

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

Subject : Chemistry

Course: CHEM1011 (MAJOR)

(Basic Chemistry-I)

Time: 2 Hours

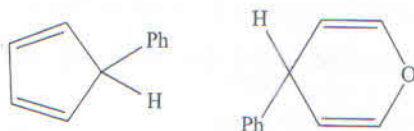
Full Marks: 40

*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  $\text{H}_2\text{PO}_4^-$ .
- (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<sup>-1</sup>. 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.

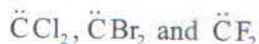
3+2

- (c) (i) Find the de Broglie wavelength of an electron which is moving with a speed of  $2 \times 10^6$  m sec<sup>-1</sup>. (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:



- (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 NO<sub>2</sub>(g) are given as 90.3 kJ/mol and 33.2 kJ/mol, respectively. Calculate the enthalpy change for the reaction  $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ .

(1+2)+4+3

- (b) (i) Ground state electronic configuration of chromium atom is  $[\text{Ar}]3d^5 4s^1$  instead of  $[\text{Ar}]3d^4 4s^2$ . —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  $\text{Ni}^{2+}$  ion.
- (ii) Calculate pH of a solution obtained by adding  $30 \text{ cm}^3$  0.1 (M)  $\text{CH}_3\text{COOH}$  solution to  $20 \text{ cm}^3$  0.1 (M) NaOH solution at  $25^\circ\text{C}$ . [Given:  $k_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$  at  $25^\circ\text{C}$ ]
- (iii) 0.084 kg of  $\text{N}_2$  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:  
 $\text{EtNH}_2$ ,  $\text{Et}_2\text{NH}$  and  $\text{Et}_3\text{N}$
- (iv) Calculate the percentage of ionic character in H—Cl bond which has dipole moment of 1.04D and bond length of  $1.275 \text{ \AA}$ . 3+2+3+2