KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University)
(Under Section 3 of UGC Act, 1956)
Coimbatore-21

M.Sc. Chemistry **2019-2020**

Semester-I

19CHP102 **INORGANIC CHEMISTRY-I** **4H 4C**

(NUCLEAR CHEMISTRY AND METALLIC CLUSTERS)

Instruction Hours/week:L: 4 T:0 P:0 Marks: Internal:40 External: 60 Total:100
External Semester Exam: 3 Hrs

Course Objectives

1. To learn the nuclear structure, stable and unstable atomic nuclei, nuclear reactions and different modes of radioactive decay.
2. To understand the detection of radioactive rays and to measure the radiation.
3. To learn about the fundamentals of metallic clusters.
4. To understand the chemistry of boranes and related compounds.

Course outcomes

1. Described the basic concepts of nuclear chemistry and types of nuclear reactions.
2. Understood the Basics of metallic clusters, preparation, properties and applications of metallic clusters
3. Learned the structure and bonding in molecules / ions and predict the structure of molecules / ions.
4. Described the type of defects in metals and about semi conductors
5. Understood the inorganic and organometallic chemistry, catalysis in the molecular level

UNIT I – Inorganic Clusters

Inorganic chains – rings - cages and clusters (definition and structure) - metal clusters - dinuclear clusters - trinuclear clusters - tetranuclear clusters - hexanuclear clusters – organometallic clusters. Silicates and siloxanes.

Boranes, boron hydrides (structure and properties) – carboranes - metallocarboranes - Wade’s theory - closo-nido and arachno structures - borazines, phosphazenes – Sulphur- Nitrogen ring compounds. Isopoly and heteropoly acids of V, Cr, Mo and W.

UNIT II – Metallic State and Organometallic chemistry

Metallic state-free electron, band and zone theories - non stoichiometry - point defects in solids - Schottky and Frenkel defects - linear effects - dislocation - effects due to dislocation - electrical properties of solids - insulators-intrinsic semiconductors - n and p type and super conductors - ceramics elementary treatment.
Basic Organometallic Chemistry: Common notation used in organometallic chemistry- Metal-ligand interactions; Basic principles of ligand-field theory; molecular orbital theory - 18-electron rule - Common organometallic bonding modes – Introduction to Metal-centered organometallic reactions.

UNIT III – Heterogenous catalytic reactions

Organometallic compounds in homogeneous catalytic reactions-coordinative unsaturation – acid-base behavior reaction – migration of atoms or groups from metal to ligand – insertion reaction – reactions of coordinated ligands – catalytic reactions of alkenes – isomerisation of alkenes – hydrogenation – hydroformylation and hydrosilation of alkenes – alkene polymerization and oligomerisation – fluxional molecules.

UNIT IV- Nuclear Chemistry

Nuclear Chemistry - the nucleus - subatomic particles and their properties, binding energy. N/P ratios in stable and meta stable nuclei - different type of nuclear forces - liquid model- shell model. Modes of radioactive decay - α, β and γ decay radiation, electron capture, nuclear isomerism and internal conversion.

UNIT V – Nuclear Reactions

Nuclear reactions - Bethes's notation, Q-value, columbic barrier, cross section, different types of nuclear reactions - projectiles capture - particle emission, spallation, fission, fusion, theories of fission, use of fission products, nuclear reactors - fissile and fertile isotopes- U^{233},U^{235},Pu^{239},Th^{232},-atomic power projects in India, stellar energy, synthetic elements - application of radio isotopes - Hot atom chemistry**.**

SUGGESTED READINGS

1. Huheey, J. E., Keitler, E. A., & Keitler, R. L. (2002). Inorganic Chemistry- Principles of Structure and Reactivity (IV Edition). Singapore: Pearson Education.
2. Shekar, C. V. (2005). A Text Book of Nuclear Chemistry (I Edition). New Delhi: Dominant publishers and Distributors.
3. Arnikar, H. J. (2003). Essentials of Nuclear Chemistry (IV Edition). New Delhi: New Age International Publishers Pvt. Ltd.
4. *B. D. Gupta*. (2011). *Basic Organometallic Chemistry*: Concepts, Syntheses and Applications. Universities Press.
5. Cotton, F. A., Wilkinson, G., Murillo, C. A., & Bochmann, M. (1999). Advanced Inorganic Chemistry (VI Edition). New York: John Wiley & Sons.
6. Glasstone, S. (1967). Source Book on Atomic Energy (III Edition). New Delhi: East West Press.
7. Gurdeep Raj, (2002). Advanced Inorganic Chemistry Vol. I (24th Revised Edition). Meerut: Goel Publishing House.
8. Madan, R. D. (2005). Modern Inorganic Chemistry. New Delhi: S. Chand & Co.
9. Puri, B. R., & Sharma, L. R. (2002). Principles of Inorganic Chemistry. New Delhi: Shoban Lal & Co.
10. Wahid Malik, Madan. R.D., and Tuli, G.D. (2004). Selected topics in Inorgani Chemistry. New Delhi. S. Chand & Co.

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Coimbatore – 641 021.

LECTURE PLAN

DEPARTMENT OF CHEMISTRY

STAFF NAME: B.Prabha **SUB.CODE**:19CHP102

SUBJECT: INORGANIC CHEMISTRY (NUCLEAR CHEMISTRY & METALLIC CLUSTERS)

SEMESTER: I **CLASS**: I M.Sc., CHEMISTRY

S.No	Lecture hour	Topics	Support material
		Unit - I	
1	1	Inorganic chains, Rings, cages and clusters	**T1:**738
2	1	Dinuclear, trinuclear, tetranuclear, hexanuclear clusters) organometallic clusters	**T1:**765-807
3	1	Silicates, Siloxanes	**T2:**1039-1043, **T1:**801-805
4	1	Boron hydrides (structure and properties)	**T1:**765-769
5	1	Carboranes - metallocarboranes	**T1:**769—773
6	1	Wade’s theory-closo-nido and arachno structures,	**T1:**769—773
7	1	Borazines, phosphazenes	**T1:**769—773
8	1	Sulphur nitrogen compounds,	**T1:**769—773
9	1	Isopoly and hetero poly acids of V, Cr, MO, and W	**T1:**773—778
	Total No of Hours Planned For Unit 1= 9		
	Unit – II		

