RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIRST SEMESTER EXAMINATION, DECEMBER 2018

FIRST YEAR [BATCH 2018-21]

Date : 14/12/2018 **INDUSTRIAL CHEMISTRY (Honours)**

Time : 11.00 am – 3.00 pm Paper : I Full Marks : 75

(Use a separate Answer Book for each group)

Group – A

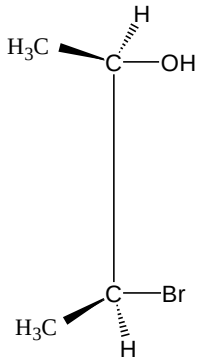
Answer **any five** questions from Question Nos.1 to 8 : [5 × 5]

1. a) Draw the orbital picture of acetonitrile (methyl cyanide) and triplet carbene indicating the state of hybridisation of carbon atoms.

   b) Resonance energy of benzene is 36 Kcal/mol. Explain. [3+2]

2. a) Draw all possible steroisomers of 2,3,4-tribromopentane [$H_3CH(Br)CH(Br)CH(Br)CH_3$] and state the relationship among themselves. Mark all the chiral centres as chirotopic, achirotopic, stereogenic and nonstereogenic as applicable.
   b) Write the necessary and sufficient condition for chirality. [4+1]

3. a) Draw the bond rotation energy diagram for 2-methylbutane (looking down the C_2-C_3 bond) with the Newman projections for each point.
   b) Convert the following molecule to Newman (staggered) and Fischer projection. [3+2]



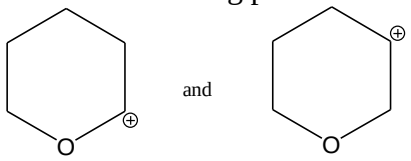
4. a) Draw the most stable conformation of 1,2-dibromoethane and 1,2-dihydroxyethane.
   b) What is the basic difference between conjugation and hyperconjugation?
   c) Between methyl benzene and tert-butylbenzene, which molecule has greater para-electron density. Provide the brief explanation. [2+1+2]

5. a) Addition of HBr to 1,3-butadiene at -15^oC yield A and at 40^oC give product B.
   (i) Give the structure of A and B.
   (ii) Draw an energy profile diagram and comment on kinetic and thermodynamic controlled products.

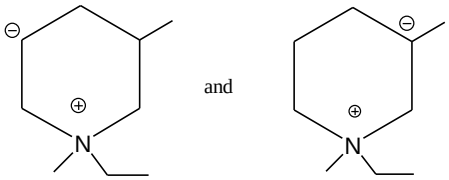
   b) Alkynes are less reactive than alkenes towards electrophilic addition reaction, why? [3+2]

6. a) Which species of each of the following pairs is more stable and why?

i)



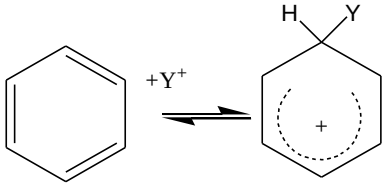
ii)



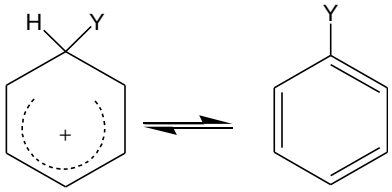
b) Arrange the following compounds in order of increasing dipole moment:
Toluene; m-dichlorobenzene, o-dichlorobenzene, p-dichlorobenzene. [3+2]

7. a) A two-step reaction with $K_H/K_D=7$ is given:

Step:1

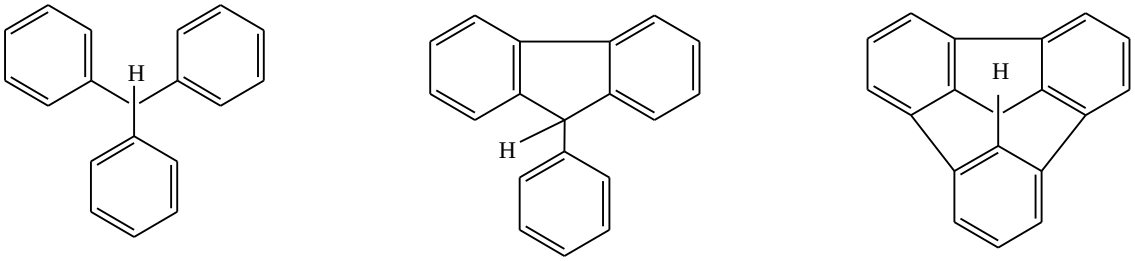


Step:2



Draw and explain the energy profile diagram for the reaction showing transition states(s) and intermediate. Indicate the rate determining step well. [3]

b) Compare the acidity of the following:



[2]

