

Roll No.

Exam Code : M-23

Subject Code—59306

B. Sc. EXAMINATION

(Main & Reappear) (Batch 2018 Onwards)

(Second Semester)

CHEMISTRY

CCL-204

Physical Chemistry-I

(Chemical Energetics and Equilibria)

Time : 3 Hours

Maximum Marks : 80

Note : Attempt *Five* questions in all, selecting *one* question from each Unit. Q. No. 1 is compulsory. All questions carry equal marks.

1. (a) What are extensive and intensive properties ? Give examples. 2
- (b) What is bond dissociation energy ? 2
- (c) Define equilibrium constant. Give its formula. 2

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- (d) Under what conditions all types of equilibrium constant become equal ? 2
- (e) What are amphoteric substances ? Give examples. 2
- (f) What are conjugate acid-base pair ? Explain with examples. 2
- (g) The aqueous solutions of salts of strong acids and strong bases are neutral, why ? 2
- (h) What is hydrolysis constant ? 2

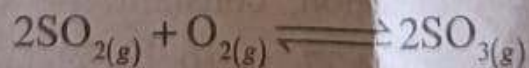
Unit I

2. (a) Derive the relation $TP^{(1-r)/r} = \text{constant}$. 6
- (b) Explain different statements of second law of thermodynamics. 4
- (c) Determine the relation to find the absolute entropy of liquids and gases. 6
3. (a) Derive Kirchhoff's equation. 6
- (b) What is third law of thermodynamics ? Derive Nernst heat theorem. 4

- (c) Derive Gibbs-Helmholtz equation.
Discuss its applications. 6

Unit II

4. (a) Derive the relationship between k_p and k_c . 4
(b) What is chemical potential ? Derive the expression for variation of chemical potential with pressure. 6
(c) Derive the relation to show variation of equilibrium constant with temperature by Vant Hoff's equation. 6
5. (a) Derive the integrated form of Clausius-Clapeyron equation. 6
(b) The equilibrium constant k_p for a reaction is 9.0 at 373 K and 12.0 at 473 K. Calculate the heat of reaction. 4
(c) What is Le-Chatelier's principle ? Discuss the effect of temperature, pressure and concentration on the following reaction :



$$\Delta H = -189 \text{ kJ/mole. } 6$$

Unit III

6. (a) What is degree of Ionisation ? Explain the factors affecting the degree of dissociation. 4
- (b) Explain Lewis concept of acid and base with examples. Also discuss its limitations. 4
- (c) Write short notes on the following : 8
- (i) Common ion effect
- (ii) Degree of ionisation of a weak acid.
7. (a) What is K_w ? Determine the value of pK_w at (i) 25°C (ii) Greater than 25°C . 4
- (b) What is dissociation constant of an acid ? How is it related to the strength of an acid ? 4
- (c) Define pH and pKa. Calculate the pH of a solution whose hydronium ion concentration is $3.16 \times 10^{-3} \text{ M}$. 4
- (d) The ionisation constant of 0.001 M aniline is 4.27×10^{-10} . Calculate the degree of ionisation of aniline. 4

Unit IV

8. (a) Derive an expression for degree of hydrolysis and pH for salt of weak acid and strong base. 8
- (b) Calculate the pH of a mixture containing 0.01 M acetic acid and 0.03 M sodium acetate solution. pK_a of the solution is 4.8. 4
- (c) What is solubility product ? Give its applications. 4
9. (a) Write notes on the following : 8
- (i) Buffer solutions
- (ii) Buffer action of basic buffers.
- (b) The solubility of AgBr at 293 K is 1.84×10^{-6} mole/litre. Calculate the value of solubility product. 4
- (c) Explain, why the salts of strong acid and weak base undergo cationic hydrolysis. 4

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CHEMISTRY

CCL-205

Organic Chemistry-II

(Functional Group Organic Chemistry)

Time : 3 Hours

Maximum Marks : 80

Note : Attempt *Five* questions in all, selecting *one* question from each Unit. Q. No. 1 is compulsory. All questions carry equal marks.

