Photophysical pathways- Jablonski diagram, Radiative and Radiationless transitions, selection rules. Photochemical kinetics of unimolecular and bimolecular processes. Quenching-collisions in the gas phase and in solution (Stern-Volmer equation). Photoisomerization, photo Fries rearrangement and Norrish type cleavage reactions with specific examples.

REFERENCES:-

1. Text book of Polymers- F.W.Billmeyer (Wiley)
2. Contemporary Polymer Chemistry-H.R. Allcock and F.W. Lampe (Prentice Hall).
3. Polymer Science and Technology-J.R. Frird (Prentice Hall).
4. Polymer Science: V.R. Gowariker, N.V.Viswanathan&T.Sreedhar.
5. Principles of Polymer Science- P.Bahadur and N.V.Sastry (Narosa Publishers)
6. Fundamentals of Photochemistry – Rohatgi and Mukherje (New Age Bangalore), 2000.
7. Physical Chemistry, 5^{th} Ed., - Atkins (ELBS) 1995.
8. Photochemistry-Gurdeep Raj, Goel Publishing House, 2^{nd} Edition, 1991.
9. Photochemistry, Carol E Wayne & Richard P. Wayne, Oxford Univ Press, , 1996

AC S 504: ORGANOMETALLIC CHEMISTRY

COURSE OUTCOME:

- The students will learn Historical development of Organometallic compounds, Classification,
- Nomenclature, Transition metal to carbon multiple bonded compounds, Transition metal-carbon pi complexes,
- Catalysis by organometallic compounds, Homogeneous catalysis by organometallics, Hydrocarbonylation of olefins,
- Ziegler-Natta catalyst and Water Gas Shift reactions in this course.

UNIT- I: **[12 Hours]**

Historical development- classification and nomenclature, bond energies and stability. 16- and 18-electron rules. Transition metal alkyls and aryls- types, routes of synthesis, stability and decomposition pathways,. Nucleophilic and electrophilic cleavage of metal-carbon sigma bonded compounds. Alkane activation.

Transition metal to carbon multiple-bonded compounds- carbenes, carbynes, synthesis, nature of bond, agostic interactions, structural characteristics and reactivity. Transition metal hydrides – synthetic routes, properties, structure and reactivity, synthetic applications.

UNIT-II: **[12 hours]**

Transition metal-carbon pi complexes: Preparative methods, nature of bonding, structural features of olefinic, acetylenic, allylic, butadiene, cyclobutadiene, η^5-cyclopentadienyl, η^6-benzene and other arenes, cycloheptatriene and cyclooctatetraene complexes. Important reactions relating to nucleophilic and electrophilic attack on ligands. Fluxional isomerism in olefin, allyl, dienyl and cyclopentadienyl complexes. Carbene complexes and metallacycles, arene complexes. Isolobal concept.

UNIT- III: **[12 hours]**

Catalysis by organometallic compounds: oxidative addition, insertion, deinsertion and reductive elimination reactions. Homogeneous catalysis by organometallics- hydrogenation, hydrosilation, hydrocyanation and isomerization of olefins, immobilisation of homogeneous hydrogenation catalysts, Hydrocarbonylation of olefins (oxo reaction–cobalt and rhodium

oxo catalysts), Wacker process. Carbonylation of alcohols- Monsanto acetic acid process. Polymerization of olefins and acetylenes: Ziegler-Natta catalyst systems. Fischer – Tropschreaction , Water Gas Shift reactions.

References:

1. J.P.Collman, L.S.hegedus, J.R.Norton and R.G.Finke: Principles and Applications of 2.Organotransition Metal Chemistry, University Science Books, 1987.
2. R.C.Mehrotra and A.Singh: Organometallic Chemistry, New Age International, 1999.
3. R.H.Crabtree:Organometallic Chemistry of Transition Metals, Wiley , 1999.
4. F.A.Cotton and G.Wilkinson : Advanced Inorganic Chemistry, Wiley, 1991.
5. Organometallic Chemistry, G. S. Sodhi, Ane books Pvt Ltd Edition 2009.

AC S 505: INORGANIC PHOTOCHEMISTRY

COURSE OUTCOME:

- This course will bring about the knowledge to students in the field of Inorganic Photochemistry like Flash photolysis,
- Photochemical reactions, Excited states of metal complexes,
- Energy transfer in metal complexes,
- Charge transfer spectra, Application of redox processes.

UNIT – I **(12 Hrs.)**

Absorption, excitation, photochemical laws, quantum yield, electronically excited states-life times- measurements of the times. Flash photolysis, stopped flow techniques. Energy dissipation by radiative and non-radiative processes, absorption spectra, Franck-Condon principle, photochemical stages – primary and secondary processes. Properties of Excited States: Structure, dipole moment, acid-base strengths, reactivity

UNIT – II **(12 Hrs.)**

Excited states of metal complexes: comparison with organic compounds, electronically excited states of metal complexes, charge-transfer spectra, charge transfer excitations methods for obtaining charge-transfer spectra. Liquid Field Photochemistry Photosubstitution, photooxidation and photoreduction, lability and selectivity, zero vibrational levels of ground state and excited state, energy content of excited state, zero-zero spectroscopic energy, development of the equations for redox potentials of the excited states.

UNIT – III **(12 Hrs.)**

Energy transfer under conditions of weak interaction and strong interaction-exciplex formation; Conditions of the excited states to be useful as redox reactions, excited electron transfer, metal complexes as attractive candidates (2,2'-bipyridinie and 1, 10-phenonthrolin complexes:. Illustration of reducing and oxidizing character of Ruthenium^{2+}(bipyridyl complex, comparison with Fe(bipy)s: role of spin-orbit coupling-life time of these complexes. Application of redox processes of electronically excited sates for catalytic purposes.

References:

1. A.W. Adamson and P.D. Fleischauer-concepts of Inorganic Photochemistry, Wiley
2. Inorganic Photochemistry, J.Chem.Educ., vol.60, no.10, 1983
3. Progress in Inorganic Chemistry, vol.30, Ed.S.J.Lippard, Wiley.
4. Coordination Chem.Revs., 1981, vol 39:121, 131;1975, 15:321, 1990, 97:313.V.
5. Balzari and V. Carassiti, Photochemistry of Coordination Compounds, Academic.