SEMESTER-IV

Core Paper – V GENERAL CHEMISTRY IV (90 Hrs) 5 Credits

Unit 1: APPLICATIONS OF THERMODYNAMICS TO EQUILIBRIUM (15 HOURS)

1.1 Chemical equilibrium –thermodynamic derivation of equilibrium constant- equilibrium constant for various homogeneous and heterogeneous equilibria.

1.2 The relationship between Equilibrium constant and free energy change – Vant Hoff reaction isotherm –The direction of chemical change.

1.3 K_p and K_c for the formation and dissociation equilibria of NH_3, $CaCO_3$ and PCl_5

1.4 Variation of equilibrium constant Kp and Kc with temperature (Vant Hoff equation or vant hoff isochore) – applications. Variation of equilibrium constants with pressure and catalyst and the principle of microscopic reversibility.

1.5 Le-Chatelier principle-Factors affecting chemical equilibrium (Concentration, temperature, pressure and addition of inert gases) –a case study of synthesis of ammonia

1.6 Third Law of Thermodynamics: Nernst heat theorem – Statement of III law – Evaluation of absolute entropy from heat capacity data with examples(N_2 and O_2). Exception to III law-The concept of residual entropy and its calculation from Boltzman law for ortho and para hydrogen, CO, N_2O and ice.

Unit 2: PHASE STUDY (15 HOURS)

2.1 Definition of terms in the phase rule –phase, components and degrees of freedom with examples.

2.2 Equilibrium- physical equilibrium of one component system - Clapeyron equation and Clausius – Clapeyron equation for various phase equilibria.

2.3 Derivation of phase rule- Phase diagram and Application of phase rule to one component system- water and CO_2 – super cooling, sublimation.

2.4 Reduced phase rule for condensed systems- Phase diagram of two component systems – solid liquid equilibria, simple eutectic (Pb-Ag & Bi-Cd), desilverisation of lead – Compound formation with congruent melting point. (Mg-Zn) and incongruent melting point (Na-K). Freezing mixtures – $FeCl_3$-H_2O and $CuSO_4$-H_2O systems.

UNIT 3: d-block Elements (15 HOURS)

3.1 Definition of a transition element-General periodic trend- study of First transition series- Electronic configuration, metallic character, atomic radii, standard electrode potential, stability of different oxidation states of transition metal ions in aqueous solution, reactivity, oxidation states, formation of coloured complexes, magnetic properties, catalytic properties, formation of non-stoichiometric compounds, interstitial compounds, alloy formation. Coinage metals-Cu, Ag and Au.

3.2 Metallurgy : Definition-Classification of ores- metallurgical processes-: concentration of the ore-hand picking, gravity separation (Wifley table method, hydraulic classifier), magnetic separation- Electrostatic separation, froath floatation-Chemical separation; calcinations, roasting; reduction to free metal-smelting- reduction by controlled heating in air (auto reduction)-reduction by aluminium. Electrometallurgy-Amalgamation method, hydrometallurgy. Fluxes- acidic and basic. Refining of metals- Zone refining, electrolytic refining, vapour phase, *van Arkel* process, vacuum arc furnace refining.

3.3 Extraction of titanium from Rutile and platinum from Sperrylite (Ni ore). Alloys and uses of Ti and Zr.

UNIT 4: Introduction to Coordination chemistry (15 HOURS)

4.1 Types of ligands- IUPAC Nomenclature- Structural Isomerism- ionization, hydrate, linkage, ligand and coordination isomerism.

4.2 Stereoisomerism-geometrical and optical isomerism of four and six coordinated complexes. Geometrical Isomerism: four coordinated complexes- $[MA_2B_2]^{n\pm}$, $[MA_2BC]^{n\pm}$, $[MABCD]^{n\pm}$, $[M(AB)_2]^{n\pm}$. Six coordinated complexes-$[MA_4B_2]^{n\pm}$, $[MA_4BC]^{n\pm}$, $[MA_3B_3]^{n\pm}$, $[MABCDXY]^{n\pm}$, $[M(AA)_2(B)_2]^{n\pm}$, $[M(AA)_2BC]^{n\pm}$, $[M(AB)_3]^{n\pm}$.

4.3 Optical Isomerism: four coordinated complexes- $[M(AB)_2]^{n\pm}$. Six coordinated complexes- $[M(AA)_3]^{n\pm}$, $[M(AA)_2X_2]^{n\pm}$, $[M(AA)_2XY]^{n\pm}$, $[M(AA)X_2Y_2]^{n\pm}$.

UNIT 5: Carboxylic acids (13 HOURS)

5.1 Preparation of monocarboxylic acids- by oxidation of alkenes with $KMnO_4$, by oxidation of alkyl benzenes, preparation using diazomethane, Arndt-Eistert synthesis, conversion of acid to acid chlorides, alcohols, Anhydrides, Esters and Amides.

5.2 Reactions of carboxylic acids – Esterification by diazomethane, Hell Volhard Zelinski reactions.

5.3 Active methylene compounds - Preparation and Synthetic applications of diazomethane . AAE and cyanoacetic ester.

5.4 Unsaturated acids: Preparation of Acrylic acid from propanoic acid, crotonic acid from β-hydroxy butyric acid , Cinnamic acid from malonic ester and cyanoacetic ester.

