

Semester VI

CHE-HC-6016: INORGANIC CHEMISTRY-IV

(Credits: Theory-04, Lab-02)

Theory: 60 Lectures

Course Objective: The unit on reaction mechanism is included for the students to get acquainted with the kinetic and thermodynamic factors governing the reaction path and stability of inorganic compounds.

Organometallic compounds are introduced so as to apprise students about the importance of metal carbon bond to form complexes and their application as catalysts. Students are expected to learn factors leading to stability of organometallic compounds, their synthesis, reactivity and uses.

Qualitative inorganic analysis is included to give students an idea and hands on experience of application of inorganic chemistry. Students should learn how differential reactivity under different conditions of pH can be used to identify variety of ions in a complex mixture.

Experiments related to synthesis and characterization of coordination compounds are included to supplement their theoretical knowledge.

Learning Outcome: By studying this course the students will be expected to learn about how ligand substitution and redox reactions take place in coordination complexes.

Students will also learn about organometallic compounds, comprehend their bonding, stability, reactivity and uses. They will be familiar with the variety of catalysts based on transition metals and their application in industry.

On successful completion, students in general will be able to appreciate the use of concepts like solubility product, common ion effect, pH etc. in analysis of ions and how a clever design of reactions, it is possible to identify the components in a mixture.

With the experiments related to coordination compound synthesis, calculation of $10Dq$, controlling factors etc. will make the students appreciate the concepts of theory in experiments.

Mechanism of Inorganic Reactions

Introduction to inorganic reaction mechanisms. Substitution reactions in square planar complexes, Trans-effect, theories of trans effect, Mechanism of nucleophilic substitution in square planar complexes, Thermodynamic and Kinetic stability, Kinetics of octahedral substitution, Ligand field effects and reaction rates, Mechanism of substitution in octahedral complexes. Electron transfer reactions.

(18 Lectures)

Organometallic Compounds

Definition and classification of organometallic compounds on the basis of bond type.

Concept of hapticity of organic ligands.

Metal carbonyls: 18 electron rule, electron count of mononuclear, polynuclear and substituted metal carbonyls of 3d series. General methods of preparation (direct combination, reductive carbonylation, thermal and photochemical decomposition) of mono and binuclear carbonyls of 3d series. Structures of mononuclear and binuclear carbonyls of Cr, Mn, Fe, Co and Ni using VBT. π -acceptor behaviour of CO (MO diagram of CO to be discussed), synergic effect and use of IR data to explain extent of back bonding. Zeise's salt: Preparation and structure, evidences of synergic effect and comparison of synergic effect with that in carbonyls.

Metal Alkyls: Important structural features of methyl lithium (tetramer) and trialkyl aluminium (dimer), concept of multicentre bonding in these compounds. Role of triethylaluminium in polymerisation of ethene (Ziegler Natta Catalyst). Species present in ether solution of Grignard reagent and their structures, Schlenk equilibrium.

Ferrocene: Preparation and reactions (acetylation, alkylation, metallation, Mannich

condensation). Structure and aromaticity. Comparison of aromaticity and reactivity with that of benzene.

(22 Lectures)

Transition Metals in Catalysis

Study of the following industrial processes and their mechanism:

1. Alkene hydrogenation (Wilkinson's Catalyst)
2. Hydroformylation (Co catalysts)
3. Wacker Process
4. Synthetic gasoline (Fischer Tropsch reaction)
5. Synthesis gas by metal carbonyl complexes

(10 Lectures)

Theoretical Principles in Qualitative Inorganic Analysis (H₂S Scheme)

Basic principles involved in analysis of cations and anions and solubility products, common ion effect. Principles involved in separation of cations into groups and choice of group reagents. Interfering anions (fluoride, borate, oxalate and phosphate) and need to remove them after Group II.

