KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Established Under Section 3 of UGC Act 1956)

Coimbatore – 641 021.

SYLLABUS-B.Sc CHEMISTRY

16CHU402 **INORGANIC CHEMISTRY IV** **4H 4C**
(Organometallic Chemistry)

Instruction Hours/week:L:4 T:0 P:0 **Marks: Internal: 40 External: 60 Total:100**

Scope

The course deals with theoretical Principles in Qualitative Analysis, the preparation and properties of organometallic compounds and also the catalytic property of organometallic compounds.

Objectives

This course enables the student to

1. Understand the Theoretical Principles in Qualitative Analysis to identify the cations and anions
2. Understand the classification of organometallic compounds based on bond type
3. Understand the catalytic property of organometallic compounds.

Methodology

Blackboard teaching, Powerpoint presentation and group discussion.

UNIT I

Theoretical Principles in Qualitative Analysis (H_2S Scheme)

Basic principles involved in analysis of cations and anions. 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.

UNIT II

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.

UNIT III

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. Ferrocene: Preparation and reactions (acetylation, alkylation, metallation, Mannich Condensation). Structure and aromaticity. Comparison of aromaticity and reactivity with that of benzene.

UNIT IV

Metal ions present in biological systems, classification of elements according to their action in biological system. Geochemical effect on the distribution of metals. Sodium / K-pump, carbonic anhydrase and carboxypeptidase. Excess and deficiency of some trace metals. Toxicity of metal ions (Hg, Pb, Cd and As), reasons for toxicity, Use of chelating agents in medicine, Cisplatin as an anti-cancer drug.

Iron and its application in bio-systems, Haemoglobin, Myoglobin; Storage and transfer of iron.

UNIT V

Catalysis by Organometallic Compounds

Study of the following industrial processes and their mechanism:

1. Alkene hydrogenation (Wilkinson's Catalyst)
2. Synthetic gasoline (Fischer Tropsch reaction)
3. Polymerisation of ethene using Ziegler-Natta catalyst

Suggested Readings

Text Books:

1. Miessler, G. L. & Tarr, Donald A. (2010). *Inorganic Chemistr*. 4th Ed. Pearson.
2. Cotton, F.A., Wilkinson, G., & Gaus, P.L.(1993). *Basic Inorganic Chemistry*. 3rd Ed. Wiley India.
3. Huheey, J. E., Keiter, E.A. & Keiter, R.L. (2006). *Inorganic Chemistry: Principles of Structure and Reactivity*. 4th Ed. Harper Collins.Pearson.
4. Gopalan R and Ramalingam V (2008), Concise Coordination Chemistry, Vikas Publishing, India
5. Douglas, B. E.; McDaniel, D.H. & Alexander, J.J.(1994). *Concepts and Models in Inorganic Chemistry*. 3rdEd. NY*:*John Wiley and Sons.
6. Lee, J.D. (2008). *Concise Inorganic Chemistry*. 5th Ed. John Wiley and sons.

Reference Books

1. Shriver, D.D., Atkins, P. and Langford, C.H. (1994). *Inorganic Chemistry*. 2nd Ed. Oxford University Press.

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LECTURE PLAN

DEPARTMENT OF CHEMISTRY

Name of the Staff : **Dr.M.GOPALAKRISHNAN** and **Dr.K.SUNDARAM**

Title of the Paper : **INORGANIC CHEMISTRY IV (ORGANOMETALLIC CHEMISTRY)**

Subject ode : **16CHU402** Class: II- B.Sc-Chemistry

Year and Semester : 2017–2018 and IV-Semester Total hours : 60 Hours

UNIT-I **Hours required- 11**

S.No	Lecture hour	Topics	Support material
1	1	Introduction of qualitative analysis	T1:1-5
2	1	Basic principles involved in analysis of cations	T1:12-32
3	1	Basic principles involved in analysis of anion	T1: 47-55
4	1	Basic Principle of Solubility products, common ion effect	T1: 35-46
5	1	Principles involved in separation of cations into groups	T1: 44-45
6	1	Selection of group reagents	T1:28-32, T1:44-45
7	1	Interfering fluoride groups	T1:51-52
8	1	Interfering borate groups	T1: 52
9	1	Interfering oxalate groups	T1:53-54
10	1	Interfering oxalate groups	T1:55-56
11	1	Recapitulation and discussion of important questions	
		UNIT-II **Hours required-14**	
S.No	**Lecture hour**	**Topics**	**Support material**
1.	1	Definition and classification of organometallic compounds	T2: 466-467
2.	1	Basis of bond type in organometallic compounds	T2:467
3.	1	Concept of hapticity of organic ligands	T2: 468-469
4.	1	18 electron rule, electron count of mononuclear metal carbonyls	T2: 468-469

5.	1	Polynuclear metal carbonyls and substituted metal carbonyls of 3d series	T2:476-477
6.	1	General methods of preparation mononuclear metal carbonyls	T2: 483-484
7.	1	Synthesis of polynuclear metal carbonyls	T3: 634-638
8.	1	Structure and bonding on mononuclear metal carbonyls (Cr, Mn, Fe, Co and Ni)	T2: 479-482
9.	1	Structure and bonding on polynuclear metal carbonyls (Cr, Mn, Fe, Co and Ni)	T2: 482-483
10.	1	Valance bond Theory of metal carbonyls structures	T2: 473-475
11.	1	π-acceptor behaviour of carbonyls CO (MO diagram of CO to be discussed)	T2:476-477
12.	1	Synergic effect of metal carbonyls	R1:562-563
13.	1	IR data to explain extent of back bonding	T2:513-516
14.	1	Recapitulation and discussion of important questions	
		UNIT-III Hours required-13	
S.No	**Lecture hour**	**Topics**	**Support material**
1.	1	Introduction of metal alkene complexes	T2: 487-491
2.	1	Synthesis and structure of Zeise’s Salt	T2:492
3.	1	Evidance and camparison of synergic effect	R1:562-563
4.	1	Syntheis of metal alkyl complexes	T3: 655-657, T3:506
5.	1	Structure features of metal lithium complexes (Tertramers)	T3:106-108
6.	1	Structure features of trialkyl aluminium complexes (Dimers)	T3:194-195, 198-200
7.	1	Introduction of Ferrocene (First sandwich compound)	T2: 494
8.	1	Preparation of Ferrocene by various method	T2: 494-495
9.	1	Acetylation and alkylation reactions in ferrocene	T3: 500

10.	1	Metallation, Mannich and Condensation reactions in ferrocene	T2:500-501
11.	1	Structure and aromaticity	T2:495-498
12.	1	Comparison of aromaticity and reactivity with that of benzene.	T2:499
13.	1	Recapitulation and discussion of important questions	
		UNIT-IV Hours required-11	
S.No	**Lecture hour**	**Topics**	**Support material**
1.	1	Introduction of bioinorganic chemistry	T4: 313,328
2.	1	Meal ions present in biological systems	T4:314
3.	1	Classification of elements according to their action in biological system	T4:319
4.	1	Geochemical effect on the distribution of metals and Sodium / K-pump in biological system	T4:890-891
5.	1	Carbonic anhydrase and carboxypeptidase enzymes	T4:616-617
6.	1	Excess and deficiency of some trace metals	T3:941-945
7.	1	Toxicity of metal ions (Hg, Pb, Cd and As). reasons for toxicity and their side effect	T4:946-949
8.	1	Use of chelating agents in medicine, Cisplatin as an anti-cancer drug	T4:167
9.	1	Iron and its application in bio-systems, Haemoglobin	T4:315-316
10.	1	Storage and transfer of iron (Myoglobin)	T4:318
11.	1	Recapitulation and discussion of important questions	
		UNIT-V Hours required-11	
S.No	**Lecture hour**	**Topics**	**Support material**
1.	1	Introduction of homogeneous and heterogeneous catalytic reactions	T2:530-531
2.	1	Organometallic compounds in homogeneous catalytic reactions	T2:544-546

3.	1	Migration of atoms or groups from metal to ligand	T2:536
4.	1	Oxidatative addition and reductive elimination in orgametallic compounds	T2:534-535
5.	1	Hydrogenation reaction of alkenes and mechanism	T2:551-553, T4: 286-287
6.	1	Hydroformylation reaction of alkenes and mechanism	T2:545, T2:291
7.	1	Synthesis of gasoline (Fisher tropsch reaction) mechanism	T4: 306-308
8.	1	Alkene polymerisation and oligomerisation by Ziegler-Natta catalyst	T2:558-559, T4: 300
9.	1	Recapitulation and discussion of important questions	
10.	1	Discussion of previous ESE question papers	
11.	1	Discussion of previous ESE question papers	

Text Book:

1. T1**.** Ramanujam, V.V (2013), Inorganic semimicro qualitative analysis, National publishing company.

2. T2. Miessler, G. L. & Tarr, Donald A. (2010). *Inorganic Chemistr*. 4th Ed. Pearson.
3. T3.Huheey, J. E., Keiter, E.A. & Keiter, R.L. (2006). *Inorganic Chemistry: Principles of Structure and Reactivity*. 4th Ed. Harper Collins.Pearson.
4. T4. Gopalan R and Ramalingam V (2008), Concise Coordination Chemistry, Vikas Publishing, India

Reference Book

1. R1: Shriver, D.D., Atkins, P. and Langford, C.H. (2009). *Inorganic Chemistry*. 5th Ed. Oxford University Press.

UNIT-I

SYLLABUS

Basics principles involved in analysis of cations and anions. Solubility products.common ion effect. Principles involved in separation of cations into group and choice of group reagent. Interfering anions (fluoride, borate, oxalate and phosphate) and need to remove them after group 2.

STEPS OF QUALITATIVE ANALYSIS

- If the sample is presented as a solid (salt), it’s important to not the shape and colour of any crystals.
- Reagents are used to separate cations into group of related elements.
- Ions in group of separated from each other. After each separation stage , a test is performed to conform certain ions truly were removed. the test is not performed on the original sample!
- Separation rely on different characteristic of ions. These may involve redox reactions to change oxidation state, differential solubility in an acid, base or water, or precipitating certain ions.

SAMPLE QUALITATIVE ANALYSIS PROTOCOL

first, ions are removed in groups from inertial aqueous solution. After each groups has been separated then testing is conducted for individual ions in each groups. Here is a common grouping of cations;

Group 1: Ag^+, Hg_2^{2+}, Pb^{2+}

Precipitated in 1 M HCl

Group 2:Bi^{3+},Cu^{2+},Hg^{2+},$Sb^{3+}$and $Sb^{5+,}$$Sn^{2+,}$$Sn^{4+}$

Precipitation in 0.1 M H_2S solutions at pH 0.5

Group 3:AL^{3+},(Cd^{2+}),Co^{2-},Cr^{3+},Fe^{2+},Fe^{3+},Mn^{2+},Ni^{2+},Zn^{2+}

Precipitated in 0.1 M H_2S solutions at pH at 9

Group 4: Ba^{2+}, Ca^{2+}, k^{+}, Mg^{2+}, Na^{+}, NH_4^{+}, Ba^{2+}, Ca^{2+},and Mg^{2+} are precipitated in 0.2 M $(NH_4)_2 CO_3$ solutions at pH 10; thw other ions are soluble

Many reagents are used in the qualitative analysis, but only a few are involved in nearly every group of procedure. The four most commonly used reagents are 6M, HCl, 6M HNO_3, 6M NaOH, 6M NH_3.. Understanding the uses if reagents is help full when planning an alalysis.

Common ions

When NaCl and KCl are dissolved in the same solutions =, the Cl- ions are common to both salts. In a system containing NaCl and KCl, the Cl- ions are common ions.

$$NaCl \rightleftharpoons Na_{+} + Cl-$$

$KCl \rightleftharpoons K_{+} + Cl-$

$CaCl_2 \rightleftharpoons Ca_{2+} + 2Cl-$

$AlCl_3 \rightleftharpoons Al_{3+} + 3Cl-$

$AgCl \rightleftharpoons Ag_{3+} + Cl-$

For an example, when AgCl is dissolved into a solution already containing NaCl(actually Na^{+} and Cl^{-} ions, the Cl^{-} ions come from the ionization of both AgCl and NaCl. Thus (Cl^{-}) differs from (Ag^{+})

Common ion effect with weak acids and bases

Adding a common ion prevents the weak acids or weak bases from ionizing as much as it would with out the added common ion. The common ion effect suppresses the ionization of a weak acid by adding more of an ion that is a product of this equilibrium.

Example 3

The common ion effect of H_3O^{+} on the ionization of acetic acid

When a strong supplies the common ion H_3O^{+} the

Equilibrium shifts to firm more $HC_2H_3O_2$

Added H_3O^+

↓

$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_2O_2^-$

↓

Equilibrium shifts to more $HC_3H_3O_2$

The common ion effect supresses the ionization of a weak base by adding more of an ion that is a product of this equilibrium.

Example 4

Consider the common ion effect of OH^- on the ionization of ammonia

When a strong base supplies the common ion OH^-

The equilibrium shifts to from more NH

Added OH^-

↓

$NH_3 + H_2O \rightleftharpoons NH_4 + OH^-$

↓

Equilibrium shifts to from more NH_3

Adding the common ion of hydroxide shift the reaction towards the left to decrease the stress (in accordance with Le chatelier principle), forming more reactants. This decreases the reaction quotient, because the reaction is being pushed towards the left to the reach equilibrium. The equilibrium consant, $K_5=1.8*10^{-5}$, does nit change, the reaction is put uot of balance, or equilibrium.

$Q_a= (NH_{+4}) (OH-) (NH_3)$

At, first when more hydroxide is added, the quotient is greater thsn equilibrium constant. The reaction then shifts right, causing the denominator to increases, decreasing the reaction quotient and pulling towards equilibrium and Q to decreases towards K.

Common ion effect in solubility

Adding common ion decreases solubility product , as the reaction shifts towards the left to relieve the stress of the excess point .adding a common ion to dissociation reaction causes the equilibrium to shift left , towards to reactants, causing precipitation.

Example 5

Consider the raction:

$PbCl_2(s) \rightleftharpoons Pb_2 + (aq) + (2Cl) – (aq)$

What happens to the solubility of ($PbCl_2$) when 0.1MNaCl is added?

Solution

$\mathbf{K_{sp}=107*10^{-5}}$

$\mathbf{Q_{sp=}}$ 1.8*-5

Identify the common ion :Cl^-

notice:$Q_{sp}>k_{sp}$ the addition of NaCl- has caused the reaction to shift out of equilibrium because there are more dissociate ions. Typically, solveing for the molarities requires the assumption that the solubility of $PbCl_2$ is the equivalent to the concentration of Pb^{2+} produce because they are in a 1 : 1 ratio.

Because $K_{sp}$for the reaction is $1.7*10^{-5,}$ the over all reaction would be (s) $(2s)^{2}1.7*10^{-5.}$ solving the equation for s givess=$1.62*10^{-2}$ M. the coefficient on $Cl^{-\ is}$ produce as $Pb^{2+,}$ hence the 2s. the solubility equilibrium constant can be used to solve for the molarities of the ions at equilibrium.

The molarity of Cl^- added would be 0.1 M because Na^+ and Cl^- are in a 1:1 ration in the ionic salt, NaCl. Therefore, the overall molarity of Cl^- would be 2s + 0.1, with 2s referring to the contribution of the chloride ion from the dissociation of lead chloride.

$Q_{sp}1.8*10\text{-}_{5s}2_{s} ====(Pb2^{+})(Cl^{-})2(s)(2s+0.1)_{2}(Pb2+)1.8*10_{-3}M(Cl-)0.1\ M$

Notice that the molarity of Pb^{2+} is lower when NaCl is added. The equilibrium constant remains the same because of the increased concentration of the chloride ion. To simplify the reaction, it can be assumed that (Cl^-) is approximately 0.1 M since the formation of the chloride ion from the dissociation of lead chloride is so small. The reaction quotient for $PbCl_2$ is greater than the equilibrium constant because of the added Cl^- . this therefore shift the reaction left towards equilibrium, causing precipitation and lowering the current solubility of the reaction. Overall, the solubility of the reaction decreases with the added sodium chloride.

The Solubility Product Expression

Silver chloride is so insoluble in water (.0.002 g/L) that a saturated solution contains only about 1.3 x 10^{-5} moles of AgCl per liter of water.

$$H_2O$$

$$AgCl(s) \qquad Ag^+(aq) + Cl^-(aq)$$

Strict adherence to the rules for writing equilibrium constant expressions for this reaction gives the following result.

(Water isn't included in the equilibrium constant expression because it is neither consumed nor produced in this reaction, even though it is a vital component of the system.)

The $[Ag^+]$ and $[Cl^-]$ terms represent the concentrations of the Ag^+ and Cl^- ions in moles per liter when this solution is at equilibrium. The third term [AgCl] is more ambiguous. It doesn't represent the concentration of AgCl dissolved in water because we assume that AgCl dissociates into Ag^+ ions and Cl^- ions when it dissolves in water. It can't represent the amount of solid AgCl in the system because the equilibrium is not affected by the amount of excess solid added to the system. The [AgCl] term has to be translated quite literally as the number of moles of AgCl in a liter of solid AgCl.

The concentration of solid AgCl can be calculated from its density and the molar mass of AgCl.

This quantity is a constant, however. The number of moles per liter in solid AgCl is the same at the start of the reaction as it is when the reaction reaches equilibrium.

Since the [AgCl] term is a constant, which has no effect on the equilibrium, it is built into the equilibrium constant for the reaction.

$[Ag^+][Cl^-] = K_c \times [AgCl]$

This equation suggests that the product of the equilibrium concentrations of the Ag^+ and Cl^- ions in this solution is equal to a constant. Since this constant is proportional to the solubility of the salt, it is called the **solubility product equilibrium constant** for the reaction, or K_{sp}.

$K_{sp} = [Ag^+][Cl^-]$

The K_{sp} expression for a salt is the product of the concentrations of the ions, with each concentration raised to a power equal to the coefficient of that ion in the balanced equation for the solubility equilibrium.

Calculating solubility products from solubilitiesI am going to assume that you are given the solubility of an ionic compound in mol dm-3. If it was in g dm-3, or any other concentration units, you would first have to convert it into mol dm-3.

Example 1

The solubility of barium sulphate at 298 K is 1.05 x 10-5 mol dm-3. Calculate the solubility product.

The equilibrium is:

Notice that each mole of barium sulphate dissolves to give 1 mole of barium ions and 1 mole of sulphate ions in solution.

That means that:

[Ba2+] = 1.05 x 10-5 mol dm-3

[SO42-] = 1.05 x 10-5 mol dm-3

All you need to do now is to put these values into the solubility product expression, and do the simple sum.

Example 2

These calculations are very simple if you have a compound in which the numbers of positive and negative ions are 1 : 1. This next example shows you how to cope if the ratio is different.

The solubility of magnesium hydroxide at 298 K is 1.71 x 10-4mol dm-3. Calculate the solubility product.

The equilibrium is:

For every mole of magnesium hydroxide that dissolves, you will get one mole of magnesium ions, but twice that number of hydroxide ions.

So the concentration of the dissolved magnesium ions is the same as the dissolved magnesium hydroxide:

[Mg2+] = 1.71 x 10-4 mol dm-3

The concentration of dissolved hydroxide ions is twice that:

[OH-] = 2 x 1.71 x 10-4 = 3.42 x 10-4 mol dm-3

Now put these numbers into the solubility product expression and do the sum.

Calculating solubilities from solubility products

Reversing the sums we have been doing isn't difficult as long as you know how to start. We will take the magnesium hydroxide example as above, but this time start from the solubility product and work back to the solubility.

If the solubility product of magnesium hydroxide is 2.00 x 10-11mol3 dm-9 at 298 K, calculate its solubility in mol dm-3 at that temperature.

The trick this time is to give the unknown solubility a symbol like x or s. I'm going to choose s, because an x looks too much like a multiplication sign.

If the concentration of dissolved magnesium hydroxide is s mol dm-3, then:

[Mg2+] = s mol dm-3

[OH-] = 2s mol dm-3

Put these values into the solubility product expression, and do the sum.

Qualitative Analysis of Anions

Preliminary Tests

Some preliminary tests are done before going to the anion analysis.

(A) Physical Examination: Colour and Smell

The physical examination of the unknown salt involves the study of colour, smell and density. Characteristic smell helps to identify some anions such as acetate, sulphide etc.

(B) Dry Heating Test

This test is performed by heating a small amount of salt in a dry test tube. Quite valuable information can be gathered by carefully performing and noting the observations. On heating, some salts undergo decomposition, thus evolving the gases.

(C) Identification of Anions (Acid Radicals)

The identification of the radicals is first done on the basis of the preliminary tests. The Dry heating test is one of the preliminary tests performed earlier which may give some important information about the acid radical present. The other preliminary tests are based on the fact that:

- CO_3^{2-}, S^{2-}, NO_2^- and SO_3^{2-} react with dil. H_2SO_4 to give out CO_2, H_2S, NO_2 and SO_2 gases respectively. These gases on identification indicate the nature of the anion present in the salt.
- Cl^-,Br^-,I^-,NO_{3-} and $C_2O_4^{2-}$ and CH_3COO^- react with conc. H_2SO_4 but not with dil. H_2SO_4 to produce characteristic gases.
- SO_4^{2-} and PO_4^{3-} react neither with dil H_2SO_4 nor with conc. H_2SO_4. These are, therefore, identified by individual tests.

Thus, these anions may be identified by performing the following tests below:

1) Dil. H_2SO_4 Tests

Treat a pinch of the salt with dil. H_2SO_4 and identify the gas evolved.

Chemical Reactions Involved in Dil.H_2SO_4 Test:

Dilute H_2SO_4 decomposes carbonates, sulphides, sulphites and nitrites in cold to give gases. These gases on identification indicate the nature of the anion present in the salt.

(a) Carbonate: On treating the solid carbonate, CO_2 is given off in the cold with brisk effervescence.

(b) Sulphide: Sulphides when treated with dil. H_2SO_4 give H_2S gas.

$$ZnS + H_2SO_4 \rightarrow ZnSO_4 + H_2S\uparrow$$

(c) Sulphite: On heating solid sulphite with dil.H_2SO_4, SO_2 gas is evolved

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + SO_2\uparrow$$

(d) Nitrite: On treating solid nitrite with dil. H_2SO_4, nitric oxide (NO) gas is evolved which readily gives brown fumes of NO_2 with the oxygen of the air.

$$KNO_2 + H_2SO_4 \rightarrow KHSO_4 + HNO_2] \times 3$$

$$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$$

$$3KNO_2 + 3H_2SO_4 \rightarrow 3KHSO_4 + HON_3 + H_2O + 2NO$$

$$\underset{\text{(Colourless)}}{2NO + O_2} \rightarrow \underset{\text{(Brown fumes)}}{2NO_2}$$

2) Conc. H_2SO_4 Test

If no action takes place with dil. H_2SO_4, warm a pinch of the salt with conc. H_2SO_4 and identify the gas evolved.

Chemical Reactions Involved in Conc. H_2SO_4 Test

(a) Chlorides: Chloride salts react with conc. H_2SO_4 to evolve hydrogen chloride (HCl) gas.

$$NaCl + H_2SO_4 \rightarrow \underset{\text{Sodium bisulphate}}{NaHSO_4} + HCl\uparrow$$

(b) Bromides: Bromide salts react with conc. H_2SO_4 to evolve bromine gas.

$$NaBr + H_2SO_4 \rightarrow \underset{\text{Sodium bisulphate}}{NaHSO_4} + HBr$$

$$H_2SO_4 + 2HBr \rightarrow SO_2 + Br_2\uparrow + 2H_2O$$

(c) Iodides: Iodide salts react with conc. H_2SO_4 to evolve vapours of iodine.

$$KI + H_2SO_4 \rightarrow KHSO_4 + HI$$

$$H_2SO_4 + 2HI \rightarrow SO_2 + I_2\uparrow + 2H_2O$$

(d) Nitrates: Upon reaction with conc.H_2SO_4 nitrates evolve NO_2 gas.

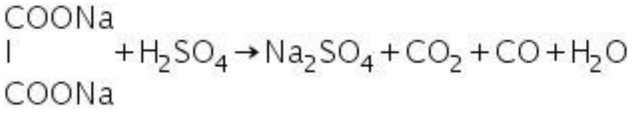
$$KNO_3 + H_2SO_4 \rightarrow KHSO_4 + HNO_3$$

$$4HNO_3 + \underset{\text{(Paper pellet)}}{C} \rightarrow 4NO_2\uparrow + CO_2 + 2H_2O$$

(e) Acetates: Acetates react with conc. H_2SO_4 to produce vapours of acetic acid.

$$CH_3COONa + H_2SO_4 \rightarrow NaHSO_4 + \underset{\text{Acetic acid}}{CH_3COOH\uparrow}$$

(f) Oxalates: Oxalates salts react with conc. H_2SO_4 to evolve a mixture of carbon dioxide and carbon monoxide.



$$\begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2SO_4 \rightarrow Na_2SO_4 + CO_2 + CO + H_2O$$

3) Independent Group. (SO_4^{2-} and PO_4^{3-}) Test

If the salt does not react with dil H_2SO_4 as well as with conc. H_2SO_4 test for $SO_4^{2-}$and PO_4^{3-} by performing their individual tests.

4) Potassium permanganate Test

This test is performed by using dilute sulphuric acid and potassium permanganate as reagents. This test helps in the detection of Cl^-, Br^-, I^- and $C_2O_4^{2-}$.

Chemical reactions involved in Potassium permanganate test

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

(a) Chlorides: $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

$$2HCl + [O] \rightarrow H_2O + Cl_2\uparrow$$

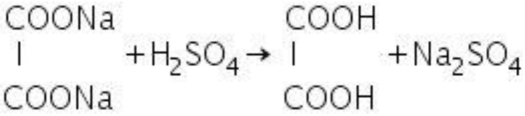
(b) Bromides: $NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$

$$2HBr + [O] \rightarrow H_2O + Br_2\uparrow$$

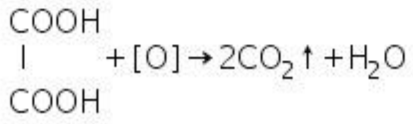
(c) Iodides: $NaI + H_2SO_4 \rightarrow NaHSO_4 + HI$

$$2HI + [O] \rightarrow H_2O + I_2\uparrow$$

(d) Oxalates:



$$\begin{array}{c}COONa\\|\\COONa\end{array} + H_2SO_4 \rightarrow \begin{array}{c}COOH\\|\\COOH\end{array} + Na_2SO_4$$



$$\begin{array}{c}COOH\\|\\COOH\end{array} + [O] \rightarrow 2CO_2\uparrow + H_2O$$

Wet Tests for Acid Radicals (Anions)

Let us discuss the chemical reactions involved in the confirmation of Anions:

Confirmation of Carbonate (CO_3^{2-})

(a) Reaction with di.lHCl

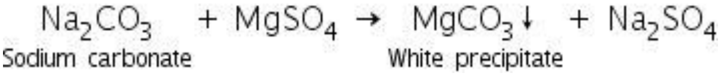
Carbonate on reaction with dil. HCl gives CO_2 gas that reacts with lime water to produce a white precipitate of calcium carbonate that turns lime water milky. In case of soluble carbonate, this test is performed with water extract and in case of insoluble carbonates, this test is performed with the solid salt.

$$\underset{\text{Calcium carbonate}}{CaCO_3} + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

$$\underset{\text{LIme water}}{Ca(OH)_2} + CO_2 \rightarrow \underset{\text{Milkness}}{CaCO_3\downarrow} + H_2O$$

(b) Magnesium sulphate test

This test is performed in the case of soluble carbonates only. Soluble carbonates react with the magnesium sulphate solution to form a white precipitate of magnesium carbonate.

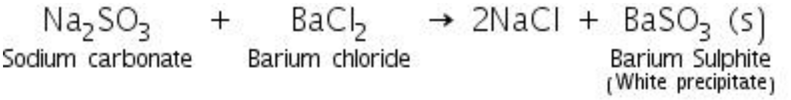


$$\underset{\text{Sodium carbonate}}{Na_2CO_3} + MgSO_4 \rightarrow \underset{\text{White precipitate}}{MgCO_3\downarrow} + Na_2SO_4$$

Confirmation of Sulphite (SO_3^{2-})

(a) Barium chloride test

Sulphites on reaction with barium chloride to form a white precipitate of barium sulphite. Barium sulphite dissolved in dil. HCl with the evolution of sulphur dioxide gas.



$$\underset{\text{Sodium carbonate}}{Na_2SO_3} + \underset{\text{Barium chloride}}{BaCl_2} \rightarrow 2NaCl + \underset{\substack{\text{Barium Sulphite}\\ \text{(White precipitate)}}}{BaSO_3\ (s)}$$

$$BaSO_3 + 2HCl \rightarrow BaCl_2 + SO_2\ (g) + H_2O$$

(b) Potassium permanganate test

The colour of potassium permanganate is discharged when it reacts with sulphite. The reaction is given below.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$Na_2SO_3 + [O] \rightarrow Na_2SO_4$$

(c) Potassium dichromate test

A green colour is obtained when sulphites react with potassium dichromate solution.

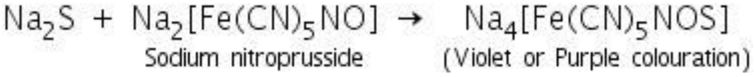
$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$Na_2SO_3 + [O] \rightarrow Na_2SO_4$$

Confirmation of Sulphide (S^{2-})

(a) Sodium nitroprusside test

Sulphides give a violet or purple colouration with the sodium nitroprusside solution due to the formation of $Na_4[Fe(CN)_5NOS]$.



$$Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5NO]} \rightarrow \underset{\text{(Violet or Purple colouration)}}{Na_4[Fe(CN)_5NOS]}$$

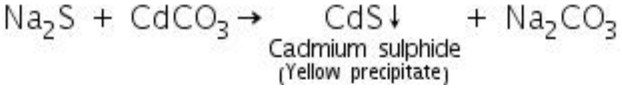
(b) Lead acetate test

Sulphides react with lead acetate to form a black precipitate of lead sulphide.

$$Na_2S + (CH_3COO)_2Pb \rightarrow \underset{\text{Black precipitate}}{PbS\downarrow} + 2CH_3COONa$$

(c) Cadmium carbonate test:

Sulphides react with a suspension of cadmium carbonate to form a yellow precipitate of cadmium sulphide.



$$Na_2S + CdCO_3 \rightarrow \underset{\substack{\text{Cadmium sulphide}\\ \text{(Yellow precipitate)}}}{CdS\downarrow} + Na_2CO_3$$

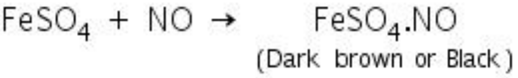
Confirmation of Nitrite (NO_2^-)

(a) Ferrous sulphate test

Nitrites give a dark brown or black colouration in Ferrous sulphate test due to the formation of $FeSO_4.NO$.

$$KNO_2 + CH_3COOH \rightarrow CH_3COOK + HNO_2$$

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$



$$FeSO_4 + NO \rightarrow \underset{\text{(Dark brown or Black)}}{FeSO_4.NO}$$

(b) Starch - Iodide test

Nitrites react with potassium iodide in the presence of dilute sulphuric acid to liberate iodine. Iodine forms a blue-black complex with starch.

$$2KI + 2H_2SO_4 + 2HNO_2 \rightarrow 2KHSO_4 + \underset{\text{Iodine}}{I_2} + 2NO + 2H_2O$$

$$I_2 + \text{Starch} \rightarrow \text{Blue-black complex}$$

(c) Diphenylamine test

In the presence of nitrites, diphenylamine is oxidised, giving a blue colouration.

Confirmation of Nitrate (NO_3^-)

(a) Diphenylamine test

In the presence of nitrates, diphenylamine is oxidised, giving a blue colouration.

(b) Copper chips test

In this reaction copper chips reduces nitrates to reddish brown NO_2 gas.

(c) Brown-ring test

This test can be performed by adding a solution of iron (II) sulphate to a solution of nitrate, followed by the slow addition of concentrated sulphuric acid, such that the sulphuric acid forms a layer below the aqueous solution. The formation of a brown ring at the junction of two layers indicates the presence of nitrate.

The overall reaction is the reduction of nitrate ion by iron (II) which reduced to iron (I) and formation of a nitrosonium complex where nitric oxide is oxidised to NO^+.

$$KNO_3 + H_2SO_4 \rightarrow KHSO_4 + HNO_3$$

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

$$FeSO_4 + NO + 5H_2O \rightarrow \underset{\text{Brown ring}}{[Fe(NO)(H_2O)_5SO_4}$$

Confirmation of Chloride (Cl^-)

(a) Silver nitrate test

Chlorides on reaction with silver nitrate solution to form a white precipitate of silver chloride which is soluble in ammonium hydroxide.

$$NaCl + AgNO_3 \rightarrow \underset{\text{White precipitate}}{AgCl\downarrow} + NaNO_3$$

$$AgCl + 2NH_4OH \rightarrow \underset{\text{Soluble Complex}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

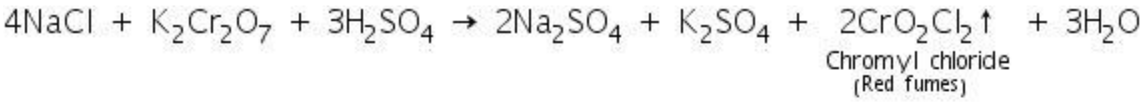
(b) Manganese dioxide test

When chloride salts react with manganese dioxide and concentrated sulphuric acid, chlorine gas is liberated.

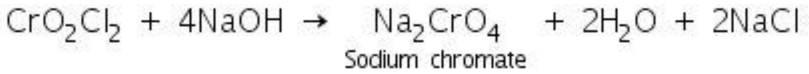
$$2NaCl + MnO_2 + 3H_2SO_4 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2\uparrow$$

(c) Chromyl chloride test

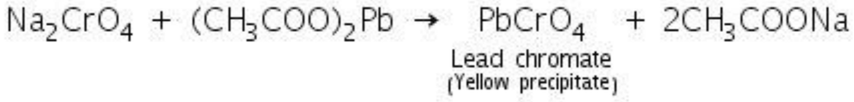
When chloride salts react with potassium dichromate and conc. sulphuric acid red fumes of chromyl chloride is formed which reacts with sodium hydroxide to form yellow solution of sodium chromate. Sodium chromate reacts with lead acetate in presence of dil. acetic acid to form yellow precipitate of lead chromate.



$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 \rightarrow 2Na_2SO_4 + K_2SO_4 + \underset{\substack{\text{Chromyl chloride} \\ \text{(Red fumes)}}}{2CrO_2Cl_2\uparrow} + 3H_2O$$



$$CrO_2Cl_2 + 4NaOH \rightarrow \underset{\text{Sodium chromate}}{Na_2CrO_4} + 2H_2O + 2NaCl$$

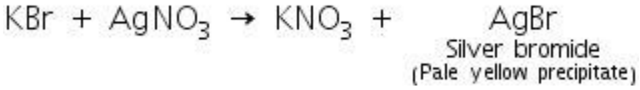


$$Na_2CrO_4 + (CH_3COO)_2Pb \rightarrow \underset{\substack{\text{Lead chromate} \\ \text{(Yellow precipitate)}}}{PbCrO_4} + 2CH_3COONa$$

Confirmation of Bromide (Br^-)

(a) Silver nitrate test

Bromides on reaction with silver nitrate solution forms a pale yellow precipitate of silver bromide which is sparingly soluble in ammonium hydroxide.



$$KBr + AgNO_3 \rightarrow KNO_3 + \underset{\substack{\text{Silver bromide} \\ \text{(Pale yellow precipitate)}}}{AgBr}$$

(b) Manganese dioxide test

When bromide salts react with manganese dioxide and concentrated sulphuric acid, bromine gas is liberated.

$$2KBr + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Br_2\uparrow$$

(c) Chlorine water test

Bromine liberated in this test being soluble in carbon disulphide imparts an orange colour to the carbon disulphide layer.

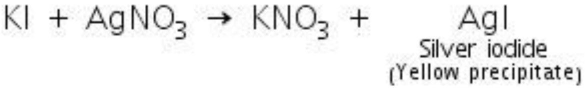
$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$

Note: Carbon tetrachloride, cyclohexane, chloroform etc can be used instead of carbon disulphide.

Confirmation of Iodide (I^-)

(a) Silver nitrate test

Iodides on reaction with silver nitrate solution forms an yellow precipitate of silver iodide which is insoluble in ammonium hydroxide.



$$KI + AgNO_3 \rightarrow KNO_3 + \underset{\text{(Yellow precipitate)}}{\underset{\text{Silver iodide}}{AgI}}$$

(b) Manganese dioxide test:

When iodide salts react with manganese dioxide and concentrated sulphuric acid, iodine gas is liberated.

$$2KI + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2\uparrow$$

(c) Chlorine water test

Iodine liberated in this test being soluble in carbon disulphide imparts a violet colour to the carbon disulphide layer.

$$2KI+Cl_2 \rightarrow 2KCl+I_2$$

Analytical Separation of Cations

Cations are positively charged fragments or ions of salt or compound. They are frequently referred to as the metals or basic radicals. In studying an unknown, a visual examination should come first.

If the unknown is a solution, what color is it ?Color is important because some inorganic ions reveal their identities through color alone.

If the unknown is a solid, the color is also important, but it does not necessarily indicate the colors of the individual ions. Thus, Pb2+ and I - are both colorless, but they combine to give the bright yellow PbI2.

Identification of cations cannot be performed by tests on the original substances (or salts), therefore .we have to some schemes for the systematic separation of cations.

Flowcharts are used to represent the steps in qualitative analysis, particularly for the analysis of cations, which is more systematic than the analysis of anions.

Common cations (basic radical) may be divided, for purposes of qualitative analysis, into a number of groups; the members of any group are precipitated by a particular group reagent.

Thus by the addition of a slight excess of dilute hydrochloric acid to a solution containing all the common cations, a precipitate is obtained consisting of the chlorides of silver; lead and mereurous, similarly by the use of the appropriate group reagents, the remaining cations are separated into different groups.

Generally, analytical separation of cations depends on the varying solubilities of their chlorides, sulphides, hydroxides and carbonates.

The steps in cations analysis fall into the following general sequence:

Separation of the cations into a series of groups

The cations of each successive group are precipitated as compounds with anions supplied by the group reagent. The precipitate (residue) containing the cations of one group are separated (usually by centrifugation). Then the group reagent for the next group is added to the remaining solution (centrifugate).

Separation of the cations in each group from each other

A series of reactions is carried out that eventually leads to the separation of each cation in a group from all of the others in that group. The reactions are carefully chosen to take advantage of similarities and differences in chemical properties.

Identification of individual cations

The presence of cation is confirmed by one or more reactions characteristic of that cation.

For ideal separation of cations

a) The groups should not be too large (3 or 5 members).

b) The precipitation of each group should be complete.

c) The precipitates should be sufficiently insoluble, (filter rapidly and wash well).

d) The precipitates should have no tendency to adsorb other ions (or cations) from the medium i.e. no interference.

The insoluble precipitate is formed by the addition of the "group reagent". This group reagent is specific for each group of cations. The active part of these reagents is the anionic part.

Possible Questions

Part-B (Two marks Questions)

1. What isuses qualitative analysis?

2. What are the group III cations (metallic radical) and what are the reagents used to identify it?

3. What are the reagents used to identify group IV metals?

4. Define the solubility product.

5. Define the common ion effect.

Part-C(Eight marks Questions)

1. Discuss the solubility products and common ion effect.

2. Calculate the 18 electron rule for following compounds
i) $Co_2(CO)_8$ ii) $V(CO)_6$

3. Expalin the principles involved in analysis of cations into groups.

4. Discuss the interfering anions such as fluoride and oxalate.

5. Write three different organometallic compounds and draw their structure.

6. Explain the general classification of metal carbonyls with examples.

7. i) What is chromyl chloride test?
ii) What are the group V cations?
iii) Why it is essential to boil of H_2S before test of group III?

8. Discuss the name of group reagents for different groups.

9. Write the general classification of metal carbonyls with examples.

10.Expalin the principles involved in analysis of cationsinto groups.

