2017

BM-(O)CH-I/17

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

1. Depict Aufbau principle for filling up of electrons in different orbitals of atoms. Represent electronic configuration of Chromium atom.

2. How deformation of ions in ionic compounds leads to passage from ionic to covalent bonding ? Comment. Enumerate the Fajan's rule in predicting type of compounds and classify $SiCl_4$ and NH_3 accordingly.

3. Critically explain the band theory of metallic bonds selecting Li as an example.

4. For each metal, lower oxidation states are basic and high oxidation states are acidic - Elucidate with suitable example. CF_3COOH is strong acid and $(CH_3)_3N$ has no basic property - Is there any common reason ?

5. Derive an expression for estimating lattice energy of NaCl from its ionization potential, electron affinity, heat of sublimation, heat of dissociation of atoms and heat of formation of Nacl using Born-Haber cycle.

4 x 5

GROUP - B

6. Show that the van der Waals equation leads to the values of $Z < 1$ and $Z > 1$, and identify the conditions for which these values are obtained.

7. Show that the interfacial tension $\gamma^{\alpha\beta}$ between two liquid phases α and β decreases with increase in the Gibbs energy of adhesion between these two phases. Under which condition the work of adhesion becomes the average of the work of cohesion between these two liquid phases.

8. Show that at constant temperature, the mean free path is inversely proportional to pressure. "A system composed of one molecule or even of a few molecules would not have a temperature, properly speaking". Justify or criticize the statement.

9. Derive the Laplace equation. What will be its form for a planar surface ?

10. A solid metal ball of radius 2 mm falls into a liquid of density 1.8 g/cm^3 and coefficient of viscosity of 54 poise with an initial velocity of 1.0 cm/sec. Find the density of the metal.

4 x 5

P. T. O.

GROUP - C

11. Comment on unusual dipolemoment of the following compound.
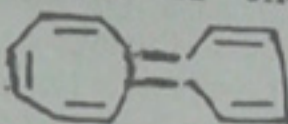
12. Show how deuterium labelling experiment may be useful to establish the mechanism of a reaction of your choice.

13. Comment on the reactions when o-bromo-anisole and m-bromoanisole are treated with $KNH_2/NH_3(\ell)$.

14. Write the possible ^1H NMR signals (chemical shift values) of four types of proton present in the following compound.
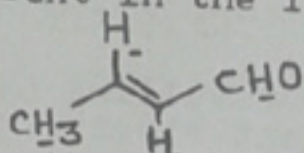
15. Predict the product(s) in the following reaction with plausible mechanism.

$$CH_3-CH(OH)-C(OH)Ph_2 \xrightarrow{H_3^+O}$$
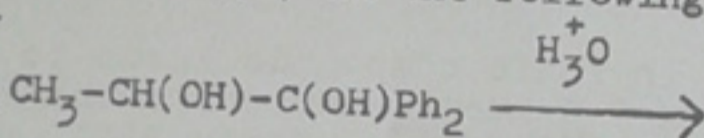
4 x 5

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) Mention different oxidation states of Manganese.

(b) Discuss π-acid complexes of Manganese.

(c) Write the structure of prucian blue, $M^I Fe^{III} \left[Fe^{II}(CN)_6 \right]$.

(d) The ferric-ferrous system has E^o value of +0.77 volt whereas formal potential in 1(M) $HClO_4$ is +0.73 volt, in 1(M) HCl is +0.70 volt and +0.50 volt only in 0.5 (M) H_3PO_4 + 1(M) H_2SO_4 - Illustrate.

(e) Cite representative compounds of ruthenium and osmium in their bivalent, tetravalent and hexavalent states.   8 x 5

17. Review on the valuable uses of coordination complexes in -

(a) as insoluble inner metallic complex in gravimetric estimation

(b) solvent extraction and separation of metal ion through complexation

(c) spectrophotometric estimation of trace metal ions

(d) complexometric estimation of metal ions using Na_2EDTA

(e) Draw a schematic for estimation of weak boric acid through chelation with polyhydric alcohol like manitol.   8 x 5

GROUP - B

18. (a) Derive the relation $C_p - C_v = \dfrac{TV\alpha^2}{\beta}$ where the terms have their usual significances.

(b) Two blocks of the same metal are of the same size but are at different temperatures T_1 and T_2, respectively. These blocks are brought into thermal contact and isolated from their surroundings. Show that the entropy change is given by $\Delta S = C_v \ln \dfrac{(T_1+T_2)^2}{4T_1T_2}$ where C_v is constant. How does this equation show that the process is spontaneous.