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(Compulsory Question)

1. (i) ✓ Out of the following alkyl halide, which alkyl halide undergo Friedel-Craft alkylation without rearrangement ? Justify your answer :
- (a) $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{Cl}$
- (b) $\text{CH}_3\text{CH}_2\text{CHClCH}_3$.
- (ii) Explain, why benzene undergo electrophilic substitution reactions instead of usual addition reaction ?
- (iii) Prepare phenol from benzene diazonium chloride.
- (iv) Explain, why phenols do not undergo substitution of the OH group like alcohols ?
- (v) Chlorobenzene reacts with sodamide in presence of liq. NH_3 but 2-bromo-1, 3-dimethylbenzene fails to react. Explain ?
- (vi) Explain Saytzeff's rule with example.

(vii) Semicarbazide has two —NH_2 group that could react with a carbonyl compound. Explain which —NH_2 group of semicarbazide reacts with carbonyl group ?

(viii) Why formaldehyde does not give aldol condensation ? 2 each

Unit I

2. (a) Explain with mechanism, why Friedel-Craft reaction between benzene and *n*-propyl chloride in presence of anhy. AlCl_3 gives considerable quantity of isopropyl benzene ? 6

(b) Explain with mechanism Sulphonation of benzene. 6

(c) How will you prepare benzene from :

(i) Benzene sulphonic acid

(ii) Phenol ? 2+2=4

3. (a) Discuss the general mechanism of electrophilic substitution reaction of benzene. Write the evidences in favour of this mechanism. 6+2

(b) Explain the role of catalyst in electrophilic aromatic substitution reaction. 4

(c) What happens when : 2+2

(i) *o*-xylene is heated with hot alkaline KMnO_4

(ii) Toluene is subjected to oxidation by chromyl chloride ?

Unit II

4. (a) Explain the mechanism by which nucleophilic substitution reaction in *p*-nitro chlorobenzene takes place ? How does it differ from nucleophilic substitution reaction in case of chlorobenzene ? 8

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(b) Point out differences between SN^1 and SN^2 reactions. 6

(c) What are SN_i (substitution nucleophilic internal) reaction ? Explain with example. 2

5. (a) *m*-Chlorotoulene when treated with $NaNH_2$ in liq. NH_3 give all the three toluidines. Explain. 4

(b) How will you prepare *n*-propyl bromide from : 2+2

(i) Alkene

(ii) Alcohol ?

(c) Explain with example how size of the base/nucleophile is helpful in determining whether secondary alkyl halide will undergo substitution by SN^2 mechanism or elimination reaction ? 4

(d) Out of alkyl and aryl halide which one is less reactive towards nucleophilic substitution reaction and why ? 4

Unit III

6. (a) Explain the following reactions with mechanism :

4+4

(i) Pinacol - Pinacolone rearrangement

(ii) Esterification reaction.

(b) Discuss the cleavage of *tert*-butyl methyl ether with HI.

4

(c) Explain the oxidation of primary alcohol with acidified KMnO_4 and PCC.

2+2

7. (a) Explain Bouveault-Blanc reduction with mechanism.

6

(b) Explain, why electrophilic substitution reaction in phenols occurs at *ortho* and *para* position ?

6

(c) Write the chemical equation for :

2+2

(i) Reimer-Tiemann reaction

(ii) Schotten-Bauman reaction.

Unit IV

8. (a) How will you convert : 2+2

(i) Benzaldehyde to styrene,

(ii) Benzoyl chloride to benzaldehyde ?

(b) Discuss the general mechanism of nucleophilic addition reactions in carbonyl compound. Also explain the role of acid catalyst in nucleophilic addition reaction. 4+4

(c) Aromatic carbonyl compounds are less reactive than their aliphatic counterpart. 4

9. (a) Explain with mechanism : 6+6

(i) Clemmensen reduction

(ii) Aldol condensation in basic medium.

(b) Which chemical test is used to distinguish between 2-pentanone and 3-pentanone ? Explain the chemistry behind the test. 4