2023

CHEMISTRY — HONOURS

Paper : DSCC-1

(Fundamentals of Chemistry - 1)

Full Marks : 75

The figures in the margin indicate full marks.

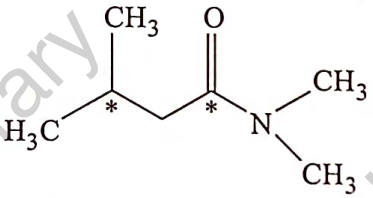
Candidates are required to give their answers in their own words as far as practicable.

Answer ***question nos.*** **1, 2, 3, 4** (compulsory) and ***any four*** questions from the rest (***question nos.*** **5** to **10**).

1. Answer ***any ten*** questions : 2×10

(a) Explain : First IP of nitrogen is greater than that of oxygen.

(b) Write down the IUPAC nomenclature of the following organic compound. Also give the state of hybridisation of carbon atoms marked (*).



(c) 'Isothermal free expansion of an ideal gas has to be adiabatic as well'.— Justify or criticise the statement with proper reasoning.

(d) Arrive at Bohr's quantisation principle from de Broglie equation.

(e) Draw the structure of [8] annulene and comment on its nature of aromaticity.

(f) Classify the following properties as extensive or intensive :

(i) Concentration, (ii) Heat capacity, (iii) Pressure and (iv) Volume.

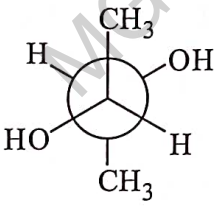
(g) Identify the smaller ion between $H^{\ominus}$ and $F^{\ominus}$ with reason.

(h) How many sp^3 hybrid orbitals are generated when one s-orbital mixes with three p-orbitals of comparable energies? Draw the shape of sp^3 hybrid orbital. Calculate the % of p-character in a sp^3 hybrid orbital.

(i) Calculate the ratio of $t_{3/4}$ and $t_{1/2}$ for a first order reaction.

(j) Gold (Au) shows the highest electron affinity among the metals. Justify or criticise.

(k) Draw any one diastereoisomer of the following compound in Newman projection formula. Write down the Fischer projection formula of the following compound also.



(l) Draw the concentration versus time curve for the following first order parallel reactions as shown below.

$$C \xleftarrow{k_2} A \xrightarrow{k_1} B \quad \text{when } k_1 > k_2$$

2. (a) Write a short note on electronegativity using the following points :

(i) Definition

(ii) Variation across the period with reason

(iii) The most electronegative element

(iv) Determination of electronegativity of Br using Allred-Rochow scale. Given covalent radius of Br = 114 pm. 1+2+½+1½

Or

(b) Calculate the effective nuclear charge of one 3d and one 4s electron of vanadium and explain why during the filling of the orbitals, the electron is added first in 4s and then in 3d, but during ionisation, 4s electrons are lost before the 3d electrons. 1½+1½+2

3. (a) Draw the π-MOs of 1,3-butadiene showing orbital diagram. Indicate HOMO and LUMO in the ground state. Also show the molecular nodes in each case. (½×4)+(½+½)+(½×4)

Or

(b) Write a short note on 'elements of symmetry' using the following points :

(i) Elements of symmetry

(ii) Centre of symmetry and one example

(iii) Plane of symmetry and one example

(iv) Alternating axis of symmetry and one example. 2+1+1+1

4. (a) Prove that :

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

and hence show that $C_P - C_V = \frac{\alpha^2 VT}{\beta}$, where $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ and $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ 3+2

Or

(b) Write a short note on consecutive reactions using the following points :

(i) Determination of concentrations of **A**, **B** and **C** at time t in terms of k_1, k_2 and initial concentration of **A** for the following first-order consecutive reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

(ii) The concentration *versus* time curves for all three three species in a single diagram when (1) $k_1 = 10\, k_2$ and (2) $10\, k_1 = k_2$. (1+1+1)+(1+1)

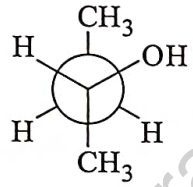
5. (a) Calculate the de Broglie wavelength of the following :

(i) A rifle bullet ($m = 2\times10^{-3}$ kg) moving with a speed of 300 ms^{-1}.

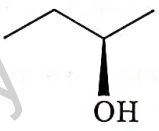
(ii) An electron moving with a speed nearly $\frac{1}{10}$th of that of light. ($m_e = 9.109\times10^{-31}$ kg).

Explain the significance of the result.

