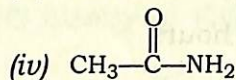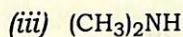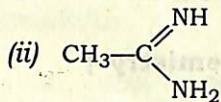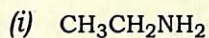
(f) The molecule does not exist. Explain.

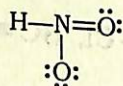(g) Between salicylic acid and p-hydroxy benzoic acid which is stronger? Explain in terms of H-bonding.

(h) The C—N bond a is shorter than b in the following compound. Explain :
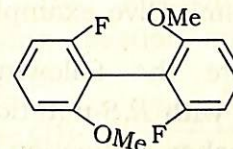

2. Answer the following questions (any four) :

2×4=8

(a) Calculate the formal charge on each of the constituent atoms of

$$H-N=\overset{..}{O}:$$
$$\overset{|}{\underset{..}{:O:}}$$

(Continued)

(b) Between toluene and tert-butyl benzene, which one is more susceptible to electrophilic substitution reaction? Explain.

(c) Explain whether [10] annulene is aromatic or not.

(d) State and explain whether the following molecule will be optically active or not :

(e) What product do you get when trans-butenedioic acid is treated with Br_2? Write equation as well.

3. Answer the following questions (any three) :

5×3=15

(a) Draw the number of possible stereo-isomers of the following molecule :

$$HOOC-CH(OH)-CH(OH)-CH(OH)-COOH$$
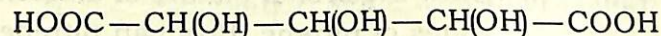
Also find the number of optical isomers and meso forms.   3+2=5

(b) Account for the fact that guanidine is a strong base. Which nitrogen of guanidine is more likely to be protonated? Explain. What are alternant and non-alternant hydro-carbons? Give example of each.   3+2=5

(Turn Over)

(c) What is resolution of a racemic mixture? What are different methods of resolution of racemic mixture? How will you separate a racemic mixture of an alcohol? 1+1+3=5

(d) Explain the cause of optical activity of biphenyls giving suitable substituents. Are their any compounds to show atrop-isomerism? Give example. 4+1=5

(e) Designate the following flying-wedge formula with R, S-notations and convert into Fischer projection. What do you understand by stereomutation? 3+2=5
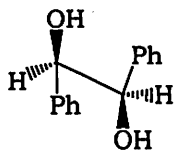
4. Answer the following questions [either (i) and (ii) or (iii) and (iv) from (a), (b) and (c)] : 10×3=30

(a) (i) Draw the orbital picture of different states of nitrene. How can nitrenes be trapped for detection? Give one important reaction of nitrene as intermediate. 2+2+1=5

(ii) Explain with example, what you mean by kinetically controlled and thermodynamically controlled reactions. Draw the energy profile diagram. 3+2=5
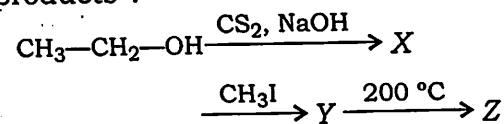
Or

(iii) The *cis*-isomer of 4-*t*-butyl cyclohexyl bromide reacts with $Ph\overset{\ominus}{S}\overset{\oplus}{Na}$ in aqueous ethanol at a much faster rate than the *trans*-isomer. Explain. 2½+2½=5

(iv) Write the mechanism of the following reaction and obtain the products :

$$CH_3-CH_2-OH \xrightarrow{CS_2, NaOH} X$$
$$\xrightarrow{CH_3I} Y \xrightarrow{200 °C} Z$$

Also name the intermediate products. 3½+1½=5

(b) (i) The rate of bromine addition to styrene is greater than that to propene. Place a suitable explanation along with the reaction intermediate formed. 2½+2½=5

(ii) (1) Which of the following would undergo solvolysis in methanol more readily? Explain : 3
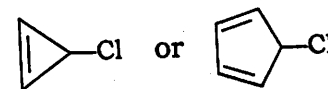
(2) Find the stereochemistry of the product for the following reaction along with the mechanism : 2

$$\underset{\substack{|\\H}}{\overset{\substack{COOH\\|}}{Me\text{''''}C}}\text{---}Br \xrightarrow{dil.\ KOH} \ ?$$
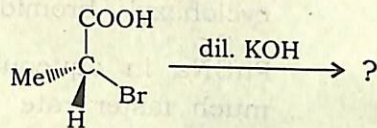
Or

(iii) What are classical and non-classical carbocations? Give example. The rate of acetolysis of exo-norbornyl brosylate is many times faster than endoisomer. Explain : 3+2=5
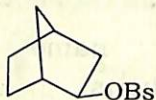
exo-norbornyl brosylate

(iv) Define carbon-free radicals. How are these detected? How can carbon-free radical be generated? 1+2+2=5

(c) (i) How are the nucleophilic substitution reactions affected by the nature of leaving group and nucleophiles? Explain with examples. 2½+2½=5

(ii) Explain the criteria for showing optical activity. Draw an allene which displays chirality. 4+1=5

(Continued)