1.	1	Metallic state free electron, band and zone theory-non stoichiometry-point defects in solids	T1:270-272
2.	1	Schottky and frenkel defects-linear effects dislocation-effects due to dislocation	**T1:**263-265
3.	1	Electrical properties of solids-insulators- intrinsic semiconductor, N and P type and superconductors	**T1:**272-280
4.		Ceramics elementary treatment.	**T3:**1229-1230
5.	1	Basic organometallic chemistry	**T1**:624-630
6.	1	Common notation used in organometallic chemistry-metal ligand interactions.	**T1:**634-640
7.	1	Basic principles of ligand field theory	**T1**:634-640
8.	1	Molecular orbital theory, 18 electron rule.	**T1**:624-630
9.	1	Common organometallic bonding modes-introduction to metal-centered organometallic reactions.	**T1**:624-630
	Total No of Hours Planned For Unit 2 =9		
		Unit - III	
1.	1	Organometallic compounds in homogeneous catalytic reactions	**T3:**1229-1230
2.	1	Coordinative unsaturation –acid base behavious reaction-migration of atoms or groups from metal to ligand	**T3:**1168-1171
3.	1	Insertion reaction-reactions of coordinated ligands	**T2:**1207-1238
4.	1	Catalytic reactions of alkenes	**T3:**1230-1258
5.	1	Isomerism of alkenes	**T3:**1230-1258
6.	1	Hydrogenation –hydroformylation	**T3:**1230-1258
7.	1	Hydrosilation of alkenes	**T3:**1230-1258
8.	1	Alkene polymerization, oligomerisation-fluxional molecules	**T3:**1230-1258
9.	1	Recaptulations and discussions of important questions	
	Total No of Hours Planned For Unit 3 =9		

		Unit - IV	
1.	1	Nuclear chemistry-the nucleus-subatomic particles and their properties	T4:1-6
2.	1	Binding energy. N/P ratios in stable and meta stable nuclei	T4: 10-13
3.	1	Different type of nuclear forces	T4:80-82
4.	1	Liquid model, Shell model	T4:80-84, 150-152
5.	1	Modes of radioactive decay-α,β,γ decay radiation	T4:150-152
6.	1	Electron capture	T4:152-156
7.	1	Nuclear isomerism,	T4:153-158
8.	1	Internal conversion	T4:153-158
9.	1	Recaptulations and discussions of important questions	
	Total No of Hours Planned For Unit 4 =9		
		Unit - V	
1.	1	Nuclear reactions –Bethe's notation, Q value, columbic barrier	T4:160
2.	1	Cross section, different types of nuclear reactions	T4:337-338
3.	1	Projectile capture, Spallation, fission	T4:741-745, 232-234
4.	1	Fusion, theories of fission	T4:248-250
5.	1	Use of fission products, stellar energy	T4:252-258, 264-268
6.		Nuclear reactors-fissile and fertile isotopes- U ^{233}, U ^{235}, Pu ^{239}, Th ^{232}	T4:256-260
7.	1	Atomic power projects in india	T4:248-250
8.	1	synthetic elements-applications of radio isotopes-hot atom chemistry	T4:248-254
9.	1	Recaptulations and discussions of important questions	
10	1	ESE question paper discussion	

11	1	ESE question paper discussion	
12	1	ESE question paper discussion	
	Total No of Hours Planned For Unit 5 =12		
Total Hours Planned	**48**		

Text Books:

T1: James E. Huheey, Ellen A. Keiter, Richard L. Keiter, Okhil K. Medhi. (2013). *Inorganic Chemistry-Principles of structure and Reactivity* (IV Edition) New Delhi pearson education, India

T2: Madan, R.D.(2014). *Modern Inorganic Chemistry*, I edition, New Delhi:S. Chand and company Ltd .

T3: Cotton, F.A,G.,Murillo,C.A., & Bochmann, M.(2007). *Advanced Inorganic Chemistry* (VI Edition).New York:John Wiley & Sons.

T4: H.J.Arnikar (2011) , Essentials of nuclear chemistry (IV Edition). New age international (P) limited publishers, New Delhi.

UNIT I

SYLLABUS

Inorganic chains-rings-cages and clusters(definition and structure)-metal clusters-dinuclear clusters-trinuclear clusters-tetranuclear clusters-hexanuclear clusters-organometallic clusteres. Silicates and siloxanes.
Boranes, boron hydrides (structure and properties)-carboranes-metallocarboranes-Wades'theory-closo-nido and arachno structures-borazines,phosphazenes-sulphur-Nitrogen ring compounds,Isopoly and heteropoly acids of V,Cr,Mo and W.

METAL CLUSTERS

Metal Clusters

In chemistry, a **cluster** is an ensemble of bound atoms or molecules that is intermediate in size between a molecule and a bulk solid. Clusters exist of diverse stoichiometries and nuclearities. For example, carbon and boron atoms form fullerene and borane clusters, respectively. Transition metals and main group elements form especially robust clusters. Clusters can also consist solely of a certain kind of molecules, such as water clusters.

The phrase cluster was coined by F.A. Cotton in the early 1960s to refer to compounds containing metal–metal bonds. In another definition a cluster compound contains a group of two or more metal atoms where direct and substantial metal bonding is present. The prefixed terms "nuclear" and "metallic" are used and imply different meanings. For example, polynuclear refers to a cluster with more than one metal atom, regardless of the elemental identities. Heteronuclear refers to a cluster with at least two different metal elements.

The main cluster types are "naked" clusters (without stabilizing ligands) and those with ligands. For transition metal clusters, typical stabilizing ligands include carbon monoxide, halides, isocyanides, alkenes, and hydrides. For main group elements, typical clusters are stabilized by hydride ligands.

Transition metal clusters are frequently composed of refractory metal atoms. In general metal centers with extended d-orbitals form stable clusters because of favorable overlap of valence orbitals. Thus, metals with a low oxidation state for the later metals and mid-oxidation states for the early metals tend to form stable clusters. Polynuclear metal carbonyls are generally found in late transition metals with low formal oxidation states. The polyhedral skeletal electron pair theory or Wade's electron counting rules predict trends in the stability and structures of many metal clusters. Jemmis mno rules have provided additional insight into the relative stability of metal clusters.

Dinuclear Clusters

Metal–metal bonding in dinuclear complexes plays a key role in inorganic and organometallic chemistry. It is the basis for development of polymers and clusters derived from this simple unit.

Its chemistry now approaches the ‘functional group’ status, typically used in organic chemistry for classes of compounds. However, owing to the array of metals and oxidation states involved, a wide range of structures, reactions, and properties are observed for this important class of compounds. This article introduces the topic of metal–metal bonded complexes and attempts to outline the synthetic strategies used to prepare metal–metal bonded complexes, some of their characteristic properties and reactions, as well as to provide a brief introduction to historical development and emerging directions of this central area of inorganic chemistry.