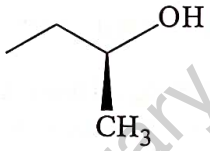
(b) Find the stereochemical relationship (enantiomer / diastereoisomer / homomer) of structure [**D**] with that of [**E**] and [**F**].



[**D**]



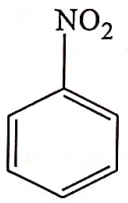
[**E**]



[**F**]

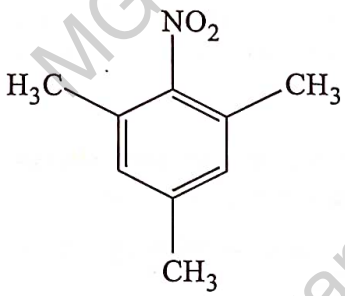
(c) Show that the pressure of an ideal gas is a state function. (1½+1½+1)+(1½+1½)+3

6. (a) Justify the dipole moments of the following molecules given in bracket with proper justification.



($\mu = 4.0$ D)

and

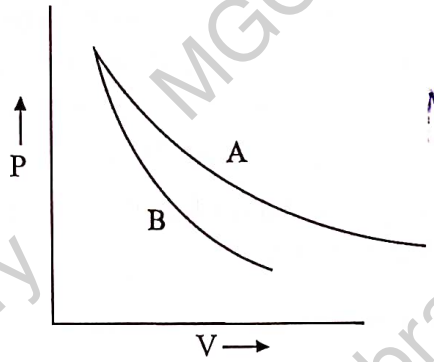


($\mu = 3.6$ D)

(b) One mole of a monatomic ideal gas $\left(\overline{C_V} = \frac{3}{2}R\right)$ at 80°C and 5 atmospheric pressure is expanded adiabatically against a constant external pressure of 1 atmosphere in such a way that the final pressure of the gas becomes 1 atmosphere. Calculate the final temperature, ΔU and ΔH, for the process.

(c) '$PbCl_4$ can act as a good oxidising agent.'— Justify the statement in the light of inert pair effect. (1+3)+(1+1+1)+3

7. (a) Following diagram shows P–V curve for reversible adiabatic and isothermal processes.



(i) Identify which one is for reversible adiabatic process and which one is for reversible isothermal process.

(ii) Prove your answer by deriving it mathematically.

(b) Draw the curves stated below for the 2s orbital of hydrogen atom.

(i) R vs. r; (ii) R^2 vs. r; (iii) $4\pi^2r^2R^2$ vs. r

where terms have their usual significance.

(c) Why is tertiary butanol more soluble in water than *n*-butanol? (2+2)+(1+1+1)+3

8. (a) State the Heisenberg's Uncertainty Principle. Give its mathematical form. Calculate the uncertainty in frequency for an electron deexcitation from an excited state of lifetime of 10^{-8}s.

(b) Draw the π-orbital picture of the following compound, clearly stating the hybridisation states of all the carbon atoms.

$$(H_3C)HC = C = CH(CH_3)$$

(c) The rate of the reaction $2A + B \longrightarrow C$ becomes doubled, when the concentration of only 'B' is doubled, and the rate becomes eight fold, when the concentrations of both 'A' and 'B' are doubled. Find the order of the reaction with respect to 'A' and 'B' and also state the units of the rate constants. 4+3+3

9. (a) Define stereogenic centre. Correlate stereogenic centre and chiral centre taking the instances of active lactic acid and *trans*-but-2-ene.

(b) Derive Kirchhoff's equation relating enthalpy change and temperature at constant pressure for the reaction shown below.

$$a\,A(g) + b\,B(g) = c\,C(g) + d\,D(g).$$

(c) What is electron affinity? Compare the electron affinities of fluorine and chlorine with proper explanation. (2+1+1)+3+(1+2)

10. (a) At 100°C, the gaseous reaction A $\longrightarrow$ 2B + C is observed to be first order. On starting with pure A, it is found that at the end of 10.0 minutes, the total pressure of the system is 176.0 mm Hg and after a long time 270.0 mm Hg. From these data find—

(i) Initial pressure of A,

(ii) The pressure of A at the end of 10.0 minutes, and

(iii) The half-life period of the reaction.

(b) Using the idea of penetration and shielding, explain the statement— 'The 3s and 3p orbitals have identical energies in hydrogen atom, but in chlorine atom, their energies are different'.

(c) Define resonance energy. Draw the resonating structures of the following compound and identify the most contributory resonating structure. (1+2+1)+3+(1+1+1)