(c) Describe any one of the suitable methods employed for the determination of surface tension of a liquid.

(d) The density of CaO is 3.35×10^3 Kg/m^3. This oxide crystallizes in one of the cubic system with a = 480 pm. Calculate the number of molecules in the unit cell. Which type of cubic system it is ?

(e) Comment on the possibility of defining a Boyle's temperature of a van der Waals gas when (i) a = 0 and when (ii) a = b = 0.

8×5

19. (a) Show thermodynamically how the internal energy changes as the volume of a system is changed isothermally for a perfect gas and for a van der Waals gas. Show how the change in enthalpy is related to the energy supplied as heat at constant temperature.

12

(b) Show that at constant temperature and pressure, the maximum non-expansion work is given by the change in Gibbs energy.   8

(c) Show that $\ln \dfrac{K_p(T_2)}{K_p(T_1)} = - \dfrac{\Delta H^\circ}{R} \left(\dfrac{1}{T_2} - \dfrac{1}{T_1} \right)$ where $K_p(T_1)$ and $K_p(T_2)$ are the equilibrium constants at T_1 and T_2 respectively. $T_2 > T_1$. 8

(d) Show that at $\left[\dfrac{\delta \left(\frac{G}{T} \right)}{\delta \left(\frac{1}{T} \right)} \right]_p = H$ 6

(e) What will be the change in surface energy when two identical mercury droplets having diameter 1.5 mm merge together isothermally to form a single drop. (Surface tension of mercury = 490 dyne/cm).
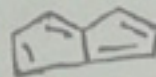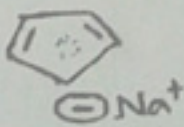
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GROUP - C

20. (a) Arrange following compounds in order of increasing SN^1 reactivity with reasons.
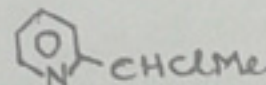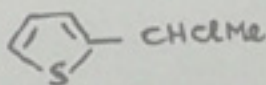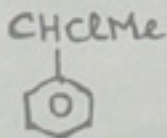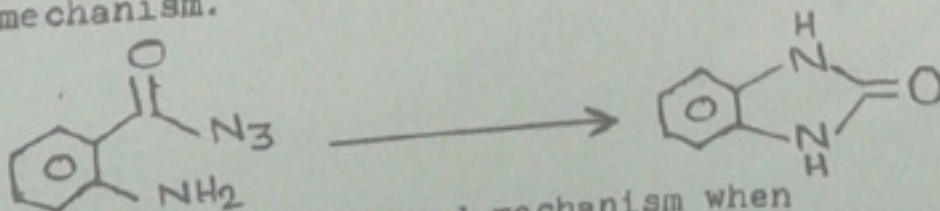

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(b) Classify the following compounds as aromatic, antiaromatic and non aromatic. Illustrate your classification.
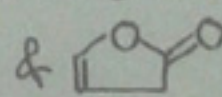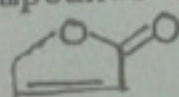

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(c) Carry out following transformation and write suitable mechanism.

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(d) Write the product and mechanism when

(i) 2,3 - Dihydroxy - 2,3 dimethyl butane is heated with Conc H_2SO_4.   8

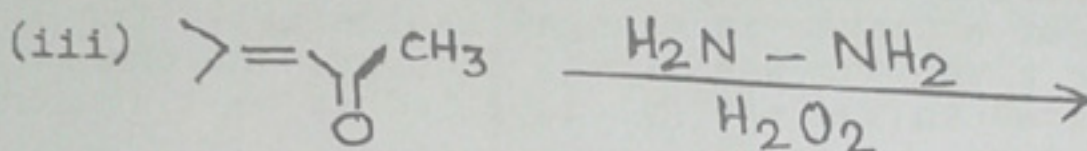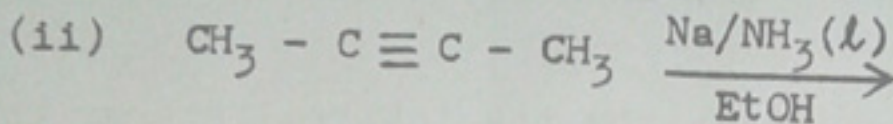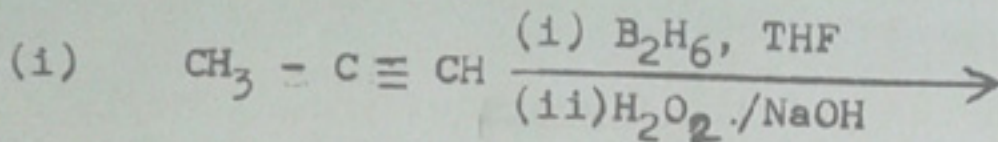(ii) 2 - Nitroaniline is treated with KCN in ethanol.   8

(e) Which one of the following compounds shows higher stretching frequency in FT.IR and why ?

