

CHEMISTRY - I

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 and 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

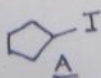
- Using VSEPR theory predict for structures of
(a) NSCl_2^- (b) XeF_5^+ (c) BrF_5 (d) O_3
- Compare the size of S^{2-} , Cl^- and K^+ using Slater's rule.
- Give four characteristics of a good redox indicator.
- State Heisenberg's uncertainty principle. Using uncertainty principle, explain why it is never possible for an electron to be present within the nucleus.
- Derive an expression for the pH of a weak monobasic acid. Hence calculate the pH of a 0.05(M) acetic acid, given that $\text{p}K_a = 4.74$.
4x5

Group - B

- Write down the expression for the probability of finding a molecule with x-component of velocity in the range between u and u+du. Using Maxwell distribution find an expression for the average speed of gas molecules. Given $\int_0^\infty x e^{-x} = 1$
- Derive an expression for the number of molecules having kinetic energies between ξ and $\xi + d\xi$, where the molecules obey Maxwell's speed distribution.
- Show that $Z = 1 + 1/RT(b-a/RT)P + a/(RT)^3(2b-a/RT)P^2$ for a gas obeying van der Waals equation of state, where Z is the compressibility factor.
- Distinguish between the number of atoms in a unit cell of a bcc and fcc lattice.
- Calculate the separation of (a) the $\{123\}$ planes and (b) the $\{246\}$ planes of an orthorhombic unit cell with $a = 0.82 \text{ nm}$, $b = 0.94 \text{ nm}$, and $c = 0.75 \text{ nm}$.
4x5

Group - C

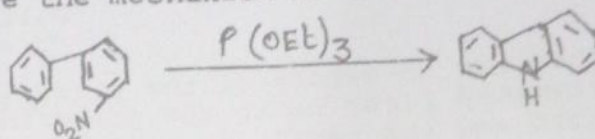
- The iodide A is rapidly solvolyzed with silver perchlorate in propionic acid whereas the compound B is not solvolyzed at all under the same conditions. Explain.



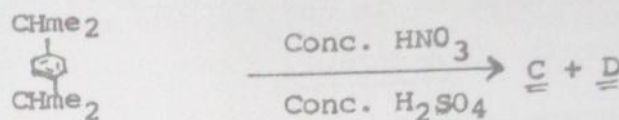
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GROUP - C

12. Give the mechanism of the following reaction



13. Identify the products C and D of the following reaction



Explain their formation.

14. The rate of solvolysis of $PhCH_2CH_2OTs$ at $75^\circ C$ in CF_3CO_2H is 3040 times than the rate for CH_3CH_2OTs . Explain.
15. How can you distinguish between ethyl butyrate and vinyl acetate from their IR spectra? 4x5

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) Compare the trend in the
- second ionization energy of S and Cl.
 - atomic size of Nb and Ta.
 - electron affinity of F and Cl.
 - electronegativity of Si and Ge.
- (b) Explain the principle involved in the estimation of copper from a solution of Cu^{2+} by iodometry.
- (c) Give a comparative account of the halides of group 14 elements with reference to
- type of halides
 - hydrolytic behaviour
 - structure
- (d) Construct the MO energy level diagram of CO and hence explain how it can behave as a ligand towards transition metal ions.
- (e) Using the concept of hybridization, explain the bonding in
- XeO_2F_2
 - NPF_2
 - NO_2^+
 - $SOCl_2$
- 3x5

GROUP - A

17. (a) What are interhalogen compounds? Why they are more reactive than the corresponding halogens? Also explain why they contain even number of halogen atoms. 2+3+3

(b) Calculate the potential at different stages of titration of 100 ml 10.1(N) Fe^{2+} sol. by 0.1(N) $\text{Cr}_2\text{O}_7^{2-}$ when

(i) 50ml 0.1(N) $\text{Cr}_2\text{O}_7^{2-}$ is added

(ii) 100 ml 0.1 (N) $\text{Cr}_2\text{O}_7^{2-}$ is added

{The conc. of H_2SO_4 maintained in 1(M)}

What indicator may be used for this titration? Explain.