OBJECTIVE QUESTIONS

S. no	Questions	Option A	Option B	Option C	Option D	Answer
1	Qualitative inorganic analysis used for detection of	Anions	Cations	Metal	Anions and cations	Anions and cations
2	Positively charged ions are called	Anions	Cations	Free radicals	carbanions	Cations
3	Negatively charged ions are called	Cations	Anions	carbanions	Free radicals	Anions
4	The detection of acidic and basic radicals present in a given inorganic mixture is called	Quantitative analysis	Qualitative analysis	Gravimetric analysis	Functional group analysis	Qualitative analysis
5	Which of the following one is not give the white precipitate?	Cu^{2+}	Ag^{+}	K^{+}	Ca^{+}	Cu^{2+}
6	What basic radical can be present in a mixture, if its colour is blue?	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Cu^{2+}
7	What basic radical can be present in a mixture, if it on heating evolves reddish brown gas?	Br^{-}	Cl^{-}	I^{-}	F^{-}	Br^{-}
8	The following basic radical is not a metal	NH_4^{+}	Ba^{+}	Sr^{+}	K^{+}	NH_4^{+}
9	Which of the following metallic salt impart colour to the flame when	Sr^{+}	Fe^{2+}	Co^{2+}	Mn^{2+}	Sr^{+}

	heated strongly in a non-luminous flame					
10	Which of the following halide is soluble in water?	AgF	AgCl	AgBr	AgI.	AgF
11	A colourless solid A produces black spots on the skin. Its aqueous solution gives brown ring test and also gives yellow precipitate with potsssium iodide solution. A could be	Copper nitrate	Zinc nitrate	Silver nitrate	Lead nitrate	Lead nitrate
12	Which of the following sulphide is completely precipitated only when the acidic solution is made dilute?	HgS	PbS	CdS	CuS	PbS
13	In qualitative analysis of basic radicals, hydrochloric acid preferred to nitric acid for preparing a solution of given substance. This is because	nitrates are not decomposed to sulphides	nitric acid contains nitrogen	hydrochloric acid is not an oxidising acid	chlorides are easily converted to sulphides.	hydrochloric acid is not an oxidising acid
14	Addition of KI to Pb salt in water gives precipitate. The colour of the precipitate is	Yellow	Black	White	Red.	Yellow
15	Which sodium thiosulphate solution is shaken with iodine, thiosulphate is changed to	Sulphite ion	Sulphate ion	Tetrathionate ion	Sulphide ion.	Tetrathionate ion

16	Certain inorganic salt, when introduced in flame produces crimson red colour. It indicates the presence of	Dichromate ion	Thiosulphate ion	Strontium ion	Calcium ion	Calcium ion
17	Sodium sulphide react with sodium nitroprusside to form a purple colured compund. During the reaction, the oxidation state of iron	Changes from + 2 to + 3	Changes from + 3 to + 2	Changes from + 2 to + 4	Remains unchanged	Remains unchanged
18	The metal whose salts do not give the borax bead test is	Cr	Ni	Pb	Mn	Pb
19	Which of the following is soluble in yellow ammonium sulphide ?	CuS	CdS	SnS	PbS	SnS
20	A moisten salt is rubbed with oxalic acid between the fingers and smells like vinegar. It indicates the presence of	Sulphur	Nitrate	Nitrite	Acetate	Acetate
21	Which types of salt produce crackcling noise in dry heating test?	Salts which have lot of water of crystallization	Salts which are hygroscopic	Salts which have lost water of crystallization	Salts which entrap mother liquor in crystals	Salts which entrap mother liquor in crystals
22	Which of the following is not a preliminary test?	Flame test	Borax bead tes	Permanganate test	Brown ring test	Brown ring test
23	A minute quantity of cupric salt is heated on borax bead in reducing	Blue	Brown red	Colourless	Green	Colourless

	foame of bunsen burner, the colour of bead after cooling will be					
24	Formation of a rose-red precipitate when a slightly alkaline solution of an inorganic salt is treated with dimethylglyoxime confirms the presence of	Cobalt	Zinc	Iron	Nickel	Nickel
25	Which of the following sulphides has lowest solubility product?	FeS	MnS	PbS	ZnS	FeS
26	Which of the following is an interfering radical?	Phosphate	Sulphate	Nitrite	Sulphide.	Phosphate
27	Carbonates of the cation of group V are	black	green	white	yellow	white
28	Which of the following is insoluble in AcOH?	Calcium oxide	Calcium carbonate	oxalate	Calcium hydroxide	oxalate
29	Which sulphides are soluble only in aqua regia?	NiS	CoS	HgS	All of the above	All of the above
30	Sulphuric acid is not used for the preparation of original solution in the analysis of basic radicals because	It forms insoluble sulphates with some of the basic radicals	It is a strong oxidising agent	It is a strong reducing agent	It decomposes many of the anions	It forms insoluble sulphates with some of the basic radicals

31	The aqueous solution of which of the following reagent will give prussian blue coloured precipitate with an aqueous solution containing iron (III) ions.	Potassium thiocyanate	Potassium hexacyanoferrate (II)	Potassium pyroantimonate	All of the above.	Potassium hexacyanoferrate (II)
32	A one litre flask is full of brown bromine vapour. The intensity of brown colour of vapour will not decrease appreciably on adding to the flask some	pieces of marble	animal charcoal powder	carbon tetrachloride	carbon disulphide	pieces of marble
33	Certain Inorganic salt gives yellow precipitate with silver nitrate. The precipitate dissolves in dilute nitric acid as well as in ammonium hydroxide. The solution contains	Bromide ions	Iodide ions	Phosphate ions	Chromate ions	Bromide ions
34	Nitric acid is generally not used for preparation of original solution in analysis of basic radicals, because	It is a strong oxidising agent	It is reducing agent	It forms insoluble nitrates	Nitrate ions cause interference with the scheme of analysis	It is a strong oxidising agent
35	The salt of which of the following metal gives violet colour in borax bead test?	Fe	Ni	Co	Mn	Mn
36	The name of the blue product of the	Thenard blue	Turnbulls blue	Prussian blue	Ultramarine	Turnbulls blue

	reaction between ferrous ion and ferricyanide ion is				blue	
37	A glassy bead formed by heating borax on a platinum wite loop is	Sodium tetraborate	Sodium metaborate	Sodiummetaborate and boric anhydride	Boric anhydride and Sodium tetraborate	Sodiummetaborate and boric anhydride
38	Which of the following sulphide is not soluble in dil HNO_3?	PbS	HgS	ZnS	Bi_2S_3	HgS
39	The two different salts A (zinc nitrate) and B (potassium bromide) were separately warmed with conc.H_2SO_4. Which of them will produce raddish brown fumes that dissolve in CS_2 giving yellow solution?	A	B	Both A and b	Neither A nor B	B
40	Which of the following is insoluble in AcOH?	Calcium oxide	Calcium oxalate	Calcium carbonate	Calcium hydroxide	Calcium oxalate
41	Which pair of ions form precipitate when their dilute aqueous solutions are mixed?	Na^+, SO_3^{2-}	NH_4^+, CO_3^{2-}	Na^+, S_2^-	Fe^{3+}, PO_4^{3-}	Fe^{3+}, PO_4^{3-}
42	Which of the salt giving white precipitate with a solution of $AgNO_3$; a white precipitate with dil. H_2SO_4 and green flame test	Copper chloride	Copper nitrate	Lead nitrate	Barium chloride	Barium chloride

43	In qualitative analysis of basic radicals, hydrochloric acid is preferred to nitric acid for preparing a solution of given substance. this is because	Nitrates are not decomposed to sulphides	Nitric acid contains nitrogen	Hydrochloric acid is not an oxidizing acid	Chlorides are easily converted to sulphides	Hydrochloric acid is not an oxidizing acid
44	In the dry heating test, a white crystalline salt produces crackling noise and also brownish fumes. The residue after heating is seen to be yellow-brown colour. When a glowing splinter is held in the fumes it is relighted. The fumes consist of	Bromine only	Nitrogen dioxide only	Mixture of O_2 and Br_2	A mixture of nitrogen dioxide and oxygen	A mixture of nitrogen dioxide and oxygen
45	Which pair of ions would be expected to form precipitate when their aqueous solutions are mixed?	K^+, SO_4^{2-}	Na^+, S^{2-}	Ag^+, NO_3^-	Al^{3+}, OH^-	Al^{3+}, OH^-
46	Lead sulphate is soluble in	Ammonium acetate	Conc. HNO_3	Ammonium hydroxide	Conc. HCl	Ammonium acetate
47	An aqueous solution of nickel sulphate is acidified by dilute HCl followed by the addition of dimethyl glyoxime reagent. The observation is	Rose red precipitate	Green precipitate	No precipitate	White precipitate	No precipitate
48	To an aqueous solution containing Cu^{2+} and Cd^{2+}, dil H_2SO_4 is added followed by iron fillings. The solution	Cu metal	CdS	Both Cu metal and CdS	None of these	Both Cu metal and CdS

	is warmed and NH4OH is added to make it alkaline followed by addition of H_2S gas . the precipitate obtained will be					
49	A mixture containing KBr + $Ca(NO_3)_2$ is warmed with dilute H_2SO_4.	No reaction will occur	Evoluation of Br_3 will take place	Gas evolved will be NBr_3	Mixture of NO_2 and Br_2 is evolved	Mixture of NO_2 and Br_2 is evolved
50	The aqueous solution of which of the following pairs of salts will give yellow precipitate separately with aqueous solution of barium bromide?	K_2CrO_4, A_gNO_3	$AgNO_3$, K_2SO_4	K_2CrO_4, K_2SO_4	$AgNO_3$, Na_2CO_3	K_2CrO_4, A_gNO_3
51	Which of the following reagent can cause the separation of precipitate of $Fe(OH)_3$ and $Cr(OH)_3$ in IIIrd group analysis?	Dil HCl	Aq. NH_3	H_2SO_4	$NaOH/H_2O_2$	$NaOH/H_2O_2$
52	A yellow coloured aqueous solution of ferric chloride acquires light green tinge on addition of reagent Y. the reagent Y can be	Aq. $SnCl_2$	Zn dust/HCl	H_2S gas	Any of the three a,b,c	Any of the three a,b,c
53	A freshly prepared aqueous solution of ferrous sulphate is added to aqueous solution of ferrocyanide, no precipitate. The addition of which of the reagent given below can cause	HCl	Dil H_2SO_4	NH_4OH	MnO_4-/H^+	MnO_4^-/H^+

	appearance of blue precipitate or colouration?					
54	Among the species X (As_2S_3), Y (CuS), Z ($AlCl_3$), W ($ZnCl_2$) which will be soluble in excess of NaOH?	X,Z only	X, Z, W	Only Z	Z, W only	X, Z, W
55	Which of following pairs of acid radicals are decomposed both dilute as well as conc. H_2SO_4?	SO_3^{2-}, SO_4^{2-}	$C_2O_4^{2-}$, SO_3^{2-}	CH_3COO^-, NO_3^-	HCO_3^-, SO_3^{2-}	HCO_3^-, SO_3^{2-}
56	A white salt gave colourless crystalline punjent smelling vapours with hot conc. H_2SO_4. On adding the piece of paper to the contents, the colorless vapours become raddish brown. The paper act as	Oxidizing agent	Catalyst	Reducing agent	agent	Reducing agent
57	An aqueous solution containing S^{2-} ions will give	Yellow precipitate with suspension of $CdCO_3$ in water	White precipitate with lead acetate solution	White precipitate with $CaCO_3$ suspension	Purple colour with sodium thiosuphate solution	Yellow precipitate with suspension of $CdCO_3$ in water
58	Brown ring test for nitrate fails, if the mixture of salts, contains along with nitrate, the	NO_2^- ions	CO_3^{2-} ions	Br^- ions	Both (a), (c)	Both (a), (c)

59	Hydrogen sulphide is a group reagent for	Group III	Group II & IV radicals	Group I radicals	Group VI radicals	Group II & IV radicals
60	The aqueous solution is prepared by dissolved a mixture containing $ZnCl_2$, $CdCl_2$ and $CuCl_2$. H_2S gas is now passed through the aqueous solution of salt to form black ppt. the precipitate contains	CdS, CuS	CdS, Cus, ZnS	Cus, ZnS	only CuS	CdS,Cus,ZnS

UNIT- II
SYLLABUS

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.

Introduction

Justus von Liebig attempted initial experiments on reaction of carbon monoxide with metals in 1834. However, it was demonstrated later that the compound he claimed to be potassium carbonyl was not a metal carbonyl at all. After the synthesis of [PtCl2(CO)2] and [PtCl2(CO)]2 reported by Schutzenberger (1868) followed by [Ni(CO)4] reported by Mond et al (1890), Hieber prepared numerous compounds containing metal and carbon monoxide.

- Compounds having at least one bond between carbon and metal are known as organometallic compounds.
- Metal carbonyls are the transition metal complexes of carbon monoxide containing metal-carbon bond.
- Lone pair of electrons are available on both carbon and oxygen atoms of carbon monoxide ligand. However, as the carbon atoms donate electrons to the metal, these complexes are named as carbonyls.
- A variety of such complexes such as mono nuclear, poly nuclear, homoleptic and mixed ligand are known.
- These compounds are widely studied due to industrial importance, catalytic properties and structural interest.
- Carbon monoxide is one of the most important π- acceptor ligand. Because of its π-acidity, carbon monoxide can stabilize zero formal oxidation state of metals in carbonyl complexes

SYNTHESIS OF METAL CARBONYLS

Direct Combination

Only Ni(CO)4 and Fe(CO)5 and Co2(CO)8 are normally obtained by the action of carbon monoxide on the finely divided metal at suitable temperature and pressure

$$\mathrm{Ni(s) + 4CO(g) \xrightarrow{30^{O}C,\,1\,atm} Ni(CO)_4(l)}$$

$$\mathrm{Fe(s) + 5CO(g) \xrightarrow{200^{O}C,\,200\,atm} Fe(CO)_5(l)}$$

$$\mathrm{2Co(s) + 8CO(g) \xrightarrow{150^{O}C,\,35\,atm} Co_2(CO)_8(s)}$$

Reductive carbonylation

Many metallic carbonyls are obtained when salts like Ru(acac)3, CrCl3, Re2O7, VCl3, CoS, Co(CO)3, CoI2 etc. are treated with carbon monoxide in presence of suitable reducing agent like Mg, Ag, Cu, Na, H2, AlLiH4 etc.

$$\mathrm{3\,Ru(acac)_3(solution) + H_2(g) + 12\,CO(g) \xrightarrow{150^{O}\,C,\,200\,atm,\,methanol} Ru_3(CO)_{12}}$$

$$\mathrm{CrCl_3(s){+}Al(s){+}6CO(g) \xrightarrow{AlCl_3,\,benzene} Cr(CO)_6(solution)}$$

$$\mathrm{2\,CoI_2 + 8\,CO + 4\,Cu \xrightarrow{200°\,C,\,200\,atm\,press.} Co_2(CO)_8 + 4\,CuI}$$

$$\mathrm{2\,FeI_2 + 5\,CO + 2\,Cu \xrightarrow{200°\,C,\,200\,atm\,press.} Fe(CO)_5 + Cu_2I_2}$$

$$\mathrm{2\,CoCO_3 + 8\,CO + 2\,H_2 \xrightarrow{120-200°\,C,\,250-300\,atm\,press} Co_2CO_8 + 2\,CO_2 + 2\,H_2O}$$

$$\mathrm{MoC1_5 + 6\,CO + 5\,Na \xrightarrow{diglyme} Mo(CO)_6 + 5\,NaC1}$$

Preparation of mononuclear carbonyls from iron pentacarbonyl

The labile carbonyl groups in iron pentacarbonyl can be replaced by chloride to give a different metal carbonyl. These reactions are characterized by low yield, which can be improved using high pressure.

$$MoCl_6 + 3Fe(CO)_5 \xrightarrow{110\ ^oC,\ ether} Mo(CO)_6 + 3FeCl_2 + 9CO$$

$$WCl_6 + 3Fe(CO)_5 \xrightarrow{110\ ^oC,\ ether} W(CO)_6 + 3FeCl_2 + 9CO$$

PHYSICAL PROPERTIES

State:

Majority of the metallic carbonyls are liquids or volatile solids.

Colour:

Most of the mononuclear carbonyls are colourless to pale yellow. V(CO)6 is a bluish-black solid. Polynuclear carbonyls exhibit are dark in colour.

Solubility:

Metal carbonyls are soluble in organic solvents like glacial acetic acid, acetone, benzene, carbon tetrachloride and ether.

Toxicity:

Due to low melting points and poor thermal stability, they show toxicity related to the corresponding metal and carbon monoxide. Exposure to these compounds can cause damage to lungs, liver, brain and kidneys. Nickel tetracarbonyl exhibits strongest inhalation toxicity. These compounds are carcinogenic over long-term exposure.

Magnetic Property:

All the metal carbonyls other than vanadium hexacarbonyl are diamagnetic. The metals with even atomic number form mononuclear carbonyls. Thus, all the electrons in the metal atoms are paired. In case of dinuclear metal carbonyls formed by metals with odd atomic number, the unpaired electrons are utilized for the formation of metal-metal bonds.

Thermal Stability:

Most of the metal carbonyls melt or decompose at low temperatures. Solid carbonyls sublime in vacuum but they undergo some degree of degradation.

Thermodynamic Stability:

Metal carbonyls are thermodynamically unstable. They undergo aerial oxidation with different rates. Co2(CO)8 and Fe2(CO)9 are oxidized by air at room temperature while chromium and molybdenum hexacarbonyls are oxidized in air when heated.

CHEMICAL PROPERTIES

Ligand substitution reactions:

Substitution of carbon monoxide ligand by various mono dentate and bidentate ligands can be carried out using thermal and photochemical reactions. Monodentate ligands likeisocyanides (CNR), cyanide (CN-), phosphine (PR3) and ethers can partially or completely replace the carbonyl group.

$$Fe(CO)_5 + 2CNR \rightarrow Fe(CO)_3(CNR)_2 + 2CO$$

$$Ni(CO)_4 + 4CNR \rightarrow Ni(CNR)_4 + 4CO$$

$$Mn_2(CO)_{10} + PR_3 \rightarrow 2Mn(CO)_4\left(PR_3\right) + 2CO$$

$$2Fe_2(CO)_{12} + 3py \rightarrow Fe_3(CO)_9(py)_3 + 3Fe(CO)_5$$

Bidentate ligands like o-phenylene-bis(dimethyl arsine) (diars) and o-phenanthroline(o-phen) can replace carbonyl groups in the multiple of two

$$Mo(CO)_6 + diars \rightarrow Mo(CO)_4(diars) + 2CO$$

$$Ni(CO)_4 + o\text{-}phen \rightarrow Ni(CO)_2(o\text{-}phen)_2 + 2CO$$

$$Cr(CO)_6 + 2\,diars \rightarrow Cr(CO)_2(diars)_2 + 4CO$$

Reaction with halogens

Most of the metal carbonyls react with halogens to give carbonyl halides

$$Fe(CO)_5 + X_2 \rightarrow Fe(CO)_4X_2 + CO$$

$$Mo(CO)_6 + Cl_2 \rightarrow Mo(CO)_4Cl_2 + 2CO$$

Halogens can cause cleavage in the metal-metal bonds in case of polynuclear carbonyls

$$Ni(CO)_4 + Br_2 \rightarrow NiBr_2 + 4CO$$

$$Co_2(CO)_8 + 2X_2 \rightarrow 2CoX_2 + 8CO$$

Reaction with hydrogen

Some of the carbonyls can be reduced by hydrogen to give carbonyl hydrides

$$Co_2(CO)_8 + H_2 \xrightarrow{165^{O}\,C,\,200\,atm} 2[Co(CO)_4H]$$

$$Mn_2(CO)_{10} + H_2 \xrightarrow{200\,atm} 2[Mn(CO)_5H]$$

Even though, these compounds are named as hydrides, they are known to behave as proton donors. The neutral hydrides like [Co(CO)4H] and [Mn(CO)5H] behave as acids as shown below

$$[Co(CO)_4H] \rightarrow [Co(CO)_4]^- + H^+$$

$$[Mn(CO)_5H] \rightarrow [Mn(CO)_5]^- + H^+$$

Reaction with nitric oxide

A good number of metal carbonyls react with nitric oxide to give carbonyl nitrosyls

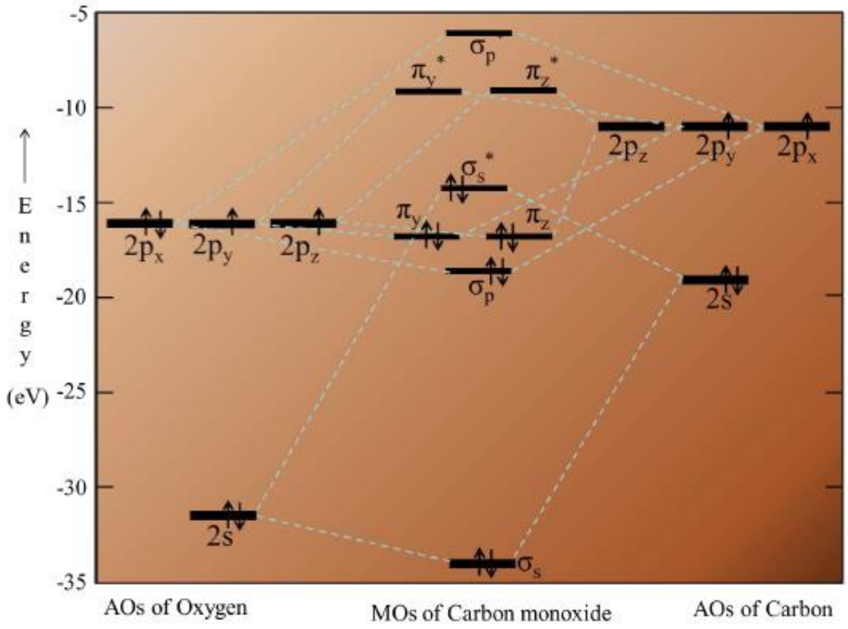
$$Fe(CO)_5 + 2NO \xrightarrow{95^0 C} Fe(CO)_2(NO)_2 + 3CO$$

$$Co_2(CO)_8 + 2NO \xrightarrow{40^0 C} 2Co(CO)_3(NO) + 2CO$$

The reaction between iron pentacarbonyl and nitric oxide involves replacement of three carbonyl groups by two nitric oxide molecules. Electronically, this is equivalent as nitric oxide is a three electron donor ligand whereas carbon monoxide is a two electron donor.

BONDING IN METALLIC CARBONYLS

In order to understand the bonding in metal carbonyls, let us first see the MO diagram of carbon monoxide

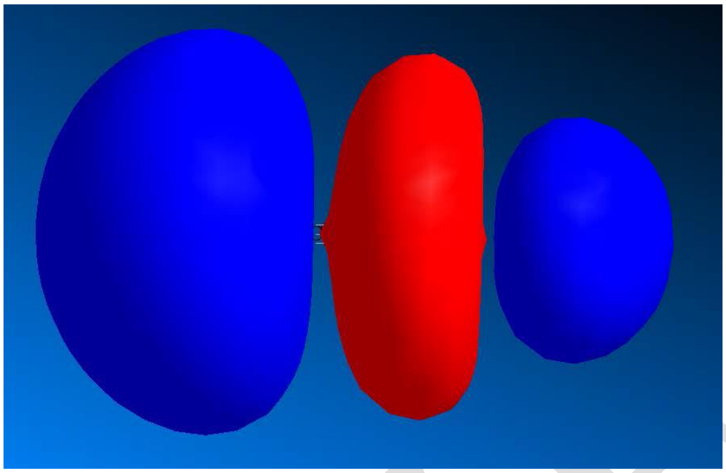


The order of energy of the molecular orbitals and the accommodation of ten electrons of the carbon monoxide can be shown as

$$(\sigma_s^b)^2 (\sigma_p^b)^2 (\pi_y^b=\pi_z^b)^4 (\sigma_s^*)^2 (\pi_y^*=\pi_z^*)^0 (\sigma_p^*)^0$$

(σ_s^*) is the highest occupied molecular orbital (HOMO) which can donate the lone pair of electrons for the formation of a OC→M σ bond

($\pi_y^*=\pi_z^*$) are the lowest unoccupied molecular orbitals (LUMO) which can accept the electron density from an appropriately oriented filled metal orbital resulting into formation of a M→CO π bond.



Red colour is for positive sign of the wave function while the blue colour indicates negative sign of the wave function

Formation of dative σ-bond

The overlapping of empty hybrid orbital (a blend of d, s and p orbitals) on metal atom with the filled hybrid orbital (HOMO) on carbon atom of carbon monoxide molecule results into the formation of a M←CO σ-bond

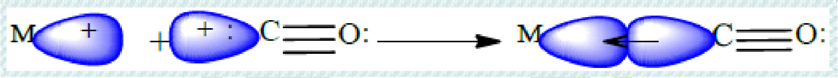
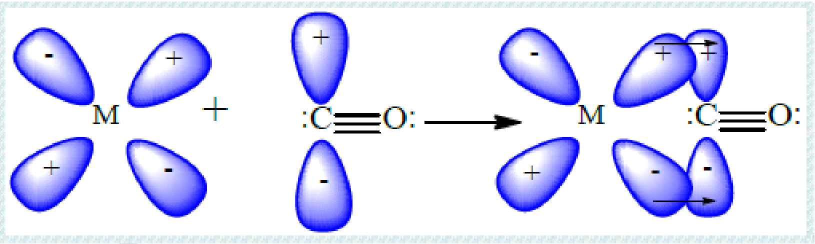


Figure: Formation of a M←CO σ-bond in metal carbonyls

Formation of π-bond by back donation

This bond is formed because of overlapping of filled dπ orbitals or hybrid dpπ orbitals of metal atom with low-lying empty (LUMO) orbitals on CO molecule. i.e. MCO π→



Bridging CO groups

In addition to the linear M-C-O groups, the carbon monoxide ligand is also known to form bridges. This type of bonding is observed in some binuclear and polynuclear carbonyls. It is denoted by μn–CO, where n indicates the number of metals bridged. While n=2 is the most common value, it reaches to be 3 or 4 in certain less common carbonyls.

In a terminal M-C-O group, the carbon monoxide donates two electrons to an empty metal orbital, while in μ2–CO group, the M-C bond is formed by sharing of one metal electron and one carbon electron.

Ni(CO)4,Nickel tetracarbonyl:

Preparation:

It can be prepared by passing carbon monoxide over nickel in the temperature range of 60-100 ^{o}C.

$$\mathrm{Ni + 4CO \xrightarrow{60^{0}\,C} Ni(CO)_4}$$

It can be made by heating nickel iodide with carbon monoxide in the presence of copper which acts as a halogen acceptor

$$\mathrm{NiI_2 + 4CO \xrightarrow{Cu} Ni(CO)_4 + CuI_2}$$

Properties:

It is a colourless liquid having melting point -25oC, boiling point 43oC and decomposition temperature in the range of 180–200oC.

It is insoluble in water but dissolves in organic solvents.

It reacts with concentrated sulphuric acid along with detonation

$$\mathrm{Ni(CO)_4 + H_2SO_4 \rightarrow NiSO_4 + H_2 + 4CO}$$

It reacts with moist nitric oxide to give deep blue coloured compound

$$\mathrm{2Ni(CO)_4 + 2NO + 2H_2O \rightarrow 2Ni(NO)(OH) + 8OH^{-} + H_2}$$

Passing gaseous hydrochloric acid in the solution of nickel tetracarbonyl results in the decomposition

$$\mathrm{Ni(CO)_4 + 2HCl_{(g)} \rightarrow NiCl_2 + H_2 + 4CO}$$

Uses:

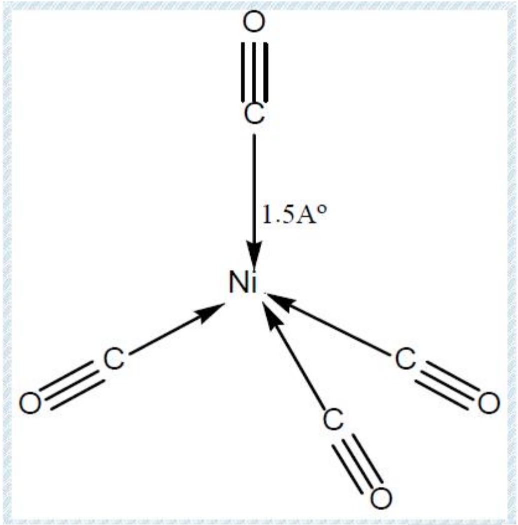
Since Ni(CO)4, on heating, decomposes to metallic nickel, it is used in the production of nickel by Mond’s process.

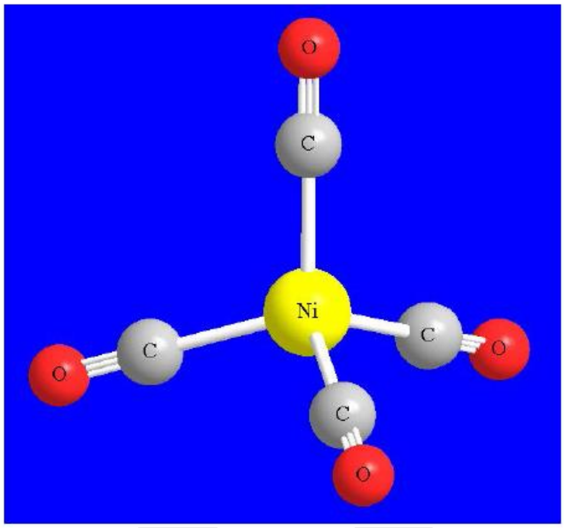
It is used for plating nickel on other metals.

It is used as a catalyst for synthesis of acrylic monomers in plastic industries

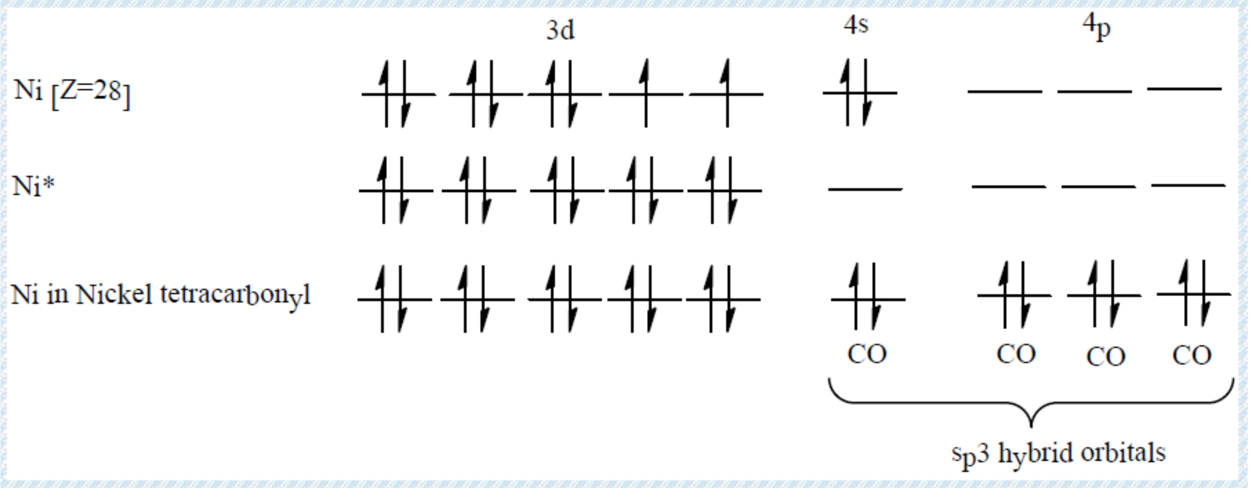
Structure:

Nickel tetracarbonyl has a tetrahedral geometry with Ni-C bond lengths of 1.5 Å. It is also found to be diamagnetic





The structure of Ni(CO) 4 can be explained by considering sp3 hybridization of Ni atom. Since it is diamagnetic, all the ten electrons present in the valence shell of Ni atom (Ni = 3d8 4s2) get paired in 3d orbitals. Thus the valence shell configuration of Ni atom in Ni(CO) 4 molecule becomes 3d10 4s0. OC→Ni bond results by the overlap between the empty sp3 hybrid orbital on Ni atom and the HOMO on C atom in CO molecule as shown below



sp3 hybridization of nickel atom in nickel tetracarbonyl

Acceptance of four electron pairs by nickel in zero oxidation state severely increases the electron density on the nickel atom. According to the electro neutrality principle given by Pauling, the atoms in a molecule share the electron pairs to the extent such that charge on each of the atom remains close to zero. Thus, the nickel atom donates back some electron density from the filled d-orbitals to the low-lying empty (LUMO) orbitals on CO molecule resulting into formation of a double bond. i.e. MCO.

Fe(CO)5, Iron pentacarbonyl

Preparation:

It can be prepared by passing carbon monoxide over iron powder at high temperature and pressure.

$$\mathrm{Fe + 5CO \xrightarrow{200^{O}\,C,\,100\ atm.} Fe(CO)_5}$$

It can also be prepared by carbonylation of ferrous sulphide/iodide in presence of Cu-metal, which acts as a reducing agent

$$\mathrm{2FeS + 10CO + 2Cu \xrightarrow{200^{O}\,C,\,200\ atm.} Fe(CO)_5 + Cu_2S}$$

Properties:

It is a pale yellow liquid having melting point -20 oC, boiling point 103 oC and decomposition temperature around 250 oC.

It is insoluble in water but soluble in glacial acetic acid, methanol, diethyl ether, acetone and benzene.

Cold solution of iron pentacarbonyl in glacial acetic acid undergoes dimerization under the influence of ultra-violet light

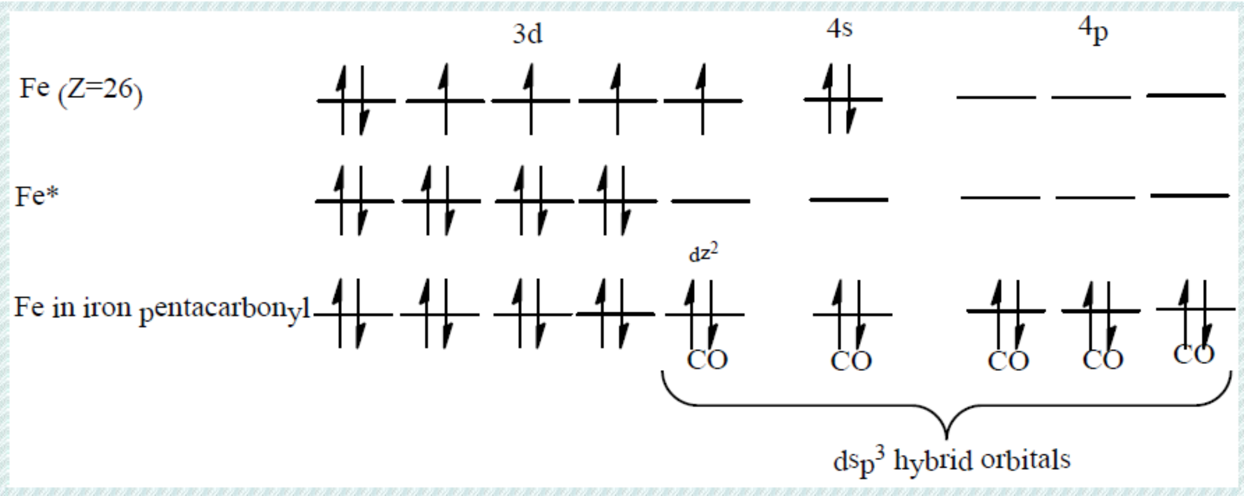
$$\mathrm{2Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO}$$

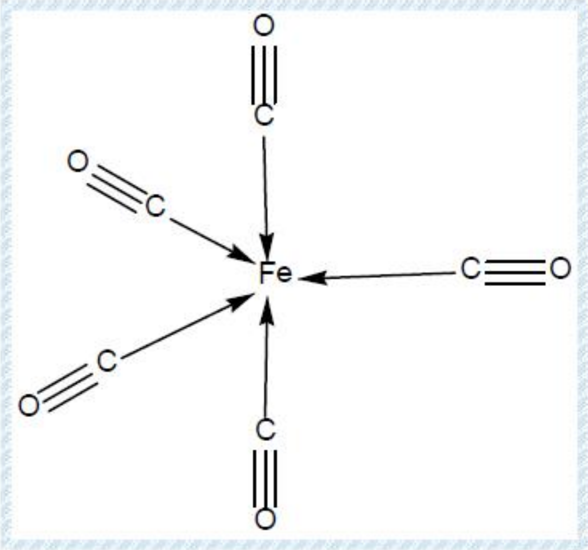
The reaction of sodium hydroxide with iron pentacarbonyl results in nucleophilic attack by hydroxide ion on the carbonyl group to give a metal carboxylic acid complex. Upon further action with sodium hydroxide, the carboxylic acid gives up carbon dioxide to form a hydrido anion. The protonation of this anion results in the formation of iron tetracarbonyl hydride (Heiber base) as shown below:

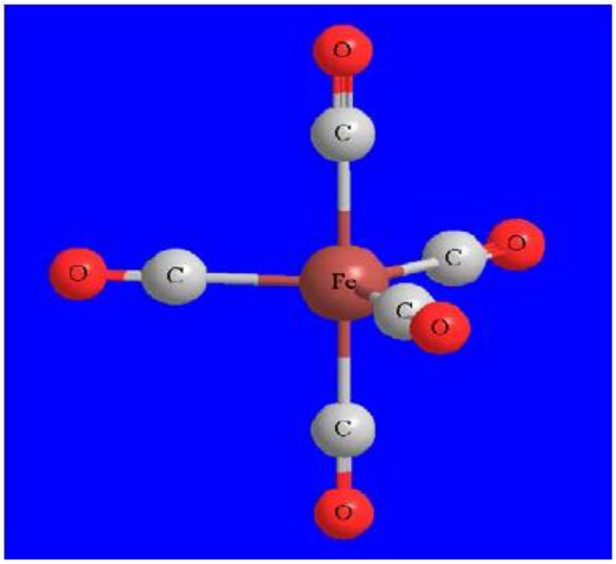
$$\mathrm{Fe(CO)_5 + NaOH \rightarrow Na[Fe(CO)_4COOH]}$$
$$\mathrm{Na[Fe(CO)_4COOH] + NaOH \rightarrow Na[HFe(CO)_4] + NaHCO_3}$$
$$\mathrm{Na[HFe(CO)_4] + H^+ \rightarrow [(H)_2Fe(CO)_4] + Na^+}$$

Structure:

The structural studies have suggested trigonal bipyramidal geometry for iron pentacarbonyl. The Fe-C distances are found to be 1.80 Å and 1.84 Å for axial and equatorial bonds respectively. The molecule is also found to be diamagnetic







The structure can be explained using dsp^3 hybridization in Fe atom. All eight electrons present in the valence shell of Fe atom (Fe:$3d^64s^2$) get paired in four 3d orbitals. Thus the valence shell configuration of Fe in $\mathrm{Fe(CO)_5}$ becomes $3d^84s^0$. The OC→Fe bond results by the overlap between the empty dsp3 hybrid orbitals on Fe atom and the HOMO on C atom in CO molecule as shown above.

Cr(CO)6, Chromium hexacarbonyl

Preparation:

It can be prepared by carbonylation of chromium chloride with carbon monoxide using a reducing agent like lithium aluminium hydride (LAH).

$$CrCl_3 + 6CO \xrightarrow{LAH, 115^{o} C, 70 \text{ atm}} Cr(CO)_6$$

An indirect method of preparation involves an action of carbon monoxide on a mixture of Grignard reagent and anhydrous chromium chloride in ether which is followed by decomposition with an acid to give chromium hexacarbonyl.

$$C_6H_5MgBr + CrCl_3 + CO \xrightarrow{35-70 \text{ atm}} Cr(CO)_2(C_6H_5)_4 + MgBrCl + MgBr_2$$

$$Cr(CO)_2(C_6H_5)_4 + 6H^+ \rightarrow Cr(CO)_6 + 2Cr^{+3} + 12(C_6H_5)^- + 3H_2$$

Properties:

It is a white crystalline solid melting above 150 $_{o}$C and boiling at 220 $_{o}$C.

It is insoluble in water but soluble in ether, chloroform, carbon tetrachloride and benzene.

It is not attacked by air, bromine, cold aqueous alkalis, dilute acids and concentrated hydrochloric acid as well as sulphuric acid. It is decomposed by Chlorine gas and concentrated nitric acid. It reacts with fluorine at -75 $_{o}$C to form chromium hexafluoride.

It reacts with sodium metal in liquid ammonia to give carbonylate anion

$$Cr(CO)_6 + 2\,py \rightarrow \underset{\text{yellowish brown}}{Cr(CO)_4(py)_2} + 2\,CO$$

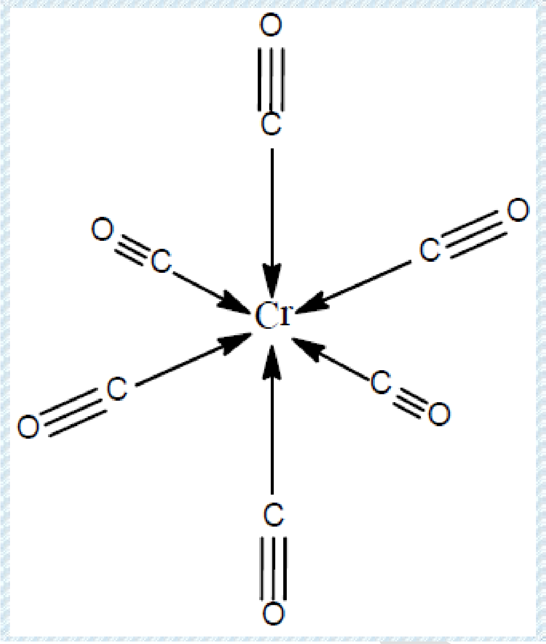
$$2\,Cr(CO)_6 + 5\,py \rightarrow \underset{\text{orange}}{Cr_2(CO)_7(py)_5} + 5\,CO$$

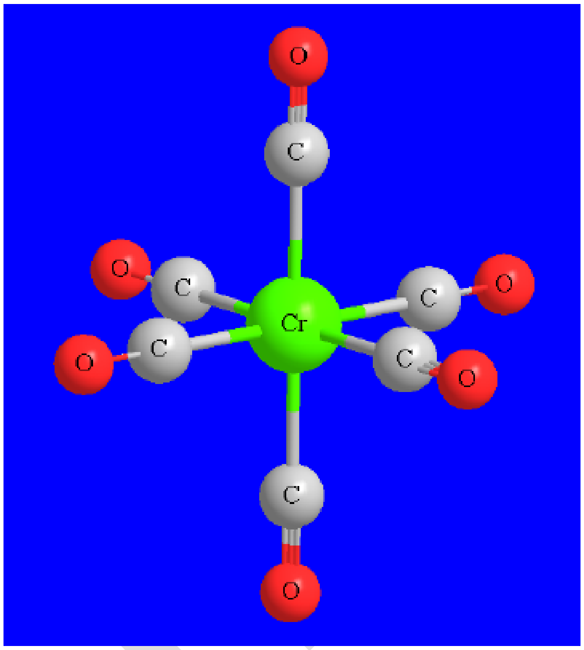
$$Cr(CO)_6 + 3\,py \rightarrow \underset{\text{bright red}}{Cr(CO)_3(py)_3} + 3\,CO$$

It gives substitution reactions with amines like en and py. At higher temperatures (>150^{o}C) several pyridyl derivatives are formed

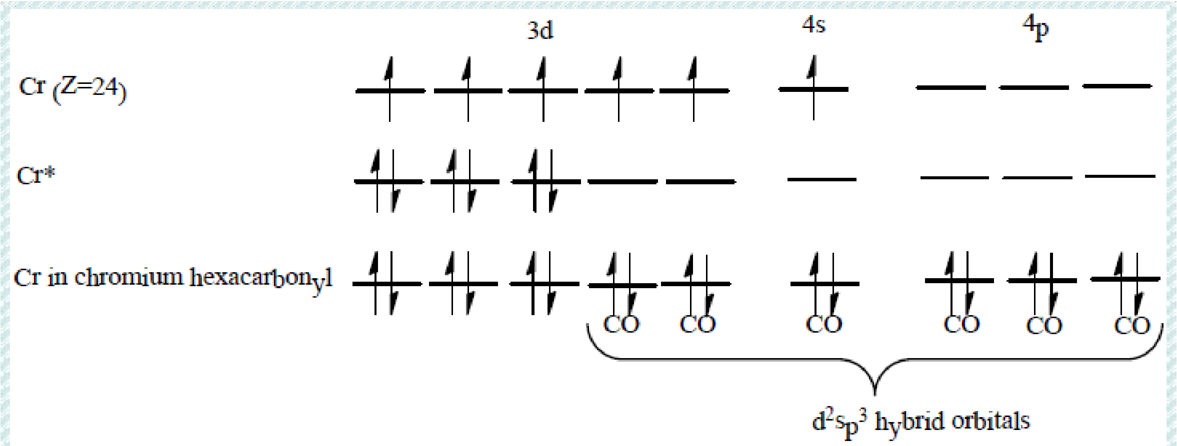
Structure

The structural studies have suggested an octahedral geometry for chromium hexacarbonyl. The Cr-C distance is found to be 1.92 Å while the C-O bond length is 1.16 Å. The molecule is also found to be diamagnetic.