5.5 Preparation of hydroxy acids - Reformatsky reaction - action of heat on α, β, γ & δ hydroxy acids.

5.6 Dicarboxylic acids – Nomenclature – General preparation of dicarboxylic acids -Succinic and Glutaric acids - Preparation of adipic acid from cyclohexanone- preparation of phthalic acid from naphthalene. Conversion of adipic acid, phthalic acids to their anhydrides.

UNIT 6: Organic Nitrogen compounds and Heterocyclic compounds (12 HOURS)

6.1 Amines –Classification - Preparation of amines from acids (Schmidt reaction)-from alkyl halides, Gabriel's Phthalimide synthesis, Hofmann Bromamide reaction –Reactions of amine - Distinction between primary, secondary and tertiary amines -Carbylamine test, Hinsberg test, with HNO_2, Schotten – Baumann Reaction.

6.2 Nitro compounds – Preparation - Difference between alkyl nitrites and nitro alkanes, distinction between primary, secondary and tertiary nitro compounds. Reduction of nitrobenzene in acidic and alkaline medium.

6.3 Five membered Heterocyclic compounds - Furan, Pyrrole, and thiophene - Hybridization, Basicity/Acidity, Orientation and aromaticity, Preparation, Reactivity towards electrophillic and nucleophillic substitution reactions - Diels alder reaction with furan.

6.4 Six-membered heterocycles - Pyridine-Aromatic character,structure, Hybridization, basicity/acidity. Orientation and reactivity- Preparation - electrophilic and nucleophilic

substitution reactions. Chichibabin reaction, Zeigler alkylation. Pyridine-N- oxide, preparation and importance.

References:

1. Principles Of Physical Chemistry , Puri, Sharma Pathania
2. Physical Chemistry: Robert G. Mortimer
3. W. Atkins Advanced Physical Chemistry Oxford Press. 1990
4. Physical Chemistry 4th Edition, Robert J. Silbey , Robert A. Alberty , Moungi G. Bawendi
5. A Text book of Physical Chemistry, A S Negi, S C Anand
6. Physical Chemistry, J. Moore- 4th edn
7. Physical Chemistry, Glasston
8. A text book of physical chemistry: KL Kapoor (Volume 2,3) (Thermodynamics)
9. Physical Chemistry, Gilbert W. Castellan, 3rd edition (Thermodynamics)
10. Phase rule and its applications, Suruchi, Sheza Zaidi
11. Puri B.R., Sharma, L.R., Kalia, K., Principles of Inorganic Chemistry 23rd edition, New Delhi, Shoban Lal Nagin Chand & Co., (1993)
12. Lee J. D., Concise Inorganic Chemistry, UK, Blackwell science (2006)
13. Madan, R.D., Tuli,G.D Malik.W.U Principles of Inorganic Chemistry, S.Chand, 1999.
14. Inorganic Chemistry III Edition, by Miessler, G. L. and Tarr, D. A. 2004.
15. Morrison R.T. and Boyd R.N., Organic Chemistry (6th edition), New York, Allyn & Bacon Ltd., (1976)
16. Bahl B.S. and Arun Bahl. Advanced Organic Chemistry, (12th edition), New Delhi, Sultan Chand & Co., (1997)

SEMESTER III AND IV

Core Paper VI MAJOR PRACTICALS II Volumetric Analysis and Inorganic preparation

CREDITS: 2 (90 hrs)

Acidimetry and Alkalimetry

1. Estimation of sodium hydroxide using standard Sodium carbonate.
2. Estimation of borax using standard Sodium carbonate.
3. Estimation of mixture of Sodium hydroxide and Sodium carbonate using standard Sodium carbonate*****.
4. Estimation of Oxalic acid using standard Potassium hydrogen phthalate.
5. Estimation of total hardness of water*.

Permanganometry

6. Estimation of Ferrous ammonium sulphate using standard Oxalic acid.
7. Estimation of Calcium using standard oxalic acid solution.

Iodometry

8. Estimation of Cu (II) sulphate using standard Potassium dichromate.
9. Estimation of Potassium dichromate using standard Cu (II) sulphate.

Iodimetry

10. Estimation of Arseneuos oxide using standard Arseneous oxide.

Argentometry

11. Estimation of Chloride by Mohr's method.

Complexometry

12. Estimation of Magnesium sulphate using EDTA as link and Zinc sulphate as standard.

Dichrometry

13. Estimation of Ferrous ion using standard Oxalic acid

Precipitation Titrations

14. Estimation of Zinc using standard Potassium ferrocyanide.
15. Estimation of Barium by back titration method*****.

*** Not for examination.**

Preparation of Inorganic Compounds

1. Preparation of Ferrous Ammonium Sulphate
2. Preparation of Sodium thiosulphate penta hydrate
3. Preparation of Manganese (II) sulphate
4. Preparation of Sodium ammonium hydrogen phosphate.

Reference:

1. Vogels Text Book of Inorganic Quantative Analysis.
2. Basic Principles of Practical Chemistry by Venkateswaran, V.; Veeraswamy, R.; Kulandaivelu, A. R. 1993, Sultan Chand & Sons.
3. Practical Chemistry for UG by Sundaram, Krishnan and Raghavan.