8. a) $CH_3CHClCH_3$ and $CD_3CHClCD_3$ show kinetic isotope effect during (i) substitution reaction using CH_3COOAg/CH_3COOH and (ii) elimination reaction using NaOMe/DMSO. Indicate the primary/secondary nature of kinetic isotope effect in the above reaction. explaining the variation of rates.

b) How does the Hammond postulate explain the greater selectivity for bromination vs. Chlorination of an alkane? [3+2]

Group – B

Answer **any five** questions from Question Nos. 9 to 16: [5 × 5]

9. a) State Pauli's exclusion principle and Hund's maximum spin multiplicity rule [3]
   b) Find out the ground state term symbol of the following electronic configurations :(i) p^5 and (ii) d^5. [2]

10. a) What is the maximum number of electrons that can be accommodated in the subshell represented by the following set of quantum numbers (i) n=2, l=1, (ii) n=5, l=3 (iii) n=3, l=2 and (iv) n=6 , l=0) [2]
    b) If an electron in Bohr orbit n=3 returns to n=1 in the Hydrogen atom, calculate the frequency of the photon that is emitted. The ionisation energy of the ground state of the H-atom is -2.17×10^{-11} erg/atom. [3]

11. a) Arrange the following subshells/sublevels according to the increase in energy : 5s,6p, 5d, 6d, and 4f. [2]
    b) Calculate the radius of the 1st Bohr orbit of Hydrogen atom after deriving the equation for radius. [3]

[Given value $\varepsilon_0 = 8.854\times10^{-12}\,kg^{-1}m^{-3}s^4A^2 h = 6.627\times10^{-34}\,J^2s^2\ \pi = 3.141, m = 9.1\times10^{-31}kg, e = 1.6\times10^{-19/}$ c]

12. a) Calculate the pauling 's electronegativity difference of H and F from the following bond energy data (K.cal/mole) in parenthesis against each, H-H(104), F-F (38) and H-F (134) [2]

    b) Why is the ionisation potential of an atom depends upon on some factors? Explain with an example of such factors. [3]

13. a) The F-F bond distance in F_2 is 141.3 pm. calculate the Allred-Rochow electronegativity of F-atom. [3]
    b) During ionisation of vanadium, the 4s electron comes but first and then the 'd' electron. Establish it using slater's rule. [2]

14. a) Using Born-Haber cycle, calculate the electron-attachment enthalpy for chlorine from the following data given below. (K.cal/mole) [3]
    ΔH_f (RbCl)= -102.9; ΔH_l(Rb)=95, ΔH_{sub}(Rb)=20.5 ΔHa(Cl_2)=54, and ΔH_L (RbCl)= -166

    b) Why Au^- (auride) is known but not Cu^-? [2]

15. a) Calculate the limiting radius of a crystal of cubic system. [3]
    b) The radius of F^- and K^+ are same, yet the hydration energy of F^- is greater than K^+. Explain [2]

16. a) Arrange and explain the solubility order of the following compounds $CaSO_4$, $MgSO_4$, $BaSO_4$ and $SrSO_4$. [2]
    b) What do you mean by p-type and n-type. semiconductor and explain it with examples. [3]

Group – C

Answer **any five** questions from Question Nos. 17 to 24: [5×5]

17. a) Distinguish between 'state function' and 'path function' with example. Explain why 'Adiabatic work' is a 'state function'. [2]
    b) Prove that cyclic rule for ideal gas whose state depends on P, V and T [3]

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$$

18. a) "In the indicator diagram of an ideal gas, adiabatic curve is steeper than isothermal curve." Illustrate. [2]
    b) One mole of an ideal monoatomic gas at 25^oC and 5 atm pressure is expanded adiabatically and reversibly. Calculate. (i) Final temperature (ii) Heat absorbed (iii) change in internal energy. [3]

19. a) Draw the T-S diagram for a Carnot cycle. [1]
    b) Derive the expression for efficiency of a Carnot cycle. involving ideal gas as the working substance. [4]
20. a) State Kelvin-planck and Clausius statement of second law of thermodynamics. [2]
    b) Show that they are equivalent. [3]

21. Starting from the TdS equation, show that $C_p - C_v = \frac{TV\alpha^2}{\beta}$ where the symbols carry their usual meaning. [5]
22. a) Define thermal equilibrium. [1]
    b) Prove that the area under the velocity distribution curve is unity at any temperature for any gas. [2]
    c) In which case the efficiency of a Carnot engine will be higher. — if the temperature of the source is increased by ΔT or the temperature of the sink is decrease by ΔT. [2]
23. a) Define degress of freedom and components in connection with Phase equilibrium. [2]
    b) Show that the greatest number of phases that can coexist in Equilibrium is one-component system is three. [3]
24. a) Write down the relations of Internal energy (U) and entropy (S) with volume (V) of the system. [1]
    b) Entropy of a system cannot be negative justify. [2]
    c) Will ΔS be positive or negative for the Isothermal process:
    N_2(gas,10 atm) $\rightarrow$ N_2 (gas, 1 atm) [2]

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