The structure can be explained using d2sp3 hybridization in Cr atom. All six electrons present in the valence shell of Cr atom (Cr: 3d54s1) get paired in three 3d orbitals. Thus the valence shell configuration of Cr in Cr(CO)6 becomes 3d64s0. The OC→Cr bond results by the overlap between the empty d2sp3 hybrid orbitals on Fe atom and the HOMO on C atom in CO molecule as shown below



The MO energy diagram for $Cr(CO)_6$ is shown in the figure below. For the molecular orbitals, 12 electrons are contributed from the lone pairs on the carbon atoms of the six carbon monoxide ligands.

The metal contributes six electrons while 24 electrons come from the π system of the six ligands. The MOs are occupied by these 42 electrons and the t_{2g} level becomes the highest occupied molecular orbital (HOMO) of the metal carbonyl.

POLYNUCLEAR CARBONYLS

$Mn_2(CO)_{10}$, Dimanganese decacarbonyl

Preparation:

It can be prepared by carbonylation of manganese iodide with carbon monoxide using magnesium as a reducing agent.

$$2\,MnI_2 + 10\,CO + \underset{\text{(diethyl ether)}}{2\,Mg} \xrightarrow{25\,^{o}C,\ 210\ atm.} Mn_2(CO)_{10} + 2\,MgI_2$$

It can also be obtained by carbonylation of anhydrous manganese chloride with carbon monoxide in presence of sodium benzophenone ketyl.

$$2\,MnCl_2 + 10\,CO + 4(C_6H_5)_2\,CONa \xrightarrow{165\,^{\circ}C,\ 140\ atm.} Mn_2(CO)_{10} + 4(C_6H_5)_2\,CO + 4\,NaCl$$

Properties:

It forms stable golden yellow crystals having melting point of 155 ^{o}C.

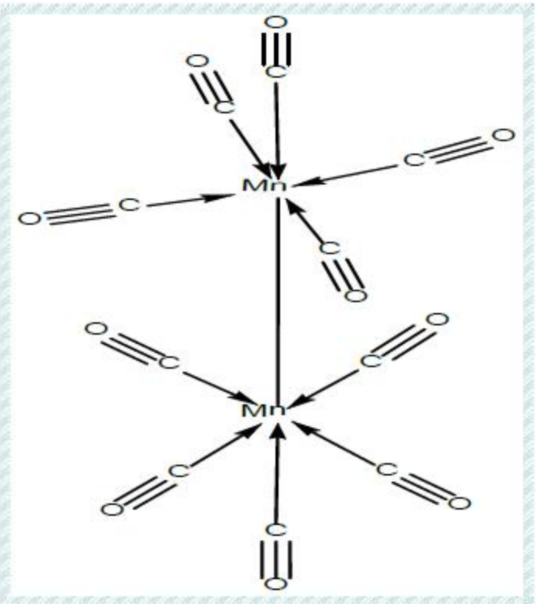
It is oxidized by trace amount of oxygen in solution. Hence, the solution must be stored in inert atmosphere.

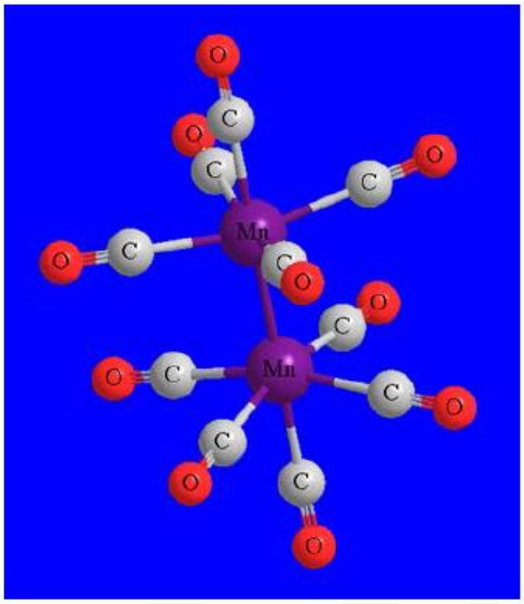
Halogenation of dimanganese decacarbonyl proceeds with breaking of Mn-Mn bond and formation of carbonyl halides

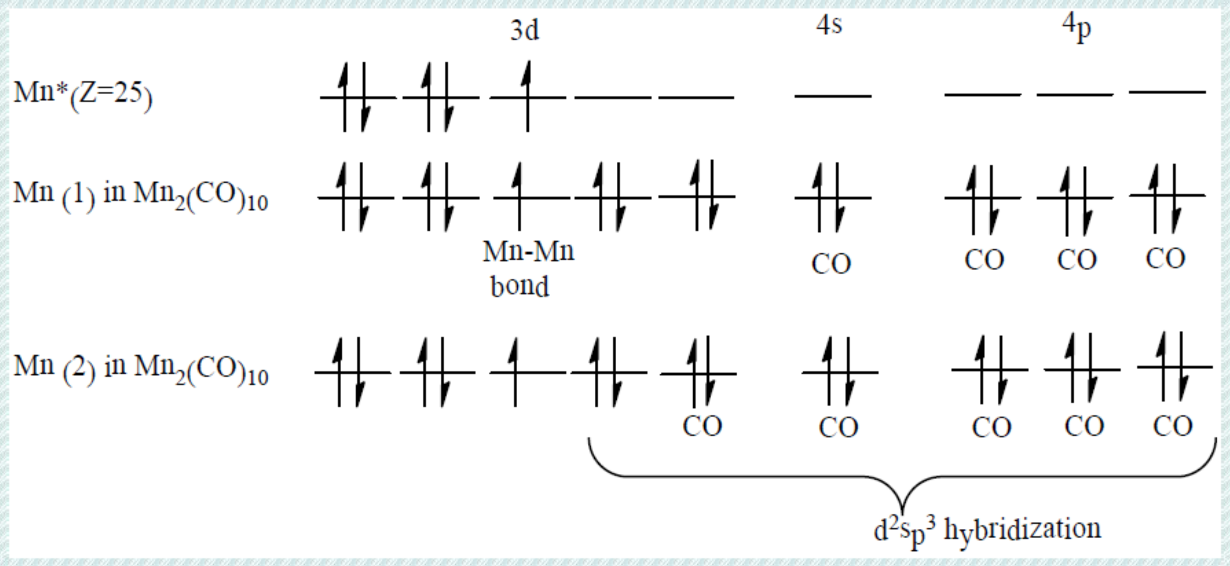
$$Mn_2(CO)_{10} + X_2\,(X = Br, I) \rightarrow 2\,Mn(CO)_5\,X$$

Manganese pentacarbonyl does not exist as Mn (Z=25) has an odd atomic number. However, the structure of dimanganese decacarbonyl consists of two manganese pentacarbonyl groups joined through a Mn-Mn (2.79 Å) bond. The formation of this inter metallic bond effectively adds one electron to each of the manganese atoms. Thus, manganese, an element with odd atomic number forms a binuclear carbonyl. Since the molecule does not have any unpaired electrons, it isdiamagnetic. The remaining two members of group VIIB viz. Technetium (Tc) and Rhenium (Re) also form decacarbonyls with similar structures.

Structure







d2sp3 hybridization in dimanganese decacarbonyl.

Co2(CO)8, Dicobalt octacarbonyl

Preparation:
It can be prepared by direct combination of carbon monoxide with cobalt metal.

$$2\,Co + 8\,CO \xrightarrow{200°\,C,\,100\ atm} Co_2(CO)_8$$

It can also be prepared by carbonylation of cobalt iodide/cobalt sulphide/cobalt carbonate using reducing agents like copper metal or hydrogen gas.

$$2\,CoS/\,2\,CuI_2 + 8\,CO + 4\,Cu \xrightarrow{200°\,C,\,200\ atm} Co_2(CO)_8 + 2\,Cu_2S/\,4\,CuI$$

$$2\,CoCO_3 + 8\,CO + 2\,H_2 \xrightarrow{120-200°\,C,\,250-300\ atm} Co_2(CO)_8 + 2\,H_2O$$

Properties:

It is an orange crystalline substance having melting point 51oC and turns deep violet upon exposure to air.

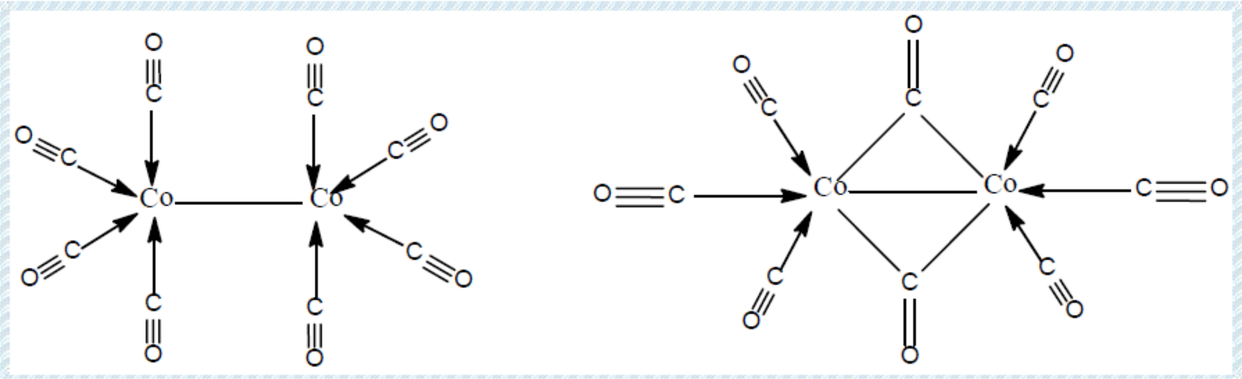
It is soluble in alcohols, ether and carbon tetrachloride.

Upon heating at 50 oC it forms tetracobalt dodecacarbonyl

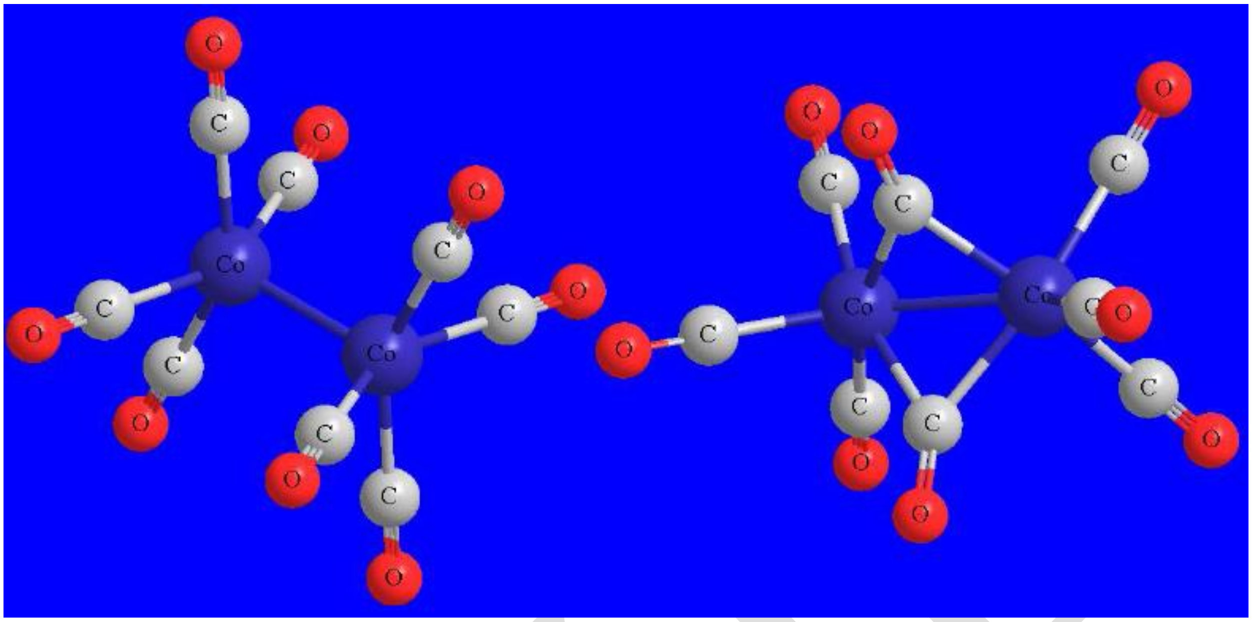
$$2\,Co_2(CO)_8 \xrightarrow{50°\,C} Co_4(CO)_{12} + 4\,CO$$

It reacts with nitric oxide to form cobalt carbonyl nitrosyl

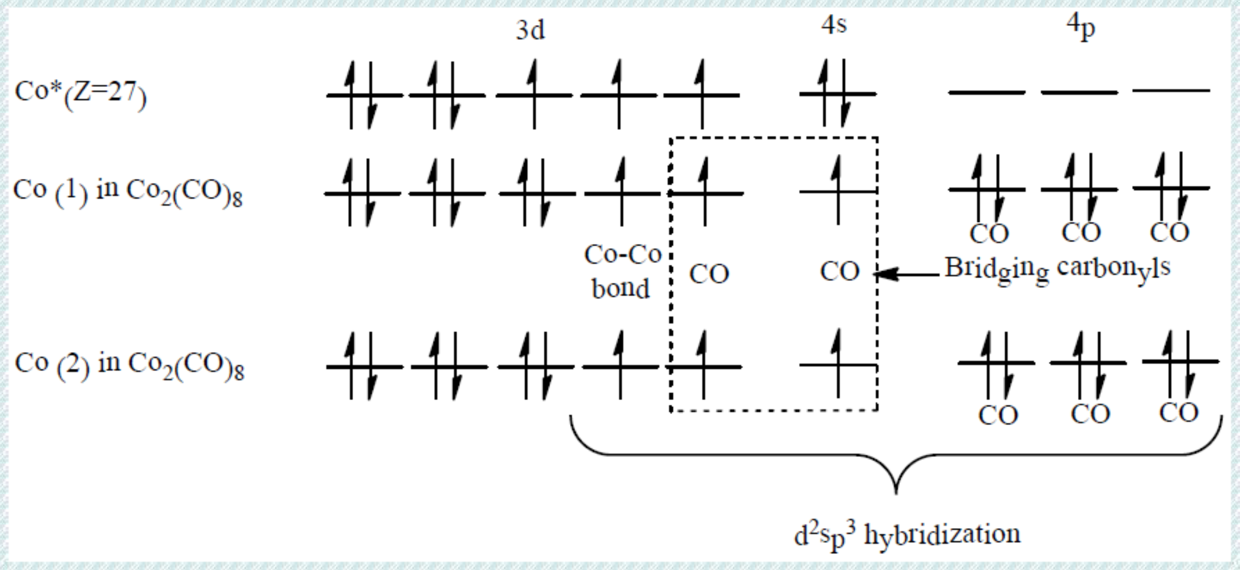
$$Co_2(CO)_8 + 2\,NO \rightarrow [Co^-(CO)_8(NO)^+]^0 + 2\,CO$$



Dicobalt octacarbonyl is known to exist in two isomeric forms. A bridged structure of this molecule is observed in the solid state as well as solution state at a very low temperature. A non - bridged structure predominates in a solution at temperatures above ambience

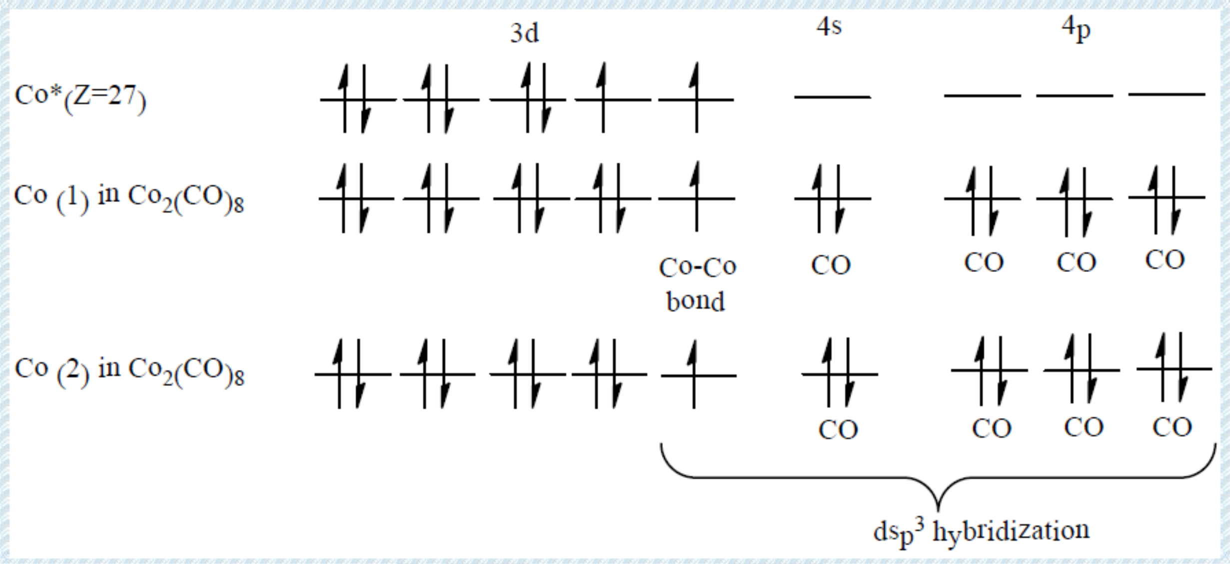


In the bridged structure, the cobalt atoms are in d2sp3 hybrid state. Three such hybrid orbitals on each cobalt atom accept lone pair of electrons from three carbon monoxide molecules to form total six Co←CO coordinate bonds. A Co-Co bond is formed by the overlapping of two half - filled d2sp3 hybrid orbitals on the cobalt atoms. Remaining two half–filled hybrid orbitals on each Co atom overlap with appropriate orbital on carbon atom of the carbonyl to form two bridging CO groups. Thus, all electrons in this molecule are paired and it is diamagnetic.



In the structure without bridge, the cobalt atoms are in dsp3 hybrid state. Out of the five hybrid orbitals on each cobalt atom, four orbitals on each cobalt atom accept a lone pair of electrons from the carbon monoxide molecules to form eight Co←CO coordinate bonds. One half–filled orbitals on each cobalt overlap to form a Co-Co bond

In case of non-bridge structure, Co atoms have dsp3 hybridization as shown below



dsp3 hybridization in dicobalt octacarbonyl

Fe2 (CO) 9, Diiron nonacarbonyl

Preparation:

Cold solution of iron pentacarbonyl in glacial acetic acid undergoes dimerization under the influence of ultra-violet light to give golden yellow crystals

$$2\,Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO$$

Properties:

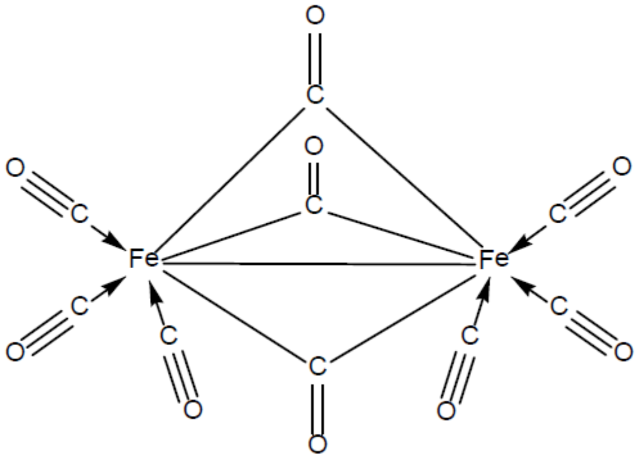
Diiron nonacarbonyl forms golden yellow triclinic crystals melting at 100 oC.

It is insoluble in water but soluble in toluene and pyridine.

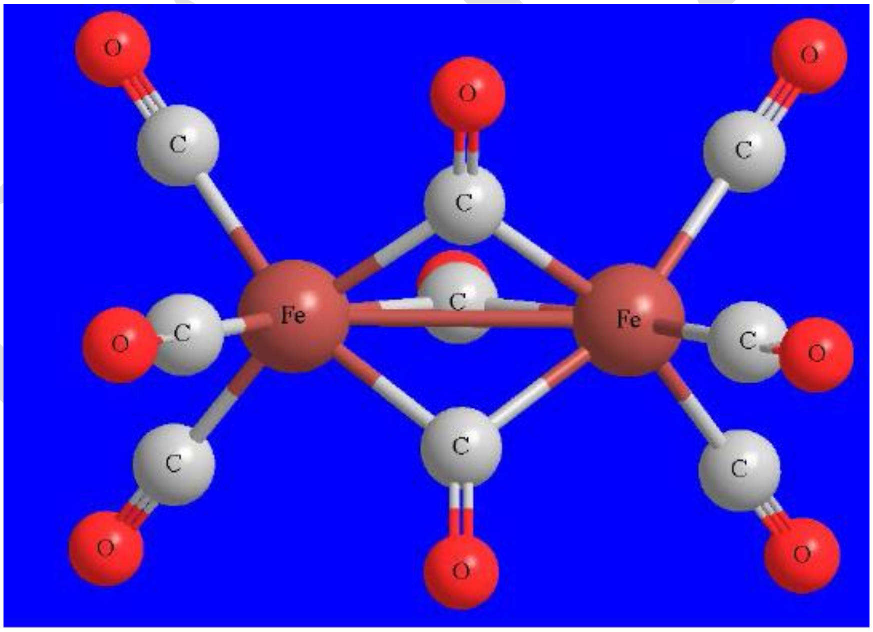
A solution of diiron nonacarbonyl in toluene disproportionates when heated to 70 oC

$$3\,Fe_2(CO)_9 \xrightarrow{70^\circ C,\ Toluene} 3\,Fe(CO)_5 + Fe_3(CO)_{12}$$

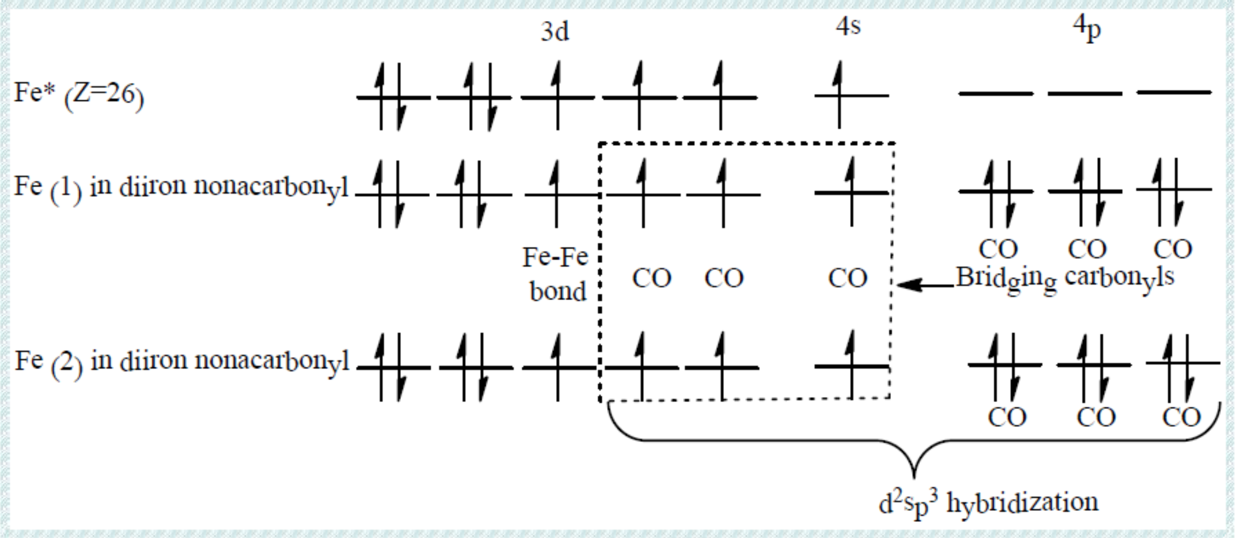
Structure:



Each of the iron atoms in diiron nonacarbonyl has three terminal carbonyl groups. The remaining three carbon monoxide ligands act as μ_2–CO groups. In addition to this, there is a weak Fe-Fe bond (2.46 Å) formed by sharing of two unpaired electrons present in the 3d orbitals of iron atoms. Thus, both the iron atoms in the molecule are identical with coordination number seven. Since the molecule does not have any unpaired electron, it is diamagnetic.



The structure of this molecule can be explained using d^2sp^3 hybridization in Fe atoms as shown in the figure.



d2sp3 hybridization in diiron nonacarbonyl

EFFECTIVE ATOMIC NUMBER (EAN) RULE:

Effective Atomic Number (EAN) is the total number of electrons surrounding the nucleus of a metal in a complex.

Sidgwick's EAN rule / Inert gas rule:

"The EAN of the metal atom in a stable complex is equal to the atomic number of a noble gas found in the same period of the periodic table."

Most of the organometallic compounds including carbonyls and nitrosyls obey the EAN rule.

It is mainly useful in predicting the number of ligands attached to the metal in such compounds.

Calculation of EAN:

An equation for calculating the EAN may be represented as follows:

EAN = Z + a + b + c

Where,

Z = Atomic number of metal atom

a = Number of electrons donated by terminal carbonyl groups

b = Number of electrons donated by bridging carbonyl groups

c = Number of electrons donated by other metal atom for the formation of M-M bonds

The EAN for nickel atom in nickel tetracarbonyl can be calculated as follows:

In nickel tetracarbonyl,

Z = Atomic number of metal atom = Atomic number of nickel atom = 28

a = Number of electrons donated by terminal carbonyl groups = 4 terminal carbonyl groups x 2 electrons donated by each group = 8

b = Number of electrons donated by bridging carbonyl groups = 0 (Because there are no bridge bonds)

c = Number of electrons donated by other metal atom for the formation of M-M bonds = 0 (Because there are no M-M bonds)

Thus,

EAN = Z + a + b + c = 28 + 8 + 0 + 0 = 36

Here, the effective atomic number is found to be 36 which is the atomic number of Krypton (Z=36) which is a noble gas lying in the same period of the periodic table as Ni (Z=28).

Thus, EAN rule is said to be obeyed in nickel tetra carbonyl.

In order to check the validity of the 18- electron rule, we have to put the number of valence electrons of the metal atom in place of atomic number (Z) in the EAN equation.

The valence shell nickel (Ni = 3d8 4s2) atom has 10 valence electrons.

Thus,

The number of valence electrons surrounding the nucleus of the metal atom

= Number of valence electrons of metal atom + a + b + c = 10 + 8 + 0 + 0 = 18

Thus, nickel tetracarbonyl obeys the 18 - electron rule.

The EAN for iron atoms in triiron dodecacarbonyl can be calculated as follows:

In triiron dodecacarbonyl, two iron atoms are bridged and have same environment while the third iron atom has a different bonding environment. Thus, we need to calculate the EAN for both the types of iron atoms separately.

For, bridged iron atoms

Z = Atomic number of metal atom = Atomic number of iron atom = 26

a = Number of electrons donated by terminal carbonyl groups = 3 terminal carbonyl groups x 2 electrons donated by each group = 6

b = Number of electrons donated by bridging carbonyl groups = 2 bridging carbonyl groups x 1electron donated by each group = 2

c = Number of electrons donated by other metal atom for the formation of M-M bonds = 2 Fe-Fe bonds x 1 electron donated by each Fe atom = 2

Thus,

EAN = Z + a + b +c = 26 + 6 + 2 + 2 = 36

Here, the effective atomic number is found to be 36 which is the atomic number of Krypton (Z=36) which is a noble gas lying in the same period of the periodic table as Fe (Z=26).

Thus, EAN rule is said to be obeyed by the bridging Fe atoms in triiron dodecacarbonyl.

In order to check the validity of the 18- electron rule, we have to put the number of valence electrons of the metal atom in place of atomic number (Z) in the EAN equation.

The valence shell nickel (Fe = 3d6 4s2) atom has eight valence electrons.

Thus,

The number of valence electrons surrounding the nucleus of the metal atom

= Number of valence electrons of metal atom + a + b + c = 8 + 6 + 2 + 2 = 18

Thus, the bridging Fe atoms in triiron dodecacarbonyl obey the 18 - electron rule.

For, un-bridged iron atom,

Z = Atomic number of iron atom = 26

a = 4 terminal carbonyl groups x 2 electrons donated by each group = 8

b = 0 (Because no bridges are formed)

c = 2 Fe-Fe bonds x 1 electron donated by each Fe atom = 2

Thus,

EAN = Z + a + b + c = 26 + 8 + 0 + 2 = 36

Here, the effective atomic number is found to be 36 which is the atomic number of krypton (Z=36) which is a noble gas lying in the same period of the periodic table as Fe (Z=26).

Thus, EAN rule is said to be obeyed by the non-bridging Fe atom in triiron dodecacarbonyl.

In order to check the validity of the 18- electron rule, we have to put the number of valence electrons of the metal atom in place of atomic number (Z) in the EAN equation.

The valence shell of nickel (Fe = 3d6 4s2) atom has 8 valence electrons.

Thus,

The number of valence electrons surrounding the nucleus of the metal atom

= Number of valence electrons of metal atom + a + b + c = 8 + 6 + 2 + 2 = 18

Thus, the non-bridging Fe atom in triiron dodecacarbonyl obeys the 18 - electron rule.

18 Electron Rule

The octahedral complexes obeying the 18-electron rule (18-electron compounds) are especially stable. In order to understand this, consider the energy level diagram of an octahedral complex in presence of a strong field ligand

Electron counting methods:

There are two popular methods giving same results for the electron count. They areNeutral Ligand method (Covalent method)

Donor Pair method (Ionic method)

Neutral Ligand method:

In this method, all the ligands are treated as electrically neutral. It takes into account the number of electrons it can donate in its neutral state. The neutral ligands capable of donating two electrons are designated as L. The ligands like Cl- which can donate one electron in their neutral state are designated as X type ligands. The ligand cyclopentadienyl (η5-C5H5) which is a five-electron donor is designated by a combined symbol L2X. This method is easy to use when the ligands are properly designated. The over emphasis on degree of covalence along with negligence of the charge over the metal ion remain shortcomings of this method. Due to this, it becomes difficult to assign oxidation states to the metal ion resulting in the loss of important information related to the ligands.

The verification of 18-electron rule for a mixed ligand carbonyl complex (η5-C5H5)Fe(CO)2Cl can be carried out as follows:

In this complex, the Fe atom has eight valence electrons.

In addition to this, the ligand η5-C5H5 when considered as a neutral ligand contributes five electrons.

CO is two-electron donor, thus two CO ligands contribute 4 electrons.

Cl, counted as a neutral species is single electron donor, which contributes one electron in total.

Thus the total electron count can be shown as below

One Fe atom	8 electrons
One (η5-C5H5) ligand (L2X)	5 electrons
Two CO ligands (L)	4 electrons

One chlorine ligand (X)	1 electron
Total electron count	**18 electrons**

An organometallic compound containing ligands designated by L and X can be shown as [MXaLb]c, where a is the number of ligands of type X, b is the number of ligands of type L and c is the charge over the complex.

Electron Count = n + a + 2b – c, where n is the group number of the metal in periodic table.

(η5-C5H5)Fe(CO)2Cl can be represented as [(L2X)M(2L)(X)] or [MX2L4]

Electron Count = n + a + 2b – c = 8 + 2 + 2 x 4 – 0 = 18

Donor Pair method:

According to this method, some ligands are treated as neutral whereas the others are treated as charged. It is assumed that the ligands donate electrons only as pairs. Neutral ligands like CO are considered as two electron donors. Ligands like halides are considered to take an electron from metal and treated as X-. The ligand (η5-C5H5) is considered as C5H5-, which becomes a six-electron donor.

The oxidation state of the metal is calculated as total charge over the complex minus charges over the ligands. The number of electrons contributed by metal is calculated as the group number minus its oxidation number. Finally, the electron count is done as the total of electrons on the metal and the electrons contributed by the ligands.

A sample calculation for (η5-C5H5)Fe(CO)2Cl is provided below:

Here oxidation state of Fe, can be calculated as

-1 + X + 0 -1 = 0

X = +2

The group number of Fe is 8.

Therefore, number of electrons contributed by Fe is 8 - 2 = 6.

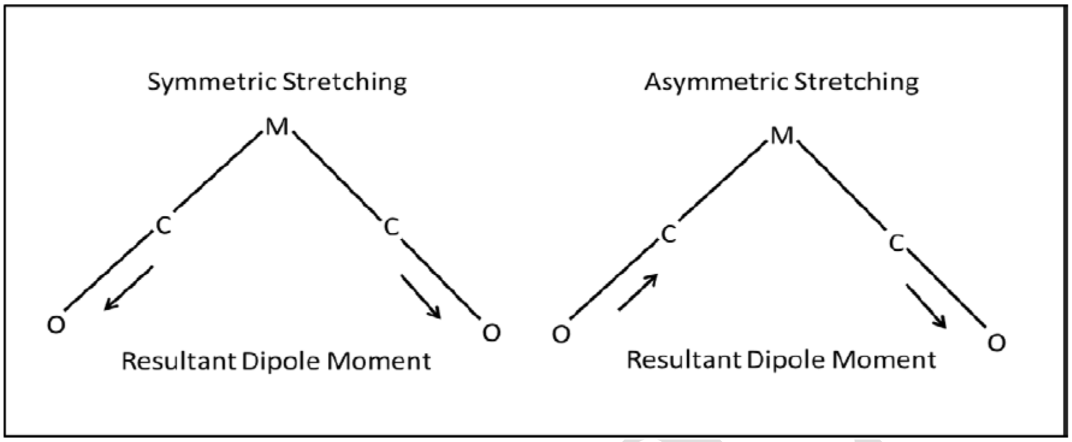
Number of electrons contributed by one C5H5- = 6.

Number of electrons contributed by two CO = 4.

Number of electrons contributed by one Cl- = 2

INFRARED SPECTROSCOPY

The carbonyl groups can have two modes of stretching



Since both of these modes result in change in dipole moment, two bands are expected in the infrared spectra of a terminally ligated carbon monoxide.

The infrared and Raman spectroscopy together can be used to determine the geometry of the metallic carbonyls.

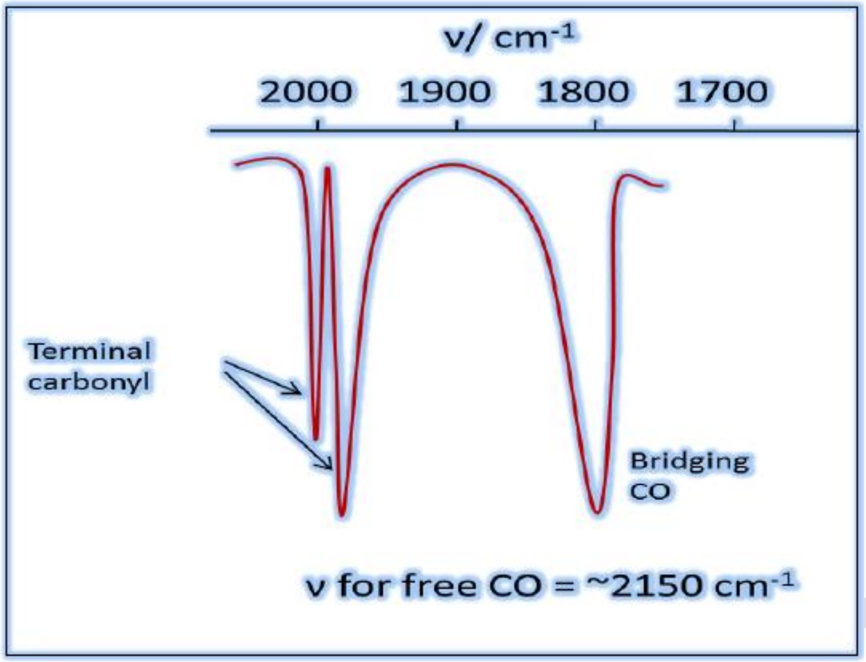
A mono nuclear pentacarbonyl can exist both in square pyramidal and trigonal bipyramidal geometry. Performing infrared spectra after calculating the IR active and Raman active bands in both the possible geometries can provide information about the actual geometry of the moleculeInfrared spectroscopy of metallic carbonyls helps in determining the bond order of ligated carbon monoxide.

The C-O bond order and the frequency related to its absorption are directly proportional. Thus, it can be predicted that the frequencies of absorption will be in the order shown below:

Free CO > metal carbonyl cation > neutral metal carbonyl > metal carbonyl anion.

The C-O bonding in terminal carbonyl groups is stronger than the bridged carbonyl groups. Therefore, it is possible to differentiate the terminal carbonyls which absorb in the region of 2050–1900 cm-1 from the bridged carbonyls absorbing below 1900 cm-1.

The change in the intensity of bands related to carbonyl group can provide information for the kinetic studies of the substitution reactions involving replacement of carbonyls



Carbonyl	*Type*	*C-O stretching frequency (cm-1)*
Carbon monoxide	Free	~2150
Mn(CO)6+	Cation	~2090
Cr(CO)6	Neutral	~2000
V(CO)6-	Anion	~1850

Possible Questions

PART-B (6 Mark Questions)

1. Write three different organometallic compounds and draw the structure
2. Explain the general classification of metal carbonyls with examples
3. Account the synthesis method of metal alkyl complexes
4. Explain α and β elimination process
5. States the bonding of alkenes to transition metals
6. Discus the Wacker process with mechanism
7. Explain the Ferrocene structure, bonding and reactivity
8. What are the group 4 metallocene? Why they act as catalyst?
9. Discuss the carboxylation of methanol-mono acetic acid process
10. Organometallic mechanisms discussed in the context of homogeneous catalytic systems.

Possible Questions

Part-B (Two marks Questions)

1. What are the polynuclear metal carbonyls?
2. What is interfering anions? Give two examples.
3. Write the all interfering anions?
4. Write 18electron rule.