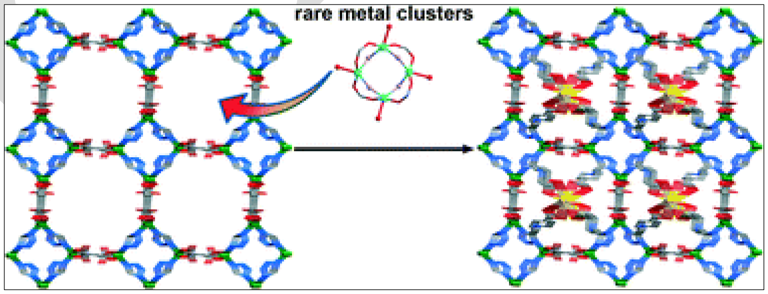
Trinuclear Clusters

Trinuclear dimethylglyoximato copper(II) complexes, $Cu_3(DMG)_2Cl_4$, $Cu_3(DMG)_2Br_4$, $4H_2O$ and $[Cu(DMG)_2]_2Cu(NO_3)_2$and an acetylacetonedioximato complex $Cu_3(AADO)_2Cl_2,2H_2O$ have been isolated. Investigations by i.r. and visible spectrophotometry revealed that both nitrogen and oxygen atoms of the oxime groups are coordinated in the halide complexes and a higher degree of conjugation occurs in the trinuclear complexes. For the nitrate complex, $[Cu(DMG)_2]_2Cu(NO_3)_2$ i.r. spectra show the presence of hydrogen bonded (O-H) bands as in $Cu(DMG)_2$and splitting occurs for the vibrational bands of (NO) groups. The structure involves the coordination of cis oxygen atoms of NO groups on one side of each of two $Cu(DMG)_2$ to a third copper(II) ion, while on the other side of $Cu(DMG)_2$ the hydrogen bonded structure remains intact.

The magnetic susceptibility of the four trinuclear compounds has been measured from ambient to 90°K in temperature. The results demonstrate antiferromagnetic exchange between one cupric ion and its neighbour on each side with no interaction between the latter.

Tetranuclear Clusters

Rare tetranuclear Zn clusters were successfully embedded into 3D energetic metal–organic framework channels by an enhanced extended hook method. The obtained metal–organic framework exhibits not only high enthalpy of combustion and low sensitivity but also strong green fluorescence.



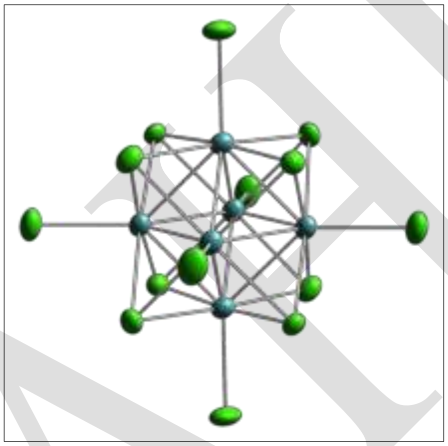
Hexanuclear Clusters

Octahedral chalcogenide and halide clusters

These compounds are bound together by metal-metal bonding as well as two kinds of ligands. Ligands that span the faces or edges of the M_6 core are labeled L_i, for inner (innen in the original German description), and those ligands attached only to one metal are labeled outer, or L_a for ausser. Typically, the outer ligands can be exchanged whereas the bridging ligands are more inert toward substitution.

Face-capped halide clusters

The premier example is of the class is $Mo_6Cl_{14}^{2-}$. This dianion is available as a variety of salts by treating the polymer molybdenum(II) chloride with sources of chloride, even hydrochloric acid. A related example is $W_6I_{14}^{2-}$ anion, which is obtained by reaction of tungsten hexacarbonyl with iodine at elevated temperatures.



Chalcohalide clusters

A related class of octahedral clusters are of the type $M_6X_8L_6$ where M is a metal usually of group6 or group 7, X is a ligand and more specifically an inner ligand of the chalcohalide group such as chloride or sulfide and L is an "outer ligand." The metal atoms define the vertices of an octahedron. The overall point group symmetry is O_h. Each face of the octahedron is capped with a chalcohalide and eight such atoms are at the corners of a cube. For this reason this geometry is called a face capped octahedral cluster. Examples of this type of clusters are the $Re_6S_8Cl_6^{4-}$anion.

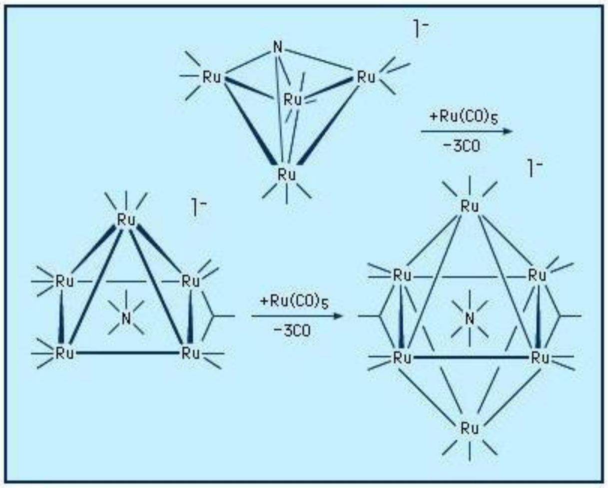
Chevrel clusters

A well-studied class of solid-state compounds related to the chalcohalides are molybdenumclusters of the type $A_xMo_6X_8$ with X sulfur or selenium and A_x an interstitial atom such as Pb. These materials, called Chevrel phases or Chevrel clusters, have been actively studied because they are type II superconductors with relatively high critical fields.[3] Such materials are prepared by high temperature (1100 °C) reactions of the chalcogen and Mo metal. Structurally related, soluble analogues have been prepared, e.g., $Mo_6S_8(PEt_3)_6$.

Organometallic Clusters

Metal cluster compounds contain metal-metal bonds. The focus here is on compounds having three or more metals in a closed array. Carbon monoxide is the most common ligand in organometallic cluster compounds, but many other organometallic ligands are bound to clusters, and the presence of several metals leads to bonding arrangements for the ligand that are not possible for monometallic compounds. A variety of metal arrays are seen in cluster compounds. Triangular, tetrahedral, and octahedral clusters are common, and much larger metal arrays are known. The structures of many clusters, which can be precisely determined by single-crystal X- ray diffraction, provide some clues to the way in which ligands are bound to the surfaces of bulk metal particles. The latter are more difficult to structurally characterize than are molecular clusters.

For many d-block clusters there is a strong correlation between their structure and the number of valence electrons (from the metal atoms and the ligands). This set of correlations for clusters is similar to the 18-electron rule for mononuclear organometallics, and these guidelines are often called Wade's rules after the British chemist Kenneth Wade, who first recognized that a triangular cluster such as $Ru_3(CO)_{12}$usually has 48 valence electrons, a tetrahedron such as $Co_4(CO)_{12}$ has 60 electrons, and an octahedron such as $Rh_6(CO)_{12}(\mu_3\text{-}CO)_4$ has 86 electrons. In some cases, it is possible to synthesize clusters in a stepwise manner. An interesting example of this type is the buildup of a ruthenium nitride cluster; in the process of cluster building, the nitrogen ligand is progressively encapsulated by metal atoms.



In chemistry, a **metal carbonyl cluster** is a compound that contains two or more metals linked in part by metal-metal bonds and containing carbon monoxide (CO) as the exclusive or predominant ligand. Simple examples include $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Mn_2(CO)_{10}$.[1]High nuclearity clusters include $[Rh_{13}(CO)_{24}H_3]^{2-}$ and the stacked Pt_3 triangules $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 2– 6).

