

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

FIRST YEAR [BATCH 2015-18]

B.A./B.Sc. SECOND SEMESTER (January – June) 2016

Mid-Semester Examination, March 2016

Date : 17/03/2016

Time : 11 am – 1 pm

CHEMISTRY (Honours)

Paper : II

Full Marks : 50

[Use a separate Answer Book for each group]

Group – A

Answer any one question :

1. a) Show that the efficiencies of all reversible engines working between same two temperatures are same. [4]
b) Write down the thermodynamic definition of entropy. [2]
c) Starting from Clausius Inequality prove that the entropy of the universe increases with time. [2]
2. a) Prove that for an ideal gas for a reversible change of state (T_i, V_i) to (T_f, V_f)
$$\Delta S = C_v \ln \frac{T_f}{T_i} + R \ln \frac{V_f}{V_i}.$$
 [3]
b) Comment whether ΔS will have same/greater/lesser than the value obtained for reversible process, has the process been carried out irreversibly. [2]
c) Calculate the change of entropy when 1 mole of water freezes to ice at 0°C , 1 atm pressure (mention all the arguments that your answer is based on). [3]

Answer any one question :

3. a) An x-ray photon of initial energy $1.0 \times 10^5 \text{ eV}$ travelling in the +X direction is incident on a free electron at rest. The photon is scattered at right angles into the +Y direction. Find the components of momentum of the recoiling electron. [3]
b) A microscope using photons is employed to locate an electron in an atom to within a distance of $0.2 \text{ \AA}$. What is the uncertainty in the velocity of the electron located in this way? [3]
c) Determine whether the function $\psi = \sin(xe^{ax})$ is an eigenfunction of the operator $\frac{d^2}{dx^2}$. [2]
4. a) What are the conditions for a well-behaved functions? Also state whether $\psi = ae^{-bx}$ is acceptable as well-behaved or not. Why? [2+2]
b) Find out the value for $[p_x, x]$. (Both are operators) [2]
c) Proof the identity relation $[A, BC] = [A, B]C + B[A, C]$. [2]

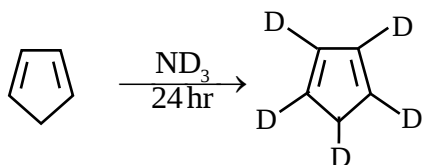
Group – B

Answer any one question :

5. a) Draw energy profile diagram indicating starting material, transition states, intermediate and product for the reaction given below which shows no primary kinetic isotope effect $\left(\frac{K_H}{K_D} \approx 1\right)$.
$$\text{ArH} + \text{NO}_2^+ \xrightleftharpoons[K_{-1}]{K_1} \text{Ar}^+ \begin{matrix} \text{H} \\ \diagup \quad \diagdown \\ \text{NO}_2 \end{matrix} \xrightarrow{K_2} \text{ArNO}_2 + \text{H}^+; K_2 \gg K_{-1}$$
 [3]

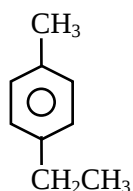
b) Explain the following observation :

[2]



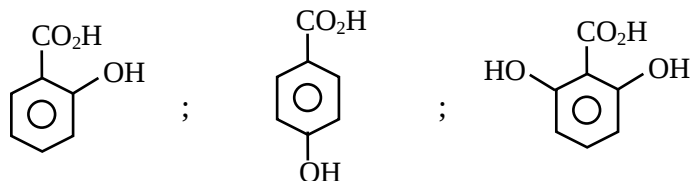
c) Indicate the relative acidity of three different kinds of aliphatic protons in the following compound. Explain.

[3]



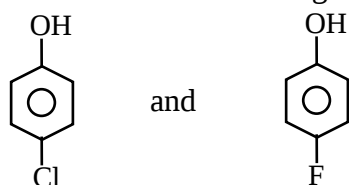
6. a) Arrange the following compounds in order of increasing acidity. Justify your answer.

[3]



b) Which one of the following is more acidic and why?

[2]



c) Sulphonation of naphthalene at 80°C gives naphthalene-1-sulphonic acid as the major product, while at 160°C the major product is naphthalene-2-sulphonic acid. Explain with a suitable energy profile diagram.