5. Write 18electron rule

Part-C (Eight marks Questions)

1. Write a note on Wade's rule and isolobal relationship of metal carbonyls.

2. Account on the synthesis of metal olefin complexes.

3. Draw the structure and Calculate the 18 electron rule for the following metal carbonyl compounds

   a) $Fe(CO)_5$ ii) $Mn(CO)_{10}$ iii) $Fe_2(CO)_9$

4. Explain the general preparation and properties of metal carbonyls with suitable examples.

5. Discuss the choice of group reagents to separate the cations.

6. Discuss the solubility products and common ion effect.

7. Explain the steps of oxidative addition and reductive elimination reaction.

8. Give the synthesis of alkenes and alkynes complexes.

9. Explain the steps of oxidative addition and reductive elimination reaction.

10. Write the reaction of interfering anions such as fluoride, borate and oxalate.

OBJECTIVE QUESTIONS

S. No.	Questions	Option A	Option B	Option C	Option D	Answer
1.	Geometry of [Cr((CO)6] is	Octahetral	Tetrahetral	Square pyramidal	Triangular bipyramidal	Octahetral
2.	The total number of electrons present in the atom of the metal forming the complex , including those gained electrons by sharing in the formation of complex is called	Effective atomic number	Effective molecular number	Exclusive atomic number	18 electron	Effective atomic number
3.	The geometry of Fe(CO)5 is	Trigonal pyramidal	Trigonal bipyramidal	Square planar	tetrahedral	Trigonal bipyramidal
4.	The magnetic property of V(CO)6 is	Diamagetic	Paramagnetic	Ferromagnetic	Non-magnetic	Paramagnetic
5.	The physical properties of the metal alkoxides depend on the ---- and ------- of the alkyl group	Size & Shape	Valency & Size	Shape &Valency	Carbonyate ions	Size & Shape
6.	The reaction of Vaskas complex with molecular hydrogen has a characteristic of an -----	Reductive elimination	Oxidative addition	Oxidative elimination	Octahetral	Oxidative addition
7.	An example of oxidative addition is the reaction of ------ molecular	Vaskas complex	Octahedral complex	tetrahedral complex	Hydride	Vaskas complex

	hydrogen					
8.	Vaskas compound absorb oxygen and become ------ colour	Yellow	Orange	Red violet	Green	Orange
9.	carbonyl hydrido complexes are formed by the acidification of ----	Carbonyate ions	Carbenes	carbines	Alkynes	Carbonyate ions
10.	Which of the following act as hydride donars	BH_4	CH_3	C_2H_5	$NaHSO_4$	BH_4
11.	Complexes with coordinated hydrogen atom are	Hydro compounds	Hydroxide	hydrochloride	Hydride	Hydride
12.	Which does not form the source of hydrogen	NaH	BH_4	$LiAlH_4$	H_2O	H_2O
13.	Metal hydride complexes acts as	Retarding agents	Oxidising agents	reducing agents	Dehydrogenating agents	reducing agents
14.	Double dihydro bridge are found in	B_2H_6	BH_4	NH_3	$H_2Cr(CO)_5$	B_2H_6
15.	When dinitrogen functions as a bridging ligand , it usually exhibits ------ coordination	End-on	Side-on	Axial	Urea	End-on
16.	Anionic carbonyl halides are obtained when metal carbonyls are treated with	Carbonyl hydrides	Ionic halides	Radical halides	Nitrosyls	Ionic halides
17.	The general formula for Carbonyl	MX(CO)YX2	HMX(CO)YX2	MX(CO)YN2	MX2	MX(CO)YX2

	halides is					
18.	Mn(CO)5Cl heated in organic solvents at 1200 c it loses	CO2	COCl2	CO	MnCO3	CO
19.	Carbonyl halides react with NH3 to form -----	Amines	Amides	Urea	Thiourea	Urea
20.	Phosgene is also known as -------	Carbonyl bromide	Carbonyl chloride	Carbonyl iodide	Carbonyl fluoride	Carbonyl chloride
21.	Carbonyl chloride is produced in large quantities to make -------	Benzene	Toluene	Xylene	Toluene di isocyanate	Toluene di isocyanate
22.	Isocyanides are better sigma donar and poorer ----- acceptor than carbonyl group complexes.	sigma acceptors	pi donars	pi acceptors	Urea	pi acceptors
23.	Which one of the following is an important building block for the synthesis of many compounds?	Carboxyhemoglobin	Carbon monoxide	Carbonylate	Carbon-di-oxide	Carbon monoxide
24.	Cyanide will preferentially leach sulfide minerals and will react with sulfur to produce ?	Thiocyanate	Potassium cyanide	Sulfocyanate	Hydrogen cyanide	Thiocyanate
25.	Which one of the following salt has a more complex cluster structure?	Sodium salt	Black-T	Potassium salt	Roussin's black	Roussin's black
26.	Metal carbonyls generally have poor solubility with ?	Water	Alcohol	Solvent	Alcohol	Water

27.	The most important technique for characterizing metal carbonyls is ?	UV spectroscopy	Mass Spectroscopy	Infra-red spectroscopy	NMR spectroscopy	Infra-red spectroscopy
28.	All metal carbonyls undergo substitution by ?	Organophosphorus ligands	Phosphine ligands	Ligands	Metal	Organophosphorus ligands
29.	Typical isocyanide ligand is ?	CO	NO	MeNC	CN	MeNC
30.	Metal nitrosyl complexes are complexes that contain ?	Nitric oxide	Nitrosyl	Metal	MeNC	Nitric oxide
31.	Metal nitrosyls are?	Physically important	Mechanically important	Chemically important	Biologically important	Biologically important
32.	Which one of the following is typically adopt one of two bonding modes?	Metal nitrosyl	NO	O2	MeNC	NO
33.	NO ligands can arise by oxidative degradation of other ?	Nitrogen ligands	Cabon ligands	Oxygen ligands	Hydrogen ligands	Nitrogen ligands
34.	Nitrogen is more electronegative than ?	Hydrogen	Oxygen	Carbon	NO	Carbon
35.	The nitroprusside anion,[Fe(CN)5NO]2−, a mixed nitrosyl cyano complex, has pharmaceutical applications as a slow release agent for ?	CN	Fe	NO	C	NO
36.	Which one of the following is an	NO	NO2	Fe	CN	NO2

	ambidentate ligand?					
37.	Which one of the following is highly paramagnetic?	[Ni(CO)4]	[FeF6]3¯	[Ni(CO)4]	[CoF6]3¯	[CoF6]3¯
38.	The Carbonyls which contain more than one metallic atoms are known as ----	Polydentate	Polynuclear	Bidentate	Mononuclear	Polynuclear
39.	[MnRe(CO)9] is an example for	Mononuclear Carbonyl	Homonuclear	Heteronuclear	carbon	Heteronuclear
40.	When Fe is directly reacted with CO at 2000C,100 atm.pressure it gives	Fe(CO)8	Fe(CO)3	Fe(CO)6	Fe(CO)5	Fe(CO)5
41.	When Ni reacted directly with CO at 2000C,100 atm. pressure it gives	Ni(CO)8	Ni(CO)4	Ni(CO)5	Ni(CO)6	Ni(CO)4
42.	When Co reacted directly with Co at 2000C,100 atm. pressure it gives	Co2(CO)8 Co(CO)8		Co3(CO)8	Co2(CO)6	Co2(CO)8 Co(CO)8
43.	The hybridization involved in the complex [Ni(CO)4] is	sp3	sp2	dsp2	dsp3	sp3
44.	Which one is an example for binuclear complex	Mn2(CO)8	Mn2(CO)10	Mn(CO)10	Mn2(CO)6	Mn2(CO)10
45.	Which one is an example for Trinuclear carbonyl	Fe3(CO)12	Co(CO)12	Fe2(CO)12	Fe (CO)12	Fe3(CO)12

46.	The anionic carbonyl complexes are known as -----	Carbonium ion	carbonylate ions	Carbanion	carbenium ion	carbonylate ions
47.	Example for carbonylate ion is	[Co(CO)12]	[Co(CO)12]+	[Mn(CO)5]-	[Mn(CO)5]+	[Mn(CO)5]-
48.	Mn2(CO)10 + H2 →	2Mn(CO)5	Mn(CO)10	2HMn(CO)5	Mn(CO)5	2HMn(CO)5
49.	The allyl group which can function as an one electron donar is known as	Monohapto	Dihapto	Trihapto	Tetra hapto	Monohapto
50.	Metal nitrosyls, compounds have	NO ligands	CO ligands	alkyl ligand	aryl ligand	NO ligands
51.	NO ligand is a stronger pi acceptor than	CO ligands	alkyl ligand	aryl ligand	alkene ligand	CO ligands
52.	Find out one is nitrosyl carbonyls compounds	Ni(CO)4	Rh2(CO)8	Rh4(CO)12	CoNO(CO)3	CoNO(CO)3
53.	Which is not metal dinitrogen compound	CoNO(CO)3	IrCl(N2)(PPh3)2	{[Ru(NH3)5]2(μ-N2)}4+	[FeH(N2)(dmpe)2)]+	IrCl(N2)(PPh3)2
54.	Which is not metal phosphene compound	Fe(PF3)5	Co2(PF3)8	Co2(PH3)8	Fe(CO)5	Fe(CO)5
55.	Which one is not metal dioxygen complexe	Myoglobin	hemoglobin	hemerythrin	vaska compounds	vaska compounds
56.	Myoglobin and hemoglobin are famous examples	Dinitrogen complexes	Dioxygen complexes	Inorganic complexes	Metal carbonyls	Dioxygen complexes
57.	Binding of O2 is usually described as proceeding	Electron transfer	Proton transfer	Oxygen transfer	Nitrogen transfer	Electron transfer

	via ………...from the metal(II) center					
58.	The reaction given below is an example of $[(CO)_5Mn(Me)] + CO \rightarrow [(CO)_5Mn\{C(O)(Me)\}]$	oxidative addition	electrophilic substitution	nucleophilic substitution	migratory	oxidative addition
59.	$CrCl3 + Al + 6\ CO \rightarrow Cr(CO)6 + AlCl3$ This reaction is	oxidation	reduction	formylation	lithiation	reduction
60.	Metal carbonyls are used in a number of industrially important ………….. reactions	chlorination	hydration	carbonylation	hydration	carbonylation

UNIT- III

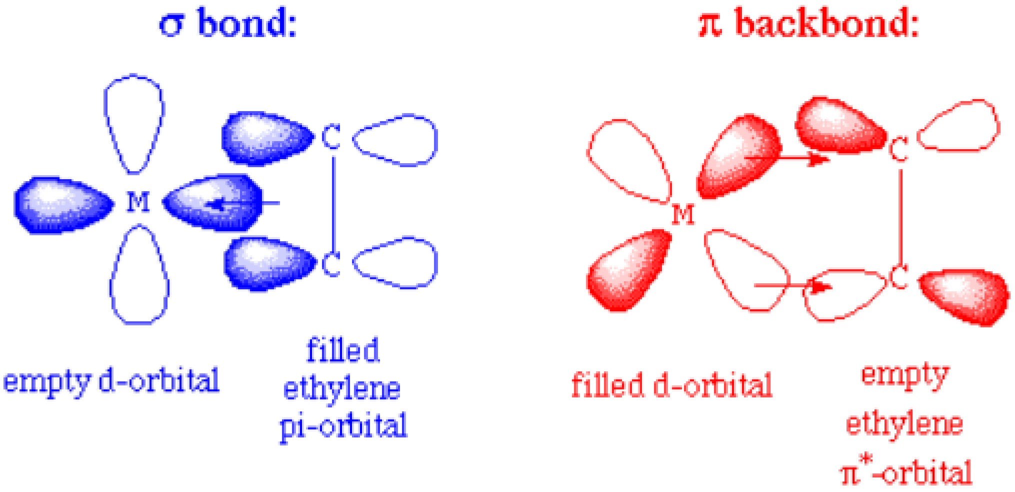
SYLLABUS

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 trialkylaluminium (dimer), concept of multicentre bonding in these compounds. Ferrocene: Preparation and reactions (acetylation, alkylation, metallation, Mannich Condensation).Structure and aromaticity. Comparison of aromaticity and reactivity with that of benzene.

Alkene or olefin ligands are common in organotransition metal chemistry. In fact, the first organotransition metal complex, Zeise's salt ($K[PtCl_3(C_2H_4]\cdot H_2O$) was an alkene complex although its true nature was not unambiguously determined until about 100 years after its discovery.

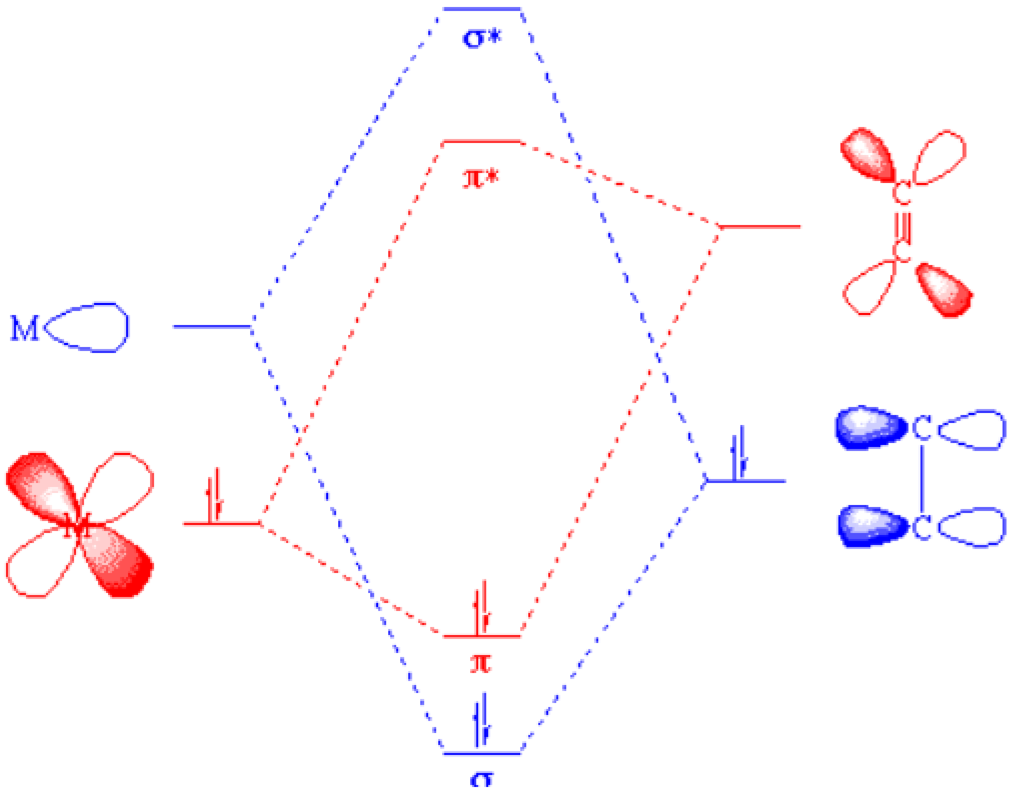
Bonding and Structure in Alkene Complexes

The bonding in alkene complexes is described by the **Dewar-Chatt-Duncanson model**, which provides us with a bonding picture not unlike that seen in carbonyl or phosphine complexes. A sigma-type donation from the C=C pi orbital with concomitant pi-backbonding into an empty pi* orbital on the ethylene presents us with a synergistic bonding situation: the greater the sigma donation to the metal, the greater the pi-backbonding:

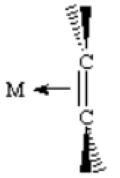


The greater the electron density back-donated into the pi* orbital on the alkene, the greater the reduction in the C=C bond order. An alternative way of stating this would be to say that the hybridization of the alkene carbon changes from sp^2 to sp^3 as back-donation increases. Either formalism describes two limiting structures: a planar olefin adduct and a metallocyclopropane.

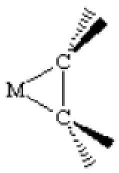
X-ray crystallographic studies confirm that the as the C-C bond length increases, the CH_2 plane is distorted from the ideal planar geometry of an alkene:



The structural distortion of a bound alkene can also be detected by NMR: the J_{CH} of alkene-like sp^2 carbons is typically around 160 Hz whereas sp^3-like carbons have a J_{CH} around 120 Hz. Unlike carbonyl stretching frequencies, the C=C IR band (around 1500 cm^{-1}) is usually weak and not well-correlated to C-C bond length.



simple alkene adduct $\beta = 90°$



metallocyclopropane $\beta = 36°$

Electronic factors play a large role in the binding of alkenes to transition metals. For example, tetrafluoroethylene will bind more tightly than ethylene to a low valent metal complex because the presence of electron-withdrawing groups on the olefin results in poorer sigma donation and lowers the energy of the pi* orbital (providing better overlap for backbonding). Likewise, ethylene (like carbon monoxide) is a poor ligand for d^0 metal complexes because there are no d-electrons to engage in back-bonding.

The stability of alkene complexes also depends on steric factors as well. An empirical ordering of relative stability would be:

tetrasubstituted<trisubstituted< trans-disubstituted< cis-disubstituted<monosubstituted< ethylene.

Synthesis of Alkene Complexes

1. Ligand substitution reactions.
2. Reduction of a higher valent metal in the presence of an alkene.
3. From alkyls and related species:
    - reductive elimination (of an allyl and hydride, for example).
    - hydride abstraction from alkyls
    - protonation of sigma-allyls
    - from epoxides (indirectly)

Substitution Reaction Mechanisms

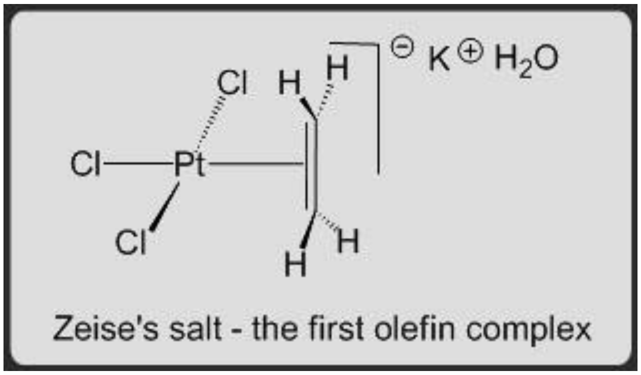
When we discuss a substitution reaction in inorganic chemistry we ask ourselves questions about these aspects of the reaction:

- **Stoichiometric mechanism** -- What are the steps involved? Does a ligand dissociate during the reaction, etc.?
- **Intimate mechanism** -- What factors specifically affect the rate constant of a particular step? Why is the rate faster for R=Me than for R=Ph etc.?

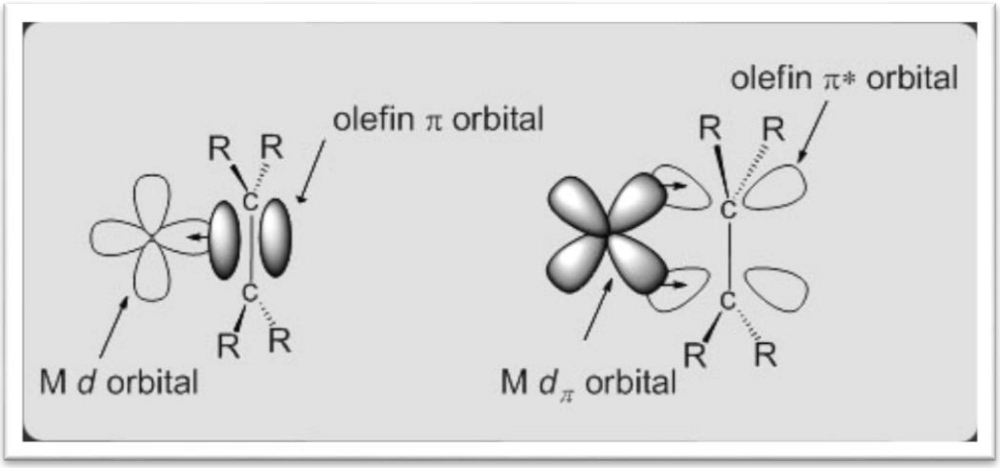
In particular, we need to ask if a reaction proceeds through an **intermediate**. This immediately raises the question, "what is an intermediate?" On the potential energy diagram shown below, an intermediate is drawn and connected to the reactants and products by the blue line. But what if the energy barrier to get out of this potential well is so small that we can't detect it? To us, the reaction coordinate might appear not to include an intermediate at all as indicated by the red line.

Though the first metal olefin complex dates back a long time to the beginning of 19th century, its formulation was established only a century later in the 1950s. While reacting K_2PtCl_4 with EtOH in 1827, the Danish chemist Zeise synthesized the famous Zeise's salt $K[PtCl_3(C_2H_4)]\cdot H_2O$

containing a Pt bound ethylene moiety and which incidentally represented the first metal–olefin complex.



The metal–olefin bonding interaction is best explained by the *Dewar−Chatt* model, that takes into account two mutually opposing electron donation involving σ−donation of the olefinic C=C π−electrons to an empty d_π metal orbital followed by π−back donation from a filled metal d_π orbital into the unoccupied C=C π* orbital. Quite understandably so, for the d^0 systems, the formations of metal–olefin complexes are not observed. The extent of the C=C forward π-donation to the metal and the subsequent π−back donation from the filled d_π orbital to the olefinic C=C π* orbital have a direct bearing on the C=C bond of the metal bound olefinic moiety in form of bringing about a change in hybridization as well as in the C−C bond distance.



If the metal to ligand π−back donation component is smaller than the ligand to metal σ−donation, then the lengthening of the C−C bond in the metal bound olefin moiety is observed. This happens primarily because of the fact that the alkene to metal σ−donation removes the C=C π−electrons away from the C−C bond of the olefin moiety and towards the metal center, thus, decreasing its bond order and increasing the C−C bond length. Additionally, as the metal to ligand π−back donation increases, the electron donation of the filled metal d_π orbital on to the π* orbital of the metal bound olefin moiety is enhanced. This results in an increase in the C−C bond length. The lengthening of the C−C bond in metal bound olefin complex can be correlated to the π−basicity of the metal. For example, for a weak π−basic metal, the C−C bond lengthening is anticipated to be small while for a strong π−basic metal, the C−C lengthening would be significant.

Another implication of ligand−metal π−back donation is in the observed change of hybridization at the olefinic C atoms from pure sp^2, in complexes with no metal to ligand π−back donation, to sp^3, in complexes with significant metal to ligand π−back donation, is observed. The change in hybridization from sp^2 to sp^3 centers of the olefinic carbon is accompanied by the substituents being slightly bent away from the metal center in the final metalacyclopropane form (Figure 3). This change in hybridization can be conveniently detected by ^{1}H and ^{13}C NMR spectroscopy. For example, in case of the metalacyclopropane systems, which have strong metal to ligand π−back donation, the vinyl protons appear 5 ppm (in the ^{1}H NMR) and 100 ppm (in the ^{13}C NMR) high field with respect to the respective position of the free ligands.

An interesting fallout of the metal to ligand π−back bonding is the tighter binding of the strained olefins to the metal center as observed in the case of cyclopropene and norbornene. The strong binding of these cyclopropene and norbornene moieties to the metal center arise out of the relief of ring strain upon binding to the metal. Lastly, in the metal−olefin complexes having very little π−back bonding component, the chemical reactivities of the metal bound olefin appear opposite to that of a free olefin. For example, a free olefin is considered electron rich by virtue of the presence of π−electrons in its outermost valence orbital and hence it undergoes an electrophilic attack. However, the metal bound olefin complexes having predominantly σ−donation of the olefinic π−electrons and negligible metal to ligand π−back donation, the olefinic C becomes positively charged and hence undergoes a nuclophilic attack. This nature of reversal of olefin reactivity is called *umpolung* character.

Alkyllithium compounds are widely used asvery strong bases, nucleophiles and reagentsfor metallations in organic synthesis. The followingtable shows, that alkanes and arenesare very weak acids, hence their correspondinglithium-derivatives are extremely strong bases.The most common members of the alkyllithiumfamilyare n-butyllithium, methyllithium andtert-butyllithium (for which 2-methylpropane isthe corresponding acid).Simple alkyllithium-compounds are soluble inhydrocarbon- and in ether-solvents (althoughthe more basic compounds can react with thelatter) forming aggregates of mostly dimeric,tetrameric or hexameric species. The aggregation8and, as a consequence, the reactivityof organolithiumcompounds can be stronglyinfluenced by the solvent and/or complexingco-solvents and additives.

Compound	Solvent	Aggregation number
MeLi	THF	4
MeLi	DEE	4
n-BuLi	Cyclohexane	6
n-BuLi	THF	4 / 2
sec-BuLi	Cyclopentane	4
sec-BuLi	THF	2 / 1
tert-BuLi	Hexane	4
tert-BuLi	DEE	2
tert-BuLi	THF	1

MeLi = Methyllithium • n-BuLi = n-Butyllithium • sec- BuLi = sec-Butyllithium • tert-BuLitert.-Butyllithium • DEE = Dietylether • THF = Tetrahydrofuran

a. Metallation

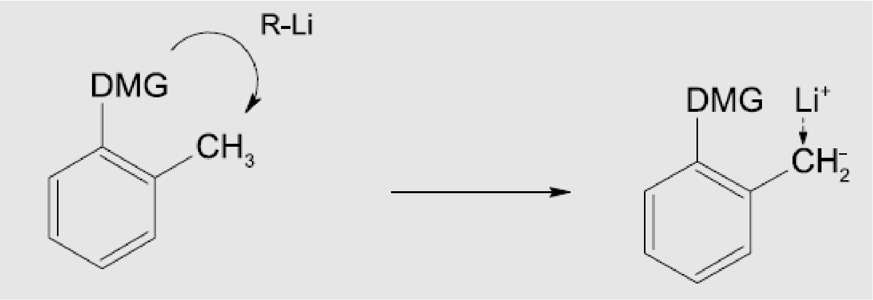
Many hundreds of functionalisedorganolithium compounds have been prepared by the metallation reaction with n-butyllithium (or other alkyllithium compounds

$$\text{R-H} + \text{n-Butyl-Li} \longrightarrow \text{R-Li} + \text{Butane}$$

The metallation uses the fact that the strong bases like n-butyllithium are capable to deprotonate organic molecules if they have “acidic” protons. Such “acidic” protons in organic molecules are mostly found at positions where a negatively charged anion is stabilised by a suitable functional group

b. Ortho-metallation

Metallation of an aromatic ring near a substituent, which acts as a "Directed Metallation Group", is called "Ortho-Metallation". Several groups can function as DMG's, i.e. sulfones, sulfonamides, amines, amides, carbamates, thio-28 and methoxy groups, they have in common the ability to coordinate the approaching cation (= lithium-ion) and/or to increase the acidity of the ortho-hydrogen.



Other synthesis

The best general method for RLi synthesis involves the reaction of an alkyl or aryl chloride with lithium metal in benzene or an aliphatic hydrocarbon (e.g., hexane),

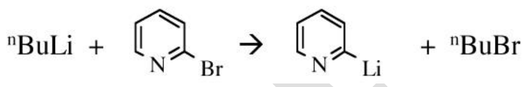
$$RCl + 2\,Li \rightarrow RLi + LiCl$$

While it is possible to use diethyl ether (Et_2O), the solvent slowly attack the resultant alkyl lithium compound

$$Et_2O + {}^nBuLi \rightarrow EtOLi + H_2C{=}CH_2 + {}^nBuH$$

Metal-hydrogen exchange, metal-halogen exchange,, and metal-metal exchange can also be used,

$$RH + R'Li \rightarrow R'H + RLi$$



$$2\,Li + R_2Hg \rightarrow 2\,RLi + Hg$$

All organolithium compounds are produced as solutions and are hence used in synthetic protocols by volume of solution. It is therefore important to know the exact concentration of RLi in solution. The simplest approach to quantify the amount of organolithium is to react a known volume with water, and then titrate (with acid) the resultant base that is formed.

$$RLi + H_2O \rightarrow LiOH + RH$$

However, while the concentration of freshly prepared samples of organolithium reagents can the theoretically measured in this way, real samples always contain some amount of LiOH or other bases. A simple titration inevitably results in an over estimation of the organolithium reagent. To overcome this a *double titration*method is used.

Gillman double titration method

The careful addition of a known volume of an organolithium reagent solution (between 0.5 and 1.5 mL) to an excess of water yields a solution of LiOH that can be titrated with a standardized solution of hydrochloric acid, using phenolphthalein as the indicator. The presence of any LiOH in the original organolithium solution will be incorporated into this titration, and thus the result will be a measure of the *total base content* in the solution, i.e.,

$$\text{Total base content} = \text{LiOH formed from the reaction of RLi with } H_2O + \text{LiOH present as impurity in the RLi solution}$$

In order to determine the amount of LiOH present as impurity in the organolithium solution it is necessary to react the RLi without the formation of base, then titrate the resulting solution. To do this, an aliquot (the same amount as used before) of the organolithium is reacted slowly with 1,2-dibromoethane ($BrCH_2CH_2Br$) dissolved in dry diethyl ether (Et_2O). After 5 min of stirring, the solution is diluted with an excess of water and then titrated with a standardized solution of hydrochloric acid, again using phenolphthalein as the indicator. The difference of the two titrations gives the exact concentration of the organolithium.

An aliquot of ^{n}BuLi in hexanes (0.50 mL) was added to degassed water (20 mL). After any visible reaction had ceased, a few drops of a phenolphthalein solution in water/methanol are added resulting in a pink color indicative of a basic pH. The resulting mixture is titrated with standardized hydrochloric acid ([HCl] = 0.1034 N) until complete disappearance of the pink color (7.90 mL).

A second aliquot of ^{n}BuLi in hexanes (0.50 mL) is added to 1,2-dibromoethane (0.20 mL, Et_2O). After 5 min of stirring, the mixture was diluted with water (20 mL) and after addition of the phenolphthalein indicator titrated (with vigorous stirring due to the biphasic nature of the system) with standardized hydrochloric acid ([HCl] = 0.1034 N) until complete disappearance of the pink color (0.25 mL).

The concentration of nBuLi is calculated as follows:

1. $$[\text{total base}] = \frac{\text{volume HCl x [HCl]}}{\text{volume }^{n}\text{BuLi}} = \frac{7.90 \text{ x } 0.1034}{0.50} = 1.633$$
2. $$[\text{residual base}] = \frac{\text{volume HCl x [HCl]}}{\text{volume }^{n}\text{BuLi}} = \frac{0.25 \text{ x } 0.1034}{0.50} = 0.013$$
3. $$[{}^{n}\text{BuLi}] = [\text{total base}] - [\text{residual base}] = 1.633 - 0.013 = 1.620 \text{ M}$$

Properties

Alkyl lithium compounds are either low melting solids or liquids, and often with high volatility (depending on the substituent) due to the covalent nature of the bonding. They are soluble in aliphatics, aromatics, and ethers. However, while the reaction with ethers is generally slow, alkyl lithium compounds can polymerize tetrahydrofuran (THF).

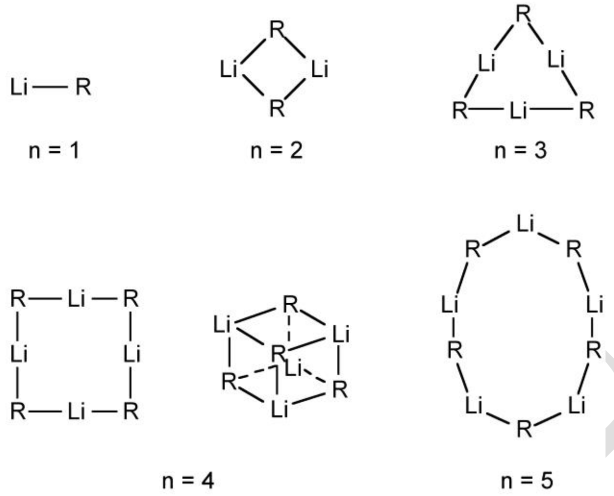
Organolithium compounds react rapidly with air and water (both vapor and liquid). The reaction with water is the basis of the Gillman double titration method for determining the concentration of organolithium reagents in solution.

Structure

The structure of organolithium compounds is dominated by their highly oligomeric nature as a result of 3-center 2-electron bridging bonds. In all cases the extent of oligomerization is dependant on the identity of the alkyl (or aryl) group. The alkyl-bridged bond is similar to those found for beryllium and aluminum compounds.

In the vapor phase any particular organolithium derivative show a range of oligomeric structures. For example, the mass spectrum of EtLi shows ions associated with both tetramers (e.g., $[Et_3Li_4]^+$) and hexamers (e.g., $[Et_5Li_6]^+$). The structures of the different oligomers have been predicted by molecular orbital calculations.

Proposed vapor phase structures for various oligomers of RLi.



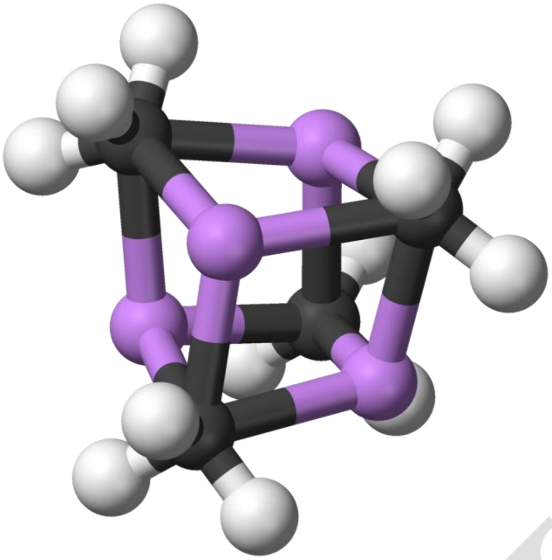
Solution molecular weight measurements indicate the oligomerization is present (in the absence of a coordinating ligand such as Et_2O or an amine). The extent of oligomerization depends on the steric bulk of the alkyl group. Oligomerization and solution structures have also been investigated by ^{7}Li and ^{13}C NMR spectroscopy.

Extent of oligomerization (n) for organolithium compounds $[RLi]_n$ in benzene solution.

R	**$[RLi]_n$**	**R**	**$[RLi]_n$**
Me	4	Et	6
^{n}Bu	6	^{t}Bu	4

There are a large number of X-ray crystallographically determined structures for organolithium derivatives. The archetypal example is MeLi, which exists as a tetramer in the solid state.The lithium atoms are arranged as a tetrahedron and the carbon atoms are positioned on the center of the facial planes, i.e., the carbon is equidistant from each of the lithium atoms. In contrast, EtLi has a similar tetrahedral structure, but the α-carbon of the ethyl groups are asymmetrically arranged such that it is closer to one lithium atom than the other two.

Solid state structure of MeLi. Copyright: Ben Mills (2007).



It is possible to prepare monomeric organolithium compounds by the addition of amines, especially chelate ligands such as ethylenediamine (en) and tetramethylethylenediamine (TMED). The reactivity of RLi is increased dramatically by the addition of such Lewis bases. For example, $PhCH_2Li$ shows an increased reactivity of 10^4 with the addition of TMED.

The bonding in organolithium compounds is difficult to describe:

- Based upon the relative electronegativity of Li (0.98) and C (2.5) it would be expected to have significant ionic character.
- Organolithium compounds form electron deficient oligomers typical of covalent bonding and clearly not as a result of ionic aggregation.
- The spin-spin coupling, *J*(C-Li), observed by NMR spectroscopy (10 – 15 Hz) are consistent with a covalent bond.
- Organolithium compounds undergo radical reactions.

However, the overall description of the bonding in RLi is that of a covalent interaction with significant polar (ionic) character, i.e., $M^{\delta+}-C^{\delta-}$.

The use of organolithium compounds in organic synthesis

Organolithium compounds perform many of the reactions commonly observed for Grignard reagents. However, lithium reagents are generally more reactive than their Grignard analogs.

Hydrolysis

Organolithium compounds react with water to give the hydrocarbon and lithium hydroxide. Lithium alkyls also react with other hydroxylic compounds such as alcohols and carboxylic acids.

$$CH_3Li + H_2O \rightarrow CH_4 + LiOH$$

$$CH_3Li + HOR \rightarrow CH_4 + LiOR$$

One important use of the hydrolysis reaction is specifically deuteration.

$$CH_3CH_2(CH_3)_2CLi + D_2O \rightarrow CH_3CH_2(CH_3)_2CD + LiOD$$

Reaction with carbonyls

Organolithium compounds react with organic carbonyls (aldehydes, ketones, and esters) to yield the alcohol on hydrolysis. This synthetic route is particularly useful since lithium reagents are far more reactive than the analogous Grignard, allowing reactions to be carried out at lower temperatures and minimizing enolization side reactions.

$$MeLi + (^tBu)_2C{=}O \rightarrow (^tBu)_2MeCOLi \xrightarrow{H_2O} (^tBu)_2MeCOH + LiOH$$

The high reactivity of alkyl lithium compounds means that they react with carboxylic acids to yield the ketone rather than the lithium carboxylate.

$$(C_6H_5)CO_2H \xrightarrow[H_2O]{2\ RLi} (C_6H_5)C(O)R$$

Organolithium compounds generally react with α,β-unsaturated ketones to give the 1,2-addition product. However, lithium dialkylcuprates, which are formed from the alkyl lithium and copper(I) iodide, add exclusively by the 1,4-addition.

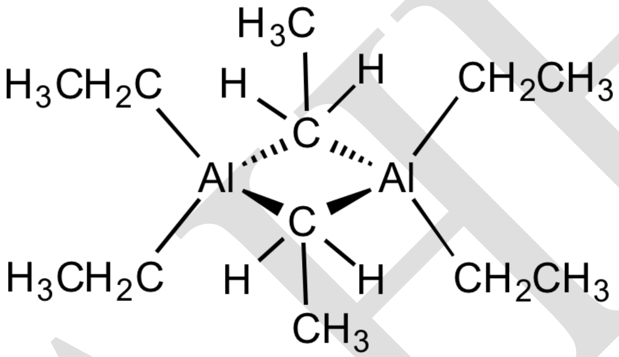
$$C_6H_5(H)C{=}C(H)C(O)C_6H_5 \xrightarrow[H_2O]{2\ C_6H_5Li} C_6H_5(H)C{=}C(H)C(OH)(C_6H_5)_2$$

$$2\ RLi + CuI \rightarrow R_2CuLi + LiI$$

$$C_6H_5(H)C{=}C(H)C(O)C_6H_5 \xrightarrow[H_2O]{R_2CuLi} C_6H_5(H)(R)CH_2C(O)(C_6H_5)_2$$

Trialkylaluminium compounds

Triethylaluminium is an organoaluminium compound. Despite its name, the formula for this compound is $Al_2(C_2H_5)_6$, shortened to Al_2Et_6 (Et = ethyl). This volatile, colorless liquid is highly pyrophoric, igniting immediately upon exposure to air. It is normally stored in stainless steel containers either as a pure liquid or as a solution in hydrocarbon solvents such as hexane, heptane, or toluene. Triethylaluminium is mainly used as a co-catalyst in the industrial production of polyethylene, polypropylene and for the production of medium chain alcohols.



The compound is a dimer of triethylaluminium. One pair of ethyl groups bridge the two Al centers, and four are terminal ligands. The two bridging carbon centres are five-coordinate. The bonding is reminiscent of that of diborane, involving 3-centred, 2-electron bonds. As in trimethylaluminium, triethylaluminium is structurally fluctional resulting in rapid interchange of the terminal and bridging ethyl groups. At higher temperatures, the dimer cracks into monomeric $AlEt_3$.

Synthesis and reactions

Triethylaluminium can be formed via several routes. The discovery of an efficient route was significant technologically. The multistep process uses aluminium metal, hydrogen gas, and ethylene, summarized as follows:

$$2\ Al + 3\ H_2 + 6\ C_2H_4 \rightarrow Al_2Et_6$$

Because of this efficient synthesis, triethylaluminium is one of the most available organoaluminium compounds.

Triethylaluminium can also be generated from ethylaluminiumsesquichloride ($Al_2Cl_3Et_3$), which arises by treating aluminium powder with chloroethane. Reduction of ethylaluminiumsesquichloride with an alkali metalsuch as sodium gives triethylaluminium:

$$3\ Al_2Cl_3Et_3 + 9\ Na \rightarrow 2\ Al_2Et_6 + 2\ Al + 9\ NaCl$$

Reactivity

The Al–C bonds of triethylaluminium are polarized to such an extent that the carbon is easily protonated, releasing ethane

$$Al_2Et_6 + 6\ HX \rightarrow 2\ AlX_3 + 6\ EtH$$

For this reaction, even weak acids can be employed such as terminal acetylenes and alcohols.

The linkage between the pair of aluminiumcentres is relatively weak and can be cleaved by Lewis bases (L) to give adducts with the formula $AlEt_3L$

$$Al_2Et_6 + 2\ L \rightarrow 2\ LAlEt_3$$

Applications

Triethylaluminium is used industrially as an intermediate in the production of fatty alcohols, which are converted to detergents. The first step involves the oligomerization of ethylene – the famed *Aufbau* reaction, which gives a mixture of trialkylaluminium compounds (simplified here as octylgroups):

$Al_2(C_2H_5)_6 + 18\ C_2H_4 \rightarrow Al_2(C_8H_{17})_6$

Subsequently, these trialkyl compounds are oxidized to aluminium alkoxides, which are then hydrolysed:

$$Al_2(C_8H_{17})_6 + 3\ O_2 \rightarrow Al_2(OC_8H_{17})_6$$

$$Al_2(OC_8H_{17})_6 + 6\ H_2O \rightarrow 6\ C_8H_{17}OH + 2\ "Al(OH)_3"$$

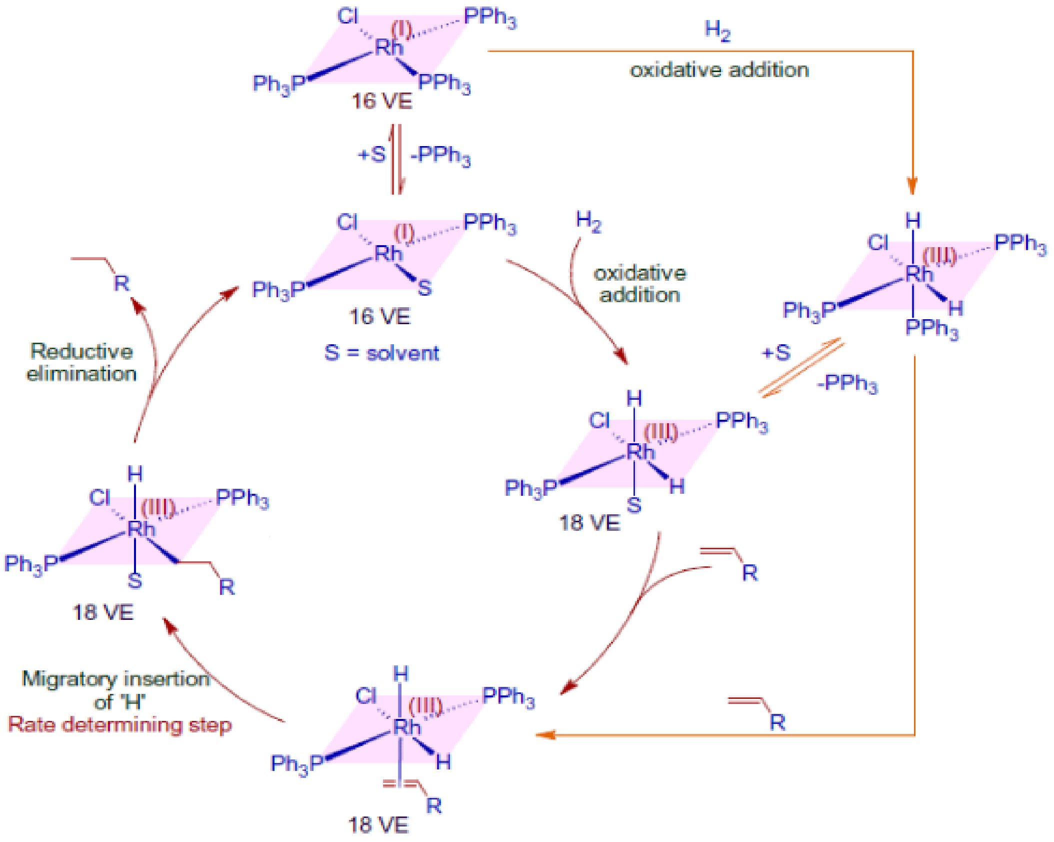
Pyrophoric agent

Triethylaluminium ignites on contact with air and will ignite and/or decompose on contact with water, and with any other oxidizer it is one of the few substances pyrophoric enough to ignite on contact with cryogenic liquid oxygen. Its easy ignition makes it particularly desirable as a rocket engine ignitor. The SpaceX Falcon 9 rocket uses a triethylaluminium-triethylborane mixture as a first-stage ignitor.

Triethylaluminium thickened with polyisobutylene is used as an incendiary weapon, as a pyrophoric alternative to napalm, e.g. in the M74 rockets for the M202A1 launchers. In this application it is known as TPA, for *thickened pyrotechnic agent* or *thickened pyrophoric agent*. The usual amount of the thickener is 6%. The amount of thickener can be decreased to 1% if other diluents are added. For example, n-hexane, can be used with increased safety by rendering the compound non-pyrophoric until the diluent evaporates, at which point a combined fireball results from both the triethylaluminium and the hexane vapors.

Olefin hydrogenation

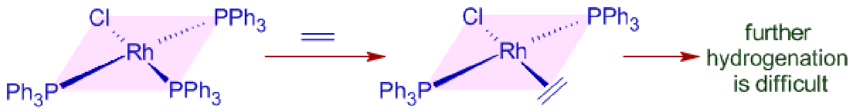
Wilkinson's catalyst is best known for catalyzing the hydrogenation of olefins with molecular hydrogen. The mechanism of this reaction involves the initial dissociation of one or two triphenylphosphine ligands to give 14- or 12-electron complexes, respectively, followed by oxidative addition of H_2 to the metal. Subsequent π-complexation of alkene, migratory insertion (intramolecular hydride transfer or olefin insertion), and reductive elimination complete the formation of the alkane product



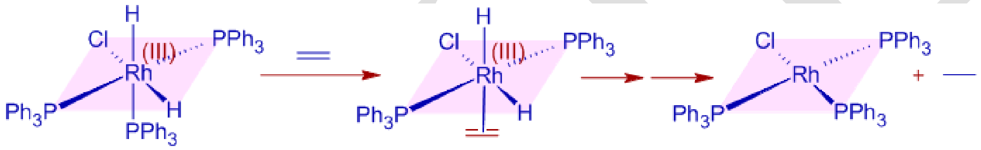
Above mechanism is supported by following observations.

