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.

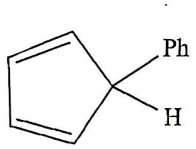
(c) "For every process in an isolated system, internal energy change $\Delta U = 0$"— Justify or criticise the statement.

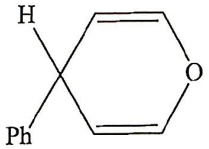
(d) On doubling the initial concentration of the reactant in a reaction, namely, A ⟶ Products, the half-life period is doubled. What is the order of the reaction?

(e) A gas obeys the equation of state : $PV = RT\left(1 + {}^{b}/_{V}\right)$. Predict the condition when the gas behaves like an ideal gas.

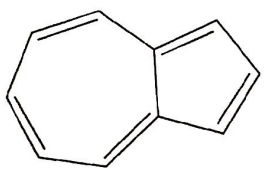
(f) What are 'Captodative radicals'? Give one example.

(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 $T \longrightarrow \infty$? 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:

$CH_2{=}CH{-}\overset{\oplus}{C}H_2$, $Ph_3\overset{\oplus}{C}$, $Ph\,\overset{\oplus}{C}H_2$

(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: $m_e = 9.1\times10^{-31}$ 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:

$\ddot{C}Cl_2$, $\ddot{C}Br_2$ and $\ddot{C}F_2$

(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 $L^2\ mol^{-2}\ s^{-1}$. 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_2(g) are given as 90.3 kJ/mol and 33.2 kJ/mol, respectively. Calculate the enthalpy change for the reaction $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$. (1+2)+4+3

(b) (i) Ground state electronic configuration of chromium atom is $[Ar]3d^5 4S^1$ instead of $[Ar]3d^4 4s^2$. —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: $R_H = 109678\ cm^{-1}$]

(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: $k_a (CH_3COOH) = 1.8\times10^{-5}$ 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: $C_V(N_2) = 29.13\ JK^{-1}\ mol^{-1}$]

(iv) What do you mean by "Double bond equivalent (DBE)"? Calculate DBE of a compound having molecular formula $C_5H_8NO_2Cl$.

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 $\dot{C}F_3$ and $\dot{C}H_3$ 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 1.275Å.

3+2+3+2