Or

(iii) Define syn- and anti-elimination reactions. Why is anti-elimination preferred over syn-elimination? Give an example. 2+2+1=5

(iv) Draw the chair-conformations of *cis*- and *trans*-1-methyl-4-*t*-butyl cyclohexane and comment on their optical activities. 3+2=5

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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) Calculate the change in the internal energy of a system that releases 2300 J of heat and that does 7043 J of work on the surroundings. 1

   (b) The value of ΔH° for the reaction below is –504 kJ :

   $$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$
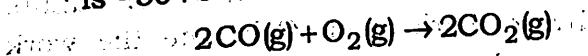
   Calculate the heat (in kJ) released to the surroundings when 12 g of CO(g) reacts completely. 1

   (c) What do you mean by inversion temperature? 2

2. (a) How do you define the criterion for the spontaneity of any process in terms of free energy? 1

(b) Explain what you understand by the term 'standard Gibbs free energy change'.   1

(c) Discuss the physical interpretation of any one of the Maxwell relations.   2

3. (a) Sketch the plot of rate versus concentration of a zero-order reaction.   1

(b) Write down the differential rate law and integrated rate law for a reaction of order $\frac{1}{2}$.   1

(c) Explain the term 'shape selective catalysis' with examples.   2

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

(a) A piece of magnesium of mass 15 g is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1·1 atm and the temperature is 23 °C.

(b) What is the physical significance of ΔH? What are the factors that affect the enthalpy of a reaction (ΔH)?

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

(Continued)

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

(a) How is the entropy of a substance affected by (i) an increase in temperature, (ii) a decrease in volume, (iii) changing from a liquid to solid and (iv) dissociating into individual atoms?

(b) Calculate ΔG°_T value at 100 °C for the following reaction :

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

Given that for—

$$N_2O_4(g);\ \Delta H^{\circ}_f = +9\cdot67\ kJ/mol\ and$$
$$S^{\circ} = +304\ J/mol\ K$$

$$NO_2(g);\ \Delta H^{\circ}_f = +33\cdot8\ kJ/mol\ and$$
$$S^{\circ} = +240\cdot5\ J/mol\ K$$

(c) Show how the third law of thermodynamics was arrived at starting from the Nernst theorem.

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

(a) Write the rate equation of a second-order reaction and explain how the half-life of this type of reaction is affected by the initial reactant concentration.

(Turn Over)

(b) A patient is given a certain amount of iodine-131 as a part of a diagnostic procedure for a thyroid disorder. Given that the half-life of radioactive iodine-131 is 8 days. What fraction of the initial iodine-131 would be present in the patient after 24 h, if none of it was eliminated through natural body processes?

(c) In what way is the rate law for a reaction related to the rate-determining step? Explain with an example.

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

(a) What do you mean by heat capacity and an adiabatic process? For the reversible adiabatic expansion of an ideal gas, show that PV^γ = constant, where

$$\gamma = \frac{C_{p,m}}{C_{v,m}}$$

What is the physical significance of γ?

2+3=5

(b) A sample of 4·50 g of methane occupies $12\cdot7\,dm^3$ at 310 K.

(i) Calculate the work done when the gas expands isothermally against a constant external pressure of 200 torr until its volume has increased by $3\cdot3\,dm^3$.

(Continued)

(ii) Calculate the work that would be done if the same expansion occurred reversibly.

(c) Deduce Kirchhoff's equation to show the variation of enthalpy of a reaction with temperature.

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

(a) Derive Gibbs-Duhem equation and show that intensive variables of a system are not independent.

(b) Starting from the definition of Gibbs' free energy (G), deduce the expressions to show the variations of G with T and P. Based on these expressions, draw the necessary graphs to show the variations of G with T and P for solid, liquid and gaseous phases of a substance.

(c) 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 a volume V_2. Volume of 1 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?

(Turn Over)

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

(a) What is a homogeneous catalyst? How does it function in general terms? What do you understand by the catalytic efficiency of an enzyme? 1+2+2=5
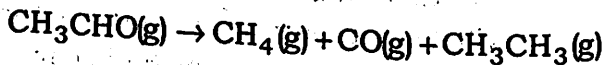
(b) Sulfuryl chloride SO_2Cl_2 is used to manufacture the antiseptic chloro-phenol. The following data were collected on the decomposition of SO_2Cl_2 at a certain temperature :

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$
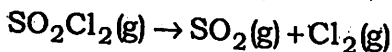
Initial concentration of SO_2Cl_2 (mol L^{-1})	Initial rate of formation of SO_2 (mol L^{-1} s^{-1})
0·100	$2·2\times10^{-6}$
0·200	$4·4\times10^{-6}$
0·300	$6·6\times10^{-6}$

What are the rate laws for the reaction? Give the reasons to justify your answer. Calculate the rate constant of the reaction from above data.

(c) Derive the rate law for the thermal decomposition of ethanal (CH_3CHO) in absence of air (shown below) considering the Rice-Herzfeld mechanism :

$$CH_3CHO(g) \rightarrow CH_4(g) + CO(g) + CH_3CH_3(g)$$

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