The rate of reaction decreases when excess of PPh_3 is added; indicating the initial dissociation of one of the PPh_3 ligand before dihydrogen activation.

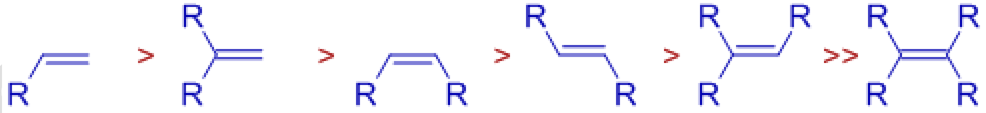
It is observed that strong π-acids like ethylene act as poisons by binding strongly with the electron rich Rh metal center and inhibit hydrogenation.



Though ethylene cannot be hydrogenated in presence of Wilkinson's catalyst under normal conditions, hydrogen transfer can be achieved with preformed dihydrido complex.

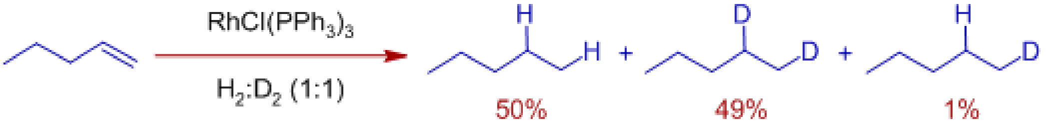


The rates of hydrogenations decrease with increase in the alkyl group substitution on double bond mirroring their relative binding affinities to the metal center. It is also partly due to steric factors.



Therefore, for a successful hydrogenation, oxidative addition of dihydrogen prior to the binding of olefin is crucial.

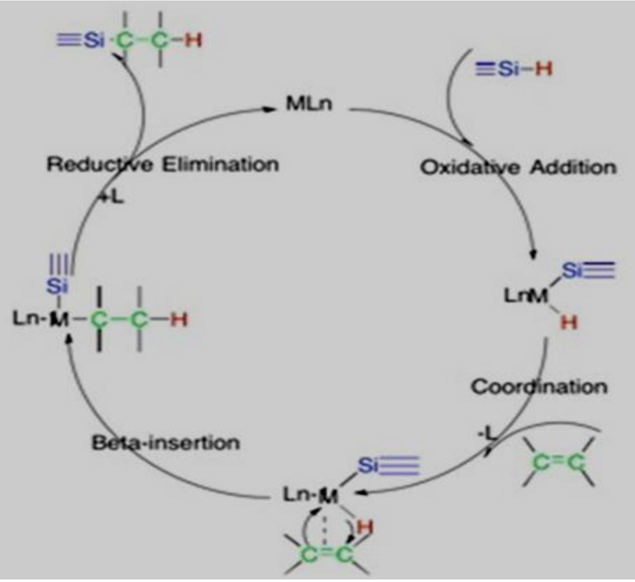
* There is minimal scrambling of H/D in the product, when an equimolar mixture of H_2 and D_2 are used.



This indicates the formation of dihydrido complex that transfers both of its hydrido ligands to the olefin and that the final reductive elimination step is very fast and irreversible.

Hydrosilation

Hydrosilylation, also known as hydrosilation, is one of the most useful catalytic reactions leading to the formation of organsilanes and organosilicones, which have a variety of applications in industry and as intermediates in organic chemistry. Hydrosilylation occurs via the addition of H-Si to an unsaturated bond such as carbon-carbon bond, carbon-oxygen bond, carbon-nitrogen bond, nitrogen-nitrogen bond and nitrogen-oxygen bond using a metal catalyst, Lewis Acid, or radical initiator. The basic reaction can be described using the following scheme:



In the first step a Si-H bond undergoes oxidative addition to a metal center. The alkene coordinates and then undergoes insertion. The hydrogen is then added to the alkene through H beta-insertion. In the final step the alkylsilylPd(II) complex undergoes reductive elimination to deliver the adduct and return the metal to the original oxidation state

The reactivity of hydrosilylation is influenced by many factors: substrate, silane, transition metal catalyst, ligand etc. which makes the reaction diverse as well as complicated. Studies have been performed to determine the reactivity influenced by each of these factors. Because there are a large variety of substrates that can be used, we will focus on alkenes. Here are some general rules:

Reaction rate: 1-alkene > 2-alkene > 3-alkene

Generally, the more substituted the alkene group, the slower the reaction would be. This is due to the more substituted alkene group being bulkier, therefore it will be harder for the alkene coordination to happen to the metal. More substituted alkene groups also make it more difficult for the H atom to undergo compete beta-insertion.

Reaction rate: $SiHCl_3$ > $(C_6H_5)_3SiH$ > $(C_2H_5)_3SiH$

$V_0(10^5)$: 110 12 1.2

From this set of data, we can derive that the rate of reactivity would increase depending on the substituted groups on the silanes. The order of reactivity is: chlorine > aromatic rings > alkanes. However, this rule is not always true. If we substituted the aromatic groups in $(C_6H_5)_3SiH$ with Cl, the reaction rate would be:

Reaction rate: $(C_6H_5)_3SiH$ > $(C_6H_5)_2SiH_2$ > $(C_6H_5)SiH_3$

$V_0(10^5)$: 12 1.7 0.69

This shows that the substituted groups do not affect the reactivity individually. The overall regularity for change of silanes is complicated and varies with each group

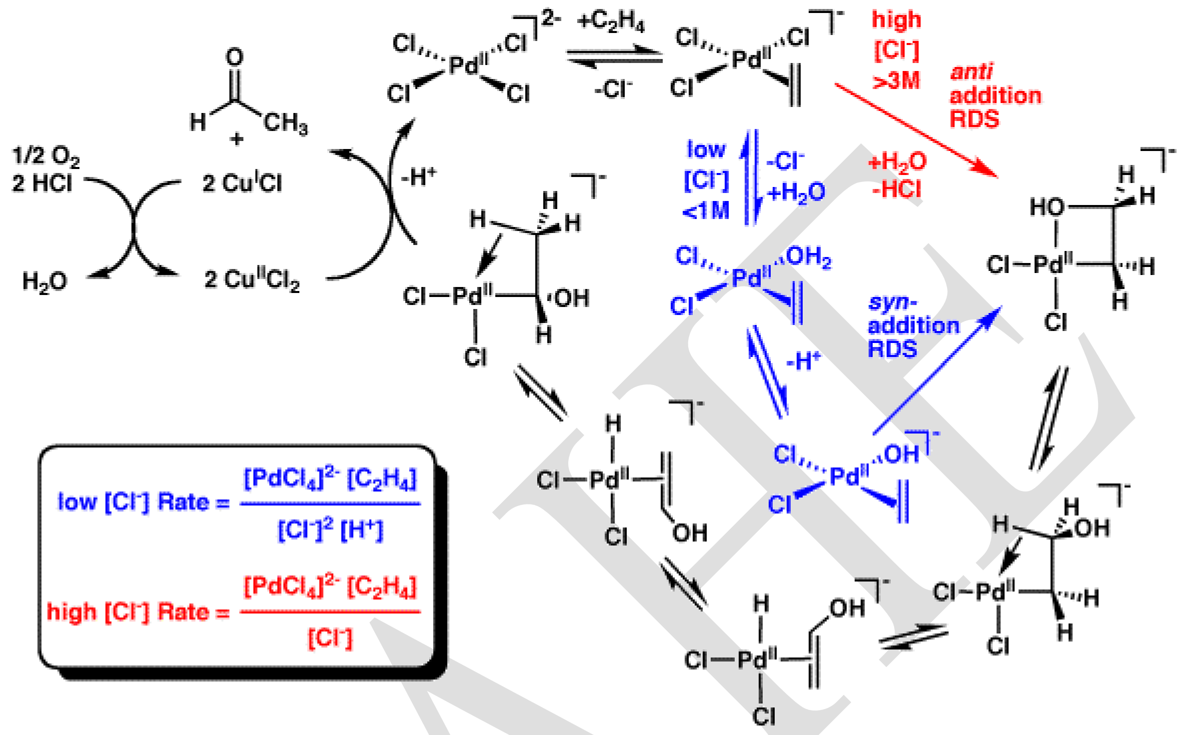
Wacker process

Acetaldehyde (CH_3CHO), also called **ethanal**, an aldehyde used as a starting material in the synthesis of 1-butanol (*n*-butyl alcohol), ethyl acetate, perfumes, flavourings, aniline dyes, plastics, synthetic rubber, and other chemical compounds. It has been manufactured by the hydration of acetylene and by the oxidation of ethanol (ethyl alcohol). Today the dominant process for the manufacture of acetaldehyde is the Wacker process, developed between 1957 and 1959, which catalyzes the oxidation of ethylene to acetaldehyde. The catalyst is a two-component system consisting of palladium chloride, $PdCl_2$, and copper chloride, $CuCl_2$.

$$2\,CH_2{=}CH_2 + O_2 \xrightarrow{PdCl_2,\ CuCl_2} 2\,CH_3CHO$$

Pure acetaldehyde is a colourless, flammable liquid with a pungent, fruity odour; it boils at 20.8 °C (69.4 °F).

The reaction mechanism for the industrial Wacker process (olefin oxidation via palladium(II) chloride) has received significant attention for several decades. Aspects of the mechanism are still debated. A modern formulation is described below



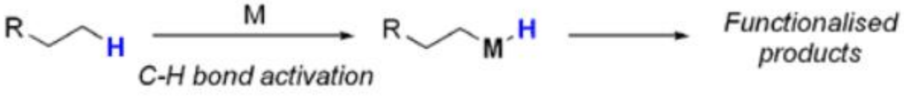
Ethylene and oxygen are passed co-currently in a reaction tower at about 130 °C and 400 kPa. The catalyst is an aqueous solution of $PdCl_2$ and $CuCl_2$. The acetaldehyde is purified by extractive distillation followed by fractional distillation. Extractive distillation with water removes the lights ends having lower boiling points than acetaldehyde (chloromethane, chloroethane, and carbon dioxide) at the top, while water and higher-boiling byproducts, such as acetic acid, crotonaldehyde or chlorinated acetaldehydes, are withdrawn together with acetaldehyde at the bottom. Due to the corrosive nature of catalyst, the reactor is lined with acid-proof ceramic material and the tubing is made of titanium.

In summary, experimental evidence seems to support that syn-addition occurs under low-chloride reaction concentrations (< 1 mol/L, industrial process conditions), while anti-addition occurs under high-chloride (> 3mol/L) reaction concentrations, probably due to chloride ions saturating the catalyst and inhibiting the inner-sphere mechanism. However, the exact pathway and the reason for this switching of pathways is still unknown.

C-H activation of alkenes

Transition metal catalysis lies at the heart of modern innovative science. As the field has matured, new areas have emerged that challenge the frontiers of synthetic organic chemistry. The capacity to activate a specific 'inert' C-H bond and transform it to a more versatile functional group is an emerging area in chemistry. To expand this area in organic synthesis, the challenge is to identify novel strategies for the formation of organo-metal intermediates under mild conditions and to discover new methods for their subsequent functionalisation. This process is perhaps the ultimate synthetic transformation and presents an exciting and fundamental challenge for chemists.

We are interested in developing new inter- and intramolecular C-C bond forming reactions catalysed by transition metals. In particular, our research focuses on the activation of C-H bonds and we are investigating methods by which *sp, sp^2 and sp^3 hybridised C-H bonds can be activated by transition metal catalysts under ambient conditions* to form a diverse range of useful molecular architectures.



C-H Activation and Functionalisation

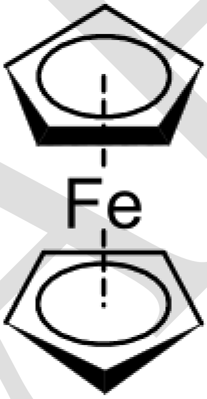
Target Structures for C-H Activation

The first reported organometallic compounds were prepared by the reductive substitution of alkyl halides, as shown in the following three equations. All these metals have strong or moderate negative reduction potentials, with lithium and magnesium being the most reactive. Halide reactivity increases in the order: Cl < Br < I. Alkylsodium and potassium compounds are not made in this way because Wurtz coupling of the alkyl moiety (giving R–R) tends to predominate. This can also be a problem when allyl or benzyl halides are converted to Grignard or lithium reagents.

R-X + Zn ——> R-Zn-X An Alkyl Zinc Reagent 1850 E. Frankland

R-X + Mg ——> R-Mg-X A Grignard Reagent 1900 V. Grignard

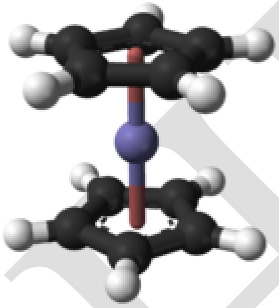
R-X + 2Li ——> R-Li + LiX An Alkyl Lithium Reagent 1917 W. Schlenk (1930 K. Ziegler)



Ferrocene

The first metallocene to be classified was ferrocene, and was discovered simultaneously in 1951 by Kealy and Pauson, and Miller et al. Keally and Pauson were attempting to synthesize fulvalene through the oxidation of a cyclopentadienyl salt with anhydrous $FeCl_3$ but obtained instead the substance $C_{10}H_{10}Fe$ At the same time, Miller *et al* reported the same iron product from a reaction of cyclopentadiene with iron in the presence of aluminum, potassium, or molybdenum oxides. The structure of "$C_{10}H_{10}Fe$" was determined by Wilkinson et al. and by Fischer et al. These two were awarded the Nobel Prize in Chemistry in 1973 for their work on sandwich compounds, including the structural determination of ferrocene. They determined that the carbon atoms of the cyclopentadienyl (Cp) ligand contributed equally to the bonding and that bonding occurred due to the metal d-orbitals and the π-electrons in the p-orbitals of the Cp ligands. This complex is now known as ferrocene and the group of transition metal dicyclopentadienyl compounds is known as metallocenes and have the general formula $[(\eta^5\text{-}C_5H_5)_2M]$. Fischer et al. first prepared the ferrocene derivatives involving Co and Ni. Often derived from substituted derivatives of cyclopentadienide, metallocenes of many elements have been prepared.

Definition



Ball-and-stick model of a metallocene moleculewhere the cyclopentadienyl anions are in a staggered conformation. The purple ball in the middle represents the metal cation.

The general name metallocene is derived from ferrocene, $(C_5H_5)_2Fe$ or Cp_2Fe, systematically named bis(η^5-cyclopentadienyl)iron(II). According to the IUPAC definition, a metallocene contains a transition metaland two cyclopentadienyl ligands coordinated in a sandwich structure, i.e., the two cyclopentadienyl anions are on parallel planes with equal bond lengths and strengths. Using the nomenclature of "hapticity", the equivalent bonding of all 5 carbon atoms of a cyclopentadienyl ring is denoted as η^5, pronounced "pentahapto". There are exceptions, such as uranocene, which has two cyclooctatetraene rings sandwiching a uranium atom.

In metallocene names, the prefix before the *-ocene* ending indicates what metallic element is between the Cp groups. For example in ferrocene, iron(II), ferrous iron is present.

In contrast to the more strict definition proposed by IUPAC, which requires a d-block metal and a sandwich structure, the term metallocene and thus the denotation *-ocene*, is applied in the chemical literature also to non-transition metal compounds, such as barocene (Cp_2Ba), or structures where the aromatic rings are not parallel, such as found in manganocene or titanocene dichloride (Cp_2TiCl_2).

Some metallocene complexes of actinides have been reported where there are three cyclopendadienyl ligands for a monometallic complex, all three of them bound η^5.

Classification

There are many (η^5-C_5H_5)–metal complexes and they can be classified by the following formulas:

Formula	Description
[(η^5-$C_5H_5)_2M$]	Symmetrical, classical 'sandwich' structure
[(η^5-$C_5H_5)_2ML_x$]	Bent or tilted Cp rings with additional ligands, L
[(η^5-$C_5H_5)ML_x$]	Only one Cp ligand with additional ligands, L ('piano-stool' structure)

Metallocene complexes can also be classified by type:

1. Parallel
2. Multi-decker
3. Half-sandwich
4. Bent or tilted
5. More than two Cp ligands

Synthesis of metallocenes

There are three main routes that are normally employed in the formation of these types of compounds:

Using a metal salt and cyclopentadienyl reagents

Sodium cyclopentadienide (NaCp) is the preferred reagent for these types of reactions. It is most easily obtained by the reaction of molten sodium and dicyclopentadiene. Traditionally, the starting point is the cracking of dicyclopentadienyl, the dimer of cyclopentadiene. Cyclopentadiene is deprotonated by strong bases or alkali metals.

$MCl_2 + 2\ NaC_5H_5 \rightarrow (C_5H_5)_2M + 2\ NaCl$ (M = V, Cr, Mn, Fe, Co; solvent = THF, DME, NH_3)

$CrCl_3 + 3\ NaC_5H_5 \rightarrow [(C_5H_5)_2Cr] + \frac{1}{2}\ "C_{10}H_{10}" + 3\ NaCl$

NaCp acts as a reducing agent and a ligand in this reaction.

Using a metal and cyclopentadiene

This technique provides using metal atoms in the gas phase rather than the solid metal. The highly reactive atoms or molecules are generated at a high temperature under vacuum and brought together with chosen reactants on a cold surface.

$M + C_5H_6 \rightarrow MC_5H_5 + \frac{1}{2} H_2$ (M = Li, Na, K)

$M + 2\ C_5H_6 \rightarrow [(C_5H_5)_2M] + H_2$ (M = Mg, Fe)

Using cyclopentadienyl reagents

A variety of reagents have been developed that transfer Cp to metals. Once popular was thallium cyclopentadienide. It reacts with metal halides to give thallium chloride, which is poorly soluble, and the cyclopentadienyl complex. Trialkyltin derivatives of Cp^- have also been used.

Many other methods have been developed. Chromocene can be prepared from chromium hexacarbonyl by direct reaction with cyclopentadiene in the presence of diethylamine; in this case, the formal deprotonation of the cyclopentadiene is followed by reduction of the resulting protons to hydrogen gas, facilitating the oxidation of the metal centre.[9]

$Cr(CO)_6 + 2\ C_5H_6 \rightarrow Cr(C_5H_5)_2 + 6\ CO + H_2$

Metallocenes generally have high thermal stability. Ferrocene can be sublimed in air at over 100 °C with no decomposition; metallocenes are generally purified by vacuum sublimation. Charge-neutral metallocenes are soluble in common organic solvents. Alkyl substituted derivative are particularly soluble, even in alkane solvents.

Possible Questions
Part-B (Two marks Questions)

1. What are the essential metals in biological system?

2. Draw the structure of $Fe_2(CO)_9$
3. Draw the structure of Zesis's salt?
4. What are interfering anions?
5. What are Na^+/K^+ pumps?

Part-C (Eight marks Questions)

1. Give an account of structure of hemoglobin and myoglobin?

2. Explain the ion channel of Na^+-K^+ charge carriers?

3. What is Zn-acid catalyst? And discuss it role in biological system.

4. Give a note on treatment of Pb, Cd and Hg toxicity?

5. What are major sources of Hg toxicity? Explain how the CH_3Hg is more toxic than Hg^{2+} ?

6. Briefly explain the function of Haemoglobin

7. Explain the synthesis of metal olefin complexes.

8. Discus the C-H activation of alkenes process

9. Synthesis of alkylidene complexes by various methods.

10. Discuss the structure and bonding in ferrocene.

OBJECTIVE QUESTIONS

S. no	Questions	Option A	Option B	Option C	Option D	Answer
1	Organometallic complexes were having------ between main group metal atoms and alkyl groups.	Sigma bond	Pi bond	Ionic bond	Covalent bond	Sigma bond
2	Which of the following is an organometallic compound	Lithium methoxide	Lithium acetate	Lithium dimethylamide	Methyl lithium	Methyl lithium
3	In the compound lithium tetrahydroaluminate, the ligands are	Al^+	H	H^-	Al^-	H^-
4	Which one of the following combination will be suitable for the preparation of $[(CH_3)_2CH]_3C\text{-}OH$:	$(CH_3)_2CHLi + [(CH_3)_2CH]_2C{=}O$	$(CH_3)_2CHMgX + [(CH_3)_2CH]_2C{=}O$	Both of these	None of these	$(CH_3)_2CHLi + [(CH_3)_2CH]_2C{=}O$
5	Which of the following organometallic compounds is the strongest base?	$(CH_3)_2CuLi$	CH_3Li	CH_3ZnBr	CH_3MgBr	CH_3Li
6	Organometallic compounds of lithium are stable in	water	air	ethyl alcohol	ether	ether
7	Which of the following statements about organometallic compounds is	Alkyllithium reagents (RLi) add to the	Grignard reagents (RMgBr) add	Alkyllithium and Grignard reagents do not	Grignard reagents are prepared in	Alkyllithium and Grignard reagents do not

	false?	carbonyl group of aldehydes and ketones	to the carbonyl group of aldehydes and ketones	add to esters	ether or tetrahydrofuran (THF)	add to esters
8	Which of the following statements about organometallic compounds is false?	An alkyllithium reagent is a very strong base	A Grignard reagent reacts as if it were a negatively charged carbanion	Grignard reagents are decomposed by water and alcohol	An organosodium compound is not very reactive compared to a Grignard reagent	An organosodium compound is not very reactive compared to a Grignard reagent
9	Trimethyl aluminium has bridged ----- group	Ethyl	Methyl	Propyl	phenyl	Methyl
10	The oxidation number of the metal in the complex $[Al(OH)(H_2O)_5]^{2+}$ is	+1	+2	+3	-2	+3
11	Organoalkali compounds are the source of	Free radicals	Electrophiles	Powerful cabanions	carbocations	
12	Which of the following condition is not suitable for the stability of the complex?	Larger basic nature of the ligand	Larger charge on the central metal ion	Smaller charge on the central metal ion	Chelation.	Smaller charge on the central metal ion

13	The correct statement for the aggregating nature of alkyl lithium (RLi) reagent is:	The carbanionnucleophilicity increases with aggregation.	The observed aggregation arises from its electron deficient nature.	Carbanionnucleophilicity does not depend on aggregation.	The extent of aggregation is maximum in polar dative solvents.	The observed aggregation arises from its electron deficient nature.
14	The final product of the reaction [Mn (CO)$_6$]$^+$ + MeLi —> is:	[Mn(CO)$_6$]$^+$ Me–	[Mn(CO)$_5$ Me]	[Mn(CO)$_6$]	[(MeCO)Mn(CO)$_5$]	[(MeCO)Mn(CO)$_5$]
15	Which one of the following will NOT undergo oxidative addition by methyl iodide?	[Rh (CO)$_2$I$_2$]$^-$	[Ir (PPh$_3$) $_2$ (CO) Cl]	[ŋ^2 – CpRh (CO)$_2$]	[ŋ^5 – Cp$_2$Ti (Me) Cl]	[ŋ^5 – Cp$_2$Ti (Me) Cl]
16	In metal-olefin interaction, the extent of increase in metal —> olefin p-back-donation would	lead to a decrease in C = C bond length	change the formal oxidation state of the metal	change the hybridisation of the olefin carbon from sp^{2}to sp^3	increase with the presence of electron donating substituent on the olefin	change the hybridisation of the olefin carbon from sp^2 to sp^3
17	The treatment of PhBr with n-BuLi yields:	2 n-BuPh + Br$_2$ + Li$_2$	PhPh + octane + 2 LiBr	n-BuPh + LiBr	PhLi + n-BuBr	PhLi + n-BuBr
18	Ferrocine is the -------- compound	Organic	Inorganic	organometallic	metallic	organometallic
19	[PtCl$_3$(C$_2$H$_4$)]-K+ is	Zeises salt	Mohr salt	Sodium salt	Ammonium salt	Zeises salt
20	Which statement about ferrocene	I$_2$ oxidizes ferrocene to	The ligands in ferrocene	The Fe centre in ferrocene	In the gas phase, the	I$_2$ oxidizes ferrocene to

	is incorrect?	give a diamagnetic cation	undergo electrophilic substitution with RCOCl in the presence of a Lewis acid	can be protonated by treatment with concentrated H_2SO_4	C_5H_5 rings in ferrocene are eclipsed	give a diamagnetic cation
21	The formula of ferrocine is	$[Fe(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-}$	$[Fe(CO)_5]$	$[(C_5H_5)_2Fe]$	$[(C_5H_5)_2Fe]$
22	What is the oxidation state of Iron in Ferrocene?	0	+1	+2	+3	+2
23	Which of the following statements about transition metal complex is false?	Metal-carbon single	Metal-carbon double	Metal-carbon triple	Carbon-metal single	Carbon-metal single
25	Grignard reagent react with excess CO_2 to yield	Aldehyde	Ketone	Ester	Acid	acid
26	Carboxylic acid obtained when Grignard reagent treated with	Carbon dioxide	Carbon monoxide	Formaldehyde	acetaldehyde	Carbon dioxide
26	Organo derivatives of groups IVB and VB are kinetically stable to attack by	Ethanol	Methanol	Water	benzene	Water
27	The hydrolysis reactions usually	Electrophilic	Nucleophilic	Free radical	Both ecetrophilic &	Nucleophilic

	involve the ---------- attack by water				nucleophilic	
28	The hydrolysis reactions usually involve the nucleophilic attack by	KOH	NaOH	H2O	$Ca(OH)_2$	H_2O
29	Me_3B is unaffected by ……… at room temperature inspite of the empty 2p-orbitals on the boron atom	KOH	NaOH	H_2O	$Ca(OH)_2$	H_2O
30	Me_3B is unaffected by waterat room temperature inspite of the empty ----- on the boron atom	2p-orbitals	2s-orbitals	3p-orbitals	3s-orbitals	2p-orbitals
31	The tetra alkyls of group IVB and trialkyls group of VB elements, metal contains low-energy orbitals and ------ attack is not favoured	Electrophilic	Nucleophilic	Free radical	Both ecetrophilic & nucleophilic	Nucleophilic
32	All organometallic compounds are thermodynamically unstable to	Reduction	Oxidation	Elimination	Addition	Oxidation
33	Olefins are ----------ligands	One electron	Two electrons	Three electrons	Four electrons	Two electrons
34	Metal olefin complexes are ---- bonded	Pi	Sigma	Covalent	ionic	Pi
35	Ferrocene is -------solid	Orange yellow	Yellow	Orange	White	Orange yellow
36	C_5H_5 is the -------- electron ligand	2	4	5	6	5

37	Metallocenes also called as	Cyclopentadienyl complexes	Cyclotetradienyl complexes	Cyclopentatrienyl complexes	Pentadienyl complexes	Cyclopentadienyl complexes
38	3d complexes possess the melting point between	182-182 °C	192-192 °C	172-172 °C	184-186 °C	172-172 °C
39	Stability order of metallocenes are	Fe > Ni > V > Cr > Ti	Ti > Fe > Ni > V > Cr	Cr > Ti > Fe > Ni > V	Cr > Fe > Ni > V > Ti	Fe > Ni > V > Cr > Ti
40	The following one is stable in air	V	Fe	Ni	Ti	Fe
41	Metallocenes oxidized in the acid solution to give	Anions	Free radicals	Cations	Neutral	Cations
42	Ferrocene is more resistant to catalytic hydrogenation than ……	Toluene	Aniline	Benzene	Phenol	Benzene
43	Ferrocene is aromatic in nature, they can undergo aromatic	Substitution	Elimination	Addition	rearrangmet	Substitution
44	The trialkyl aluminium compounds are generally	Monomeric	Dimeric	Trimeric	Tetrameric	Dimeric
45	The platinum ion in the Zeises salt is ----coordinated	3	4	5	1	4
46	The geometry of Zeises salt is	Square planar	Tetrahedral	Trigonal	Trigonal pyrimidal	Square planar
47	Ferrocene is a	Cluster	Sandwich	Carbide	hydride clusters	Sandwich

		compounds	compounds	clusters		compounds
48	The reaction of ferrocene, formaldehyde and N,N-dimethylamine is known as	Claisen condensation	Mannich condensation	Michael condensation	Perkin condensation	Mannich condensation
49	The fridel-craft reaction of Ferrocene gives	1-acetyl ferrocene	2-acetyl ferrocene	3-acetyl ferrocene	4-acetyl ferrocene	2-acetyl ferrocene
50	The reaction of ferrocene with acetylchloride gives	3-acetyl ferrocene	4-acetyl ferrocene	1-acetyl ferrocene	2-acetyl ferrocene	2-acetyl ferrocene
51	Which of the following mechanism takes place in ferrocene?	Electrophilic	Nucleophilic	Addition	Elimination	Electrophilic
52	In donar pair method, :CR_3^- donates	2 electrons	4 electrons	6 electrons	1 electron	2 electrons
53	Lithium is an	Alkaline metal	Alkaline earth metal	Transition metal	Inner transition metal	Alkaline earth metal
54	Carbine complexes containing	Metal carbon double bonds	Metal single carbon bonds	Metal carbon triple bonds	Carbob carbon double bonds	Metal carbon double bonds
55	Carbyne complexes containing	Metal carbon double bonds	Metal single carbon bonds	Metal carbon triple bonds	Carbob carbon double bonds	Metal carbon triple bonds
56	C_5H=- is planar with a symmetrical	Pentagonal shape	Hexagonal shape	Tetragonal shape	octagonal shape	Pentagonal shape
57	The first organometallic compound,	$K_2[Pt(C_2H_4)Cl_3$	$K_3[Pt(C_2H_4)Cl_3$	$K[Pt(C_2H_4)Cl_2]$	$K[Pt(C_2H_4)Cl_3]$.	$K[Pt(C_2H_4)Cl_3]$

	an alkene complex with formula is	].H_2O	].H_2O	.H_2O	$2H_2O$	.H_2O
58	Metal carbonyls of diamagnetic with the exception of	$Ni(CO)_4$	$Fe(CO)_5$	$V(CO)_6$	$V(CO)_5$	$V(CO)_6$
59	Purification of nickel by ------- processes makes use of the formation of nickel tetracarbonyl.	Mond’s	Wilkinson	Mannich	Fisher	Mond’s
60	The instability of ------------- in lights has been used for the preparation of blueprints pertaining to building plans.	Iron penta carbonyl	Nickel penta carbonyl	Iron tetra carbonyl	Cobalt penta carbonyl	Iron penta carbonyl

UNIT IV
SYLLABUS

Metal ions present in biological systems, classification of elements according to their action in biological system. Geochemical effect on the distribution of metals.Sodium/K-pump, carbonic anhydrase and carboxypeptidase. Excess and deficiency of some trace metals. Toxicity of metal ions (Hg, Pb, Cd and As), reasons for toxicity, Use of chelating agents in medicine, Cisplatin as an anti-cancer drug.
Iron and its application in bio-systems, Haemoglobin, Myoglobin; Storage and transfer of iron.

INTRODUTION

The role of metal ions in biological systems has been realized for a long time. Some metals are essentials. Others are considered toxic. When it comes to transition metals, the story is not different from that of the main group metals. Some have no known biological effects, such as Scandium in its +2 and +3 oxidation states in its various isotopic forms. Some are hypoallergenic such as Titanium (Ti), while others are essential to all forms of life such as iron and zinc. It appeared that Zinc plays an essential role in 300 enzymes in biota

The aim of this special issue is to make the biologically associated and related scientists pay more and close attention to the essential or the toxic effects of the elements in the first transition metal series of the periodic table. For example,iron ($Fe^{2+/3+}$), by far, is the most important metal ion not only within the first transition series, but also within the entire periodic table. Without iron, there will be no life. On the other hand, Chromium (III) or (Cr^{3+}) may have a role to play in glucose metabolism as has been seen by Mertz and Vincent. On the other hand, the toxic effect of Cr (VI) or (Cr^{6+}) is undeniable which prompted researches to search for specific Cr^{6+}chelators. Cr^{6+}also is considered to be mutagenic and/or carcinogenic.

In this special issue of eJBio, the Associate editor is presenting original research articles that deal with the most abundant first series transition ions in humans ($Fe^{3+}$and Zn^{2+}) and their interactions with one of agonists of one of mammalian nuclear receptors.The rest of the first transition metal series are: V, Mn, Co, Ni, and Cu. The experts on the biochemistry of these metal ions are welcome to contribute to this special issue. Biologists know the limited role of V in biology. Also, they know the role of Mn in photosynthesis, the role of Co in Vitamin B12, and the role of Ni in urease. We will give a very brief account for one of these remaining metal ions (copper). Cu2+ is an essential trace metal ion involved in many metalloproteins including: ceruloplasmin, cytochrome oxidase, superoxide dismutase, dopamine-β-hydroxylase, ascorbate oxidase, lysyl oxidase, and tyrosinase

Classification of elements according to their action in the biological system

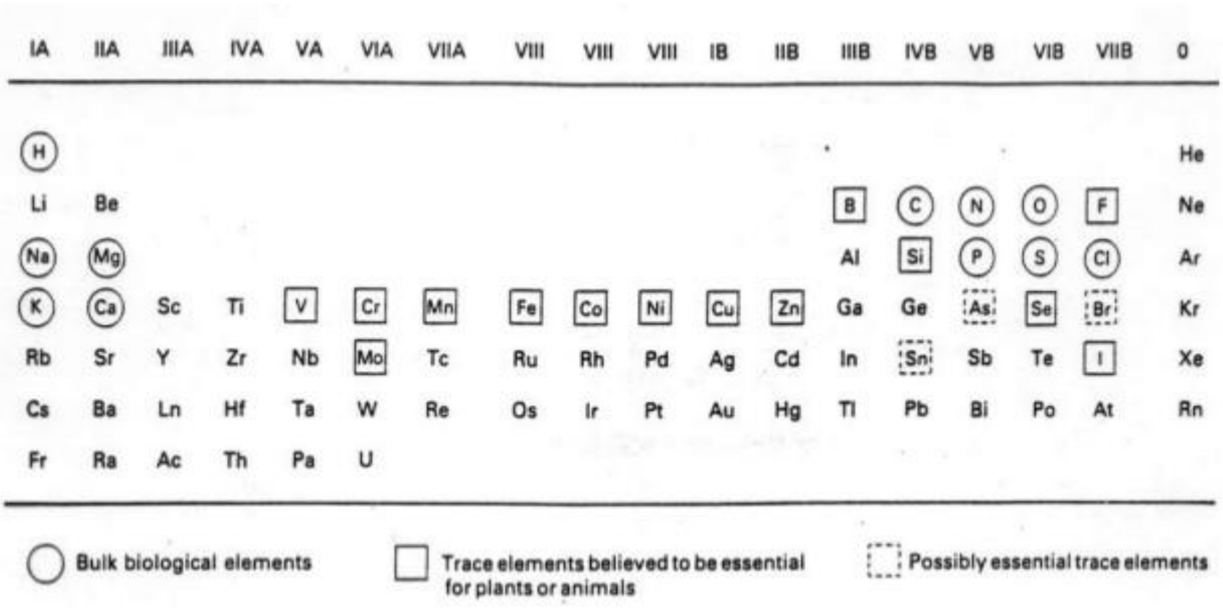
ESSENTIAL:Essential elements are absolutely essential or necessary for life processes.eg:O,C,H,N,P,Na,K,Mg,Cl,Ca,S etc.

TRACE:Trace elements are also necessary for life processes.eg I,Fe,Cu,Zn,Mn,Co,Mo etc.

NON ESSENTIAL:Non-essential elements are not essential. If they are absent other elements may serve the same function.eg Al,Sr,Ba,Snetc

TOXIC: Toxic elements disturb the natural functions of the biological system.eg Cd,Pb,Hgetc

Periodic Distribution of Biologically Important Elements



IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII	VIII	VIII	IB	IIB	IIIB	IVB	VB	VIB	VIIB	0
○ H																	He
Li	Be											□ B	○ C	○ N	○ O	□ F	Ne
○ Na	○ Mg											Al	□ Si	○ P	○ S	○ Cl	Ar
○ K	○ Ca	Sc	Ti	□ V	□ Cr	□ Mn	□ Fe	□ Co	□ Ni	□ Cu	□ Zn	Ga	Ge	⬚ As	□ Se	⬚ Br	Kr
Rb	Sr	Y	Zr	Nb	□ Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	⬚ Sn	Sb	Te	□ I	Xe
Cs	Ba	Ln	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U												

○ Bulk biological elements

□ Trace elements believed to be essential for plants or animals

⬚ Possibly essential trace elements

Geochemical effects on the distribution of metals

All the most essential elements, except Mo are fairly abundant in the earth's crust. Al (8.2%), Si (28.2%), Ti (0.57%) and Zr (0.02%) are although abundant but these are not essential elements. Because all these form insoluble oxides at biological pH values and do not form stable complexes with complexing agents of biological significance. 3No common element is toxic at levels normally encountered though almost anything can be harmful at too high levels. All the wellknown toxic elements, which are currently of much concern in environmental pollution problems, are extremely rare in abundance in the earth crust. As (~ 2 x10P-4 P%), Pb (~ 1.3 x10P-3 P%), Cd (~ 2 x10P-5 P%) and Hg (~ 5 x10P-5 P%).

The Sodium(Na+)–Potassium(K+)Pump

BIG IDEAS:

1. Uses energy supplied by the cell in the form of ATP totransport Na+out of the cell and K+into the cell
2. Both Na+ and K+ are moved against the concentration gradient(from low to high)
3. Creates an electrical gradient across the membrane(outside of the cell is + while the insideoff the cell is -)
4. This difference in chargeacross the cell membrane is important for the conduction of nerve impulses

SUMMARY:

The sodium-potassium pump is a form of active transport in that it uses ATP to "pump"3 sodium ions(3 Na+)out of the cell (against the flow of diffusion) and 2 potassium ions (2 K+)into the cell (also against the flow of diffusion). The sodium-potassium pump is important in the movement of ions across cell membranes of muscle cells (to help muscle contraction) and also for creating charge imbalances acrossthe cell membranes of nerve cells (for generating electrical impulses)

Steps involved in the Sodium-Potassium Pump(Na+-K+pump):

SUMMARY:

1.3 Na+ions from inside the cell bind to the Na+-K+pump

2.The pump changes shape, transporting the 3 Na+ionsacross the cell membrane and releases them on theoutside of the cell membrane.

3.The pump is now exposed to the outside surface of thecell. 2K+ions from outside the cell bind to the pumpand the pump changes shape again.

4.K+ions are transported across the cell membrane andare released inside the cell

5.During this process, ATP is split into ADP and inorganic phosphate. The breaking of this bond releases energy to power the pump.

6.Overall, because 3 positively charged ions LEFT the cell and ONLY 2 positively charged ions ENTEREDthe cell, a charge gradient develops across the cell membrane suchthat the outside of thecellhas more positive charge and the inside of the cell has more negative charge.

STEP-BY-STEP DETAILS

1. A molecule of adenosine triphosphate (ATP, a source of chemical energy) binds to a site on the intracellular side of the Na+-K+ pump protein.

2. Three sodium ions (3 Na+, shown as red balls) from the cytoplasm bind to “lock and key” sites on the Na+-K+ pump.

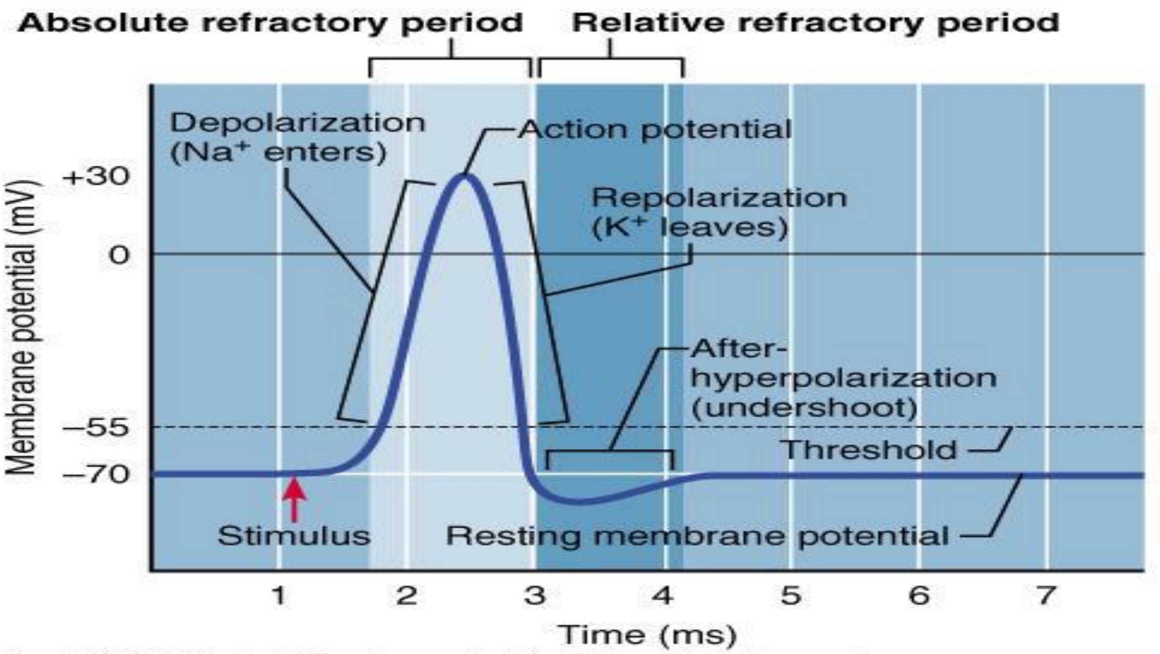
3. The bound ATP is then split into ADP and inorganic phosphate (the ADP is released back into the cytoplasm, while the inorganic phosphate, P, remains bound to the pump). The breaking of this bond releases energy that powers a change in the shape of the Na+-K+ pump protein , releasing the three sodium ions (3 Na+) outside the cell.

4. Two potassium ions (2 K+, shown as blue triangles) from outside the cell bind to “lock and key sites” on the protein of the Na+-K+ pump.

5. The protein of the Na+-K+ pump changes shape again as the remaining inorganic phosphate group leaves the protein's active site.

