

3 Yr. Degree/4 Yr. Honours 1st Semester Examination, 2023 (CCFUP)

Subject : Chemistry

Course: CHEM1011 (MAJOR)

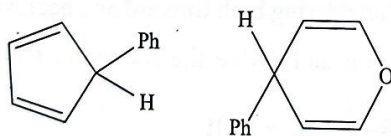
(Basic Chemistry-I)

Time: 2 Hours

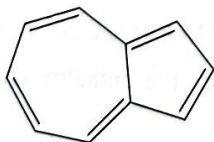
Full Marks: 40

*The figures in the right hand margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.*1. Answer any five questions from the following: 2×5=10

- (a) What do you mean by "super acid"? Write down the formula of the conjugate acid of H_2PO_4^- .
- (b) Calculate effective nuclear charge (Z^*) for a 3d-electron of iron atom.
- (c) "For every process in an isolated system, internal energy change $\Delta U = 0$ "— Justify or criticise the statement.
- (d) On doubling the initial concentration of the reactant in a reaction, namely, $A \rightarrow \text{Products}$, the half-life period is doubled. What is the order of the reaction?
- (e) A gas obeys the equation of state : $PV = RT \left(1 + \frac{b}{V} \right)$. Predict the condition when the gas behaves like an ideal gas.
- (f) What are 'Captodative radicals'? Give one example.
- (g) Which one is more acidic and why?



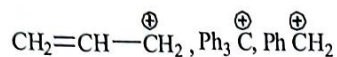
- (h) Account for the considerable dipole moment of the following compound:



2. Answer any two questions from the following:

5×2=10

- (a) (i) How does the Arrhenius equation, $K = Ae^{-E_a/RT}$ look at $T \rightarrow \infty$? Mention its significance.
 (ii) For a van der Waals' gas $P_c = 112.2$ atm and $b = 0.03707$ litre mole⁻¹. Find the reduced temperature of the gas at 27°C. 2+3
- (b) (i) Arrange the following carbocations in increasing order of their stability with explanation:



- (ii) Define "Homo-aromatic compounds" with a suitable example. 3+2
- (c) (i) Find the de Broglie wavelength of an electron which is moving with a speed of 2×10^6 m sec⁻¹. (Given: $m_e = 9.1 \times 10^{-31}$ Kg; $h = 6.626 \times 10^{-34}$ J. sec).
 (ii) Define ionisation energy. Why is the second ionisation energy of an element always greater than the first? 2+1½+1½
- (d) (i) Compare the stability of the following carbenes with brief explanation:
 $\ddot{\text{C}}\text{Cl}_2, \ddot{\text{C}}\text{Br}_2$ and $\ddot{\text{C}}\text{F}_2$
 (ii) "Acetic acid exerts less levelling effect on the strengths of acids than water."— Explain the statement.
 (iii) The rate constant for a reaction has an unit of $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$. What is the order of the reaction? 2+2+1

3. Answer any two questions from the following:

10×2=20

- (a) (i) Write down the van der Waals' equation in the virial form. Hence, deduce the expression for the Boyle temperature.
 (ii) Consider the opposing reaction $A \rightleftharpoons B$ with rate constants k_1 and k_2 for the forward and backward reaction, respectively. Considering both forward and backward reactions are of first order, write the rate equation and derive the following relation:

$$\ln \left[\frac{x_e}{x_e - x} \right] = (k_1 + k_2)t$$

where x_e is the equilibrium value of x , (x is the concentration of B at time t).

- (iii) Given that standard molar enthalpies of formation of NO(g) and NO₂(g) are given as 90.3 kJ/mol and 33.2 kJ/mol, respectively. Calculate the enthalpy change for the reaction $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$. (1+2)+4+3

- (b) (i) Ground state electronic configuration of chromium atom is $[\text{Ar}]3d^54s^1$ instead of $[\text{Ar}]3d^44s^2$. —Explain with the help of exchange energy calculation.
- (ii) In between AgCl and AgI which one is more stable? Explain with the help of HSAB concept.
- (iii) Calculate the shortest wavelength in H-atom spectrum of the Lyman series. [Given: $R_H = 109678 \text{ cm}^{-1}$]
- (iv) What do you mean by the term inert pair effect? And give suitable example of this. 2+3+2+(2+1)
- (c) (i) Find out the ground state term symbol of Ni^{2+} ion.
- (ii) Calculate pH of a solution obtained by adding 30 cm^3 0.1 (M) CH_3COOH solution to 20 cm^3 0.1 (M) NaOH solution at 25°C . [Given: $k_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$ at 25°C]
- (iii) 0.084 kg of N_2 gas initially at 300 K and 10 atm expands adiabatically against a constant pressure of 1 atm. Assuming ideal behaviour of the gas, calculate final temperature and final volume. [Given: $C_V(\text{N}_2) = 29.13 \text{ JK}^{-1} \text{ mol}^{-1}$]
- (iv) What do you mean by “Double bond equivalent (DBE)”? Calculate DBE of a compound having molecular formula $\text{C}_5\text{H}_8\text{NO}_2\text{Cl}$. 2+2+4+(1+1)
- (d) (i) Draw Frost diagrams of cyclopropenyl radical, cyclopropenyl cation and cyclopropenyl anion. Which one is aromatic in nature? Explain.
- (ii) Compare the geometry of $\dot{\text{C}}\text{F}_3$ and $\dot{\text{C}}\text{H}_3$ with suitable reason.
- (iii) Explain the basicity order of the following in aqueous medium:
 EtNH_2 , Et_2NH and Et_3N
- (iv) Calculate the percentage of ionic character in H—Cl bond which has dipole moment of 1.04D and bond length of 1.275 \AA . 3+2+3+2