4

21. (a) Draw and explain the ^{1}H-NMR spectrum of pure ethanol in $CDCl_3$.

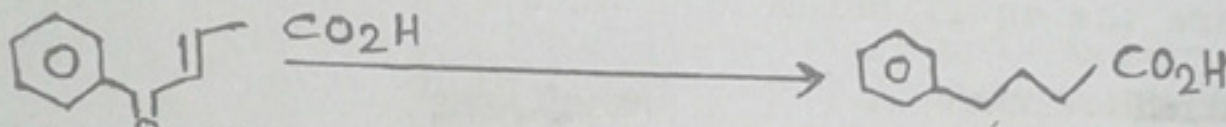   (b) Predict products of the following reaction. Give possible mechanistic pathways.

   (i) $CH_3 - C \equiv CH$ $\xrightarrow[\text{(ii)}H_2O_2./\text{NaOH}]{\text{(i) } B_2H_6, \text{ THF}}$

   (ii) $CH_3 - C \equiv C - CH_3$ $\xrightarrow[\text{EtOH}]{\text{Na/NH}_3(l)}$

   (iii) $\xrightarrow[\text{H}_2O_2]{\text{H}_2N - NH_2}$
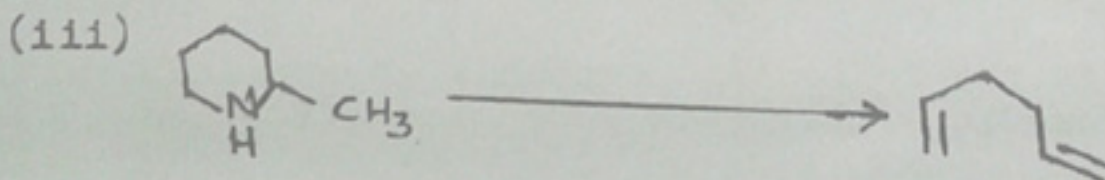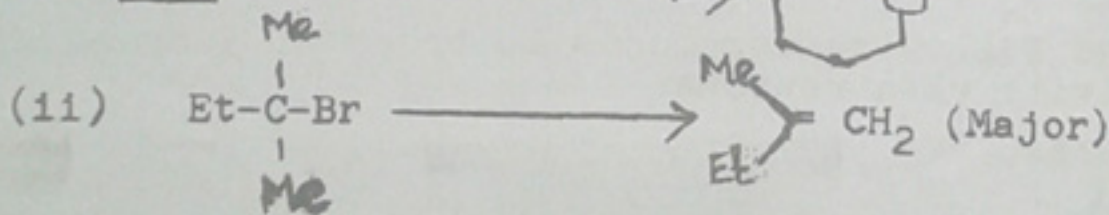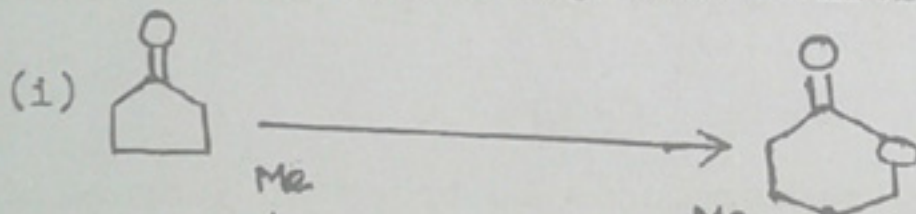
   4 x 3

   (c) What happens when erythro-3-bromo-2-butanol is heated with HBr ? Explain possible mechanistic pathway.

   4

   (d) How would you detect the following organic transformation by IR spectroscopy ?

   4

   (e) Illustrate McLaf_erty rearrangement with appropriate example.

   4

   (f) Carry out the following transformation with mechanism.

   (i)

   (ii) $Et-\overset{Me}{\underset{Me}{C}}-Br$ $\longrightarrow$ CH_2 (Major)

   (iii)

   4 x 3