

(Time: Three Hours)

(Marks: 100)

Please check whether you have got the right question paper.

- N.B:
1. All questions are compulsory.
 2. Answers to the same questions must be written together.
 3. Figures to the right indicate full marks.
 4. The use of log table/non-programmable calculators is allowed.

Q.1 A. Select the correct option and complete the following sentences **12**
(any twelve):

- i) The van-der Waal's constant 'a' is expressed in the unit-----.
a) $\text{atm.lit}^{-2}.\text{mol}^{-2}$ b) atm.lit.mol^{-1} c) $\text{atm.lit}^{-1}.\text{mol}^{-1}$
- ii) The velocity for which the fraction of molecule is maximum is called -----.
a) maximum velocity b) most probable velocity
c) minimum velocity
- iii) Entropy of the medium ----- when salt is dissolved in water.
a) increases b) decreases c) remains constant.
- iv) If the pressure and absolute temperature of the 3 litre of a gas are doubled its volume will be -----.
a) 2L b) 3L c) 6L
- v) The value of equilibrium constant depends on-----.
a) temperature b) pressure c) concentration of reactants
- vi) A gas which follows all assumptions of kinetic theory of gases is called ----- gas.
a) non-ideal b) ideal c) real
- vii) Cations have _____ charges.
a) positive b) negative c) neutral
- viii) Reddish brown gas _____.
a) chlorine b) bromine c) iodine
- ix) The evolution of CO_2 can be detected by _____.
a) lime water b) starch water c) plain water
- x) HSO_4^- is an example of _____.
a) conjugated acid b) conjugated base c) amphiprotic ion

- xi) Acidic and basic character in non aqueous solvent is not explained by _____.
 a) Arrhenius concept b) Lowry Bronsted concept
 c) Lewis concept
- xii) Cu^+ is toxic when present in the body at concentration of _____ mg/kg of body weight.
 a) 5 b) 10 c) 15
- xiii) Bromination of propane gives _____.
 a) 1-bromopropane as major product
 b) 2-bromopropane as major product
 c) equal quantities of 1-bromopropane and 2-bromopropane as product
- xiv) The product of Wurtz reaction is _____.
 a) higher alkane b) lower alkane c) lower alkene
- xv) The products of ozonolysis of 2-butene are _____.
 a) 2 molecules of CH_3CHO
 b) 2 molecules of CH_3COCH_3
 c) 1 molecule of CH_3CHO and 1 molecule of CH_3COCH_3
- xvi) Oxymercuration-demercuration is a method for _____ of an alkene.
 a) hydrogenation b) hydration c) hydroxylation
- xvii) The ease of dehydration of alcohols is _____.
 a) $3^\circ > 2^\circ > 1^\circ$ b) $2^\circ > 3^\circ > 1^\circ$ c) $1^\circ > 2^\circ > 3^\circ$
- xviii) Hydroxylation of alkenes using OsO_4 is a _____ addition.
 a) anti b) trans c) syn

B. State whether the following statements are true or false (**any three**).

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- At equilibrium free energy does not changes.
- The free path is the distance travelled by the molecule before collision.
- According to Pearson, Class 'a' metal ions are hard acids.
- Sulphur dioxide is basic in nature.
- Addition of HBr to propene in absence of peroxides follows Anti-Markownikoff rule.
- Relative reactivities of halogens is $\text{I}_2 > \text{Br}_2 > \text{Cl}_2$.

- C. Match the following columns (**any five**): **5**
- | | |
|-------------------------------------|------------------------|
| i) Avogadro law | a) carbocation |
| ii) Gibbs free energy | b) hard acid |
| iii) $\text{Co}(\text{SCN})_4^{-2}$ | c) carbanion |
| iv) I^- | d) $V \propto n$ |
| v) E_1 mechanism | e) blue complex |
| vi) E_1cB mechanism | f) state function |
| | g) carbon free radical |
| | h) soft base |

Q.2Answer **any four** of the following:

- A. Define Joule-Thompson effect. Show that Joule Thompson effect is isoenthalpic. **5**
- B. Explain the deviation of gases from ideal behaviour using van-der Waal's equation. **5**
- C. The free energy change for a reaction at 300 K is -67KJ, the enthalpy change is -42KJ. Calculate the entropy change of the reaction. What will be ΔG of the reaction at 350K? **5**
- D. What is meant by equilibrium constant? Derive the relation between K_p and K_c . **5**
- E. Derive Van-der Waal's equation. **5**
- F. For a reaction $\text{CO}_{(g)} + 2\text{H}_{2(g)} \rightleftharpoons \text{CH}_3\text{OH}_{(g)}$, calculate the value of K_c and K_p at 327 °C. The equilibrium concentration of H_2 , $\text{CO}_{(g)}$, and $\text{CH}_3\text{OH}_{(g)}$ are 0.06mol.dm^{-3} , 0.02mol.dm^{-3} and 0.02mol.dm^{-3} respectively. (Given: $R=8.314\text{J.K}^{-1}.\text{mol}^{-1}$). **5**

Q.3Answer **any four** of the following:

- A. How will you detect the presence of ions in the given sample using reagent paper sulphites, sulphides and Ni^{+2} . **5**
- B. Explain the term precipitation equilibria in qualitative analysis. **5**
- C. What is ionic strength? Discuss it's relation with activity of ions. **5**
- D. Explain classification of substances of acids and bases of solvent system. **5**
- E. What are the different types of Lewis acids and bases? Give examples. **5**
- F. What are the limitations of Bronsted-Lowry concept? **5**

Q. 4

Answer **any four** of the following:

- A. What is a β -elimination? Explain E_2 mechanism with a suitable example. **5**
- B. i) How would you prepare methyl iodide from methane? Why is the yield of the reaction low and how can it be increased? **3**
 ii) Explain the reactivity-selectivity principle as applied to halogenation of alkanes. **2**
- C. Write a reaction to show the action of 20% H_2SO_4 on 2-methyl-2-butanol. Predict the major and minor products. Give reasons for your answer. **5**
- D. Give stepwise reactions for the hydroboration-oxidation of ethane. Name the rule according to which addition takes place. **5**
- E. Explain why :- **5**
 i. Terminal alkynes are weakly acidic in nature.
 ii. Tertiary alkyl halides prefer to undergo E_1 mechanism as compared to primary alkyl halides.
- F. Write short notes on the following: **5**
 i. Diels Alder reaction
 ii. Peroxide effect

Q.5

Answer **any four** of the following:

- A. State Le-Chatelier principle. How does it explain the effect of change of variables on the equilibrium? **5**
- B. 11.0 g of CO_2 occupied $1.5 dm^3$ at 298K. Calculate the pressure exerted by the gas using ideal gas equation and Van-der Waal's equation. **5**
 Given: $R=8.314 Nm K^{-1} mol^{-1}$, $a = 0.3640 Nm^4 mol^{-2}$, $b = 4.267 \times 10^{-5} m^3 mol^{-1}$, molar mass of $CO_2 = 44$.
- C. What are dry and wet test? Explain. **5**
- D. Calculate the pH of solution when $10 cm^3$ of 0.1M NaOH added to 0.1M HCl, using following stages of titration. **5**
 a) $5.0 cm^3$ of NaOH added
 b) $9.9 cm^3$ of NaOH added
- E. What is a conjugated diene? Explain 1,2- and 1,4- addition reactions to conjugated dienes with a suitable example. **5**
- F. Explain the mechanism of oxymercuration-demercuration reaction. **5**
