# 2 0 1 9

## 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) A system in which exchange of both matter and energy with the surroundings is possible is called

   (i) homogeneous system

   (ii) closed system

   (iii) open system

   (iv) isolated system

   ( Choose the correct option )

(b) State the first law of thermodynamics.

(c) For an ideal gas, calculate the difference between molar heat capacity at constant pressure and molar heat capacity at constant volume.

(d) State the entropy statement of second law of thermodynamics.

(e) Calculate the entropy change for fusion of 1 mole of a solid which melts at 300 K. The latent heat of fusion of the solid is 2930 J mol$^{-1}$.

(f) Give the SI unit of rate constant of a zeroth-order reaction.

(g) Give the statement of steady-state approximation.

2. Answer the following :  2×4=8

(a) Give the molecular interpretations of heat and work.

(b) Calculate the work done during isothermal expansion of 2 moles of an ideal gas from 50 bar pressure to 5 bar pressure at 300 K.

( Continued )

(c) Define chemical potential. Give its physical significance.

(d) Define half-life time of a reaction. Show that half-life time of a first-order reaction is independent of initial molar concentrations of the reactants.

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

(a) State and explain the Hess's law of constant heat summation. Given bond enthalpies of H—H and O=O bonds respectively are 436 kJ mol$^{-1}$ and 498 kJ mol$^{-1}$ and enthalpy of formation of $H_2O$(g) is –242·0 kJ mol$^{-1}$. Calculate the bond enthalpy of O—H bond.  2+3=5

(b) Define heat capacity at constant pressure and heat capacity at constant volume. Show that

$$C_P - C_V = \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P$$  2+3=5

(c) What is Joule-Thomson effect? Show that the process in Joule-Thomson experiment takes place at constant enthalpy. Define Joule-Thomson coefficient.  1+3+1=5

( Turn Over )

(d) Define Helmholtz function and Gibbs' function. Show that decrease in Helmholtz function in any process at constant temperature gives the maximum work that can be obtained from the system during any change.

$$1+1+3=5$$

(e) Derive integrated rate equation for a first-order reaction. For a first-order reaction, $t_{0.5}$ is 100 s. Calculate the time required for the reaction to be completed by 75%.

$$3+2=5$$

4. Answer *either (a) and (b) or (c) and (d)* :

(a) For an adiabatic process, show that

$$TV^{\gamma-1} = \text{a constant}$$

where, $\gamma = \overline{C}_P / \overline{C}_V$

Hence for an ideal gas show that $PV^{\gamma} = \text{constant}$.

$$4+2=6$$

(b) One mole of an ideal gas at STP is compressed adiabatically and reversibly to occupy a volume of 2·24 L. Calculate the amount of work done during the process. 4

(c) Using the relation $\Delta G = \Delta H - T\Delta S$, give the conditions when $\Delta G$ can be positive or negative. Obtain the relation between Gibbs' free energy change and equilibrium constant of an equilibrium reaction.

$$2+4=6$$

(d) Of the following pairs, which has higher chemical potential?

(i) $H_2O(l)$ at 298 K, 1 atm and $H_2O(g)$ at 298 K, 1 atm

(ii) $H_2O(s)$ at 273 K, 1 atm and $H_2O(l)$ at 273 K, 1 atm

(iii) $H_2O(s)$ at 268 K, 1 atm and supercooled $H_2O(l)$ 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. 4

5. Answer *either (a) and (b) or (c) and (d)* from the following :

(a) What are Maxwell's relations? By using Maxwell relation, show that

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

$$2+4=6$$

*(b)* 4·0 g of helium gas is allowed to expand reversibly and isothermally at 300 K from a pressure of 1 atm to a pressure of 0·1 atm. If helium gas behaves ideally, calculate the change in Gibbs' free energy. Also predict whether the expansion is spontaneous or not.   4
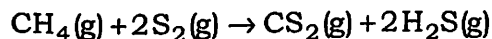
*(c)* Deduce the Gibbs-Helmholtz equation. Give the physical significance of this equation.   4+2=6