6. The two potassium ions (2 K+) are released into the cytoplasm, as another ATP molecule binds to the active site on the Na+-K+ pump protein and the process starts over. When this process repeats many times, an imbalance of charge forms across the membrane. There will be more positive charged ions outside the membrane than inside. This creates a chemical potential energy which can be used by the cell to later generate lots more ATP, for

generating electrical impulses, or for muscle contractions. Neurons communicate with one another when this charge difference is used to generate an "**action potential**" along the axon of a neuron



Polarity of cell membrane.

- Active transport by the Na+-K+ pump creates a concentration gradient
- Na+ is moved from the inside of the cell (low concentration) to the outside of the cell (high concentration)
- K+ is moved from the outside of the cell (low concentration) to the inside of the cell (high concentration)
- There are more Na+ ions outside the cell than there are K+ ions inside of the cell.
- As a result there is a net electrical charge across the cell membrane

Action Potential Stages

(a) The Resting State – known as the Polarized State:

 The**outside** of the cell membrane is **positive** and contains a high concentration Na+ ions (and a low concentration of K+ ions)

 The**inside** of the cell membrane is **negative** and contains a high concentration of K+ ions (and a low concentration of Na+ ions)

 Neither ion type (Na+ ions or K+ ions) is passing through the cell membrane.

 The net electrical energy (usually measured in millivolts) generated by this charge difference is called the **resting (membrane) potential** of the neuron.

(b) Depolarization:

 A stimulus occurs (such as release of a chemical neurotransmitter or the depolarization of a neighboring section of the cell membrane)

 As a result, sodium (Na+) channels in the cell membrane open and **Na+ ions rush** across the membrane **into the cell** via facilitated diffusion.

 There is a decrease in the **resting (membrane) potential** as the membrane is **depolarized** and the
interior of the cell **becomes positive.**

 If the stimulus is strong enough and reaches the depolarization **threshold**, an **action potential** is initiated.

(c) Propagation of the Action Potential:

 The positive patch in the membrane acts as a stimulus to the adjacent patch of the membrane.

 As a result, sodium (Na+) channels in the cell membrane open and **Na+ ions rush** across the membrane **into the cell** via facilitated diffusion.

 Thus the **resting potential** in this area of the cell membrane also decreases and depolarization spreads.

 The action potential thus travels rapidly along the axon of a neuron.

(d) Repolarization :

 Immediately after the action potential passes the membrane permeability changes again

 Na+ ion channels close and K+ ion channels open.

 K+ ions rush across the membrane and **out of the cell** via facilitated diffusion

 This ion movement restores the resting state **electrical conditions** (but not the resting concentration gradient of ions).
 Thereafter the **Na+-K+ pump** restores the ion concentration gradient by pumping Na+ out and K+ in.
 Until repolarization is complete, the neuron will be in a **refractory period**, meaning it cannot be stimulated again (until repolarization is complete).

Carbonic anhydrase

Carbonic anhydrases is a metalloenzymes with zinc ligands that catalyze the reversible hydration of carbon dioxide to bicarbonate. Among the most efficient enzyme, carbonic anhydrases acts over a broad spectrum of pH. Knowledge of carbonic anhydrase activity in plants has expanded significantly since the first scientific report was published 78 years ago . During this time majority of studies have focused on the key role of carbonic anhydrases in inorganic carbon fixation, respiration and CO2 transport and electrolyte secretion among other things and it was found that carbonic anhydrases helps in the regulation of chloroplast pH and protect stroma enzymes against denaturation during rapid and drastic changes in light conditions. Betacarbonic anhydrase involvement in the CO2 concentrating mechanism (CCM), which increases the content of this gas in close proximity to RuBisCO and consequently decreases photorespiration. •Carbonic anhydrase plays an important role in the mitigation of climate change in response to increasing concentration of CO2 in the atmosphere.

Carboxypeptidase

Carboxypeptidase A is a good illustration of the induced-fit theory, because the active site changes appreciably when the substrate binds. Figures 2 and 3 show three-dimensional representations of the carboxylase protein with and without a bound substrate. Note how the active site changes shape when it is complexed with a substrate. As the protein substrate binds to carboxypeptidase, the active site closes in around it. Hydrolysis of the peptide bond is most likely to occur if the terminal residue has an aromatic or bulky hydrocarbon side chain. A zinc ion (Zn^{2+}) is tightly bound near the active site and assists in catalysis. Three hydrogen bonding and electrostatic interactions are critical for the enzyme to recognize the terminal amino acid in the peptide chain. The intermediate is stabilized by interactions with $Zn^{2+}$and the carboxypeptidase molecule. The last step is a proton transfer and cleavage of the peptide bond. This entire process requires considerable mobility of the carboxypeptidase A protein itself.

Trace metals

The word "trace elements" is used for elements existing in natural and perturbed environments in small amounts, with excess bioavailability having a toxic effect on the living organism . Trace elements are chemical micronutrients which are required rather in minute quantity but play a vital role in maintaining integrity of various physiological and metabolic processes occurring within living tissues. The deficiency of any of the trace elements may be apparent as a combination of various clinical manifestations rather than a specific presentation as each trace element is related to many enzyme systems.

Healthy nutritional habits with regular intake of essential vitamins and minerals are of immense significance to general as well as oral health. As there had been limited knowledge among the oral physicians regarding significance of trace elements in human nutrition, the current review focuses on the role of those essential trace elements which have a proven role in maintaining oral health and their implications in various oral diseases and disorders.

Magnesium

Magnesium, an abundant element in the earth's crust, is vital to both plant andanimal life. Chlorophyll pigment in plants is a Mg-porphyrin complex. All enzymaticreaction in animals and men that are catalyzed by ATP require Mg as a cofactor.Oxidative phosphorylation, DNA transcription, RNA function, protein synthesis andcritical cell membrane functions are all dependent upon optimal Mg concentrations. Anaverage man has about 35g Mg, out of this 99% is either intracellular or in bone, of the60% in bone, two-third is tightly incorporated into the mineral lattice, but one-third is inan apparently exchangeable bone surface pool.

Dietary sources high in Mg include nuts,sea foods, legumes and vegetables, meat is intermediate in Mg content.

Potassium

An adult human has approximately 140 g K of which >90% is both intracellular and exchangeable (K is the predominant cation in intracellular water) since musclecontains most of the body’s intracellular water, it also contains most of the K. Since K is found in most animal and vegetable foods, dietary deficiency is exceedingly rare exceptunder unusual conditions (such as diets very high in refined sugars, alcoholic individualsderiving most of their calories from low-K alcoholic beverages in the states of starvationetc.).

Sodium

Sodium is the predominant extracellular cation in animals and man. An adulthuman has about 105 g Na, about 24% is located in bone and about 65% in extracellularwater. Sodium ion equilibrium is maintained primarily by the kidney, the key organ inwater and electrolyte balance. Sodium chloride (salt) is the predominant dietary source.Although excessive dietary Cl appear to have no significant ill effect on health, there ismuch evidence that excessive Na intake results in elevated blood pressure (hypertension)and that reduces Na intake or increased K intake helps to reduce high blood pressure.

Cobalt

Cobalt is an essential element for humans, but its pathway through the food chainto human being remains elusive. Only a little over 1 mg Co is present in an adult human. Itis useful to man, insofar as is known, only in the form of vitaminB12(cobalamin).Vitamin B12is synthesized only by bacteria. Vitamin enters the human food chain asanimal organs or muscle. In man dietary Co deficiency is only likely among strictvegetarians or when the intrinsic factor from the stomach that facilitates v. B12 absorption isabsent or severely decreased as in pernicious anaemia.

Zinc

An adult has about 1.5-3.0 g Zn with the largest amounts being in liver and bone.There is evidence that Zn concentrations in blood and several tissues vary considerably inresponse to many stimuli. Zinc appears to be critical in many functions. Human Zndeficiency in an inherited form in infants is termed acrodermatitisenteropathica and ischaracterized by behavioral disturbances, diarrhoea, hair loss and severe peri-orificialskin rash, all of which respond with remarkable promptness to Zn administration. Similarsyndromes have now been reported many times with penicillamine treatment of otherdisorders, presumably due to chelation of Zn, as well as during total parenteral nutritionwhen Zn was not added to the nutritional solutions for even as short a time as two weeks.A more chronic dietary deficiency of Zn (combined with other deficiencies) includedwarfism, hypogonadism and sexual immaturity, the latter devised with Zn therapy.

There is much evidence for marginal dietary deficiencies in humans. The effects includedecreased acuity of taste (hypogeusia), importance, delayed wound healing. Dietary source range in Zn concentrations from1400 μg g-1 to 2 μg g-1 orless in fresh fruit and vegetables. Bioavailability of Zn is especially high from animal issues and is low from milk and from grains. The latter effect is apparently due tobinding to phytic acid and fibre.

Molybdenum

The essentiality of Mo in animals and human beings is assumed from it'spresence in the metalloemzymes xanthine oxidase and aldehyde oxidase. Mo is also partof the enzyme sulphite oxidase, an inherited deficiency of which cause severe neurologicdisorders and early death in humans. However, no naturally occurring Mo deficiency hasever been documented in animals or man, even though several animal deficiencies havebeen produced experimentally, particularly by using the Mo antagonist. Molybdenum ispresent in very small quantities. Molybdenum appears to be readily absorbed from the GItracts and excreted primarily through the kidneys (though human studies are lacking).

Chromium

The designation of Cr as an element essential to animals and man is quite recent.Insofar as is known, the major biological function of Cr is an integral part of an organiccomplex originally isolated from yeast termed “glucose tolerance factor” (GTF). Thiscomplex apparently includes one Cr (III) ion and two nicotinic acid molecules and maycoordinate with three amino-acid molecules, probably glycine, cysteine and glutamicacid. Chromium is a known carcinogen and toxic metal present abundantly in tannery effluents in India. As anestimate, about 80-90% of the tanneries use chromium as a tanning agent. Ofthisquantity, the hides take up only 50-70%, while the rest is discharged as effluent.

Copper

Normal adult human has about 100-110 mg Cu, highest concentrations are foundliver, kidney, heart and brain. The prototype functional deficiency of Cu in humans is anX-linked inherited disorder called Menke’s syndrome (Kinky or steely hair syndrome).Cu insufficiency was first suspected by analogy with abnormal wool in Cu-deficientsheep. Ferroxidase (better known as ceruloplasmin before its role in mobilizing and oxidizing Fefrom storage sites was recognized) is believed to account for 95% of serum Cu, andappears to be a multi-functional protein serving as a major transport system for Cu aswell. Copper is widely distributed in the food chain, a notable exception being cow’s milk. Copper concentration ranges from 20-60 μg g-1Bin animal tissues to lessthan 2 μg g -1 in leafy green vegetables and fruits to less than 0.2 μg g-1 in cow’s milk, which is muchless than in human milk. Infants, especially if premature and not breast-fed, are thereforemost susceptible to dietary deficiencies; excessive loss of Cu from gastro-intestinal tractdue to diarrhoea is the most common precipitating factor

Toxicity

Mechanism of the toxicity of metals is very complicated. Generally toxicity of metals may result from one of the following:

i) Blocking the essential biological functional groups of biomolecules such as enzymes.Amino acid residues like serine is –OH functional group, cysteine is –SH group and histidine –N group often constitute the active sites of enzymes. Atoxic metal ion may bind with these functional groups and block the activity of the enzyme.

ii) Displacing the essential metal ions from biomolecules.A biomolecule with a foreign metal ion loses its activity.

iii) Modifying the active conformation of biomolecules.Biomolecules are having specific active conformations and if this active conformation is lost due to the coordination of a metal ion, the activity of thebiomolecule is lost.

Toxic Metals

Mercury:

Sources of Mercury pollution are industrial waste, mining (as mercury is tracecomponent of many minerals), pesticides, coal &lignite (containing about 100 ppb ofHg). It is a well known toxic metal came to lime light after the incidence of “Minamatadisease” in 1953-60 in Japan. One hundred eleven cases of mercury poisoning werereported who had eaten mercury contaminated fish from Minamata Bay. Among them 45people died. The sea fish were found to be containing 27-102ppm of Hg in the form ofmethyl mercury. The mercury source was the effluent (Hg containing catalyst wastes)from a vinyl chloride plant (Minamata Chemical Company) releasing into the bay. Thiswas followed by more tragic report of mercury poisoning from Iraq in 1972, where 450villagers died after eating wheat which had been dusted with mercury containingpesticides. These two tragic events boosted the awareness of mercury as pollutant; andultimately resulting in its being studied more extensively than any other trace elements

Reason for Toxicity: Toxicity of mercury is based on the strong affinity (very highformation constant between 10P16P and 10P22P) for the deprotonated forms of thiol ligandssuch as Cysteine; therefore, thiols, RSH, with sulfhydryl group, -SH are also calledmercaptans (Mercuriumcaptans). So Hg (II) binds strongly with the thiol group ofproteins and enzymes and this binding changes the confirmation of protein about theactive site. Mercury is a soft acid and –S of –SH group is a soft base so strong interaction between mercury and -SH group can be explained on the basis of stronger soft-softbinding**.**

Cadmium:

The source of Cd pollution in urban areas are metallurgical plants, Cd plating and battery fabricators. Acute Cd poisoning leads to nausea, salivation, vomiting, diarrheaand abdominal pain. Cd deposition tends to be cumulative in the kidney with lower9concentrations in the liver. Another characteristics of Cd poisoning is brittleness ofbones. Cd occurs in nature in association with Zn minerals. A severe outbreak of chronicCdpoisoning occurred along the Jintsu river of North-West Japan and was known as Itai-Itai or ouch-ouch disease. Over 20 year period around 100 people died. In 1961 Cd wasfound to be the cause. The region was due to a old disused zinc mine and river waterwhich was containing Cd used for irrigation of rice and people died after eating the rice.

Reason for toxicity: Cd is similar to zinc. Therefore Cd (II) can displace Zn (II) in manyzinc enzymes. Like Hg (II), Cd (II) also binds strongly with the –SH groups of Cysteineresidues of enzymes e.g., Carbonic anhydrase, dipeptidase, carboxy peptidase etc. Cd (II)like other toxic metal ions effects the active confirmation of biomolecules due to thestrong binding.

Lead :

Sources of pollution : Battery industry is the largest single user of lead. Butleaded petrol accounts for more than 20% of total lead consumed per year and 90% of

lead released to atmosphere is from gasoline exhaust. The triethyl lead cation, (CB2BHB5B)B3BPbP+P, is formed from tetraethyl lead by the dissociation of a carbanion. Toxicity; of thisorganometallic cation results from the permeability of membranes, including the verydiscrimination blood-brain barrier causing several disorders of central and peripheralnervous system (cramps, paralysis, loss of coordination). One of the characteristicsymptoms of lead poisoning is anemia.

Reason for toxicity: Like Hg (II) and Cd (II) lead inhibits SH-enzyme but less strongly.Major biochemical effect of Pb is its interference with heme synthesis by inhibiting several of key enzymes involved in the overall process of heme synthesis.

Arsenic:

Arsenic toxicity has become a global health problem affecting millions of people. Aside from causing gastrointestinal, respiratory, cardiovascular, genitourinary, endocrine, hematopoietic system and skin diseases , acute and chronic arsenic exposure is associated with neurologic consequences in adults. Arsenic is a known neurotoxicant that affects the peripheral nervous system, with effects which may last for several years or even a lifetime, causing a symmetrical peripheral neuropathy characterized by sensory nerves being more sensitive than motor nerves to arsenic effects, and neurons with large axons being more affected than neurons with short axons . Acute arsenic exposure was reported to cause central nervous system (CNS) alterations , including learning, memory, and concentration. When exposure occurs in the early developmental stages, the CNS is more susceptible to toxic agents. Although neurotoxic effects of arsenic in adults have been well documented, there is no review addressing the effects of arsenic on neurodevelopment. The purpose of this review is to integrate the reports on possible interactions of arsenicals with neurodevelopment and to promote interest in exploring the mechanisms of arsenic developmental neurotoxicity.

Reason for toxicity

Long-term exposure to arsenic can cause more severe symptoms. You should seek emergency help if you experience any of the following after a suspected arsenic exposure:

- darkening skin
- constant sore throat
- persistent digestive issues

Use of chelating agents in medicine; or chelation therapy

Treatment of Metal poisoning detoxification by chelating agents:

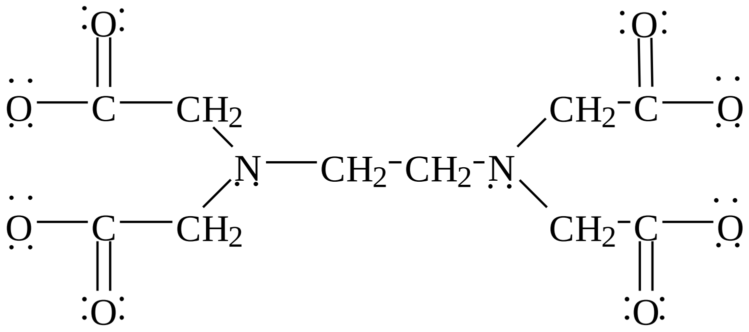
Mostly the treatment of metal poisoning is done by the use of chelating agents. It is hoped that the chelating agent will form soluble, stable and non-toxic complexes whichare readily excreted.Criteria for a potential chelating drug.

1. It must bind the metal strongly to complete for it with biological ligands and excreting as soluble chelate.
2. It should be selective for the metal ion. If it is non-selective then there will he harmful side effects from the removal of other metals, particularly calcium and zinc from the body.
3. Chelate must be of low toxicity and not metabolized i.e. it should remainunchanged in biological system.
4. It should be capable of penetrating in to metal storage sites.
5. Chelate should be less toxic than the ‘free’ metal ions.A suitable multidentate ligand that can satisfy all the coordination positions of the metalion would be ideally suited in the elimination of the metal ion. So that the chelated metal ion cannot bind to any binding sites of enzymes and proteins e.g. EDTA is the mostfamiliar example of chelating agents used in chelation therapy.

(i) EDTA (Ethylenediaminetetraacetic acid)

EDTA was synthesized in Germany in 1930 by Munz as a substitute for the expensive imported chemical citric acid, used as a calcium-sequestering agent in thetextile industry. EDTA was patented for this use in 1935. Due to the greater demand ofchelating agents for the removal of toxic elements and increasing risk of nuclear fissionproducts entering the human body, Pfeiffer, Schwarzenbach and others introduced EDTAto medical research in 1945. The first administration to human beings was in the form ofNi-EDTA

complex for the treatment of breast cancer, but it remained unchanged andexcreted in the urine. Later in 1952 it was effectively used against lead poisoning.Sodium salt of EDTA depletes blood calcium levels and produces hypocalcaemic tetany.This danger is minimal if calcium disodium EDTA is used as the chelating agent and I thas now become the material of choice in cases of lead poisoning. Calcium-EDTA hasthe lowest stability constant in comparison to other metal ions in the body. Hence thesemetals readily exchange in vivo to form soluble EDTA complexes that are excreted in theurine. Except in massive doses it is almost nontoxic and treatment with [CaNa2EDTA]
results in a rapid depletion of lead.

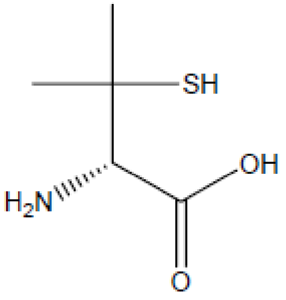


(ii) British anti-Lewisite (BAL) or
2, 3-dimercapto-1-propanol : [CHB2BSH-CHSH-CHB2BOH]

It was used by British army during world war to treat patients poisoned by the gasLewisite ClCH=CHAsClB2B. It binds to the enzymes containing SH group. But BAL bindsstrongly to arsenic and removes it. It is also used for the treatment of poisoning caused byHg, As, Gold etc.

(iii) D-Penicillamine :

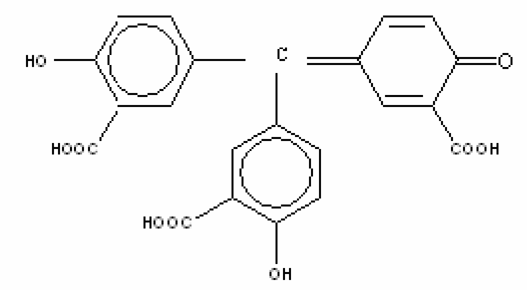
It is used for urinary excretion of copper in Wilson's disease.



D-penicillamine

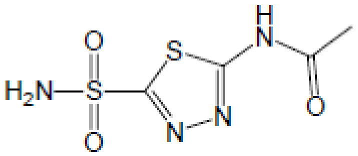
(iv) Aurine tricarboxylic acid :

Effective in the treatment of Beryllium poisoning



(v) Diuretics:

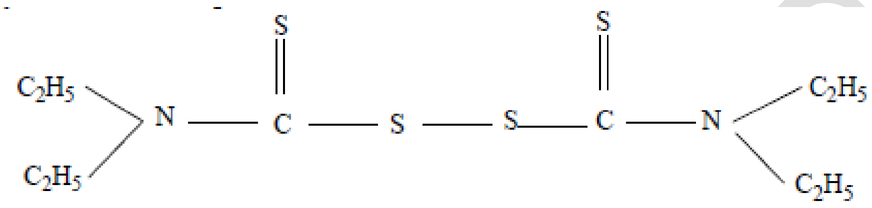
These are the drugs that promote the formation of urine e.g. Diacarb or acetazolamide.Coordinates with zinc of zinc containing enzyme carbonic anhydrase and stopsthe enzymatic activity of catalyzing the reactionCO_2+ H_2O ↔ H^++ HCO_3^- in whichwater combines with CO2 to form bicarbonate ion. When this reaction stopped, there willnot be conversion of carbondioxide and water to bicarbonate ion, resulting in theformation of more urine.



Acetazolamide

(vi) Disulfiram:-

Tetraethyl thiuramdisulphide Used in the treatment of chronic alcoholism. It inhibits Molybdenum containingmetalloenzymealdehydeoxidase. So the metabolism of ethanol stops with the formationof acetaldehyde producing unpleasant symptoms and discouraging further indulgence.Drug inhibits aldehydeoxidase presumably via the soft-soft Mo-S interaction.



(vii) Tetracycline and its analogues:

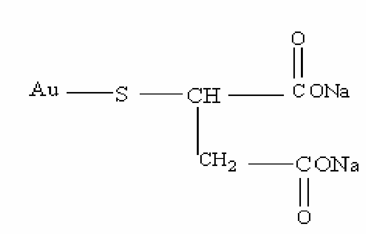
It has been shown that there is a correlation between the possession ofantibacterial properties and the ability to form stable chelates. Tetracycline and itsanalogues have a number of sites to form metal chelates of fairly high stability.Certain metal ions stabilize the DNA double helix. Unwinding of helix normallyarises from the repulsion between negatively charged phosphate groups. Binding ofcations to the phosphate neutralizes the charge and stabilizes the double helix. MgP2+P mosteffective in stabilizing the structure. It is now generally accepted that the action of thetetracyclines is directed towards the ribosomes of the bacterial cells and hence results ininhibition of protein synthesis. It seems that the ultimate target of tetracydines is the MgP2+Pwhich is necessary for the stabilization and function of the ribosomes.

ix) Lithium:

Lithium is used in the treatment of the manic phase of manic depressive patients. One in two thousand people in the U.K. receive such lithium treatment. Manic depressive psychoses involve alternating phases of depression and over excitement. Very little is known about the mechanism of lithium action. From a general point of view it is possible that lithium could be interfering with aspects of Na^+, K^+, Mg^{2+} or Ca^{2+} metabolism. The existenes of diagonal relationship suggests that competition between Li+ and Mg2+ for Mg2+ sites must be considering as a priority.

(xi) Gold:

Gold compound were first used in 1927 for the treatment of rheumatoid arthritis and are still used. The major role of gold compounds in chemotherapy involves the treatment of rheumatoid arthritis with gold (I) compounds such as disodium gold (I) thiomalate (Myocrisin)



CISPLATIN

Chemotherapy is one of the main weapons in the fight against cancer. A crucialevent happened in 1962 when B.Rosenberg, a physicist, who was investigating the effectof electric field (using platinum electrodes) on the division of cultured bacterial cellfound that the field generated between platinum electrodes seemed to prevent the divisionof bacterial cell without simultaneous inhibition of bacterial growth which eventually ledto the formation of long, filamentous cells. Further experiments showed that it was notthe electric field but cisdiamminedichloroplatinum (II) {cis [Pt (NH3)2BCl2]}, laterknown as cisplatin that were responsible for this effect.

These species were formed bytiny amounts of platinum from the 'inert' electrodes reacting with the chloride andammonia that were present in the electrolytic medium. In subsequent studies theantitumour activity of cisplatin has been studied in tumors induced in animals and thepromising results led to the first clinical trials in 1972. In 1978 it was officially approvedas an anticancer drug in US. Since 1983, cisplatin has been the drug with the highestturnover in the United States; annual revenues are in excess of US$ 100 million, andabout 30000 patients per year have regularly been treated successfully.

For a long time,this compound has topped the list of the most successful patent application granted toAmerican Universities (Michigan State University). Although effective against the broadspectrum of tumors, the compound is almost universally sued in the treatment oftesticular and ovarian cancer, as well as some other types of cancer. The cure rate isapproaching 100 percent, especially for early-recognized testicular cancer.

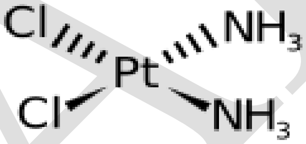
The mostcommon side effects of a cisplatin therapy include kidney and gastrointestinal problems,including nausea, which may be attributed to the inhibition of enzymes throughcoordination of the heavy metal platinum to sulfhydryl groups in proteins. Accordingly, atreatment with sulfur compounds such as sodium diethyldithiocarbamate or thiourea andsubsequent diuretics may counteract these symptoms.Now it is well established fact that the mechanism of cisplatin is based on Pt-DNA interaction. The first clue came from the filamentous growth observed byRosenberg. This growth is to be caused by inhibiting DNA replication while the RNAsynthesis and protein synthesis are relatively unaffected. Studies in vitro as well as invivo indicate that Pt binds with NB7B of two intrastand adjacent guanine bases ofDNA. Thisbinding changes the active conformation of DNA leading to inhibiting of DNAreplication or cell division. The binding of cisplatin to DNA seriously interferes with theability of guanine bases to undergo Watson-Crick base pairing.

cis-Pt (NH3)2 Cl2 + H2O ---------- cis- [Pt (NH3)2 (OH2) Cl]++ Cl-

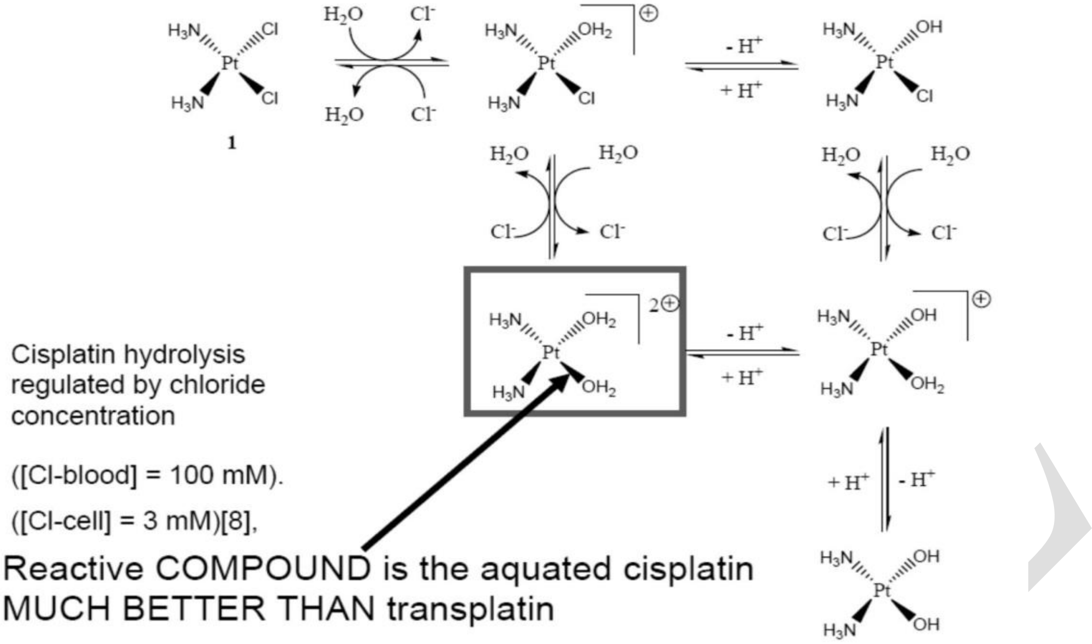
Cisplatin is administered by intravenous injection as an aqueous saline solution.Approximately half the platinum binds to serum proteins and is excreted. The rest isdistributed among various tissues. In serum, the drug remains largely as cis-Pt (NH3)2Cl2, owing to the relatively high chloride concentration (0.1M). As a neutral molecule,cisplatin diffuses passively across cell membranes into the cytoplasm, where itencounters a substantially lower chloride ion concentration (3mM). Hydrolysis producescationic complexes such as cis- [Pt (NH3)2 (OH2) Cl]+ that diffuses to DNA, itself apolyanion, they bind to form cytotoxic lesions. The hydrolysis reactions of cisplatin arean important aspect of its biological activity.Since cis- as well as transplatin alter the double helical structure of

DNA and itsreplication, the answer of the question that why only cis is active, is veryinteresting.

Thetrans isomer is resorbed more rapidly than cis-platin; however the concentration of theDNA coordinated trans complex begins to decrease after six hours whereas the cis-isomeris then still accumulated in the cell nucleus. Only very little trans compound is stillcoordinated to DNA after 24 hours. These results indicate that the changes in the DNAstructure caused by the trans isomer are sensed differently by the endogenous repairmechanism from those caused by coordination of cisplatin. Recently it has been foundthat as the cisplatin binds with DNA, a structure specific recognition protein (SSRP)recognizes the bending of DNA containing cis platin and binds with DNA. This proteinbinds specifically to DNA containing cisplatin and not with trans. Though the mechanismis not clear but this binding of SSRP may be the reason activity of cisplatin and inactivityof trans.



Reactions of *cis-platin*under physiological conditions



Disadvantages of *cis*-platin

1.Applicable in relatively narrow range of tumors.

2.Limited solubility in Aqueous solution.

3.Intravenous administration, inconvenience to outpatient treatment. Nephrotoxicity,neurotoxicity and nausia.

4.Higher toxicity leading to lower doses of 100 mg/day.

Iron in biology

The average human adult has about 4-5 g Fe. Of this amount, about 60-70% ispresent in haemoglobin in red blood cell, 3-5% is in muscle myoglobin, 15% is bound tothe Fe storage cellular protein, ferritin, 0.2% occurs as a component of critical respiratoryenzymes and 0.004% is bound to the serum transport protein transferin. Iron deficiencycauses anemia because red cells of blood containing less hemoglobin than in normalcondition. Acute iron poisoning leads to vomiting, pallor, shock, circulatory collapse andcoma. Chronic conditions are also known in which iron is deposited in tissues and organsof the body. This condition is known as siderosis.

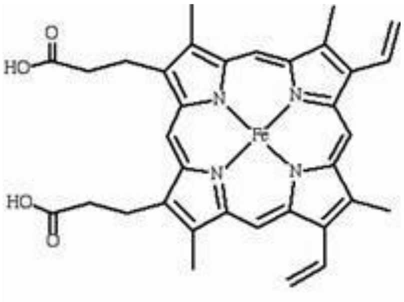
Peroxidases are hemecontaining enzymes that use hydrogen peroxide (H2O2) as the electron acceptor to catalyse a number of oxidative reactions.

Most heme peroxidases follow the reaction scheme-

Heme proteins by function

- Catalysis
- Electron transfer
- Oxygen transport and storage
- Nitric oxide transport
- Peroxidases typically catalyze a reaction of the form:

ROOR' + electron donor (2 e-) + $2H^+ \rightarrow$ ROH + R'OH

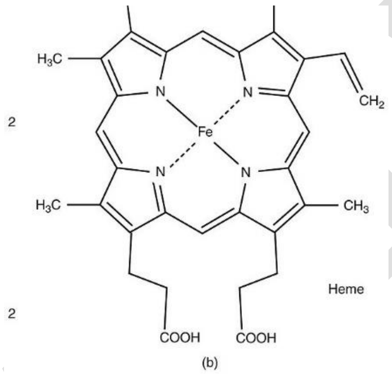


Heme *b*

Structure and functions of haemoglobin-myoglobin

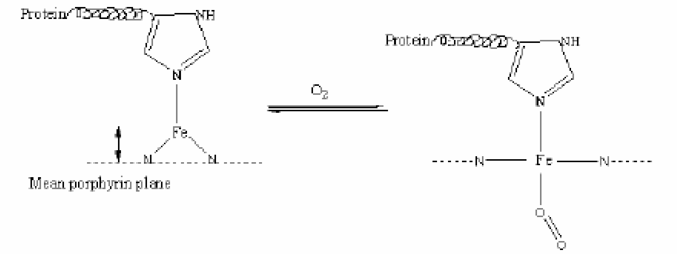
Whereas hemoglobin is the oxygen-carrying protein of blood, myoglobin is the oxygen-carrying protein of the muscle. Myoglobin is particularly abundant in the muscles of diving mammals, like seals and whales, allowing. Hemoglobin is the oxygen-carrying protein thatmakes red blood cells red.them to continue to use oxygen even whenthey are underwater for extended periodsof time.

The structures of hemoglobin andmyoglobin have some notable similarities,which are related to their oxygen-bindingfunctions. None of the amino acids are well
suited to bind oxygen, so both of theseproteins have an additional iron-containing
group (**heme**) as part of their structure.Fe2+ is commonly used inbiological systems to reversibly bind O2.A notable difference between the twoproteins, which relates to their specificroles in the body, is that hemoglobincontains four polypeptide chains butmyoglobin has only one .Each chain withits attached heme group is called a “subunit.”

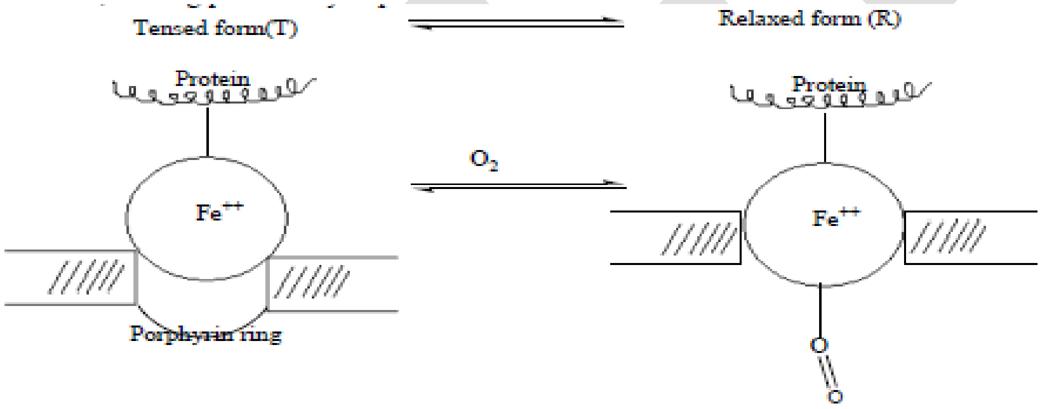


Mechanism of oxygenation in Hb and Mb

Hb may be viewed as tetrameric Mb. It has four heme groups bound to fourprotein chains. The differences between Hb and Mb in their behavior towards oxygen isrelated to the structure and movements of the four chains. It is found that, uponoxygenation of Hb, two of the heme groups move about 1AP oP towards each other whiletwo other separate by about 7APoP. These movements seem responsible for the cooperativeeffect observed. Detailed study of the mechanism has been accomplished by Perutz.According to Perutz, changes in the coordination of the iron play a crucial role. DeoxyHb contains iron (II) in a high spin state, with two electrons occupying eg. orbitals, thebonding radius of the iron is so large (0.78AP oP) that it cannot fit into the plane of four Natoms of the heme porphyrin. It therefore lies around 0.75APoP out of the plane. The iron isthus pentacoordinate with square pyramidal coordination provided by four porphyrinnitrogen atoms in the basal position and an imidazole nitrogen atom from histidine in theapical position.



When an oxygen molecule is bound in the position opposite to this histidine, the iron atom goes in to a low spin state, eg. orbitals are then empty and the radius of the irondecreases (by 0.17 APoP) so much that it now fits in to the plane of the porphyrin system.Thus the iron atom moves down when deoxy Hb becomes oxygenated. Since it remainsattached to the side chain of histidine this shift is transmitted to various parts of thesubunits, causing particularly important movements of the entire helical section.



Two forms tensed (T) and Relaxed (R) 0f Hbare present as an equilibriummixture. With no OB2B present, the T state is more stable than the R state and the Hb is thusfound to be almost exclusively in the T form. The OB2B affinity of Hb in the T state is muchless than the OB2B affinity of Hb in the R state. Thus the initialOB2B affinity of Hb issignificantly lower than that observed for the individual subunits. Addition of OB2B todeoxy Hb changes the equilibrium between T and R state. As the Hb picks up oxygen, theequilibrium shifts towards the R state. Thus the more OB2B molecules bound to Hb, thehigher the probability that Hb will be in the R state. As the oxygen affinity of the R stateis approximately same as that of an isolated subunit, the OB2B affinity of almost completelyoxygenated Hb should be approximately equal to that of the isolated chain. It is thisstructural change, which occurs in the binding of the O2 to the heme that results in thedecrease in the stability of T conformation relative to the R form and causes the observed cooperativity.

Storage and transfer of iron

When you absorb more iron than your body needs for immediate purposes, some of it is stored in your cells as ferritin (ferritin is a storage protein for iron in your cells). These stores can supply iron when your body needs it later and will be depleted before iron deficiency begins.

Ferritin: The Iron-Storage Protein

Fortunately, most of us are able to maintain appropriate levels of available iron in the body, even if our iron consumption does not always exactly match the body's iron loss. This regulation of blood-iron levels is mediated by the protein **ferritin** . Ferritin can release iron if the blood has a low iron concentration, and it can help to store excess iron if the blood and tissues have a high iron concentration. Hence, ferritinfunctions as a "buffer" against iron deficiency and, to a lesser extent, against iron overload. Ferritin has the shape of a hollow sphere. Inside the sphere, iron isstored in the Fe(III) oxidation state. It is incorporated in the mineral ferrihydrite,$[FeO(OH)]_8[FeO(H_2PO_4)]$, which is attached to the inner wall of the sphere. To release iron when the body needs it, the iron must be changed from the Fe(III) to the Fe(II) oxidation state. Then, the iron leaves through channels in the spherical structure. To understand how ferritin controls storage and release of iron, we need to first study its structure.

