3 Yr. Degree/4 Yr. Honours 1st Semester Examination, 2024 (CCFUP)

Subject : Chemistry
Course: CHEM1011 (MAJOR)
### (Basic Chemistry-I)

Time: 2 Hours
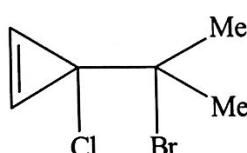
Full Marks: 40

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

   (i) Cite an example of a process where heat is completely converted into work.

   (ii) What is meant by 'Critical coefficient' of a gas?

   (iii) "Activation energy of some reactions may be zero."— Justify or criticise.

   (iv) Which one is more basic and why? MgO and AL_2O_3.

   (v) What is 'Sacrificial hyperconjugation'? Give an example.

   (vi) Compare dipole moment between fluorobenzene and chlorobenzene.

   (vii) Identify the halogen atom to be precipitated in presence of $AgNO_3$ solution and why?

   (viii) An element with mass number 81 contains 31.7% more neutrons as compared to protons. Assign the atomic symbol.

2. Answer *any two* questions from the following: 5×2=10

   (a) (i) The virial equation of state in terms of P is given by

   $$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)P + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)P^2 + \ldots\ldots$$

   Set up an expression for the initial slope of Z vs P curve (at P → 0) of a real gas and obtain the expression for Boyle temperature. 2+1
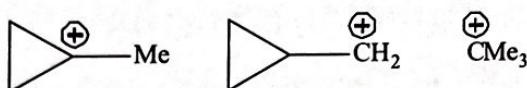
   (ii) Show that PdV – VdP is not an exact differential. 2

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(b) (i) Draw π-molecular orbitals with electron occupancy of the allyl radical system. 3

(ii) Compare the stability of the following carbocations: 2

(c) (i) Arrange the following Lewis acids in order of increasing acidic character: 3

BF_3, BCl_3, BBr_3

(ii) The ionisation potential of H-atom is 13.6 eV. Calculate the ionisation potential of Li^{2+} ion. 2

(d) (i) Is cyclo-octatetraene an aromatic compound?—Comment. 2
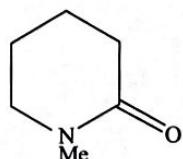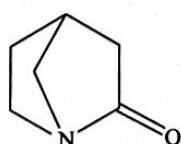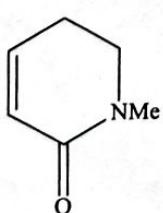
(ii) In what condition pH = pKa for an acidic buffer? 1

(iii) Calculate the half-life of the decomposition reaction at 300K of a substance having initial concentration 0·05 mole L^{-1}. (Given, rate constant = $6·8 \times 10^{-4}$ L $mole^{-1}$ S^{-1}) 2
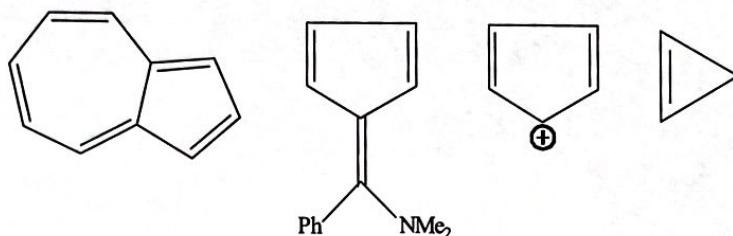
3. Answer *any two* questions from the following: 10×2=20

(a) (i) The temperature variation of rate constant (k) of a reaction is given by $k = ATe^{-Ea/RT}$ (Terms have their usual significance). Suggest a suitable plot for the determination of E. 2

(ii) For a second order reaction, A ⟶ Products, show that the time required for the three-fourths of the reactants to decay ($t_{3/4}$) is equal to $3t_{1/2}$, where $t_{1/2}$ indicates half-life. 3

(iii) Heat of neutralisation of HCl with NaOH is estimated to be–13·7 kcal. When 10 ml of (N/10) acetic acid is neutralised by 10 ml of (N/10) NaOH, enthalpy change is –12·5 kcal. Calculate the heat of dissociation of acetic acid. 3

(iv) Show that $\left(\dfrac{\partial P}{\partial T}\right)_v = \alpha / \beta$ $\begin{bmatrix} \alpha = \text{coefficient of volume expansion} \\ \beta = \text{coefficient of compressibility} \end{bmatrix}$ 2

(b) (i) Arrange the following compounds in order of increasing basic strength. Justify your answer. 3

(ii) Categorize the following species as aromatic/anti-aromatic/non-aromatic with brief reason: 4

(iii) C—C bond distance in CCl_3CHO is calculated to be $1·54Å$ (same as ethane) while that in CH_3CHO is observed to be $1·50Å$. —Explain. 3

(c) (i) Write short notes on (*any two*): 3×2=6

    (I) Inert pair effect

    (II) Allred-Rochow's electronegativity scale

    (III) Drago-Wayland equation
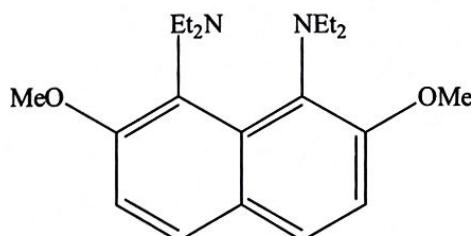
(ii) Calculate pH of a 10^{-8}(M) aqueous HCl at 25°C. 2

(iii) Should methyl orange be used as indicator in the titration of acetic acid by NaOH? —Explain. 2

(d) (i) What do you mean by 'The law of correspondig state'? Derive the necessary equation in this regard starting from the van der Waal's equation of state. 1+3

(ii) Calculate the mass of a photon having wavelength $3·6Å$. 2

(iii) The following compound is a strong base. Explain why. 2

(iv) Arrange the following ions in ascending order of radius: 2

Na^+, F^-, O^{2-}, Mg^{2+}