$$E^\circ \text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+} = 1.33 \text{ V}$$

$$E^\circ \text{Fe}^{3+}/\text{Fe}^{2+} = 0.77 \text{ V}$$

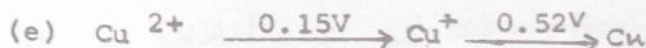
4+4

- (c) Discuss the structure and bonding in polythiazyl. Also explain how can it be synthesized from S_4N_4 . 6+2

- (d) Derive an expression of pH of a solution of ammonium acetate and hence explain why such solution is always neutral.

(pK_a of $\text{AcOH} = 4.74$

pK_b of $\text{NH}_3 = 4.75$) 6+2



Construct a Frost Diagram of Cu from the above Latimer Diagram and hence explain whether Cu^+ is prone towards disproportionation. Also explain whether the disproportionation will be favoured in presence of KI. 4+2+2

GROUP - B

18. (a) As a first approximation, the compressibility factor of the van der Waals gas is given by

$$PV/RT = 1 + (b-a/RT)P. \text{ Show that } \left(\frac{\partial S}{\partial P}\right)_T = -\left[\frac{R}{P} + \frac{Ra}{(RT)^2}\right] \quad 10$$

- (b) Show that $\left(\frac{\partial S}{\partial P}\right)_V = \frac{\beta C_V}{\alpha T}$

and $\left(\frac{\partial S}{\partial V}\right)_P = \frac{C_P}{\alpha V T}$ where the terms have their usual significances. 8

- (c) At 20°C the interfacial tension between water and benzene is 35 mN m^{-1} . If the surface tension $\gamma = 28.85 \text{ mN m}^{-1}$ for benzene and 72.75 mN m^{-1} for water, calculate (i) the work of adhesion between water and benzene (ii) the work for cohesion for benzene and for water, and (iii) the spreading coefficient for benzene on water. 8

- (d) Deduce the expression for the Van't Hoff reaction isotherm. 10

- (e) The first order reflection from a crystal plane in a cubic crystal occurs at $13^\circ 41'$. Find the Miller indices of the plane. [Given, $a = 5.63 \text{ \AA}$, $\lambda = 1.54 \text{ \AA}$, $\sin^2 13^\circ 41' = 0.056$] 4

GROUP - B

19. (a) (i) State and explain Nernst heat theorem.

(ii) A spherical drop of a liquid weighing 0.04 g is dispersed into 1500 microglobules of radius 0.02 cm. Find the resultant increase in surface energy.

(b) Show that $C_p - C_v = \left[V - \left(\frac{\partial H}{\partial P} \right)_T \right] \left(\frac{\partial P}{\partial T} \right)_V$

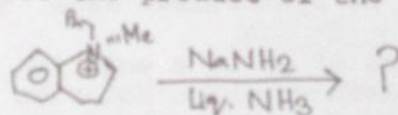
(c) Find $\left(\frac{\partial H}{\partial V} \right)_T$ for n-mole of a van der Waals gas and n-mole of an ideal gas.

(d) Show that $\left(\frac{T_2}{T_1} \right)^{5/2} = \frac{V_1 - b}{V_2 - b}$ for reversible, adiabatic expansion of 1 mol of a diatomic gas that obeys the equation of state $P(V-b) = RT$

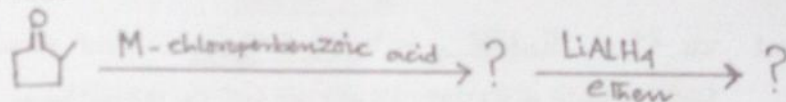
(e) At 20°C water with an absolute viscosity of 0.01009 dyne.sec.
cm⁻² requires 102.2 seconds to flow through the capillary of an Ostwald viscometer, whereas, toluene requires 68.9 seconds. If the densities of water and toluene be 0.998 g.cm⁻³ and 0.866 g.cm⁻³, respectively, calculate the viscosity of toluene

GROUP - C

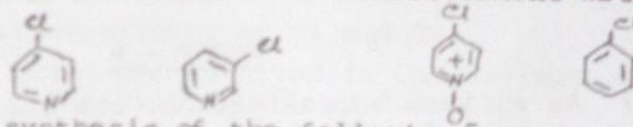
20. (a) Predict the product of the following reaction. Explain.