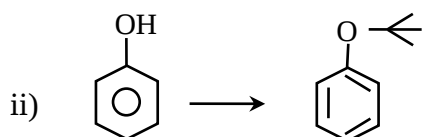
[3]

Answer any one question :

7. a) Carry out the following conversions. Give mechanism.

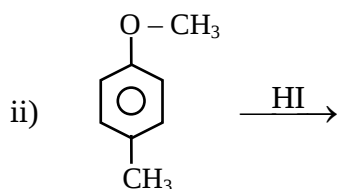
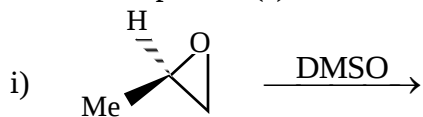
[2×2]

i) (R) – 2 – phenylethanol $\longrightarrow$ (R) – 2 – phenylethylchloride

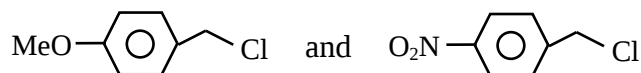


b) Predict the product(s) of the following reactions. Give mechanism.

[2×2]



8. a) Compare the S_N^1 reactivity of the following compounds :



[2]

- b) Ethanolysis of the following two compounds gives same product mixture. Justify. [2]
 $\text{Me}-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$ and $\text{Me}-\underset{\text{Cl}}{\underset{|}{\text{CH}}}-\text{CH}=\text{CH}_2$.
- c) Which one of the following is a better nucleophile? Justify your answer. [2×2]
 i) MeS^- or MeO^- in DMSO
 ii) LiCl or $\text{Bu}_4\text{N}^+\text{Cl}^-$ in acetone.

Group – C

Answer any one question :

9. a) Explain : [2+2]
 i) Atomization energy (KJ/mol) of lithium (161) is higher than Na (108).
 ii) $-\Delta H_f$ (KJ/mol) of LiF (612) > NaF (569) while that of LiI (271) < NaI (288).
- b) Discuss the structural similarity of basic beryllium acetate and basic beryllium nitrate. [3]
- c) State, with equation, what will happen when dilute aqueous potassium salt solution is treated with sodium cobaltinitrite solution in acetic acid medium. [2]
10. a) Explain : [2+2]
 i) Solubility of BeO increases in aqueous BeSO_4 solution.
 ii) Golden yellow flame of sodium shows doublet structure.
- b) Reduction potential of Li^+/Li (–3.05V) is highest of the Group-1 elements and that of Be^{2+}/Be (–1.85V) is lowest of the Group-2 elements – rationalize. [2]
- c) Compare the stability of complexes of the alkali metal ions with 18-crown-6 ether and explain the variation. [3]

Answer any one question :

11. a) SbCl_6^{3-} and TeCl_6^{2-} is regular octahedral where as XeF_6 is distorted octahedral, explain with reasons. [3]
 b) Write Born Lande equation and explain all the terms. [3]
 c) Formation of divalent cation and anion are endothermic yet MgO is a stable ionic solid, comment. [2]
 d) Comment on the thermal stability of BeO, MgO, CaO, SrO, BaO. [1]
12. a) What is proton affinity? Starting from gaseous N_2 , H_2 and Cl_2 construct the Born Haber cycle for the formation of NH_4Cl and from the given data calculate the proton affinity of NH_3 .
 Bond dissociation enthalpies, $\Delta H_{\text{diss}}^\circ$: H_2 436(D_1); Cl_2 242 (D_2)
 Standard enthalpy of formation, ΔH_f° : NH_3 : –46 ; NH_4Cl : –314
 Lattice energy of NH_4Cl : –683
 Ionisation enthalpy of H(I) : 1310; $\Delta H_{\text{EA}}^\circ$ of Cl = – 348
 all are in KJmol^{-1} . [1+2+2]
- b) Comment on the shape of $\cdot\text{CH}_3$ and $\cdot\text{CF}_3$. [2]
- c) With an example explain the exception of Bent's rule. [2]

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