(10 Lectures)

Recommended Books:

1. Vogel, A.I. *Qualitative Inorganic Analysis*, Longman, 1972.
2. Svehla, G. & Sivasankar, B., *Vogel's Qualitative Inorganic Analysis*, 7th Ed., Prentice Hall, 2012.
3. Cotton, F.A., Wilkinson, G. and Gaus, P. L., *Basic Inorganic Chemistry*, 3rd Ed., Wiley, 2007.
4. Cotton, F.A. & Wilkinson, G., *Advanced Inorganic Chemistry*. 6th Ed., Wiley-VCH, 2007.
5. Huheey, J. E., Keiter, E. A., Keiter, R. L., Medhi, O. K., *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th Ed., Pearson Education India, 2006.
6. Sharpe, A.G. *Inorganic Chemistry*, 4th Indian Reprint (Pearson Education) 2005
7. Douglas, B.E. and Mc Daniel, D.H., *Concepts and Models of Inorganic Chemistry*, 3rd Ed. Wiley India, 2006.
8. Greenwood, N.N. & Earnshaw, A., *Chemistry of the Elements*, 2nd Ed., Elsevier India, 2010.
9. Lee, J. D., *Concise Inorganic Chemistry*, 5th Ed., Oxford University Press, 2008.
10. Powell, P. *Principles of Organometallic Chemistry*, Chapman and Hall, 1988.
11. Shriver, D.D. & Atkins, P., *Inorganic Chemistry 2nd Ed.*, Oxford University Press, 1994.
12. Basolo, F. & Person, R. *Mechanisms of Inorganic Reactions: Study of Metal Complexes in Solution* 2nd Ed., John Wiley & Sons Inc; NY.
13. Purcell, K.F. & Kotz, J.C., *Inorganic Chemistry*, W.B. Saunders Co. 1977
14. Miessler, G. L. & Tarr, D. A., *Inorganic Chemistry* 4th Ed., Pearson, 2010.
15. Crabtree, Robert H. *The Organometallic Chemistry of the Transition Metals*. j New York, NY: John Wiley, 2000.
16. Spessard, Gary O., & Gary L. Miessler. *Organometallic Chemistry*. Upper Saddle River, NJ: Prentice-Hall, 1996.

LAB

60 Lectures

- Qualitative semimicro analysis of mixtures containing 3 anions and 3 cations. Emphasis should be given to the understanding of the chemistry of different reactions. The following radicals are suggested: CO_3^{2-} , NO_2^- , S^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, CH_3COO^- , F^- , Cl^- , Br^- , I^- , NO_3^- , BO_3^{3-} , $\text{C}_2\text{O}_4^{2-}$, PO_4^{3-} , NH_4^+ , K^+ , Pb^{2+} , Cu^{2+} , Cd^{2+} , Bi^{3+} , Sn^{2+} , Sb^{3+} , Fe^{3+} , Al^{3+} , Cr^{3+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+}
- Mixtures should preferably contain one interfering anion, **or** insoluble component (BaSO_4 , SrSO_4 , PbSO_4 , CaF_2 or Al_2O_3) **or** combination of anions e.g. CO_3^{2-} and SO_3^{2-} , NO_2^- and NO_3^- , Cl^- and Br^- , Cl^- and I^- , Br^- and I^- , NO_3^- and Br^- , NO_3^- and I^- .
- Spot tests should be done whenever possible.
- Synthesis of ammine complexes of Ni(II) and their ligand exchange reactions involving bidentate ligands like acetylacetonate, dimethylglyoxime, glycine, etc.
- Preparation of acetylacetonate complexes of $\text{Cu}^{2+}/\text{Fe}^{3+}$.
- Controlled synthesis of two copper oxalate hydrate complexes: kinetic vs. thermodynamic factors.
- Determination of ϵ_{max} value from UV-visible spectra of complexes.
- Measurement of 10 Dq by spectrophotometric method, verification of spectrochemical series.

Recommended Books

1. Vogel's *Qualitative Inorganic Analysis*, Revised by G. Svehla.
 2. Marr, G. and Rockett, R.W. *Practical Inorganic Chemistry*, Van Nostrand Reinhold. 1972.
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