Classes of carbonyl clusters

Binary metal carbonyl clusters

Binary carbonyl clusters consist only of metal and CO. They are the most widely studied and used metal carbonyl clusters. They arise in general by the condensation of unsaturated metal carbonyls. Dissociation of CO from $Ru(CO)_5$ would give $Ru(CO)_4$, which could trimerize to $Ru_3(CO)_{12}$. The reaction mechanisms are more complicated than this simple scenario. Condensation of low molecular weight metal carbonyls requires decarbonylation, which can be induced thermally, photochemically, or using various reagents. The nuclearity (number of metal centers) of binary metal carbonyl clusters is usually no greater than six.

Metal	Parent carbonyl	Cluster
Fe	$Fe(CO)_5$	$Fe_2(CO)_9$, $Fe_3(CO)_{12}$
Ru	$Ru(CO)_5$	$Ru_3(CO)_{12}$
Os	$Os(CO)_5$	$Os_3(CO)_{12}$
Co	$Co_2(CO)_8$	$Co_4(CO)_{12}$
Rh	$Rh_2(CO)_8$	$Rh_4(CO)_{12}$
Ir	$Ir_2(CO)_8$	$Ir_4(CO)_{12}$

SILICATES

A **silicate** is a compound containing an anionic silicon compound. The great majority of the silicates are oxides, but hexafluorosilicate ($[SiF_6]^{2-}$) and other anions are also included.

"Orthosilicate" is the anion SiO^{4-} 4 or its compounds. Related to orthosilicate are families of anions (and their compounds) with the formula $[SiO_{2+n}]^{2n-}$. Important members are the cyclic and single chain silicates $\{[SiO_3]^{2-}\}_n$ and the sheet-forming silicates $\{[SiO_{2.5}]^{-}\}_n$.

Silicates constitute the majority of Earth's crust, as well as the other terrestrial planets, rocky moons, and asteroids. Sand, Portland cement, and thousands of minerals are examples of silicates. Silicate compounds, including the minerals, consist of silicate anions whose charge is balanced by various cations. Myriad silicate anions can exist, and each can form compounds with many different cations. Hence this class of compounds is very large. Both minerals and synthetic materials fit in this class.

SILICONES

Silicones, also known as **polysiloxanes**, are polymers that include any inert, synthetic compound made up of repeating units of siloxane, which is a chain of alternating silicon atoms and oxygen atoms, frequently combined with carbon and/or hydrogen. They are typically heat- resistant and rubber-like, and are used in sealants, adhesives, lubricants, medicine, cooking utensils, and thermal and electrical insulation. Some common forms include silicone oil, silicone grease, silicone rubber, silicone resin, and silicone caulk.

BORANES

In chemistry, **boranes** comprise a large group of the group 13 hydride compounds with the generic formula of B_xH_y. Due to the high affinity of boron for oxygen, these compounds do not occur in nature. Many of the boranes readily oxidise on contact with air, the lighter explode violently. The class is named after the parent chemical called "borane" itself, chemical formula BH_3. This compound is only known to exist as a transient intermediate since it dimerises to form diborane, B_2H_6. The larger boranes all consist of boron clusters that are polyhedral. In addition to the charge-neutral boranes, a large number of anionic boron hydrides are known. The most important boranes are diborane B_2H_6 and two of its pyrolysis products, pentaborane B_5H_9 and decaborane $B_{10}H_{14}$. The development of the chemistry of boron hydrides led to new experimental techniques and theoretical concepts. Boron hydrides have been studied as potential fuels, for rockets and for automotive uses, but the only commercial applications involve derivatives of borane.

Generic formula of boranes

The four series of single-cluster boranes have the following general formulae, where "n" is the number of boron atoms:

Type	Formula	Notes
closo−	$B_nH_n^{2-}$	No neutral B_nH_{n+2} boranes are known
nido−	B_nH_{n+4}	Examples include hexaborane(10) (B_6H_{10}) and decaborane(14 ($B_{10}H_{14}$)

arachno	B_nH_{n+6}	
hypho−	B_nH_{n+8}	only adducts established
klado−	B_nH_{n+10}	

There also exists a series of substituted neutral hypercloso-boranes that have the theoretical formulae B_nH_n. Examples include $B_{12}(OCH_2Ph)_{12}$, a derivative of the unstable hypercloso- $B_{12}H_{12}$.

Naming conventions

The naming of neutral boranes is illustrated by the following examples, where the Greek prefix shows the number of boron atoms and the number of hydrogen atoms is in brackets:

- B_5H_9 pentaborane(9)
- B_6H_{12} hexaborane(12)

The naming of anions is illustrated by the following, where the hydrogen count is specified first followed by the boron count, and finally the overall charge in brackets:

- $B_5H_8^-$ octahydridopentaborate(1−) Optionally **closo− nido−** etc. can be added:

- B_5H_9, nido−pentaborane(9)
- B_4H_{10}, arachno−tetraborane(10)
- $B_6H_6^{2-}$, hexahydrido−closo−hexaborate(2−)

Understandably many of the compounds have abbreviated common names.

CARBORANES

A **carborane** is a cluster composed of boron, carbon and hydrogen atoms. Like many of the related boranes, these clusters are polyhedra and are similarly classified as closo-, nido-, arachno-, hypho-, etc. based on whether they represent a complete (closo-) polyhedron, or a polyhedron that is missing one (nido-), two (arachno-), or more vertices. Carboranes are a notable example of heteroboranes.

The icosahedral closo-carboranes are particularly stable. These boron-rich clusters exhibit unique **organomimetic** properties with chemical reactivity matching classical organic molecules, yet structurally similar to metal-based inorganic and organometallic species[2]

A prominent example is the charge-neutral $C_2B_{10}H_{12}$ or **o-carborane** with the prefix o derived from ortho. This derivative has been consider for a wide range of applications from heat-resistant polymers to medical applications. The electronic structure of these cluster compounds has been described by Wade-Mingos rules. Carborane acid is the chlorinated superacid H($CHB_{11}Cl_{11}$), which has the structure shown at right.

Sulphur-Nitrogen ring compounds

A **heterocyclic compound** or **ring structure** is a cyclic compound that has atoms of at least two different elements as members of its ring(s). **Heterocyclic chemistry** is the branch of organic chemistry dealing with the synthesis, properties, and applications of these **heterocycles**.

Examples of heterocyclic compounds include all of the nucleic acids, the majority of drugs, most biomass (cellulose and related materials), and many natural and synthetic dyes.

Classification

Although heterocyclic compounds may be inorganic, most contain at least one carbon. While atoms that are neither carbon nor hydrogen are normally referred to in organic chemistry as heteroatoms, this is usually in comparison to the all-carbon backbone. But this does not prevent a compound such as borazine(which has no carbon atoms) from being labelled "heterocyclic". IUPAC recommends the Hantzsch-Widman nomenclature for naming heterocyclic compounds.