Possible Questions

Part-B (Two marks Questions)

1. State the EAN rule

2. What is Hydrophobic Pocket?

3. What are carrier proteins?

4. Draw the structure of ferrocene?

5. Draw the structure of $Co_2(CO)_8$?

Part-C (Eight marks Questions)

1. Briefly explain the bonding and reactivity of ferrocene.

2. Explain the polymerization reactions with Ziegler-Natta catalysis?

3. Discuss the preparation of alkyl lithium and aluminium compounds.

4. Brief reaction mechanism of Ziegler-Natta catalyst.

5. Explain the structure and reactivity of ferrocene.

6. Explain the synthesis of metal-olefin complexes.

7. Briefly explain the function of Myoglobin.

8. Discuss the brief reaction mechanism of Ziegler-Natta catalyst.

9. What are the biochemical importance of Co and Zn?

10. Give an account of biological oxygen carriers?

OBJECTIVE QUESTIONS

S. No	Questions	Option A	Option B	Option C	Option D	Answer
1.	The sodium-potassium pump passes	more Na+ out than K+ in	K+ out and Na+ in on a one-for-one basis	Na+ out and K+ in on a one-for-one basis	K+ and Na+ in the same direction	more Na+ out than K+ in
2.	Which of the following are not components of the cell membrane?	cell surface markers	transmembrane proteins	interior protein network	plasmodesmata	plasmodesmata
3.	Red blood cells have a characteristic concave shape because of	spectrin	dextrin	hemoglobin	hemocyanin	spectrin
4.	ATP is required in the transport of	water molecules	all molecules across a membrane	molecules to areas of lower concentrations	molecules to areas of higher concentrations	molecules to areas of higher concentrations
5.	A ______ protein combines with a substance and helps to move it across the membrane.	carrier	channel	receptor	enzymatic	carrier
6.	Sodium and potassium ions are transported across the plasma membrane by a ______ protein.	carrier	channel	receptor	enzymatic	carrier

7.	______ is the net movement of any type of molecule from a region of higher concentration to a region of lower concentration.	Osmosis	Diffusion	Active transport	Facilitated diffusion	Diffusion
8.	The diffusion of water across a differentially permeable membrane is called ______.	simple diffusion	facilitated diffusion	osmosis	exocytosis	osmosis
9.	Which of the following processes uses a carrier protein and ATP?	Osmosis	Diffusion	Active transport	Facilitated diffusion	Active transport
10.	Which of the following conditions does NOT apply to active transport?	requires ATP	transports molecules from a high to low concentration area	requires a carrier protein	carrier proteins bind reversibly to transported substances	transports molecules from a high to low concentration area
11.	Why are proteins involved in active transport often called "pumps"?	They use energy to move a substance with its concentration gradient.	They use energy to move a substance against its concentration gradient.	They use energy to bind the substance to the carrier.	They use energy to dislodge the substance from the carrier.	They use energy to move a substance against its concentration gradient.
12.	The principal intracellular cation is:	Na+	Cl-	K+	Ca2+	K+
13.	Which of the following is an example of primary active transport	Cl--HCO3- exchange	Na+ - H+ exchange	Na+-Ca2+ exchange	The Na+, K+ ATPase	The Na+, K+ ATPase

14.	The sodium pump	Exchanges extracellular Na^+ for intracellular K^+	Is important for maintaining a constant cell volume	Can only be inhibited by metabolic poisons	Is an ion channel	Is important for maintaining a constant cell volume
15.	Which of the following values is closest to the resting membrane potential of mammalian cells:	-20 mV	-60 mV	+60 mV	+20 mV	-60 mV
16.	The principal extracellular cation is	Sodium (Na^+)	Potassium (K^+)	Chloride (Cl^-)	Calcium (Ca^{2+})	Sodium (Na^+)
17.	The resting membrane potential is mainly determined by	the Cl^- gradient	the Ca^{2+} gradient	the Na^+ gradient	the K^+ gradient	the K^+ gradient
18.	Nucleoside is a pyrimidine or purine base	covalently bonded to a sugar	ionically bonded to a sugar	hydrogen bonded to a sugar	none of the above	covalently bonded to a sugar
19.	Which pyrimidine base contains an amino group at carbon 4?	Thymine	Cytosine	Adenine	Uracil	Cytosine
20.	Nucleotide bases and aromatic amino acids absorb light respectively at	260 and 280 nm	270 and 280 nm	280 and 260 nm	260 and 270 nm	260 and 280 nm
21.	Nucleic acids can be analyzed experimentally by their	molecular weight	absorption of visible light	absorption of uv light	equivalent weight	absorption of uv light
22.	The most stabilizing force for nucleic acids is	Van der Waals	electrostatic bond	hydrogen bonds	conformational entropy	Van der Waals

23.	The basic unit of nucleic acid is	pentose sugar	nucleotide.	nucleoid	nucleoside	nucleotide.
24.	Adenine is	purine	pyrimidine	nucleoside	nucleotide.	purine
25.	Living cell contains 60 – in human body is	65 – 70%.	50 – 55%	75 – 80%	65 – 70%.	65 – 70%.
26.	Amino acids are produced from	fatty acids	essential oils	proteins	a-keto acids.	proteins
27.	Amino acids are mostly synthesised from	a-ketoglutaric acid.	mineral salts	fatty acids	volatile acids	a-ketoglutaric acid.
28.	What are the most diverse molecules in the cell?	proteins	lipids	mineral salts	carbohydrates.	proteins
29.	The major role of minor elements inside living organisms is to act as	co-factors of enzymes	building blocks of important amino acids	constituent of hormones	binder of cell structure	co-factors of enzymes
30.	nucleic acid is one of the	pentose sugar unit	nucleotide uit	nucleoid unit	nucleoside unit	nucleotide unit
31.	purine base with nucleoside is	covalently bonded to a sugar	ionically bonded to a sugar	hydrogen bonded to a sugar	none of the above	covalently bonded to a sugar
32.	pyrimidine base with nucleoside is	covalently bonded to a sugar	ionically bonded to a sugar	hydrogen bonded to a sugar	none of the above	covalently bonded to a sugar
33.	Hydrogenation involve the saturation of which type of	Carbon-carbon	Carboxyl group	Hydroxyl group	All of the mentioned	All of the mentioned

	linkage?					
34.	Which catalyst carry hydrogenation to the maximum?	Mild Catalyst	Vigorous catalyst	All the above	Both mild and vigorous catalyst	Vigorous catalyst
35.	Which of the following is a vigorous catalyst?	Nickel	gold	copper	Zinc	Nickel
36.	Which of the following is mild hydrogenation catalyst?	Nickel	gold	copper	Zinc oxide	Zinc oxide
37.	What are the hydrogenation reactions catalysed by molybdenum compounds?	Reduction in unsaturated	Cleavage of C-C	Dehydroisomerization	All the above	All the above
38.	Which of the following is a Nobel-metal catalyst?	Nickel	gold	copper	Platinum	Platinum
39.	What are the commonly used catalysts for the Fischer Tropsch synthesis?	Nickel	gold	copper	Zinc	Nickel
40.	Cobalt catalyst is used when which type of products are desired?	Solid	Liquid	vapour	both solid and liquid	Liquid
41.	Complete the following reaction: 3Fe2C + 4H20 —–> 2_____ + 3C + 4H2.	Fe3O4	Fe3O6	Fe3O2	Fe3O5	Fe3O4
42.	Which catalyst is prepared by precipitation from a nitrate solution with potassium	Nickel	gold	copper	Zinc	Nickel

	carbonate?					
43.	The magnetite catalysts are reduced to what?	Metallic iron	Metallic zinc	Metallic cobalt	Metallic nickel	Metallic iron
44.	By which process Iron can not be prepared?	From magnetite	Iron oxide	Oxidation of metals	Reduction of metals	Reduction of metals
45.	Enzymes	make endergonic reactions proceed spontaneously	lower the activation energy of a reaction	are not very specific in their choice of substrates	are needed in large quantities because they are used up during catalysis	lower the activation energy of a reaction
46.	NAD+ is a(n)	Enzyme	CoEnzyme	active site	high-energy bond	CoEnzyme
47.	Which of the following is a reduced compound?	CO_2	O_2	N_2	NADH	NADH
48.	The initial steps in breaking down glucose are called	glycolysis	intramolecular catalysis	chemiosmosis	intermolecular catalysis	glycolysis
49.	Cofactors	break hydrogen bonds in proteins	help facilitate enzyme activity	increase activation energy	decrease activation energy	help facilitate enzyme activity
50.	Enzyme B requires Zn^{2+} in order to catalyze the conversion of substrate X. The zinc is best identified as a(n)	coenzyme	enzyme	Cofactor	Substrate	Cofactor
51.	Redox reactions (oxidation-	do not occur in	involve the loss of electrons	involve the gaining of energy by an oxidized	require the presence of	involve the loss of electrons

	reduction)	living systems	termed oxidation	substance	oxygen	termed oxidation
52.	The actions of an enzyme can be affected by all of the following except	p/PH	allosteric inhibitors	temperature	availability ATP	availability ATP
53.	Which of the following are mismatched	anabolic reactions-expend energy	reduction-gain of an electron	activation energy-entropy	exergonic reaction-catabolism	activation energy-entropy
54.	The activation energy of a chemical reaction is the energy that	initiates the reaction	activates the catalyst	must be removed from the mixture	must be released from the mixture	initiates the reaction
55.	In hemoglobin, allosteric effects occur	Only in humans	For maintaining Fe in the Fe^{2+} state	To minimize oxygen delivery to the tissues	To maximize oxygen delivery to the tissues	To maximize oxygen delivery to the tissues
56.	Small molecules affect hemoglobin (Hb) by	Decreasing Hb affinity for O_2	Increasing Hb affinity for O_2	Increasing $[H^+]$	Increasing $[H^+]$ and decreasing Hb affinity for O_2	Increasing $[H^+]$ and decreasing Hb affinity for O_2
57.	Myoglobin was the first protein to have its	Two-dimensional structure	Three-dimensional structure	Four-dimensional structure	Five-dimensional structure	Three-dimensional structure
58.	Hydrogen fluoride is an example for	Redox reaction	Oxidation reaction	Reduction reaction	Reducing agent	Redox reaction
59.	Which one of the following is a chemical species that undergoes a	Oxidizing agent	Reducing agent	Redox agent	Divising agent	Oxidizing agent

	chemical reaction that removes one or more electrons from another atom					
60.	The oxidation state of an individual atom is	Zero	One	Two	Three	Zero
61.	Low counts of hemoglobin leads to	Anemia	Pellagra	Sterility	Scurvey	Anemia
62.	Which one of the following has 153 amino acids residues?	Hemoglobin	Myoglobin	Oxyhemoglobin	Coenzyme	Myoglobin
63.	Which one of the following has smaller monomer of polypeptide structure	Hemoglobin	Myoglobin	Oxyhemoglobin	Coenzyme	Myoglobin
64.	Muscle injury is commonly associated with the release of	Hemoglobin	Myoglobin	Oxyhemoglobin	Coenzyme	myoglobin

UNIT-V

SYLLABUS

Study of the following industrial processes and their mechanism:
1. Alkene hydrogenation (Wilkinson's Catalyst)
2. Synthetic gasoline (Fischer Tropsch reaction)
3. Polymerisation of ethene using Ziegler-Natta catalyst

Homogeneous catalysis

Contribution of homogeneous catalytic process in chemical industry is significantly smaller compared to heterogeneous catalytic process, it is only about 17-20 %. But importance of homogeneous catalysis is increasing significantly. The significance of homogeneous catalysis is growing rapidly particularly in the area of pharmaceutical and polymer industry. Some of the important industrial processes include:

1. Oxidations of alkenes such as production of acetaldehyde, propylene oxide etc.
2. Polymerization such as production of polyethylene, polypropylene or polyesters.

A new major development in homogeneous catalysis is the application of organometallic complexes as catalysts. The use of organometallic catalysts has revolutionized the homogeneous processes increasing economic viability. Another new area is bio-catalysis involving enzymes catalysts. Enzyme catalysts are highly selective and active for production of fine chemicals, pharmaceuticals etc. Enzyme catalysts are discussed in a separate section.

In homogeneous catalysis, all the reactants and catalysts are present in a single fluid phase and usually in the liquid phase. Homogeneous catalysts are the simple molecules or ions such as HF, H2SO4, Mn+2 as well as complex molecules such as organometallic complexes, macrocyclic compounds and large enzyme molecules.

Advantages

Advantages of homogeneous processes can be summarized as follows:

- In many reactions, homogeneous catalysts are more active and/or selective compared to heterogeneous catalysts.

- In homogeneous catalysis, the catalysts are molecularly dispersed within the fluid. Hence, pore diffusion limitations are absent. However, bulk phase mass transfer limitation may occurs.

- Catalytic chemistry and mechanism for homogeneous catalysis are better studied and understood. Therefore, it is easier to control and manipulate the process parameters.

Types of reactions

Several homogeneous catalytic systems are :

1. Acid base catalysis
2. Catalysis by metal ions
3. Catalysis by organometallic complexes
4. Catalysis by Lewis acids

1. Catalysis by acids or bases

Acid –base catalysts are used in the following types of reactions:

i. Condensation
ii. Dehydration
iii. Hydrolysis
iv. Halogenations

a) Acid catalyzed condensation

Acid catalyzed condensation of phenol and acetone to bisphenol which is an important intermediate in the manufacture of epoxy resin and polycarbonates.

$$CH_3COCH_3 + 2\phi - OH + 2H^+ \longrightarrow OH - \phi - C\left(CH_3\right)_2 - \phi - OH + H_2O$$

$$\phi = benzyl\ group$$

ii. Acid catalyzed synthesis of ethyl acetate ester from ethanol and acetic acid

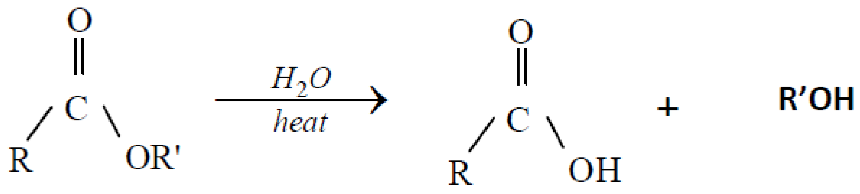
$$\mathrm{CH_3CH_2OH + CH_3COOH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O}$$

b) Acid catalyzed dehydration of ethyl alcohol to ethylene

$$CH_3CH_2OH \xrightarrow{H^+} CH_2 = CH_2 + H_2O$$

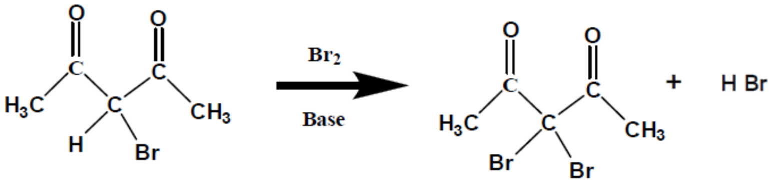
Hydrolysis of esters

Hydrolyses of carboxylic esters to form the parent carboxylic acid and an alcohol.



d) Acid or base catalyzed halogenations

Ketones can be halogenated in the presence of acid or base and X2(X= Cl, Br).



2. Catalysis by metal ion

Metal ions can act as catalysts. Metal ions function in different ways

1. Metal ion can act as a “super acid”. It introduces positive charge into the substrate, making it more susceptible toward nucleophilic attack.

2. Metal ions can also act as templates. Metal ions are able to coordinate to more than 2 ligands and thereby bring the molecules together.

3. Metal ions can act as redox catalysts. Many metal ions can accept or donate electrons by changing their oxidation state and thereby participate in redox reactions.

a) Catalysis by Cu2+ ions

Cu2+ ions are very effective catalysts for the hydrolysis of α-amino acid esters.

$$CHRNH_2 - COOCH_3 \xrightarrow[H_2O]{Cu^{2+}} CHRNH_2 - COOH + CH_3OH$$

b) Catalysis by Mg2+ ions

Hydrolysis of phosphate esters is catalyzed by metal ions, usually Mg^{2+}.

$$CH_3 - COOPO_3 \xrightarrow[H_2O]{Mg^{2+}} CH_3COOH + H_3PO_4$$

3. Catalysis by organometallic complexes

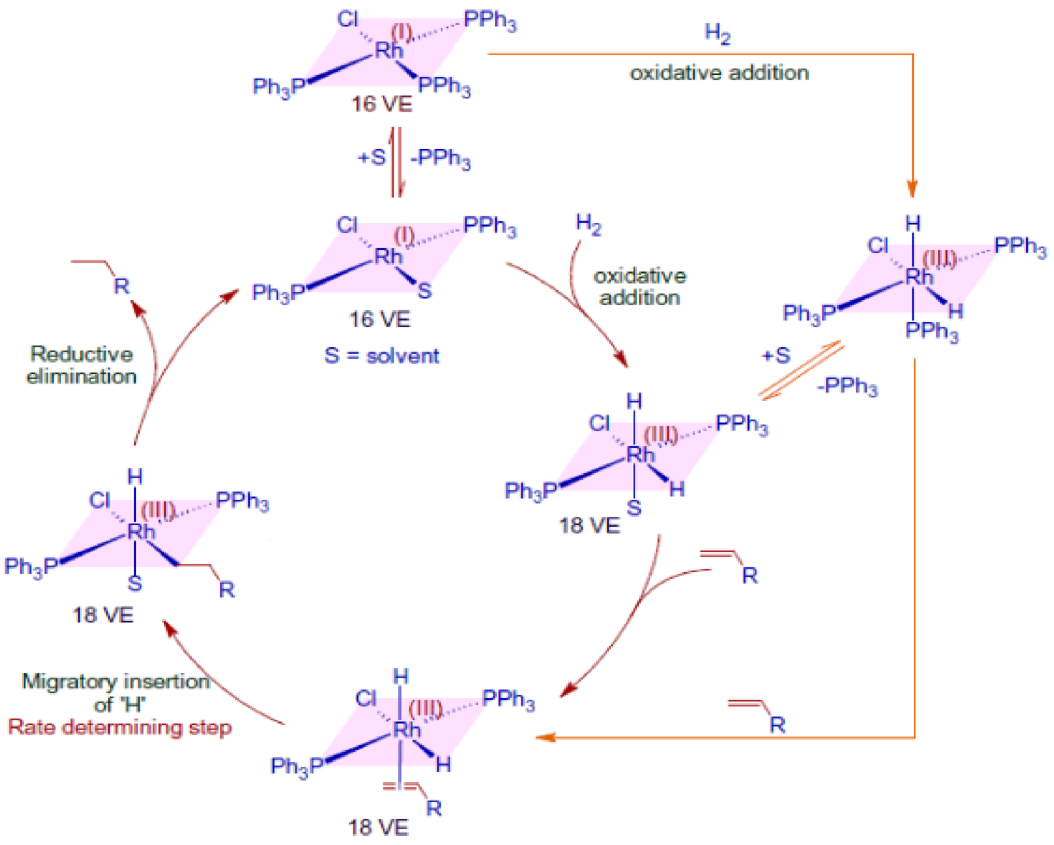
Presently, organometallic catalysts play major role in homogeneous catalysis. Organometallic complex consist of a central transition metal ion bonded to organic ligands such as R2C=CR2, RCO, R3P, R3N, CO etc. Catalysis occurs through dissociation of ligands followed by co-ordination of reactant molecule to the metal ion. The transition metal ions react through exchange of d electrons. Organometallic complexes usually have octahedral or tetrahedral geometry. Reactions catalyzed by organometallic complexes include hydrogenation, hydroformylation, carbonylation and decarbonylation, hydrocarbon rearrangement, partial oxidations etc.

Effect of ligands

The nature of surrounding ligands is very important in organometallic catalysis and known as ligand effect. The product distribution depends on the ligand environment around the metal center. Using the same metal center, different products can be obtained with the same substrate when associated ligands are changed around the metal center.

Olefin hydrogenation

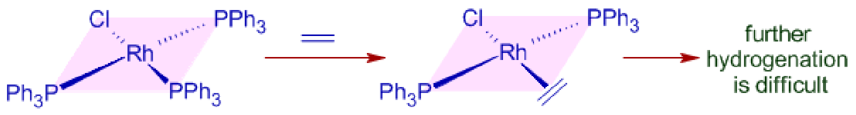
Wilkinson's catalyst is best known for catalyzing the hydrogenation of olefins with molecular hydrogen. The mechanism of this reaction involves the initial dissociation of one or two triphenylphosphine ligands to give 14- or 12-electron complexes, respectively, followed by oxidative addition of H_2 to the metal. Subsequent π-complexation of alkene, migratory insertion (intramolecular hydride transfer or olefin insertion), and reductive elimination complete the formation of the alkane product



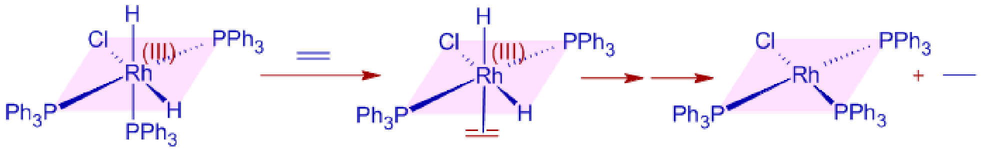
Above mechanism is supported by following observations.

The rate of reaction decreases when excess of PPh_3 is added; indicating the initial dissociation of one of the PPh_3 ligand before dihydrogen activation.

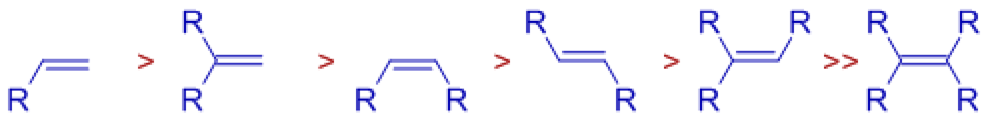
It is observed that strong π-acids like ethylene act as poisons by binding strongly with the electron rich Rh metal center and inhibit hydrogenation.



Though ethylene cannot be hydrogenated in presence of Wilkinson's catalyst under normal conditions, hydrogen transfer can be achieved with preformed dihydrido complex.

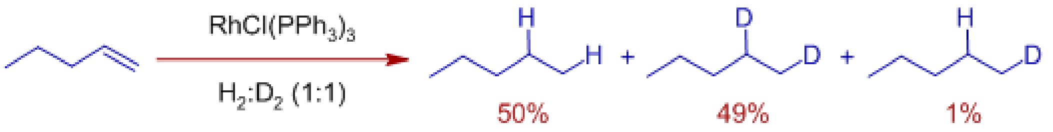


The rates of hydrogenations decrease with increase in the alkyl group substitution on double bond mirroring their relative binding affinities to the metal center. It is also partly due to steric factors.



Therefore, for a successful hydrogenation, oxidative addition of dihydrogen prior to the binding of olefin is crucial.

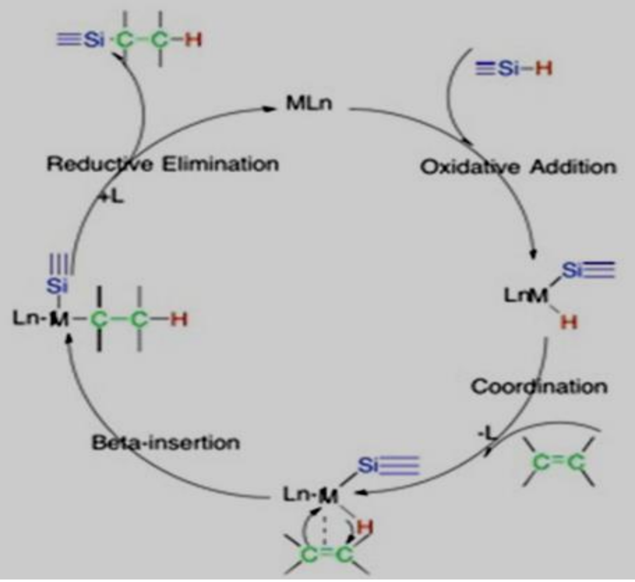
* There is minimal scrambling of H/D in the product, when an equimolar mixture of H_2 and D_2 are used.



This indicates the formation of dihydrido complex that transfers both of its hydrido ligands to the olefin and that the final reductive elimination step is very fast and irreversible.

Hydrosilation

Hydrosilylation, also known as hydrosilation, is one of the most useful catalytic reactions leading to the formation of organsilanes and organosilicones, which have a variety of applications in industry and as intermediates in organic chemistry. Hydrosilylation occurs via the addition of H-Si to an unsaturated bond such as carbon-carbon bond, carbon-oxygen bond, carbon-nitrogen bond, nitrogen-nitrogen bond and nitrogen-oxygen bond using a metal catalyst, Lewis Acid, or radical initiator. The basic reaction can be described using the following scheme:



In the first step a Si-H bond undergoes oxidative addition to a metal center. The alkene coordinates and then undergoes insertion. The hydrogen is then added to the alkene through H beta-insertion. In the final step the alkylsilyl Pd(II) complex undergoes reductive elimination to deliver the adduct and return the metal to the original oxidation state

The reactivity of hydrosilylation is influenced by many factors: substrate, silane, transition metal catalyst, ligand etc. which makes the reaction diverse as well as complicated. Studies have been performed to determine the reactivity influenced by each of these factors. Because there are a large variety of substrates that can be used, we will focus on alkenes. Here are some general rules:

Reaction rate: 1-alkene > 2-alkene > 3-alkene

Generally, the more substituted the alkene group, the slower the reaction would be. This is due to the more substituted alkene group being bulkier, therefore it will be harder for the alkene coordination to happen to the metal. More substituted alkene groups also make it more difficult for the H atom to undergo compete beta-insertion.

Reaction rate: $SiHCl_3 > (C_6H_5)_3SiH > (C_2H_5)_3SiH$

$V_0(10^5)$: 110 12 1.2

From this set of data, we can derive that the rate of reactivity would increase depending on the substituted groups on the silanes. The order of reactivity is: chlorine > aromatic rings > alkanes. However, this rule is not always true. If we substituted the aromatic groups in $(C_6H_5)_3SiH$ with Cl, the reaction rate would be:

Reaction rate: $(C_6H_5)_3SiH > (C_6H_5)_2SiH_2 > (C_6H_5)SiH_3$

$V_0(10^5)$: 12 1.7 0.69

This shows that the substituted groups do not affect the reactivity individually. The overall regularity for change of silanes is complicated and varies with each group

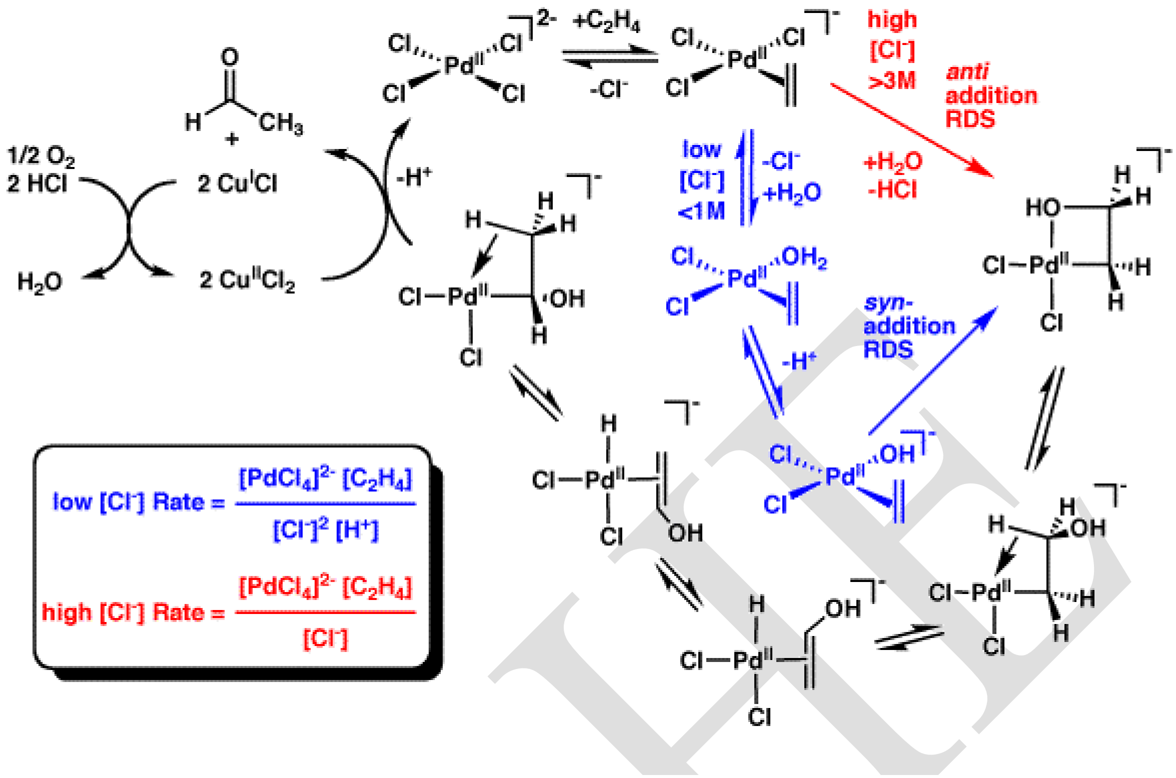
Wacker process

Acetaldehyde (CH_3CHO), also called **ethanal**, an aldehyde used as a starting material in the synthesis of 1-butanol (*n*-butyl alcohol), ethyl acetate, perfumes, flavourings, aniline dyes, plastics, synthetic rubber, and other chemical compounds. It has been manufactured by the hydration of acetylene and by the oxidation of ethanol (ethyl alcohol). Today the dominant process for the manufacture of acetaldehyde is the Wacker process, developed between 1957 and 1959, which catalyzes the oxidation of ethylene to acetaldehyde. The catalyst is a two-component system consisting of palladium chloride, $PdCl_2$, and copper chloride, $CuCl_2$.

$$\underset{\text{ethylene}}{2\,CH_2{=}CH_2} + O_2 \xrightarrow{PdCl_2,\ CuCl_2} \underset{\text{acetaldehyde}}{2\,CH_3CHO}$$

Pure acetaldehyde is a colourless, flammable liquid with a pungent, fruity odour; it boils at 20.8 °C (69.4 °F).

The reaction mechanism for the industrial Wacker process (olefin oxidation via palladium(II) chloride) has received significant attention for several decades. Aspects of the mechanism are still debated. A modern formulation is described below



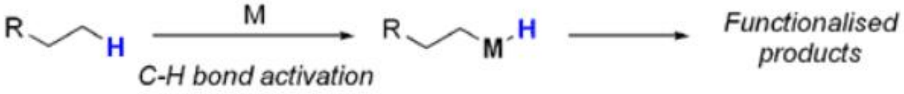
Ethylene and oxygen are passed co-currently in a reaction tower at about 130 °C and 400 kPa. The catalyst is an aqueous solution of $PdCl_2$ and $CuCl_2$. The acetaldehyde is purified by extractive distillation followed by fractional distillation. Extractive distillation with water removes the lights ends having lower boiling points than acetaldehyde (chloromethane, chloroethane, and carbon dioxide) at the top, while water and higher-boiling byproducts, such as acetic acid, crotonaldehyde or chlorinated acetaldehydes, are withdrawn together with acetaldehyde at the bottom. Due to the corrosive nature of catalyst, the reactor is lined with acid-proof ceramic material and the tubing is made of titanium.

In summary, experimental evidence seems to support that syn-addition occurs under low-chloride reaction concentrations (< 1 mol/L, industrial process conditions), while anti-addition occurs under high-chloride (> 3mol/L) reaction concentrations, probably due to chloride ions saturating the catalyst and inhibiting the inner-sphere mechanism. However, the exact pathway and the reason for this switching of pathways is still unknown.

C-H activation of alkenes

Transition metal catalysis lies at the heart of modern innovative science. As the field has matured, new areas have emerged that challenge the frontiers of synthetic organic chemistry. The capacity to activate a specific 'inert' C-H bond and transform it to a more versatile functional group is an emerging area in chemistry. To expand this area in organic synthesis, the challenge is to identify novel strategies for the formation of organo-metal intermediates under mild conditions and to discover new methods for their subsequent functionalisation. This process is perhaps the ultimate synthetic transformation and presents an exciting and fundamental challenge for chemists.

We are interested in developing new inter- and intramolecular C-C bond forming reactions catalysed by transition metals. In particular, our research focuses on the activation of C-H bonds and we are investigating methods by which *sp, sp^2 and sp^3 hybridised C-H bonds can be activated by transition metal catalysts under ambient conditions* to form a diverse range of useful molecular architectures.



C-H Activation and Functionalisation

Target Structures for C-H Activation

The first reported organometallic compounds were prepared by the reductive substitution of alkyl halides, as shown in the following three equations. All these metals have strong or moderate negative reduction potentials, with lithium and magnesium being the most reactive. Halide reactivity increases in the order: Cl < Br < I. Alkylsodium and potassium compounds are not made in this way because Wurtz coupling of the alkyl moiety (giving R–R) tends to predominate. This can also be a problem when allyl or benzyl halides are converted to Grignard or lithium reagents.

R-X + Zn ––> R-Zn-X An Alkyl Zinc Reagent 1850 E. Frankland

R-X + Mg ––> R-Mg-X A Grignard Reagent 1900 V. Grignard

R-X + 2Li ––> R-Li + LiX An Alkyl Lithium Reagent 1917 W. Schlenk (1930 K. Ziegler)

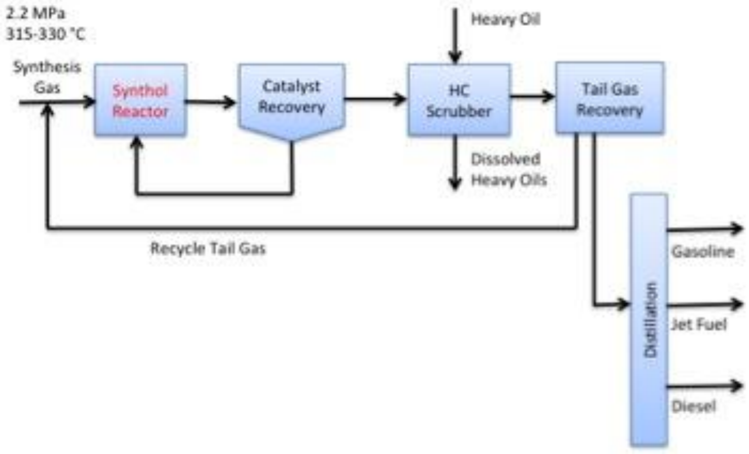
Fischer Tropsch reaction

What can be done with synthesis gas? It can be burned and used in a gas turbine to heat exchange the heat to produce steam and operate a second turbine for electricity. The gas can be fed to a solid oxide fuel cell to generate electricity. We can also use the synthesis gas to generate fuels, chemicals, and materials. In fact, the dominant application of synthesis gas from coal is the production of synthetic hydrocarbons for transportation fuels – Fischer Tropsch (FT) synthesis. This is what is primarily done in South Africa by the company Sasol and was also one of the methods used by the Germans in WWII to generate liquid fuels; in fact, direct liquefaction was the primary method used to produce liquid fuels in Germany in the 1940s. However, it is not the only gasification to liquids process. As noted in Lesson 4, the FT synthesis reaction can be presented by:

$$CO + nH2 \rightarrow (\text{-}CH2-)x + H2O$$

We are taking carbon atoms and building them up as alkanes, containing up to at least 20 carbon atoms. It is really a polymerization process, and it follows polymerization statistics. Figure 8.9 shows a typical polymerization statistical function. You will not obtain one single pure alkane from the FT process, and there will be a distribution of products. As with all chemical reactions, you will have reaction variables to adjust, such as temperature, pressure, residence, and addition of a catalyst. By skillful selection of variables (T, P, t, and catalyst), we can, in principle, make anything from methane to high molecular weight waxes. The intent is to maximize liquid transportation fuel production.

The primary process for FT is the Synthol Process; the schematic is shown in Figure 8.10. The synthesis gas goes into the reactor at 2.2 MPa of pressure and 315-330°C. The product leaves the reactor where catalyst is recovered, oils are removed by a hydrocarbon scrubber, and the tail gas recovered. The gas part is recycled, and the rest of the material is then distilled into the gasoline, jet fuel, and diesel fractions. The Synthol reactor is a fluid bed reactor that uses an iron-based catalyst.



The liquids produced make very clean fuels. The product is near zero sulfur and low in aromatic compounds, and it is composed of mainly straight chain alkanes. When considering the carbon-steam reaction, it is an endothermic reaction (the gasification, need to add heat). In this case, the reaction is “backwards," or going the other direction. Therefore, the FT synthesis reaction is an exothermic reaction. Because the reaction is exothermic, heat is generated, so Synthol reactors have internal cooling tubes with steam that when heated generate high pressure steam that can be used in other processes.

FT diesel fuel is high quality diesel fuel – we want to have linear alkanes, low aromatic content, and low sulfur. FT diesel fuel has all three aspects of diesel fuel that we want, and has a cetane number ≥ 70 – it is an ideal diesel fuel (recall that a good diesel fuel has a cetane number of 55).

Jet fuel made from FT synthesis makes a decent fuel. It is low in aromatic and sulfur content. It is the first bio-based jet fuel that has been certified for use in aircraft and has been tested in blends with major airlines (Virgin). However, for use in military jets, it must be blended because newer designs use the fuel as coolant for electronics, as the fuel can have issues in these aircraft. For example, alkanes have the lowest density of various compound classes in jet fuel, so FT jet fuel has borderline volumetric density. Alkanes are also likely to undergo pyrolysis reactions at certain high temperatures, and if the fuel is used as a heat-exchange fluid to reduce the heat load, carbon formation can occur – this is mainly a problem for some of the newer military jet aircraft.

FT gasoline that comes straight off of the reaction is not a great gasoline, as it has a low octane number. Recall that branched alkanes and aromatic compounds have higher octane numbers. Since FT compounds tend to be straight chain alkanes, the isomerization is required, and an appropriate catalyst must be used for catalytic reforming.

The primary location for gasification and FT synthesis is in South Africa – the gasoline being sold in South Africa has an octane number of 93. An integrated plant will also produce aromatics, waxes, liquid petroleum gas, alcohols, ketones, and phenols in addition to liquid hydrocarbon fuels. The reasoning behind marketing multiple products is because all the products will go up and down in price; when something goes up in price, you make more of it, when something goes down in price, you may make less. This is a way for plants to maximize their profits.

Methanol Production

Synthesis gas can also be used to produce methanol, CH3OH. The current technology for making methanol is fairly mature. Typically natural gas is used as the feedstock, which is steam reformed to make CO and hydrogen:

$$CH4 + H2O \rightarrow CO + H2$$

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Then methanol is synthesized by the reaction:

$$CO + 2H2 \rightarrow CH3OH$$

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However, another methanol synthesis reaction allows for CO2 to be in the feed gas:

$$CO2 + 3H2 \rightarrow CH3OH + H2O$$

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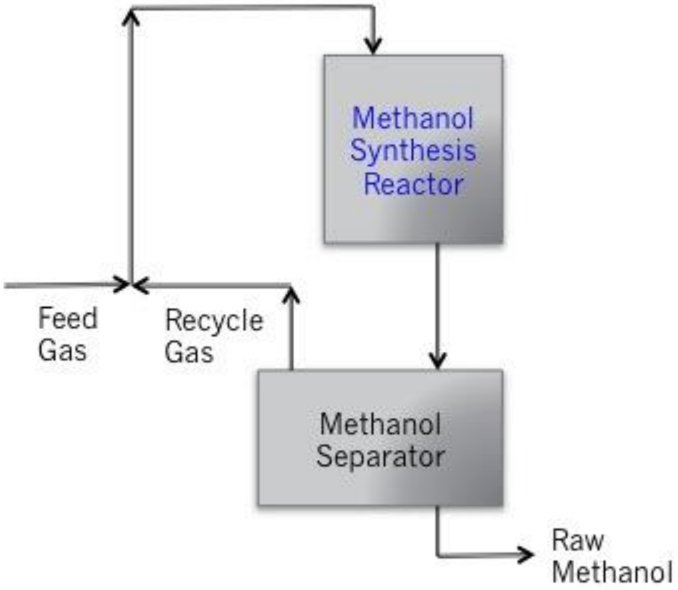
But because water and methanol are infinitely soluble, an additional step is required downstream to isolate methanol from water. Typical operating conditions in the methanol synthesis reactor are: 5-10 MPa pressure, 250-270°C, using a copper/zinc catalyst. The reaction is extremely exothermic, so heat must be removed to keep the reaction under control. Similar to the FT reaction, the reactor has a shell and tube heat exchanger where coolant is circulated through the shell and catalyst particles are packed into the tubes where the reactant/product liquids flow. Figure 8.11 shows a schematic of the methanol synthesis process.



So, what can methanol be used for? It is periodically used as a replacement for gasoline, particularly for racing fuel, as it has a high octane number. It has no sulfur in it, will produce almost no NO_X due to the low flame temperature, and can be blended with gasoline.

There are also some disadvantages to using methanol as a fuel. It is infinitely miscible with water, it has health and safety issues, provides only half the volumetric energy density of gasoline, and may have compatibility issues with materials in some vehicles.

Enormous tonnages of methanol are produced and handled annually with excellent safety – but within the chemical process industry. However, if the general public is handling methanol, safety may be an issue, because methanol has toxic properties. Methanol is being seriously considered as the fuel of choice in use of fuel cells. However, there is a process to make methanol directly into gasoline, so concerns about methanol aren't an issue then.

Methanol-To-Gasoline (MTG)

Methanol can be used to make a gasoline product. The process uses a special zeolite catalyst with pore size such that molecules up to C10 can get out of the catalyst. Larger molecules cannot be made with this process; therefore, a product is made with no carbon molecules greater than C10, which boils in the gasoline range. In this process, aromatics and branched chain alkanes are made, which means the MTG process produces a very high octane gasoline. Gasoline is the only product. In the reaction, methanol is converted into dimethyl ether (which can be a good diesel fuel) by the following reaction:

$$2CH3OH \rightarrow CH3OCH3 + H2O$$

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As the reaction progresses, the dimethyl ether is dehydrated further to the product hydrocarbons. The overall reaction is:

$$CH3OH \rightarrow -(CH2)-n+H2O$$

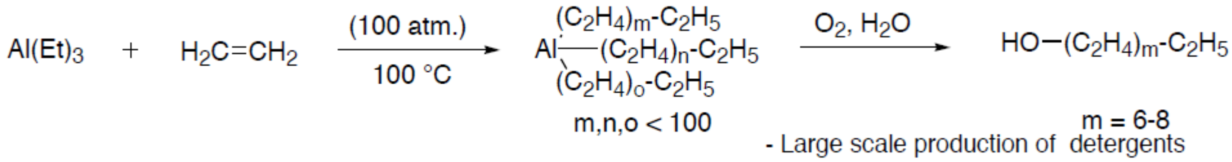
This equation is not rendering properly due to an incompatible browser. See Technical Requirements in the Orientation for a list of compatible browsers.

As with the other reactions we’ve looked at in this section of the lesson, the reaction is highly exothermic, so the reactor and process has to be designed to remove heat from the reaction to keep it under control. The conditions for this reaction are 330-400°C and 2.3 MPa. If one wanted to envision how a plant could incorporate all of these processes together, the following would be one scenario:

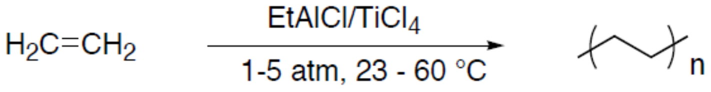
1. Add a MTG unit to existing natural gas fed methanol plants (produce high octane gasoline).
2. Replace the natural gas units with coal and/or biomass gasification and gas conditioning.
3. Add parallel trains of Synthol reactors (produce high cetane diesel).
4. Add a third section, using a solid oxide fuel cell to generate electricity using synthesis gas as the feed material.

The plant then produces gasoline, diesel, and electricity.

Ziegler and Natta

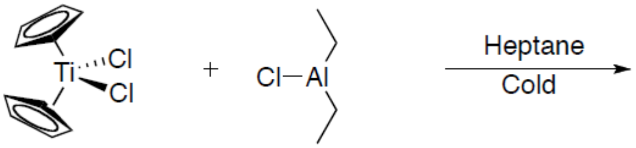


Polymerization of ethylene

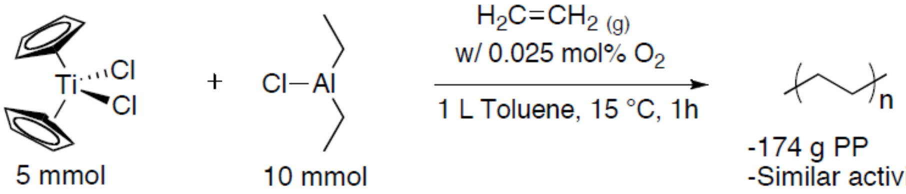


-high molecular weight, Linear PE
-low pressures and temperatures

Homogeneous Metallocene Catalysts



Blue Crystaline Solid (Air Sensitive)
-EA, EPA, and Colorimetric Analysis suggest Ti(III)/Aluminum complex
$(C_5H_5)_2Ti(III)Cl \cdot 1/2(C_2H_5)_2AlCl \cdot 1/2C_2H_5AlCl_2$



-174 g PP
-Similar activity to Ziegler Catalysts
-Linear polymer (0.05% Methyl content)

A brief description of the Ziegler process will be explained in the following paragraph. First, the organometallic compound (i.e. titanium tetrachloride) is reacted in a reaction vessel with a metal alkyl at a temperature between 100-130 degrees Celsius in the presence of a solvent. The pressure of the reaction vessel is between atmospheric and 20 atm. Ethylene is introduced into the reactor vessel in the gas phase. The boiling point of ethylene is approximately 100 degrees Celsius. The ethylene reacts with the active site of the catalyst to produce polyethylene. The solvent is used to dissipate heat. The solvent must not vaporize or react with any of the compounds in the reactor (inert solvent). The melting point of high-density polyethylene is approximately 130 degrees Celsius. Therefore, the polyethylene formed is in the solid phase. This type of polymerization is called slurry polymerization or suspension polymerization. The slurry solution is passed to a catalyst decomposition bed where the catalyst is deactivated. The catalyst is not completely used in the polymerization process. Catalyst decomposition is achieved with the addition of an alcohol. Polyethylene is then recovered with the extraction of the solvent, and a filtration and drying process. The polyethylene can then be processed and manufactured. The polyethylene created by the Ziegler process has a molecular weight 20,000 and 1.5 million. The molecular weight is controlled in a number of different ways: pressure of the reactor vessel (higher pressure, less branches), temperature in preparation of catalyst (too high of temperature deactivates catalyst), chain transfer reagents, and the ratio of Al/Ti catalyst added to reactor. The table below shows the weight average for different Al/Ti ratios for the Ziegler process at atmospheric pressure.