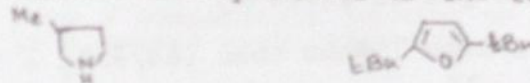
(b) Identify the products of the following reaction sequence. Explain.



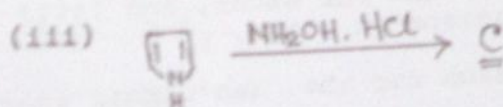
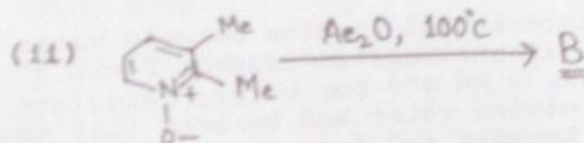
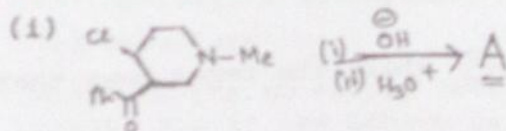
(c) Arrange the following chloro compounds in the increasing order of rates of nucleophilic displacement with NaOMe . Explain.



(d) Outline the synthesis of the following compounds

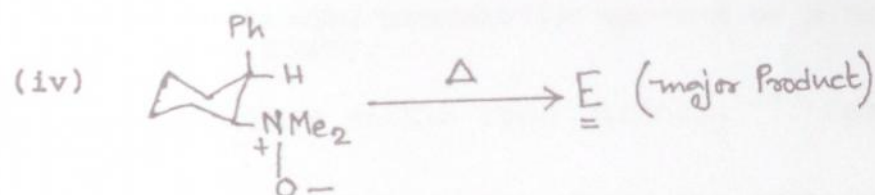
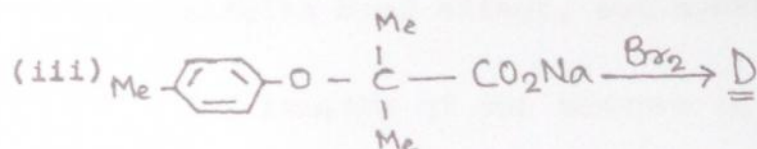
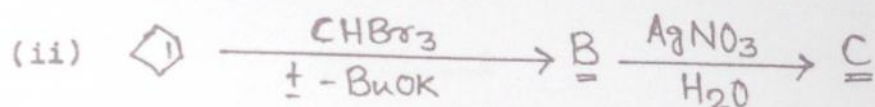
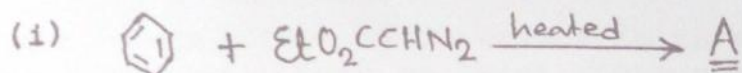


(e) Identify the products A - C of the following reactions. Give mechanism in each case.



GROUP - C

21. (a) There is deuterium in the recovered alkene, $\text{Cl}_2\text{C}=\text{CHCl}$ when it reacts with NaOD to give $\text{ClC}\equiv\text{CCl}$ and the reaction is stopped before completion. No such deuterium incorporation is found for similar reaction with $\text{PhCH}_2\text{CH}_2\text{Br}$. Explain. 6
- (b) Identify the products A - E of the following reactions. Explain their formation and comment on their stereochemistry, if required.



5x4

- (c) What is a metastable ion peak in mass spectrum of organic compounds? Why they frequently occur at non-integral values of m/z ? 4
- (d) How can you distinguish isopropyl-benzene and n-propyl benzene from their mass spectral features? 6
- (e) Give an example of free radical initiator organic compound. Explain the mechanism of benzylic bromination of toluene with N-bromosuccinimide (NBS) 4