Heterocyclic compounds can be usefully classified based on their electronic structure. The saturated heterocycles behave like the acyclic derivatives. Thus, piperidine and tetrahydrofuran are conventional amines and ethers, with modified steric profiles. Therefore, the study of heterocyclic chemistry focuses especially on unsaturated derivatives, and the preponderance of work and applications involves unstrained 5- and 6-membered rings. Included are pyridine, thiophene, pyrrole, and furan. Another large class of heterocycles are fused to benzene rings, which for pyridine, thiophene, pyrrole, and furan are quinoline, benzothiophene, indole, and benzofuran, respectively. Fusion of two benzene rings gives rise to a third large family of compounds, respectively the acridine, dibenzothiophene, carbazole, and dibenzofuran. The unsaturated rings can be classified according to the participation of the heteroatom in the pi system.

3-membered rings

Heterocycles with three atoms in the ring are more reactive because of ring strain. Those containing one heteroatom are, in general, stable. Those with two heteroatoms are more likely to occur as reactive intermediates.

Common 3-membered heterocycles with one heteroatom are:

Heteroatom	Saturated	Unsaturated
Nitrogen	Aziridine	Azirine

Oxygen	Oxirane (ethylene oxide epoxides)	Oxirene
Sulfur	Thiirane (episulfides)	Thiirene
Boron	Borirane	Borirene
Phosphorus	Phosphirane	Phosphirene

Those with two heteroatoms include:

Heteroatom	**Saturated**	**Unsaturated**
Nitrogen	Diaziridine	Diazirine
Nitrogen/oxygen	Oxaziridine	
Oxygen	Dioxirane	

4-membered rings

Compounds with one heteroatom:

Heteroatom	**Saturated**	**Unsaturated**
Nitrogen	Azetidine	Azete
Oxygen	Oxetane	Oxete
Sulfur	Thietane	Thiete

Compounds with two heteroatoms:

Heteroatom	Saturated	Unsaturated
Nitrogen	Diazetidine	Diazete
Oxygen	Dioxetane	Dioxete
Sulfur	Dithietane	Dithiete

Borazines

Borazine is an inorganic compound with the chemical formula $(BH)_3(NH)_3$. In this cyclic compound, the three BH units and three NH units alternate. The compound is isoelectronicand isostructural with benzene. Like benzene, borazine is a colourless liquid. For this reason borazine is sometimes referred to as "inorganic benzene".

Synthesis

The compound was reported in 1926 by the chemists Alfred Stock and Erich Pohland by a reaction of diborane with ammonia.

Borazine is synthesized from diborane and ammonia in 1:2 ratio at 250–300 °C with a conversion of 50%.

$$3\ B_2H_6 + 6\ NH_3 \rightarrow 2\ B_3H_6N_3 + 12\ H_2$$

An alternative more efficient route begins with lithium borohydride and ammonium chloride: 3

$$LiBH_4 + 3\ NH_4Cl \rightarrow B_3H_6N_3 + 3\ LiCl + 9\ H_2$$

In a two-step process to borazine, boron trichloride is first converted to trichloroborazine: $3\ BCl_3 + 3$

$$NH_4Cl \rightarrow Cl_3B_3H_3N_3 + 9\ HCl$$

The B-Cl bonds are subsequently converted to B-H bonds:

$$2\ Cl_3B_3H_3N_3 + 6\ NaBH_4 \rightarrow 2\ B_3H_6N_3 + 3\ B_2H_6 + 6\ NaCl$$

Properties

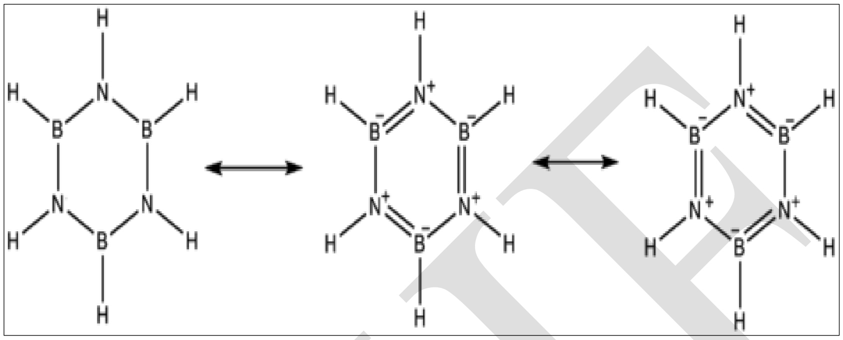
Borazine is a colourless liquid with an aromatic smell. In water it hydrolyzes to boric acid, ammonia, and hydrogen. Borazine, with a standard enthalpy change of formation ΔH_f of −531 kJ/mol, is thermally very stable.

Structure and bonding

Borazine is isostructural with benzene. The six B-N bonds have length of 1.436 Å. The carbon–

carbon bond in benzene is shorter length at 1.397 Å. The boron–nitrogen bond length is between that of the boron–nitrogen single bond with 0.151 nm and the boron–nitrogen double bond which is 0.131 nm. This suggests partial delocalisation of nitrogen lone-pair electrons.

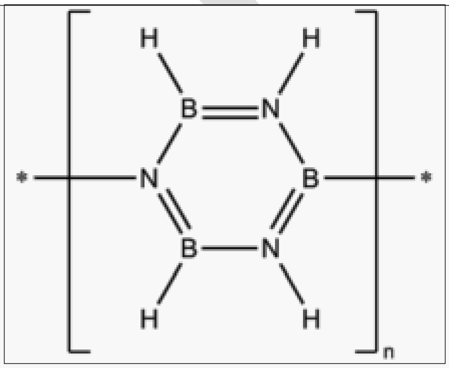
The electronegativity of boron (2.04 on the Pauling scale) compared to that of nitrogen (3.04) and also the electron deficiency on the boron atom and the lone pair on nitrogen favor alternative mesomer structures for borazine.



Boron is the Lewis acid and nitrogen is the Lewis base.

Reactions

Although often compared with benzene, borazine is far more reactive. With hydrogen chloride it forms an adduct, whereas benzene is unreactive toward HCl.



Polyborazylene

$B_3N_3H_6 + 3\ HCl \rightarrow B_3N_3H_9Cl_3$

Addition reaction of borazine with hydrogen chloride $B_3N_3H_9Cl_3 + NaBH_4 \rightarrow (BH_4N)_3$

Reduction with sodium borohydride

The addition reaction with bromine does not require a catalyst. Borazines undergo nucleophilicattack at boron and electrophilic attack at nitrogen. Heating borazine at 70 °C expels hydrogen with formation of a borazinyl polymer or polyborazylene, in which the monomer units are coupled in a para fashion by new boron-nitrogen bonds. Boron nitride can be prepared by heating polyborazylene to 1000 °C. Borazines are also starting materials for other potential ceramics such as boron carbonitrides. Borazine can also be used as a precursor to grow boron nitride thin films on surfaces, such as the nanomesh structure which is formed on rhodium.

Polyborazylene has been proposed as a recycled hydrogen storage medium for hydrogen fuel cell vehicle applications, using a "single pot" process for digestion and reduction to recreate ammonia borane.

