

2016

CHEMISTRY -II

Time Allowed: 3 Hours

Full Marks: 200

If the questions attempted are in excess of the prescribed number, only the question attempted first up to the prescribed number shall be valued and the remaining ones ignored. Answer may be written either in English or in Bengali but all answers must be in one of the same language.

SECTION - I

This section comprises 15 questions in three groups. Answer any ten questions taking at least three questions from each group.

GROUP A

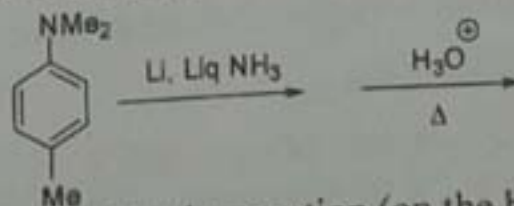
1. Compare the spin state of $\text{Ni}(\text{CO})_4$ and $\text{Ni}(\text{CN})_4^{2-}$ ion. 4
2. Predict the number of stereochemical isomers of $[\text{PtClBrFI}]^{2-}$ ion. 4
3. What is cytochrome C? State the role of it. 4
4. Illustrate the structure of $\text{Fe}_2(\text{CO})_9$. 4
5. What is Berlin green? State the origins of its colour. 4

GROUP B

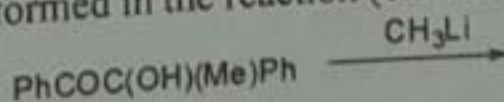
6. Two liquids A and B, form an ideal solution. At the specified temperature, the vapour pressure of pure A is 200 mm Hg and that of pure B is 75 Hg. If the vapour over the mixture consists of 50 mol percent A, what is the mole percent of A in the liquid? Given the total pressure of $P = 109$ mm. 4
7. What do you understand by 'Langmuir film'? Give one example.
Show how the surface pressure π would vary with the area A of a monolayer film at a certain fixed temperature. Indicate the 'Pockels point' and how an estimate of the cross sectional area per molecule may be obtained. 4
8. Integrate the rate expression for the reaction $A \longrightarrow \text{Pds.}$ $\text{Rate} = -\frac{d[A]}{dt} = k[A]^n$
From here show that the time required for the completion of the reaction, $t_{\text{comp}} = 2t_{1/2}$. 4
9. What is meant by 'quantum yield' of a photochemical reaction? Can it be greater than 1? How can you account for a $\phi \approx 10^5$ for the photochemical reaction, $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ at $\lambda = 4000 \text{ \AA}$? 4
10. Point out the shortcomings of SHO model of a chemical bond. The equilibrium vibration frequency of the I_2 molecule is 215 cm^{-1} . What is its 'zero point energy'? 4

Group C

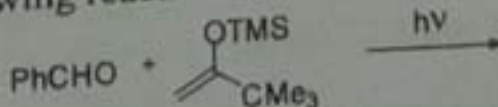
11. Comment on the chirality of trans-cyclooctene. Is trans-cyclodecene resolvable? Explain. 4
12. Draw the structure of the preferred conformer of 1-methyl-1-phenylcyclohexane. Explain. 4
13. Predict the product of the following reaction sequence. Explain its formation. 4



14. Predict the major diastereomer to be formed in the reaction (on the basis of Cram's rule). Explain. 4



15. Predict the major product of the following reaction. Give reasons. 4

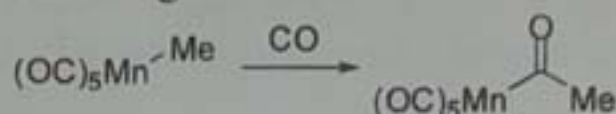


SECTION - II

This section comprises 6 questions in three groups. Answer any four questions taking at least one question from each group.

GROUP A

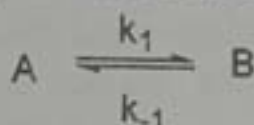
16. (a) CoCl_4^{2-} and $\text{Co}(\text{H}_2\text{O})_6^{3+}$ exhibit different colour with different intensity. Explain. 8
 (b) $[\text{Co}(\text{en})_3]^{3+}$ is more stable than $[\text{Co}(\text{NH}_3)_6]^{3+}$. Explain. Delineate the optical activity of two complexes. 8
 (c) Describe the electronic state of the oxyhemoglobin. How does the oxygenation of hemoglobin depend on the pH? 8
 (d) Describe the structure and bonding of $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ and compare it with $\text{C}_2(\text{CN})_4$ analogue. 8
 (e) Illustrate the structure of $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$. Explain the features. 8
 17. (a) Establish the mechanism of the following reaction: 8



- (b) Predict the total number of stereoisomers of $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2]^+$ ion with illustration. 8
 (c) What is the active site of hemerythrin? How does it bind O_2 molecule? Explain the features mentioning the oxidation state of the iron centers. 8
 (d) Predict two ions which exhibit magnetic moment higher than spin only values. Explain their features. 8
 (e) cis-Platin is prepared from $[\text{PtCl}_4]^{2-}$ via $[\text{PtL}_4]^{2-}$ ion. Explain. 8

GROUP B

18. (a) The energy level of a real oscillator is given by the equation
 $\epsilon_v = \left(v + \frac{1}{2}\right) \bar{\nu}_e - \bar{\nu}_e x_e \left(v + \frac{1}{2}\right)^2 \text{ cm}^{-1}$. How would you proceed to obtain v_{max} , the vibrational quantum no. corresponding to the dissociation of the molecule? What is the expression for the zero point energy of the molecule? What would be the bond dissociation energy if x_e , the anharmonicity constant is 0.007? Given $\bar{\nu}_e = 1903.98 \text{ cm}^{-1}$ 8
 (b) Consider the following chemical reaction, first order in both directions. 12



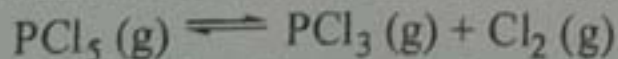
- i. Write down the rate law for the reaction.
 ii. Let the initial concentration of A be 'a' and the concentration of B formed at anytime t be 'x'. Let x_e be the equilibrium concentration of B. Relate 'x' and ' x_e '.
 iii. Draw the time profile of [A] and [B] if $k_1 = 2k_{-1}$.

(c) Deduce the Clausius-Clapeyron equation for a general $\text{liq} \rightleftharpoons \text{vap}$ equilibrium.

The vapour pressure of solid selenium is given by $\log p(\text{mm}) = -\frac{7440}{T} + 12.78$ and that of the liquid selenium by $\log p(\text{mm}) = -\frac{5390}{T} + 8.63$

- i. Determine the triple point temperature of selenium.
 ii. What is the vapour pressure at the triple point? 14

(d) What do you understand by 'degrees of freedom' in a heterogeneous system of P phases in equilibrium? Determine the number of components in the system. 6



19. (a) Why is 'phosphorescence' not usually observed at room temperature? Explain. What is usually done to obtain phosphorescence spectra? Justify 'phosphorescence bands are red-shifted with respect to fluorescence bands'. 6
 (b) Obtain the expression for the depression of freezing point of a nonvolatile, non-associative solute dissolved in a volatile solvent. Use the chemical potential of the solution and the pure solvent in your derivation.

Under what condition would you have freezing point elevation? Discuss with the help of μ vs T diagram. 6