*(d)* What are partial molar quantities? Show that

$$\left(\frac{\partial G}{\partial P}\right)_{T,\, composition} = V$$

   4

**6.** Answer *either (a)* and *(b)* or *(c)* and *(d)* from the following :

*(a)* Define activation energy of a reaction. The gas-phase reaction between methane and diatomic sulphur is given by the equation

$$CH_4(g) + 2S_2(g) \rightarrow CS_2(g) + 2H_2S(g)$$

For this reaction, the rate constant at 300 K is $1·1\, dm^3\, mol^{-1}\, s$ and at 400 °C the rate constant is $6·4\, dm^3\, mol^{-1}\, s$. Calculate activation energy of the reaction.   1+4=5

*( Continued )*

*(b)* What are competing reactions? Give one suitable example of competing reaction showing the different steps involved in it. How can a desired product be obtained as major product in the competing reactions?   1+3+1=5

*(c)* What are homogeneous catalyses? Give a suitable example of homogeneous catalysis. Explain how a homogeneous catalyst changes the rate of a reaction.
   1+1+3=5

*(d)* Distinguish between order and molecularity of a reaction. Give one example of reaction in which order and molecularity are the same. The rate of reaction $2NO + Cl_2 \rightarrow 2NOCl$ becomes doubled when the concentration of $Cl_2$ is doubled. But when the concentrations of both the reactants are doubled, the rate becomes eight times. Determine order of the reaction.   2+1+2=5

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# 2 0 1 9

## CHEMISTRY

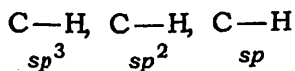( Major )

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 :  1×7=7

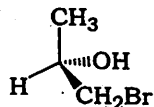   (a) Arrange the C—H bond lengths in increasing order :

   $$C\underset{sp^3}{—}H, \quad C\underset{sp^2}{—}H, \quad C\underset{sp}{—}H$$

   (b) Why is the boiling point of *n*-pentane more than neopentane?

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

*( Turn Over )*

( 2 )

(d) Why does pentane-2,4-dione mostly exist in the enol-form?

(e) Assign R- or S-configuration for the molecule :

$$CH_3$$
$$|$$
$$\text{......OH}$$
$$H \quad CH_2Br$$

(f) What is the state of hybridization of carbon in $\overset{\ominus}{C}H_2-NO_2$?

(g) Why is the dipole moment of *ortho*-dichlorobenzene not zero?

2. Answer any *four* of the following questions :
$$2×4=8$$

(a) Draw the Newman projections for all the conformers that result from rotation about the C-2 and C-3 bonds of butane and identify the most stable amongst them.

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

(c) Between *ortho*-nitrophenol and *para*-nitrophenol, which has higher boiling point and why?

( 3 )

(d) Explain why $Ph-S\diagup\diagdown\diagup Cl$ reacts with water 100 times faster than $\diagup\diagdown\diagup^{Cl}$.

(e) Which of the following carbocations is more stable and why?

$$\triangleright\overset{\oplus}{\underset{\triangle}{C}}\triangleleft \quad \text{and} \quad CH_2=CH-\overset{\oplus}{C}H_2$$
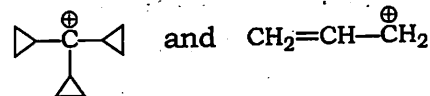
3. Answer any *three* of the following questions :
$$5×3=15$$

(a) What do you mean by kinetically controlled and thermodynamically controlled reactions? Draw the energy profile diagram for these two reactions.
$$2+3=5$$

(b) (i) What is $S_N2$ mechanism? Give an example to explain it. $1+1=2$

(ii) Explain why *trans*-2-chloro-cyclohexanol gives epoxy-cyclohexane in high yield on treatment with a base whereas the *cis*-isomer does not react with the base. 3