Among other B-N type compounds mixed amino-nitro substituted borazines have been predicted to outperform carbon based explosives such as CL-20.

Related compounds

Carborazine is another six-membered aromatic ring with two carbon atoms, two nitrogen atoms and two boron atoms in opposing pairs.

PHOSPHAZENES

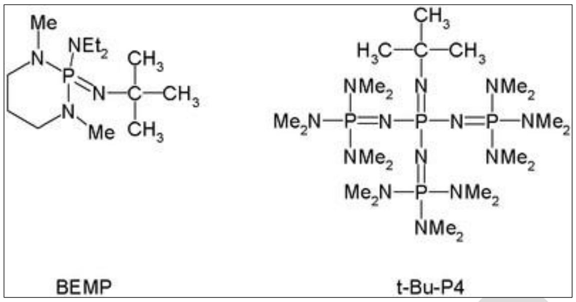
Phosphazenes are a class of chemical compounds in which a phosphorus atom is covalently linked to a nitrogen atom by a double bondand to three other atoms or radicals by single bonds. While other substitutions produce relatively persistent compounds, in organic synthesis the term largely refers to species with three amino substituents bound to phosphorus. The compounds are unusually stable examples of the phosphorane class of molecules and have a remarkable proton affinity. As such, they are one of the eminent examples of neutral, organic superbases.[1] Two examples are hexachlorocyclotriphosphazene and bis(triphenylphosphine)iminium chloride. Phosphazenes are also known as **iminophosphoranes** and **phosphine imides**.

The corresponding polymers are polyphosphazenes. Phosphinimide ligands can be used in catalysis.

Phosphazene bases

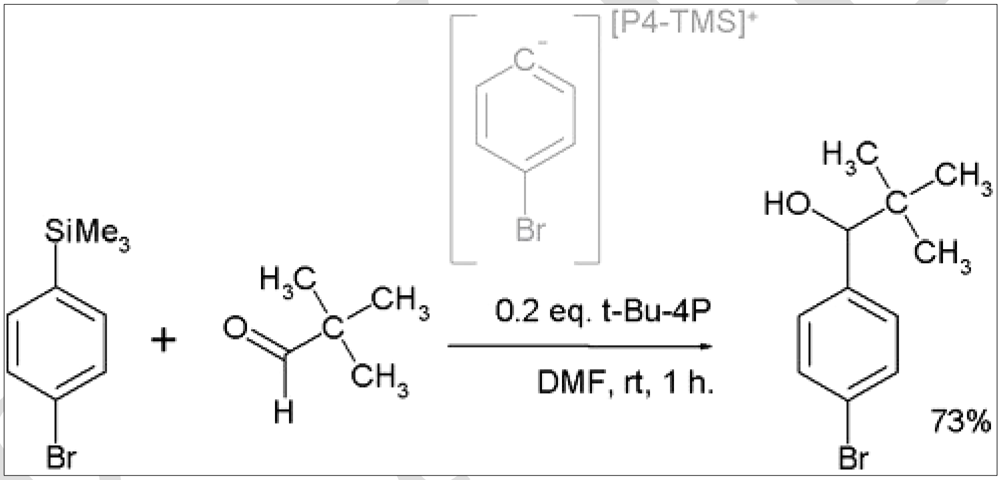
Phosphazene bases are strong non-metallic non-ionic and low-nucleophilic bases. They are stronger bases than regular amine or amidine bases such as Hünig's base or DBU. Protonation takes place at a doubly bonded nitrogen atom. Related to phosphazene bases are the proazaphosphatrane bases, which have a saturated $P(NR)_3$ structure and protonate at phosphorus.

Though the simplest phosphazene superbase, P1-Me, was first synthesized in 1975, chemists assumed that the compounds were highly unstable, like their alkyl-substituted derivatives. The species was regarded at that time as little more than an academic curiosity.



By now phosphazene bases are established reagents in organic synthesis. Perhaps the best known phosphazene bases are BEMP with an acetonitrile pKa of the conjugate acid of 27.6 and the phosphorimidic triamide t-Bu-P4 ($pK_{BH}+$ = 42.7) also known as Schwesinger base after one of its inventors.

In one application t-Bu-P4 is employed in a nucleophilic addition converting the pivaldehyde to the alcohol:



The active nucleophile is believed to be a highly reactive phosphazenium species with full negative charge on the arene sp_2 carbon.

Besides organic synthesis, phosphazene bases are used as basic titrants in non-aqueous acid-base titration. Their advantages for this are: they are very strong bases in many solvents and their conjugate acids are inert and non-HBD cations.

Isopolyand heteropolyacids

A **heteropoly acid** is a class of acid made up of a particular combination of hydrogen and oxygen with certain metals and non-metals. This type of acid is a common re-usable acid catalyst in chemical reactions.

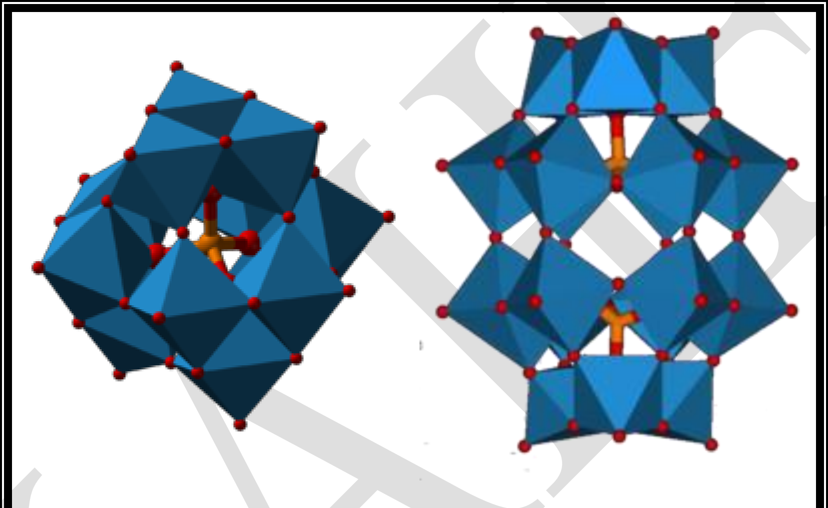
To qualify as a heteropoly acid, the compound must contain:

- a metal such as tungsten, molybdenum or vanadium, termed the addenda atom;

- oxygen;
- an element generally from the p-block of the periodic table, such as silicon, phosphorus or arsenic, termed the hetero atom;
- acidic hydrogen atoms.

The metal addenda atoms linked by oxygen atoms form a cluster with the hetero-atom inside bonded via oxygen atoms. Examples with more than one type of metal addenda atom in the cluster are well known. The conjugate anion of a heteropoly acid is known as a polyoxometalate.

Due to the possibilities of there being different combinations of addenda atoms and different types of hetero atoms there are a lot of heteropolyacids. Two of the better known groups of these are based on the Keggin, $H_nXM_{12}O_{40}$, and Dawson, $H_nX_2M_{18}O_{62}$, structures.