The results show the greatest yield is when the ratio is when the Al/Ti ratio is 0.9. The molecular weight continues to rise over an Al/Ti ratio of 2.0, however, the weight average remains constant. The Ziegler process produced a high-density polyethylene at pressures as low as atmospheric pressure. High-density polyethylene is a more durable polymer when compared to low-density polyethylene due to its lower degree of branching.

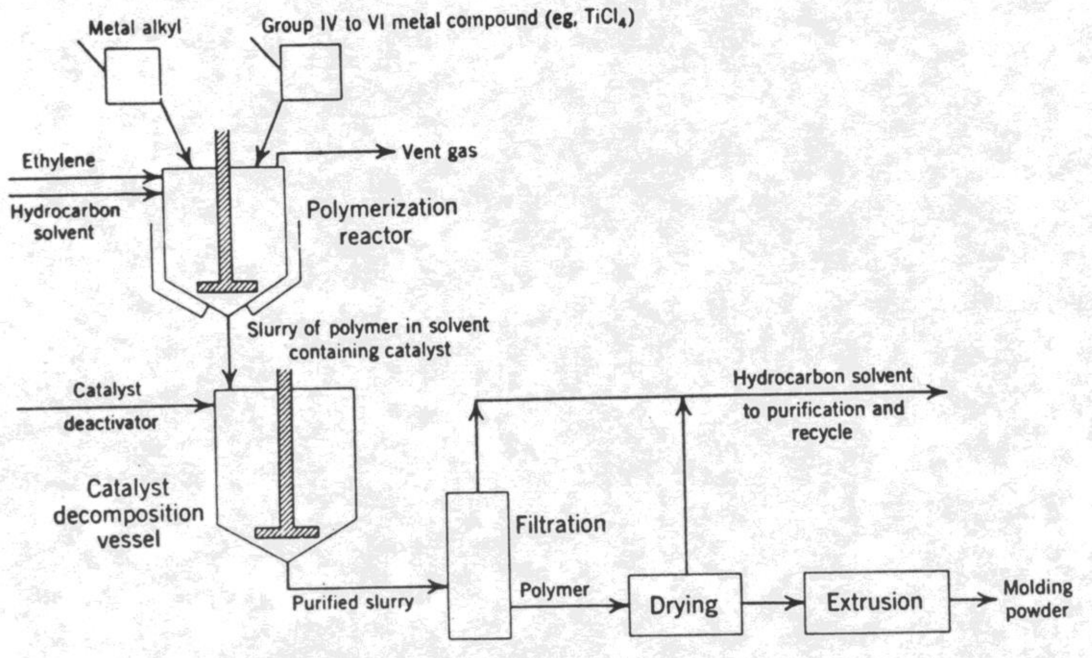


FIG. 6.5 *Flow Diagram of Ziegler Process*[6]

PART-B (6 Mark Questions)

1. Writeeffective atomic number rule with examples
2. The general preparation methods of metal carbonyls hydride with examples
3. Explain the steps ofoxidative addition and reductive elimination reaction
4. Insertions reaction of alkenes and alkynes complexes
5. Synthesis of metal alkene complexes by various methods.
6. Discus the C-H activation of alkenes process
7. Preparation of the half sandwich compound, reactivity
8. Brief reaction mechanism of Ziegler-Natta catalyst
9. Write the reaction and mechanism of Cobalt catalysed alkyne cycloaddition?
10. Brief reaction mechanism of Wilkinson's catalyst

Possible Questions

Part-B (Two marks Questions)

1. What is Ziegler-Natta catalyst?

2. What is oxo process?
3. What is agostic interaction?
4. Write the alkene hydrogenation reaction.
5. Write the Fischer Tropsch reaction.

Part-C (Eight marks Questions)

1. Discuss the Redox reactions in Vaska’s complexes

2. Explain the hydrogenation of olefin with mechanism

3. Account on the synthesis of gasoline by Fischer Tropsch reaction

4. Give the conditions for the hydrogenation of a simple alkene.

5. Discuss the Fischer Tropsch reaction for synthesis of gasoline.

6. Explain the homogeneous mechanisms of Alkene hydrogenation.

7. What is Zn-acid catalyst? And discuss it role in biological system

8. Explain the reaction mechanism of Wilkinson's catalyst.

9. Discuss the brief reaction mechanism of Olefin Polymerization with Ziegler-Natta Catalyst.
10. Write the reaction mechanism of gasoline.

OBJECTIVE QUESTIONS

S. No	Questions	Option A	Option B	Option C	Option D	Answer
1.	The process in which the catalytic addition of molecular oxygen to alkene is called	a) Wacker process	b) Contact process	c) Heat process	d) Haber process	a) Wacker process
2.	The product of wacker process is given as	a) Aldehydes	b) Ketones	c) Ozonide	d) Alkane	a) Aldehydes
3.	The product formed , when the acidification of carbonylate ion	a)Carbonyl hydrido complex	b) Carbonyl complex	c) Carboxylate anion	d) none	a)Carbonyl hydrido complex
4.	Which is the relatively expensive catalyst used in hydroformylation	a) Cobalt	b) Rhodium	c) Copper	d) Nickel	b) Rhodium
5.	The uses of which catalyst will continue to increase in hydroformylation chemistry	a) Cobalt	b) Copper	c) Rhodium	d) Zinc	c) Rhodium
6.	who proposed the most widely accepted mechanism for hydrofomylation	a) Watson and Crick	b) Cannzaro	c) Wittig	d) Heck and Breslow	d) Heck and Breslow
7.	Hydroformylation is carried out in such a way that aldehydes are reducesd to give ----	a) Alcohols	b) Acids	c) ketones	d) none	a) Alcohols
8.	The reaction of an alkene with carbnmonoxide and hydrogen, catalysed	a) Hydroformylati	b) Hydroxylation	c) Hydrogenation	d) None	a) Hydroformylati

	by cobalt or rhodium salt, to form an aldehyde is called	on				on
9.	In hydroformylation cobalt and ----- are used as catalysis	a) Rhodium	b) Bismath	c) copper	d) Nickel	a) Rhodium
10.	(Ph3P)3RhCl is a ---------catalyst	Wilkinson's	dewar	albert	alexander	Wilkinson's catalyst
11.	An alkene can coordinate and react with a coordinated hydrogen ligand to form an -----group	alkyl	aryl	keto	acid	alkyl
12.	----------------is commonly chosen to illustrate homogeneous hydrogenation with wilkinsons catalyst	propylene	ethylene	butylene	methylene	ethylene
13.	Etylene competes effectively with the solvent for the vacant coordination site created when--------------------dissociation from wilkinsons catalyst and thus serves inhibitor	triphenyl phosphine	tetraphenyl phosphine	diphenyl phosphine	phenyl phosphine	triphenyl phosphine
14.	Oxidative addition reactions lead to products that appear to have had a --------atom inserted into a bond	metal	atom	molecule	proton	metal
15.	Insertion reactions are enormously important in ---------------------cylces	catalytic	polymeric	material	dimeric	catalytic
16.	A classic example of a CO insertion reaction is found in the work of ------------	einstein	albert	noack	clausius	noack

	-and calderazzo					
17.	The reverse of insertion is called --------------	decarbonylation	carbonylation	oxidation	reduction	decarbonylation
18.	The CO of the acetyl ligand has a choice of --------------cis positions	3	4	5	6	3
19.	Insertion involves ligands which are-------------------to one another	cis	trans	exo	endo	cis
20.	The reverse reaction in isertion cannot occur unless a --------------------is first eliminated	acid	base	ligand	keto	ligand
21.	Inversion of configuration is expected for-------------migration	ethyl	methyl	propyl	pentyl	ethyl
22.	Retention is expected for ------------- insertion	carbonyl	keto	acids	aldehyde	carbonyl
23.	---------------of configuration is observed in nitromethane	retention	inversion	insertion	elimination	inversion
24.	β elimination represents the chief pathway for decompositionof a ---------------metal alkyl complexs	s block	p block	transition	inner transition	transition
25.	β elimination cannot take place unless there is a ---------------site for hydrogen to occupy in the diinsertion step	3 site	2 site	one site	vacant	vacant

26.	Coordinatively saturated catalyst precursors become activated by --------------loss	electron	ligand	metal	proton	ligand
27.	Ligand dissociation is most commonly induced by ---------------and is assisted by the solvent	cooling	heating	polymerising	condensing	heating
28.	At higher temperature the red mononuclear complex is converted to the ------------halide bridged species	orange	red	white	Yellow	orange
29.	The degree of ligand dissociation is dependent on sigma-------and pi ----------------	acceptor and donor	donor and acceptor	acceptor and acceptor	donor and donor	donor and acceptor
30.	In metal-olefin interaction, the extent of increase in metal → olefin π-back donation would	leads to a decrease in C = C bond length	change the formal oxidation state of the metal	change the hybridization of the olefin carbon from sp^2 to sp^3	increases with the presence of electron electron donating substituent on the olefin	change the hybridization of the olefin carbon from sp^2 to sp^3
31.	The oxidation state of molybdenum in $[(\eta^7 -$ tropylium$) Mo(CO_3)]^+$ is	+2	+1	0	-1	+1
32.	The nature of metal-metal bonds in $[W_2(OPh)_6]$ is	1	2	3	4	3
33.	The reaction given below is an example of $[(CO)_5Mn(Me)] + CO \rightarrow$	oxidative addition	electrophilic substitution	nucleophilic substitution	migratory insertion	migratory insertion

	$[(CO)_5Mn\{C(O)(Me)\}]$					
34.	Which of the following is not suitable as catalyst for hydroformylation ?	C8H82-	HCo(CO)3PBu3	HRh(CO)(PPh3)3	H2Rh(CO)(PPh3)2Cl	H2Rh(CO)(PPh3)2Cl
35.	The ligand(s) that is (are) fluxional in $[(\eta^5 - C_5H_5)(\eta^1 - C_5H_5)Fe(CO)_2]$ in the temperature range 221-298K, is (are)	$\eta^5 - C_5H_5$	$\eta^1 - C_5H_5$	$\eta^5 - C_5H_5$ & CO	$\eta^1 - C_5H_5$ & CO	$\eta^1 - C_5H_5$
36.	The oxidation state of the Ni & the number of metal – metal bonds in $[Ni_2(CO)_6]^{2-}$ that are consistent with the 18 electron rule are	Ni(-2) & 1 bond	Ni (IV), 2 bond	Ni (-1), 1 bond	Ni (IV), 3 bond	Ni (-1), 1 bond
37.	The product of the reaction of the propene, CO & H_2 in the presence of $Co_2(CO)_8$ as a catalyst is	Butanoic Acid	Butanal	2-butacarbon	Methylpropanoate	Butanal
38.	The hapticities 'K' & 'L' of the arene moieties in the diamagnetic complex $[(\eta^K - C_6H_6)Ru(\eta^L - C_6H_6)]$ respectively are	6 & 6	4 & 4	4 & 6	6 & 2	4 & 6
39.	Reductive elimination step in the hydrogenation of alkenes by Wilkinson catalyst results in (neglecting solvent in coordination sphere of Rh)	T-shaped $[Rh(PPh_3)_2Cl]$	Trigonal -planar $[Rh(PPh_3)_2Cl]^{2+}$	T-shaped $[Rh(H)(PPh_3)_2Cl]^+$	Trigonal-planar $[Rh(H)(PPh_3)_2]$	T-shaped $[Rh(PPh_3)_2Cl]$
40.	The oxidative addition & reductive elimination steps are favoured by	Electron rich metal centers	Electron deficient	Electron deficient & electron rich metal centers	Electron rich & electron deficient metal centers respectively	Electron rich & electron deficient metal centers

				respectively		respectively
41.	Identify the order according to increasing stability of the following organometallic compounds, $TiMe_4$, $Ti(CH_2Ph)_4$, $Ti(i\text{-}Pr)_4$ & $TiEt_4$.	$Ti(CH_2Ph)_4 < Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4$	$TiEt_4 < TiMe_4 < Ti(i\text{-}Pr)_4 < Ti(CH_2Ph)_4$	$Ti(i\text{-}Pr)_4 < TiEt_4 < TiMe_4 < Ti(CH_2Ph)_4$	$TiMe_4 < TiEt_4 < Ti(i\text{-}Pr)_4 < Ti(CH_2Ph)_4$	$TiMe_4 < TiEt_4 < Ti(i\text{-}Pr)_4 < Ti(CH_2Ph)_4$
42.	Among the metals, Mn, Fe, Co, & Ni, the ones those would react in its native form directly with CO giving metal carbonyl compounds are	Co & Mn	Mn & Fe	Fe & Ni	Ni & Co	Fe & Ni
43.	In the hydroformylation reaction, the intermediate $CH_3CH_2CH_2Co(CO)_4$	Forms an acyl intermediate $CH_3CH_2CH_2COCo(CO)_3$	Forms an adduct with an olefin reactant	Reacts with H_2	Eliminates propane	Forms an acyl intermediate $CH_3CH_2CH_2COCo(CO)_3$
44.	Reaction of $Fe(CO)_5$ with OH^- leads to complex A which on oxidation with MnO_2 gives B. Compounds A & B respectively are	$[HFe(CO)_4]^-$ & $Fe_3(CO)_{12}$	$[Fe(CO)_5(OH)]^-$ & $Fe_2(CO)_9$	$[Fe(CO)_4]^{2-}$ & $Mn_2(CO)_{10}$	$[HF(CO)_4]^-$ & Fe_2O_3	$[HFe(CO)_4]^-$ & $Fe_3(CO)_{12}$
45.	The number of metal-metal bonds in the dimers $[CpFe(CO)(NO)]_2$ & $[CpMo(CO)_3]_2$ respectively are	two & two	two & three	one & three	zero & one	zero & one
46.	The greater stability of $((CH_3)_3C\text{-}CH_2\text{-})_4Ti$ (A) compared to that of $((CH_3)_2CH\text{-}CH_2\text{-})_4Ti$ (B) due to	Hyperconjugation present in complex (A)	β-hydride elimination is not possible in complex (A)	Steric protection of titanium from reactive species in complex (A)	The stronger nature of Ti-C bond in complex (A)	β-hydride elimination is not possible in complex (A)

47.	The carbonyl resonance in ^{13}C NMR spectrum of $[(\eta^5 - C_5H_5)Rh(CO)]_3$ (^{103}Rh, nuclear spin I = ½, 100 %) shows a triple at -65° owing to the presence of	Terminal CO	μ2 - CO	μ3 - CO	η^5 - C_5H_5	μ2 - CO
48.	The complex that DOES NOT obey 18 – electron rule is :	$[(\eta-C_5H_5)]RuCl(COPPh_3)]$	$[W(CO)_3(SIMe_3)(Cl)(NCMe)_2]$	$[IrCl_3(PPh_3)_2(AsPh_2)]^-$	$[Os(N)Br_2(PMe_3)(NMe_2)]^-$	$[Os(N)Br_2(PMe_3)(NMe_2)]^-$
49.	The final product of the reaction $[Mn(CO)_6]^+ + MeLi \rightarrow$ is	$[Mn(CO)_6]^+ Me^-$	$[Mn(CO)_5Me]$	$[Mn(CO)_6]$	$[(MeCO)Mn(CO)_5]$	$[(MeCO)Mn(CO)_5]$
50.	Which statement about a catalyst is incorrect?	The presence of a catalyst speeds up a reaction	The presence of a catalyst changes the rate of a reaction	In some reactions, one of the products acts as a catalyst for the forward reaction	During use, a catalyst may be poisoned	The presence of a catalyst speeds up a reaction
51.	Which of the following criteria is least important for a homogeneous, organometallic catalyst?	The metal centre must normally be able to accommodate both a 16 or 18 valence electron count	The metal centre must be able to tolerate more than one ligand geometry	The metal centre must be able to undergo oxidation and reduction reactions	The catalyst must be contain a third row d-block metal	The catalyst must be contain a third row d-block metal
52.	Match the compound formula to its application as a catalyst or catalyst precursor in the stated process. Which	cis-[Rh(CO)2I2]–; Monsanto	RhCl(PPh3)3; alkene	HRh(PPh3)3; asymmetric	HCo(CO)4; hydroformylation	HRh(PPh3)3; asymmetric

	pair is incorrect?	acetic acid synthesis	hydrogenation	hydrogenation	of alkenes	hydrogenation
53.	Hydroformylation of alkenes may lead to alcohol and aldehyde products. Which statement is correct?	The stereoselectivity of the reaction gives the aldehyde:alcohol ratio	The chemoselectivity of the reaction gives the n:i aldehyde ratio	The regioselectivity of the reaction gives the aldehyde:alcohol ratio	The regioselectivity of the reaction gives the n:i aldehyde ratio	The regioselectivity of the reaction gives the n:i aldehyde ratio
54.	In the Tennessee–Eastman acetic anhydride process, the catalyst is cis-[Rh(CO)2I2]–. Which sequence of steps best describes the primary catalytic cycle?	Oxidative addition of MeI and loss of CO; Me migration; addition of 2 CO; elimination of MeC(O)I	Oxidative addition of MeI; Me migration; CO addition; elimination of MeC(O)I		Loss of CO; oxidative addition of MeI; Me migration; addition of 2 CO; elimination of MeC(O)I	Oxidative addition of MeI; Me migration; CO addition; elimination of MeC(O)I
55.	Which statement is incorrect about chemisorption of CO on a metal (M) surface?	CO molecules are activated	IR spectroscopy can be used to study the system	M–C bonds are formed	The CO molecules must be terminally bound	The CO molecules must be terminally bound
56.	Which statement is incorrect about the industrial Haber process for NH3 production?	The catalyst used commercially is α-Fe; catalyst promoters are added	Chemisorption of N2 and H2 activates the molecules, weakening and cleaving their	A high temperature is needed because the forward reaction is endothermic	Both a high temperature and pressure are required	A high temperature is needed because the forward reaction is endothermic

			bonds			
57.	The following statements are about catalytic converters. Which one is incorrect?	Permissible emission gases are CO2, N2 and H2O	The precious metals Rh, Pt and Pd are used in 3-way converters	Ce2O3/CeO2 is an "O2 storage" additive	Rh catalyses the oxidation of NO	Rh catalyses the oxidation of NO
58.	In the hydrogenation of alkenes using Wilkinson's catalyst, the active catalyst is RhCl(PPh3)2 (or RhCl(PPh3)2(solvent)). The first step in the catalytic cycle is:	alkene coordination	oxidative addition of H2	loss of PPh3	loss of Cl–	oxidative addition of H2
59.	A key feature of the Fischer-Tropsch process is:	hydrocarbon formation	alkene hydrogenation	alkene polymerization	hydroformylation	hydrocarbon formation
60.	Which step, taken from a catalytic cycle, is an example of reductive elimination?	Loss of RCH2CH3 from Rh(H)2(CO)(PPh3)2(CH2CH2R)	Conversion of Rh(CO)2(PPh3)2(CH2CH2R) to Rh(CO)(PPh3)2(COCH2CH2R)	Reaction of Rh(CO)(PPh3)2(CH2CH2R) with H2	Loss of RCH=CHR from PdX(PPh3)2(CHRCH2R) and formation of Pd(H)X(PPh3)2	Loss of RCH2CH3 from Rh(H)2(CO)(PPh3)2(CH2CH2R)
61.	Which of the following compounds is a 16-electron species and is an active catalyst?	HCo(CO)3	HRh(CO)(PPh3)3	[Rh(CO)2I4]–	Pd(PPh3)4	HCo(CO)3
62.	Typical Grubbs' catalysts contain:	Ru; a carbene ligand	Rh; a carbene ligand	Ru; an alkene ligand	Mo; a carbene ligand	Ru; a carbene ligand

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INORGANIC CHEMISTRY IV: ORGANOMETALLIC CHEMISTRY

Time: 2 Hours **Maximum: 50 Marks**
Date:

PART-A

20 × 1 = 20 Marks

ANSWER ALL QUESTIONS

1. Which of the following metal sulphide is completely precipitated only when the acidic solution is diluted
a) HgS b) PbS c) CdS d) CuS

2. Which of the following halide is soluble in water?
a) AgF b) AgCl c) AgBr d) AgI

3. In qualitative analysis of basic radicals, hydrochloric acid is preferred to nitric acid for preparing
a solution of given substance. This is because
a) Nitrates are not decomposed to sulphides
b) Nitric acid contains nitrogen
c) Hydrochloric acid is not an oxidizing acid
d) Chlorides are easily converted to sulphides.

4. Addition of KI to Pb salt in water gives precipitate. The colour of the precipitate is
a) Yellow b) Black c) White d) Red

5. When sodium thiosulphate solution is shaken with iodine, it get coverted in to
a) Sulphite ion b) Sulphate ion c) Tetrathionate ion d) Carbonate ion

6. An inorganic salt, when introduced in to the flame produces crimson red colour. It indicates the
presence of
a) Dichromate ion b) Thiosulphate ion c) Strontium ion d) Calcium ion

7. Sodium sulphide react with sodium nitroprusside to form a purple colured compund. During the reaction, the oxidation state of iron is
a) Changes from + 2 to + 3 b) Changes from + 3 to + 2
c) Changes from + 2 to + 4 d) Remains unchanged +3

8. The metal whose salts do not give the borax bead test is
a) Cr b) Ni c) Pb d) Mn

9. Which of the following is soluble in yellow ammonium sulphide?
a) CuS b) CdS c) SnS d) PbS

10. Which types of salt produce crackling noise in dry heating test?
a) Salts which have lot of water of crystallization
b) Salts which are hygroscopic
c) Salts which have lost water of crystallization
d) Salts which entrap mother liquor in crystals

11. Which of the following is not a preliminary test?
a) Flame test b) Borax bead test c) Permanganate test d) Brown ring test

12. Which of the following is an interfering radical?
a) Phosphate b) Sulphate c) Nitrite d) Sulphide

13. Formation of a rose-red precipitiate when a slightly alkaline solution of an inorganic salt is treated with dimethylglyoxime confirms the presence of
a) Cobalt b) Zinc c) Iron d) Nickel

14. Which one of the bond is called Organmetallic bond?
a) M–Cl b) M–N c) M–O d) M–**C**

15. The carbonyls which contain more than one metal atom are known as ----
a) Polydentate b) Polynuclear c) Bidentate d) Mononuclear

16. Carbon monoxide is one of the most important ……… Ligand
a) π- Donor b) π- acceptor c) σ-Donor d) σ- acceptor

17. Which of the following metal carbonyl contains $17e^-$?
a) $Cr(CO)_6$ b) $Mn_2(CO)_{10}$ c) $V(CO)_6$ d) $Fe(CO)_5$

18. Identify the metal carbonyl containing trigonal bipyramidal geometry
a) $V(CO)_6$ b) $Mn_2(CO)_{10}$ c) $W(CO)_6$ d) $Fe(CO)_5$

19. The e^- donation from filled metal d orbital to the vacant anti-bonding π^* orbital of carbonyl ligand. this process called as
a) σ-donation b) π-donation c) π-back donation d) σ and π donation

20. The most important technique for characterizing metal carbonyls.
a) UV spectroscopy b) Mass Spectroscopy
c) FT-IR Spectroscopy d) NMR spectroscopy

PART-B

3 × 2 = 6 Marks

ANSWER ALL THE QUESTIONS

21. What are the group III cations (metallic radical) and what are the reagents used to identify it?

22. What is interfering anions? Give two examples.

23. Calculate the number of outer electrons in $Fe(CO)_5$.

PART-C

3 × 8 = 24 Marks

ANSWER ALL THE QUESTIONS

24. a) Expalin the principles involved in analysis of cations into groups.

OR

b) Discuss the solubility products and common ion effect.

25. a) Write the reaction of interfering anions such as fluoride, borate and oxalate.

OR

b) What is organometallic chemistry? Give four examples and discuss the bond type

26. a) Draw the structure and calculate the 18 electron rule for the following metal carbonyl compounds. i) $Fe_2(CO)_9$ ii) $Co_2(CO)_8$

OR

b) Explain the general preparation of metal carbonyls with suitable examples.

B.Sc., DEGREE INTERNAL EXAMINATION, JANUARY 2018
INTERNAL TEST-I
INORGANIC CHEMISTRY IV: ORGANOMETALLIC CHEMISTRY

Time: 2 Hours **Maximum: 50 Marks**
Date: 18-01-2018

Answer Key

1. b) PbS
2. a) AgF
3. c) Hydrochloric acid is not an oxidizing acid
4. a) Yellow
5. c) Tetrathionate ion
6. d) Calcium ion
7. d) Remains unchanged +3
8. c) Pb
9. c) SnS
10. d) Salts which entrap mother liquor in crystals
11. d) Brown ring test
12. a) Phosphate
13. d) Nickel
14. d) M–C
15. b) Polynuclear
16. b) π- acceptor
17. c) $V(CO)_6$
18. d) $Fe(CO)_5$
19. c) π-back donation
20. c) FT-IR Spectroscopy

PART-B

3 × 2 = 6 Marks

21. What are the group III cations (metallic radical) and what are the reagents used to identify it?

Ans: Fe, Al and Cr / NH_4Cl and NH_4OH

22. What is interfering anions? Give two examples.

Ans: Interfering radicals are oxalate, tartrate, fluoride, borate and phosphate and they are anionic radicals. They form complex with IIIrd gr group reagent ammonium chloride and ammonium hydroxide. This leads to incomplete precipitation of IIIrd group cations and causes immature precipitation of IVth and Vth group cations in alkaline medium. Let's try to understand it.

If you remember, for 1stand 2nd analysis medium remain acidic (dilute HCl) that's why they do not interfere then. But for 3rd group analysis the medium becomes alkaline by group reagents ammonium chloride and ammonium sulphide. Here interfering radicals come into action and disturb the solubility product of cations which causes their premature or incomplete precipitation.

23. Calculate the number of outer electrons in $Fe(CO)_5$.

Ans: Fe = $4S^2\ 3d^6$ = 8 e^-

5CO = 5x 2 = 10 e^-

Total = 18 e^-

PART-C

3 × 8 = 24 Marks

24. a) Expalin the principles involved in analysis of cations into groups.

Ans: The common metal cations are classified into five groups for systematic qualitative analysis. This classification is based on the differences of their behaviour against some reagents and solubilities of their chlorides, sulphides and carbonates. Each group of cations reacts with a particular reagent and forms precipitates. This particular reagent is known as the group reagent of corresponding group.

Group I: Cations of this group are lead(II) Pb^{2+}, mercury(I) Hg^+ and silver(I) Ag^+.

Group reagent of this group is dilute Hydrochloric acid. These cations form chloride precipitates with dilute HCl. Solubility product of Chlorides of lead, mercury and silver are lowest so they are precipitated first.

Group II: Cations of this group are divided in to two groups IIA and IIB on the basis of their solubility in ammonium polysulphide $(NH_4)_2S_x$. IIA group consists of mercury(II) Hg^{2+}, lead(II) Pb^{2+}, bismuth(III) Bi^{3+}, copper(II) Cu^{2+}, cadmium(II) Cd^{2+} and they are insoluble in ammonium polysulphide. IIB group consists of arsenic(III) As^{3+}, arsenic(V) As^{5+}, antimony(III) Sb^{3+}, antimony(V) Sb^{5+}, tin(II) Sn^{2+} and tin(IV) Sn^{4+} and these are soluble in ammonium polysulphide.

Group reagent: Hydrogen sulphide (gas or saturated aqueous solution). Cations of this group form precipitate in the form of sulphides on reacting with H_2S.

Did you notice? Lead(II) is common among two groups. That is because when lead reacts with 1st group reagent dil HCl it forms lead chloride, while other cations get precipitated as chloride, it doesn't precipitate completely because its chloride is more soluble than others. Its complete precipitation can be done as sulphide in 2nd group.

Group III: cations of this group are cobalt(II) Co^{2+}, Nickel(II) Ni^{2+}, iron(II) Fe^{2+}, iron(III) Fe^{3+}, chromium(III) Cr^{3+}, aluminium(III) Al^{3+}, zinc(II) Zn^{2+}, manganese(II) Mn^{2+}, manganese(VII) Mn^{7+},

Group reagent: ammonium sulphide solution or hydrogen sulphide gas in the presence of ammonia and ammonium chloride. Cations of this group don't react with group reagents of 1st or 2nd group. They all precipitate with ammonium sulphide in the form of sulphides.

Group IV: calcium(II) Ca^{2+}, strontium(II) Sr^{2+} and barium(II) Ba^{2+}

Group reagent: 1M solution of ammonium carbonate in neutral or alkaline medium. Cations of this group don't react with previous three group reagents; they give precipitate with ammonium carbonate in the form of carbonates.

Group V: Magnesium(II) Mg^{2+}, sodium(I) Na^+, potassium(I) K^+ and ammonium ion NH_4^+. You might be surprised here to see ammonium with metal cations. It has similar characteristics to alkali metals. Its general properties are similar to that of potassium as the sizes of both ions are identical.

Group reagent: this group has no group reagent.

These groups are arranged in increasing order of solubility of chloride, sulphides and carbonates of cations. For example, chlorides of Ist group cations have lowest solubility so they precipitate prior to others. Cations of any one group don't react with group reagent of any other group. Let's see how we can detect which metal cation is present in a given mixture.

Class A: Anions of class A can be identified by volatile products they evolve on treating with acids. This further can be divided into two subclasses.

Dilute acid group: This class of anions gives response with dilute hydrochloric or dilute sulphuric acid. These are Carbonate (CO_3^{2-}), Hydrogen carbonate or bicarbonate (HCO_3^-), Sulphite (SO_3^{2-}), Thiosulphate ($S_2O_3^{2-}$), Sulphide (S^{2-}), Nitrite (NO_2^-), Cyanide (CN^-), Cyanate (OCN^-), Hypochlorite (OCl^-).

Concentrated acid group: This class of anions gives response with concentrated sulphuric acid. These are Fluoride (F^-), Chloride (Cl^-), Bromide (Br^-), Iodide (I^-), Nitrate (NO_3^-), Sulphate (SO_4^{2-}), Acetate (CH_3COO^-), Oxalate $(COO)_2^{2-}$, Chlorate (ClO_3^-), perchlorate (ClO_4^-), Bromate (BrO_3^-), Thiocyanate (SCN^-), Citrate ($C_6H_5O_7^{3-}$), Tartrate ($C_4H_4O_6^{2-}$), permanganate (MnO_4^-), Hexacyanoferrate (I) and (II),

Class B: Anions of class B are subdivided into two categories on the basis of reaction they give in solution.

1. Anions of this group give Precipitation Reaction in solution. Anions of this group are: Sulphate (SO_4^{2-}), Phosphate (PO_4^{3-}), Succinate ($C_4H_4O_4^{2-}$), Arsenate (AsO_4^{3-}), Chromate (CrO_4^{2-}), Silicate (SiO_3^{2-}), Salicylate ($C_6H_6(OH)COO^-$), Phosphite (HPO_3^{2-}), Arsenite (AsO_3^{3-}), Dichromate ($Cr_2O_7^{2-}$), Benzoate ($C_6H_6COO^-$).

2. Anions of this group give Oxidation or Reduction Reaction in solution. Anions of this group are: Manganate (MnO_4^{2-}), Permanganate (MnO_4^-), Chromate (CrO_4^{2-}), Dichromate ($Cr_2O_7^{2-}$).

OR

b) Discuss the solubility products and common ion effect.

Ans: Silver chloride is so insoluble in water (.0.002 g/L) that a saturated solution contains only about 1.3 x 10^{-5} moles of AgCl per liter of water.

$$\mathrm{AgCl}(s) \overset{H_2O}{\rightleftharpoons} \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

Strict adherence to the rules for writing equilibrium constant expressions for this reaction gives the following result.

$$K_c = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

(Water isn't included in the equilibrium constant expression because it is neither consumed nor produced in this reaction, even though it is a vital component of the system.)

The $[Ag^+]$ and $[Cl^-]$ terms represent the concentrations of the Ag^+ and Cl^- ions in moles per liter when this solution is at equilibrium. The third term [AgCl] — is more ambiguous. It doesn't represent the concentration of AgCl dissolved in water because we assume that AgCl dissociates into Ag^+ ions and Cl^- ions when it dissolves in water. It can't represent the amount of solid AgCl in the system because the equilibrium is not affected by the amount of excess solid added to the system. The [AgCl] term has to be translated quite literally as the number of moles of AgCl in a liter of solid AgCl.

The concentration of solid AgCl can be calculated from its density and the molar mass of AgCl.

This quantity is a constant, however. The number of moles per liter in solid AgCl is the same at the start of the reaction as it is when the reaction reaches equilibrium.

Since the [AgCl] term is a constant, which has no effect on the equilibrium, it is built into the equilibrium constant for the reaction.

$$[Ag^+][Cl^-] = K_c \times [AgCl]$$

This equation suggests that the product of the equilibrium concentrations of the Ag^+ and Cl^- ions in this solution is equal to a constant. Since this constant is proportional to the solubility of the salt, it is called the **solubility product equilibrium constant** for the reaction, or K_{sp}.

$$K_{sp} = [Ag^+][Cl^-]$$

The K_{sp} expression for a salt is the product of the concentrations of the ions, with each concentration raised to a power equal to the coefficient of that ion in the balanced equation for the solubility equilibrium.

25. a) Write the reaction of interfering anions such as fluoride, borate and oxalate.

Ans: In acidic medium these salts produce their corresponding acids like oxalic acid, phosphoric acid, hydrofluoric acid, boric acid and tartaric acid. For example, barium oxalate reacts with HCl and produces oxalic acid.

$$BaC_2O_4 + 2HCl \longrightarrow BaCl_2 + H_2C_2O_4$$

These interfering acids are weak acids so they do not dissociate completely and remain in solution in their unionised form. Equilibrium is developed between dissociated and un-dissociated acid.

$$H_2C_2O_4 \rightleftharpoons 2H^+ + C_2O_4^{2-}$$

Hydrochloric acid is a strong acid and is ionised completely.

$$HCl \longrightarrow H^+ + Cl^-$$

Hydrogen ions acts as common ion among them and higher concentration of H^+ suppresses the ionization of interfering acid. Therefore, ionic product of $C_2O_4^{2-}$ and Ba^{2+} doesn't exceed the solubility product of barium oxalate which is why Ba^{2+} remains in the solution as barium oxalate. That's how interfering radicals do not interfere as long as the medium remains acidic enough. But when we make the medium alkaline by adding 3rd group reagent ammonium hydroxide NH_4OH, OH^- ions combine with H^+ and neutralise them. This decreases the concentration of H^+ ions which shifts the equilibrium of dissociation of interfering acid forward and increases the concentration of $C_2O_4^{2-}$. Thus the ionic product of $C_2O_4^{2-}$ and Ba^{2+} exceeds the solubility product of barium oxalate and Ba^{2+} gets precipitated in the 3rd group, which actually belongs to the 4th group.

One or more interfering radicals can be present in the solution. They have to be removed in the following order: first we remove oxalate and tartrate, then borate and fluoride, then silicate and in the last phosphate.

Procedure for the removal of borate and fluoride: Take the filtrate and evaporate it to dryness. Add concentrated HCl and again evaporate to dryness.

$$F^- + H^+ \longrightarrow HF$$

$$CaF_2 + 2HCl \longrightarrow CaCl2 + 2HF$$

On heating with HCl fluoride forms hydrofluoric acid and Borate forms orthoboric acid which evaporate on heating.

$$BO_3^{3-} + 3H^+ \longrightarrow H_3BO_3$$

$$Na_3BO_3 + 3HCl \longrightarrow 3NaCl + H_3BO_3$$

Extract the residue with dilute HCl and filter. Use this filtrate for analysis of 3rd group or use for removal of other interfering radicals.

If fluoride is absent and borate is present then residue use a mixture of 5ml ethyl alcohol and 10ml conc. HCl and evaporate to dryness.

$BO_3^{3-} + 3H^+ \longrightarrow H_3BO_3$

$H_3BO_3 + 3C_2H_5OH \longrightarrow (C_2H_5O)_3B\uparrow + H_2O$

Procedure for the removal of silicate: Evaporate the filtrate of 2nd group or residue obtained from removal of interfering radicals with concentrated HCl to dryness. Repeat this treatment for 3-4 times.

$SiO_3^{2-} + 2H^+ \longrightarrow H_2SiO_3\downarrow$

$H_2SiO_3\downarrow \longrightarrow SiO_2\downarrow + H_2O$

On heating with HCl silicate converts to metasilicic acid (H_2SiO_3) which is converted into white insoluble powder silica (SiO_2) on repetitive heating with concentrated HCl.

OR

b) What is organometallic chemistry? Give four examples and discuss the bond type

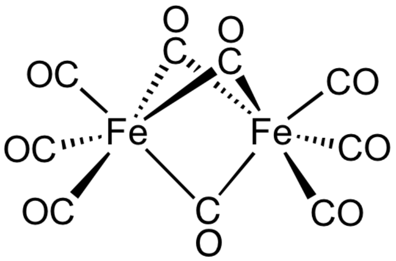
Ans: Compounds that contain a metal-carbon bond, R-M, are known as "*organometallic*" compounds. Organometallic compounds of Li, Mg (Grignard reagents) are amongst some of the most important organic reagents.
Many other metals have been utilised, for example Na, Cu and Zn.

Organometallic compounds provide a source of nucleophilic carbon atoms which can react with electrophilic carbon to form a new carbon-carbon bond. This is very important for the synthesis of complex molecules from simple starting materials.

To rationalise the general reactivity of organometallics it is convenient to view them as ionic, so R-M = R^-M^+

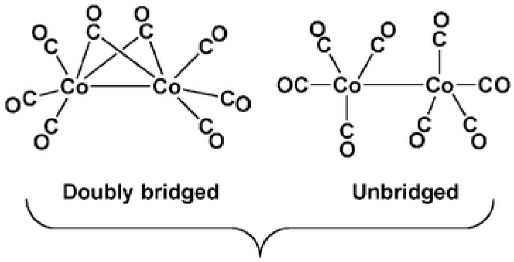
The most important reactions is this chapter are the reactions of organolithiums, RLi, and Grignard reagents, RMgX, with the carbonyl groups in aldehydes, ketones and esters to give alcohols. However, we will also look at some useful reactions involving Cu, Zn and Hg (mercury).

26. a) Draw the structure and calculate the 18 electron rule for the following metal carbonyl compounds. i) $Fe_2(CO)_9$



2Fe	$4S^2 3d^6$	$= 16\ e^-$	
9 CO	9×2	$= 18\ e^-$	
M-M	1×2	$= 02\ e^-$	
Tatal		= 36/2	$= 18e^-$

ii) $Co_2(CO)_8$



$Co_2(CO)_8$ structures

2Co	$4S^2 3d^7$	$= 18\ e^-$	
8 CO	8×2	$= 16\ e^-$	
M-M	1×2	$= 02\ e^-$	
Tatal		= 36/2	$= 18e^-$

OR

b) Explain the general preparation of metal carbonyls with suitable examples.

Ans: Direct Combination

Only Ni(CO)4 and Fe(CO)5 and Co2(CO)8 are normally obtained by the action of carbon monoxide on the finely divided metal at suitable temperature and pressure

$$Ni(s) + 4CO(g) \xrightarrow{30^{O}C, 1\,atm} Ni(CO)_4(l)$$

$$Fe(s) + 5CO(g) \xrightarrow{200^{O}C, 200\,atm} Fe(CO)_5(l)$$

$$2Co(s) + 8CO(g) \xrightarrow{150^{O}C, 35\,atm} Co_2(CO)_8(s)$$

Reductive carbonylation

Many metallic carbonyls are obtained when salts like Ru(acac)3, CrCl3, Re2O7, VCl3, CoS, Co(CO)3, CoI2 etc. are treated with carbon monoxide in presence of suitable reducing agent like Mg, Ag, Cu, Na, H2, AlLiH4 etc.

$$3\,Ru(acac)_3(solution) + H_2(g) + 12\,CO(g) \xrightarrow{150^{O}\ C,\ 200\,atm,\ methanol} Ru_3(CO)_{12}$$

$$CrCl_3(s) + Al(s) + 6CO(g) \xrightarrow{AlCl_3,\ benzene} Cr(CO)_6(solution)$$

$$2\,CoI_2 + 8\,CO + 4\,Cu \xrightarrow{200°\,C,\ 200\ \text{atm press.}} Co_2(CO)_8 + 4\,CuI$$

$$2\,FeI_2 + 5\,CO + 2\,Cu \xrightarrow{200°\,C,\ 200\ \text{atm press.}} Fe(CO)_5 + Cu_2I_2$$

$$2\,CoCO_3 + 8\,CO + 2\,H_2 \xrightarrow{120 - 200°\,C,\ 250 - 300\ \text{atm press}} Co_2CO_8 + 2\,CO_2 + 2\,H_2O$$

$$MoCl_5 + 6\,CO + 5\,Na \xrightarrow{\text{diglyme}} Mo(CO)_6 + 5\,NaCl$$

Preparation of mononuclear carbonyls from iron pentacarbonyl

The labile carbonyl groups in iron pentacarbonyl can be replaced by chloride to give a different metal carbonyl. These reactions are characterized by low yield, which can be improved using high pressure.

$$MoCl_6 + 3\,Fe(CO)_5 \xrightarrow{110\ ^{o}C,\ \text{ether}} Mo(CO)_6 + 3\,FeCl_2 + 9\,CO$$

$$WCl_6 + 3\,Fe(CO)_5 \xrightarrow{110\ ^{o}C,\ \text{ether}} W(CO)_6 + 3\,FeCl_2 + 9\,CO$$