(c) What are non-classical carbocations? Give example of it. Discuss the stability of non-classical carbocations. $1+1+3=5$

## ( 4 )

(d) Why is it difficult to separate racemic mixture? Describe a method of resolving a racemic mixture. $1\frac{1}{2}+3\frac{1}{2}=5$

(e) What is atropisomerism? What types of isomerism are shown by 3-bromopent-2-ene? Give their structures along with their designation. Why are enantiomers not easily separated?

$$1+1+2+1=5$$

**4.** Answer *either (a) or (b), (c) or (d)* and *(e) or (f)* from the following questions : $10\times3=30$

(a) (i) Explain why C—N bond length in methylamine is more than that in urea. 2

(ii) What is hyperconjugation and what are its types? What are the conditions for any organic species to exhibit hyperconjugation? $1+2+2=5$

(iii) Arrange the following $C_a$—$C_b$ bond lengths in increasing order and explain the observation : 3

$$CH_3-C_a\equiv C_b-CH_3, \ CH_2=C_aH-C_bH=CH_2,$$

$$CH_3-C_aH_2-C_bH_2-CH_3$$
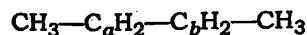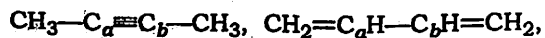
(b) (i) What is $pK_a$? How is it related to acid strength? Explain why $pK_a$-value of picric acid is much lower than phenol. $1+1+2=4$

## ( 5 )

(ii) What is diagonal hybridization? What are its characteristics? $1+2=3$

(iii) What is inductive effect? What are its applications in determining the stability of carbocations? $1+2=3$

(c) (i) Which of the two alkenes, 1-pentene or 2-pentene on reaction with HBr will produce 2-bromopentane exclusively? Explain the reason. 3

(ii) How can you generate carbocations? Arrange the following carbocations in increasing order of stability and explain the reasons : $2+3=5$
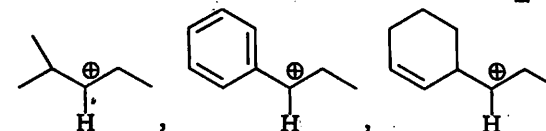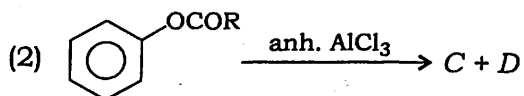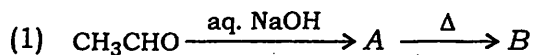


(iii) Write a reaction to show evidence that $S_N1$ mechanism involves carbocation intermediate. 2

(d) (i) What are pyrolytic eliminations? Give an example. Propose a mechanism for the pyrolytic elimination reaction. $1+1+3=5$

*(ii)* Write a general mechanism for elimination reactions proceeding via the $E1$ pathway. Provide two evidences in support of the mechanism. 3+2=5

*(e)* *(i)* Explain why the chair-conformation of cyclohexane is more stable than the boat-conformation. Which conformer of cis-1,3-cyclohexane-diol is more stable and why? 3+2=5

*(ii)* How many stereoisomers are there for 2,3-diphenylbutane? Use Fischer projection 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=5

*(f)* *(i)* Explain why benzylchloride is more reactive than alkyl chloride in nucleophilic substitution. 2

*(ii)* Give the products $A$, $B$, $C$ and $D$ in the following reactions : 1×2=2

(1) $CH_3CHO \xrightarrow{\text{aq. NaOH}} A \xrightarrow{\Delta} B$

(2)  $\xrightarrow{\text{anh. AlCl}_3} C + D$

*( Continued )*

*(iii)* Olefinic double bonds are prone to electrophilic addition whereas carbonyl $C=O$ bonds are prone to nucleophilic addition. Explain. 3

*(iv)* Explain why elimination reactions always complete with substitution reaction. 3

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