$^{n-}$Keggin structure, $XM_{12}O_{40}$ Dawson structure, $X_2M_{18}O_{62}^{n-}$

Some examples are:

- $H_4X^{n+}M_{12}O_{40}$, X = Si, Ge; M = Mo, W
- $H_3X^{n+}M_{12}O_{40}$, X = P, As; M = Mo, W
- $H_6X_2M_{18}O_{62}$, X=P, As; M = Mo, W

The heteropolyacids are widely used as homogeneous and heterogeneous catalysts, particularly those based on the Keggin structureas they can possess qualities such as good thermal stability, high acidity and high oxidising ability. Some examples of catalysis are:

- Homogeneous acid catalysis
  - hydrolysis of propene to give propan-2-ol by $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$
  - Prins reaction by $H_3PW_{12}O_{40}$
  - polymerisation of THF by $H_3PW_{12}O_{40}$
- Heterogeneous acid catalysis
    - dehydration of propan-2-ol to propene and methanol to hydrocarbons by $H_3PW_{12}O_{40}$

a)reformation of hexane to 2-methylpentane (isohexane) by $H_3PW_{12}O_{40}$ on SiO_2
b)Homogeneous oxidation
c)cyclohexene + H_2O_2 to adipic acid by the mixed addenda $H_3PMo_6V_6O_{40}$ d)ketone by O_2 to acid and aldehyde by mixed addenda $H_5PMo_{10}V_2O_{40}$

Heteropolyacids have long been used in analysis and histology and are a component of many reagents e.g. the Folin-Ciocalteu reagent, folins phenol reagent used in the Lowry protein assay and EPTA, ethanolic phosphotungstic acid

<u>ISOPOLY & HETEROPOLY ACIDS</u> (poly oxometallates)

The polymerization of simple monomeric oxide anions of Cr, Mo, W,V, Nb& Ta occurs when their alkaline solutions are gradually acidified. If from any oxyacid, the O atoms are replaced by radicals of the same acid (eg. introduction of one or more Cr O_4 radicals in H_2 Cr O_4) the resulting compounds are termed as poly acids . They can also be defined as compounds derived from a simple acid by the elimination of water between two or more molecules of the acid.

$$2\ H_2CrO_4 \rightarrow H_2Cr_2O_7 + H_2O$$

$$3\ H_2CrO_4 \rightarrow H_2Cr_3O_{10} + 2\ H_2O$$

$$4\ H_2CrO_4 \rightarrow H_2Cr_4O_{13} + 3\ H_2O$$

The acids which are obtained as a result of the apparent condensation of number of simple O containing acid molecules to give compounds containing more than a single molecule of acid anhydride is called **poly acid** . The ions of the polyacids are similarly derived from those of the simple acids by the elimination of O^{2-} ions are known as **poly anions** A familiar example is, the reaction of chromate solution $(Cr\ O_4)^{2-}$ which is yellow, with excess acid to form dichromate $(Cr_2\ O_7)^{2-}$ which is orange in colour.

The anions of the weak acids derived from the metals of group V A & VI A and particularly vanadium, molybdenum & tungsten have the property of condensing reversibly as the p H of their solutions is lowered to give a series of larger anions known as poly anions & the corresponding acids are called poly acids . Mo(VI), W(VI), V(V), Nb(V), Ta(V)etc have the tendency to form polymeric oxoanions containing MO_6 octahedra. In general, the acidification of basic solutions of vanadate$(VO_4)^{3-}$, niobate $(NbO_4)^{3-}$, molybdate $(Mo\ O_4)^{2-}$, tungstate (WO_4) etc leads to their polymerization yielding poly acids & poly anions.

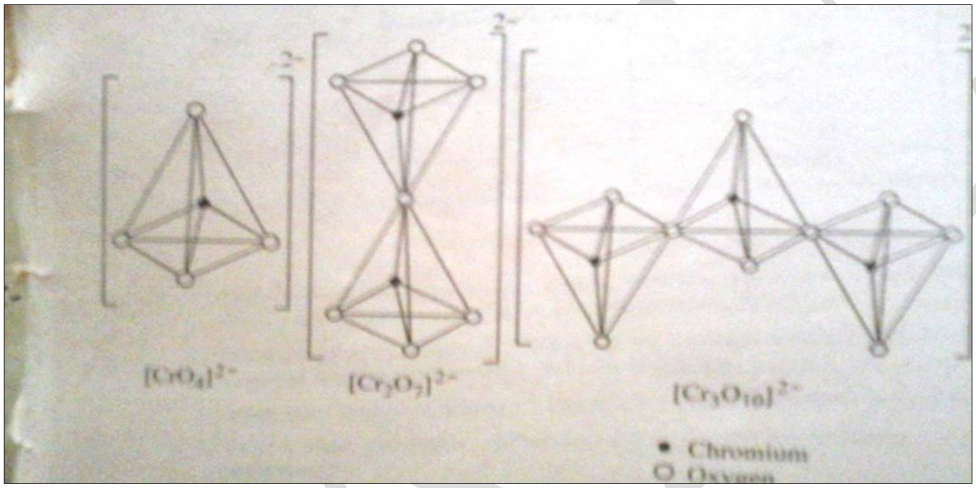
The polyacids can be divided into two groups

1) **Isopolyacids :** where the acids/anions which condense together are all of the same type. ie, all Mo O_6 groups or all WO_6 groups.
2) **Hetropolyacids :** where two or more different types of anions condense together ie, molybdate or tungstate groups with phosphate $(PO_4)^{3-}$, silicate $(Si\ O_4)^{4-}$ or borate groups.

Isopolychromate

The oxide of chromium CrO_3 is strongly acidic & dissolve in aq. NaOH forming discrete tetrahedral chromate CrO_4^{2-} . They exist both in solution & as solids. Chromates are stable only at high p H. The basic unit of isopolychromate is CrO_4 tetrahedra. As the p H is lowered (on acidifying) protonation & dimerisation takes place. On gradually decreasing the p H of the solution, the ions such as $(Cr_2O_7)^{2-}$, $(Cr_3O_{10})^{2-}$, & $(Cr_4O_{13})^{2-}$ are formed by corner tetrahedral CrO_4^{2-} .

CrO_4^- & $(Cr_2O_7)^{2-}$ exist in equilibrium over a wide range of p H from 2 – 6 . Below p H = 1 (treatment with con. H_2SO_4), the red chromium oxide (chromic acid) precipitates. The structure of CrO_3 consists of infinite number of linear chains of CrO_4^{2-} tetrahedra. Thus on acidifying CrO_4^{2-} form $HCrO_4^-$ & orange red dichromate $(Cr_2O_7)^{2-}$ in which two tetrahedral units join together by sharing the O atom at one corner. The sharing of O atom in dichromate $(Cr_2O_7)^{2-}$ may be represented in either in the traditional way (A) or by the polyhedral representation(B) .



There is some evidence for further polymerization giving a limited number of polychromates. Tri chromates $(Cr_3O_{10})^{2-}$, & tetra chromates$(Cr_4O_{13})^{2}$ have been found. Polymerization does not normally go beyond $(Cr_4O_{13})^{2-}$. These anions as well as dichromate ion are formed by corner sharing CrO_4^{2-} tetrahedra. The tendency for Cr to form large number of polyacids is limited. The small size of Cr^{6+} evidently limits it to the tetrahedral rather than octahedral coordination with oxygen. CrO_4 tetrahedra link only through corners & simultaneously favouring the Cr –O double bonds & so inhibiting the sharing of the attached oxygen. But it is found that for 5 & 6 coordinate metal oxo complexes which are common with
4d & 5d metals can share their O atoms either by their corners or by edges. Edge sharing result in too close approach of the metal units, lead to a richer variety of polyacids than found with 3d metals. The stability of radicals derived from one acid decreases with increase in the degree of condensation.,

$$(Cr_2O_7)^{2-} > (Cr_3O_{10})^{2-} > (Cr_4O_{13})^{2}.$$

Other polyacids

For other polyacids (except for polychromates) during the condensation process the C.N of the metal change from 4 to 6 & the basic building unit in the polymerization process becomes MO_6 octahedra . Unlike tetrahedra, which can link up only by sharing an apex , an octahedra can link up by sharing either an apex or edge but not by faces. Edge sharing results in larger clusters of octahedra in the discrete polyanions. Face sharing brings metal ions closest to each other & thus causes highest metal ion – metal ion repulsion .

Isopolymolybdate

When the trioxide of molybdate is dissolved in aqueous alkali, the resulting solution contain tetrahedral $[Mo\,O_4]^{2-}$. If these solutions are made strongly acidic, precipitates of yellow molybdic acid $Mo\,O_3.\,2H_2O$ is obtained which convert into the monohydrate if warmed. At the pH between these two extremes, polymeric anions made up of $Mo\,O_6$ octahedra are formed & their salts can be crystallized.

The only ion present in a molybdate solution at a pH of about 10 is simple $[\,Mo\,O_4]^{2-}$. But if the pH is lowered to about 6-8 , polyanion formation commences.

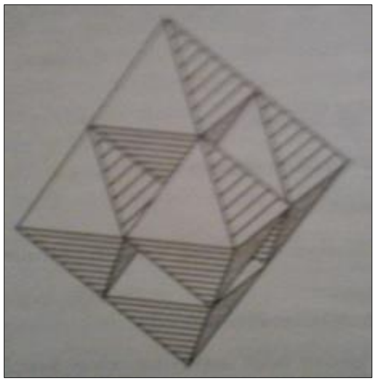
$$6\,[Mo\,O_4]^{2--} + 10H^{+\ -} \xrightarrow{\quad} [Mo_6\ O_{19}]^{2--} + 5H_2O$$

$$8\,[Mo\,O_4]^{2--} + 12H^{+\ -} \xrightarrow{\quad} [Mo_8\ O_{26}]^{4--} + 6H_2O$$

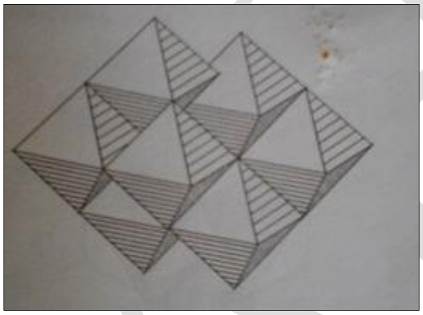
The first stable isopolymolybdate is $[Mo_7\ O_{24}]^{6-}$, the hepta molybdate or paramolybdate. When this solution is further acidified to pH of about 1.8 – 2.9, the octamolybdate ion $[Mo_8\,O_{26}]^{4-}$ is formed.

At a pH of 1.8, the largest isopolyanion $[Mo_{36}\ O_{112}\ (H_2O)_{16}]^{8-}$ is formed. Final product is polymeric $Mo\,O_3.\,2H_2O$ consisting of sheets of corner shared $Mo\,O_6$ octahedra . All these ions are formed from the basic unit $Mo\,O_6$ joined by sharing corners or edges.

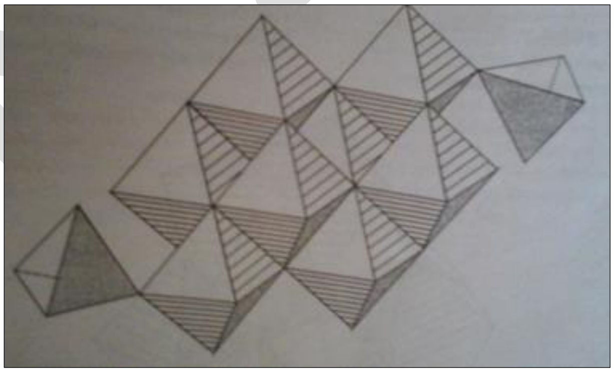
$$\mathbf{[Mo\,O_4]^{4-} \xrightarrow{\quad} [Mo_7\,O_{24}]^{6-} \xrightarrow{\quad} [Mo_8\,O_{26}]^{4-} \xrightarrow{\quad} [Mo_{36}\,O_{112}\,(H_2O)_{16}]^{8}}$$



$[Mo_6 O_{19}]^{2-}$

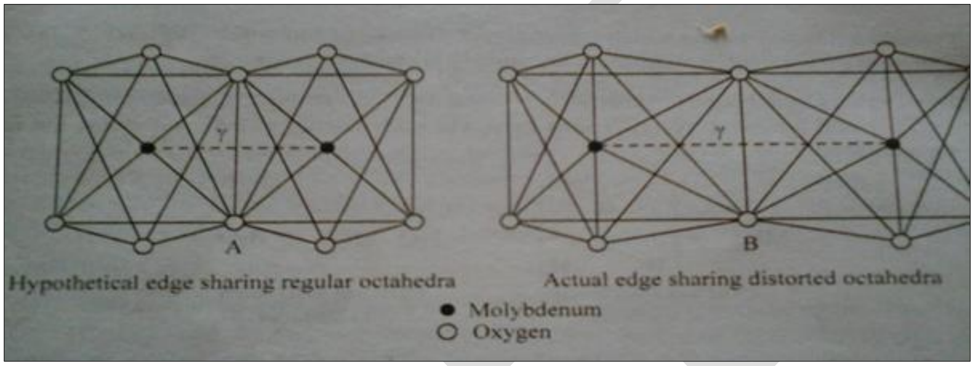


$[Mo_8 O_{26}]^{4-}$



$[Mo_{10} O_{34}]^{8-}$

The sharing of edges between MO_6 octahedra causes repulsion between the metal ions . This repulsion is reduced partially by displacement of M from the exact centre of the octahedra . For O atom bonded only to one metal atom , the M–O bond length ~ 1.70 A^0 , while the M-O-M bond length is 1.90 A^0. Repulsion should increase with increase in the ionic radius. V^{5+}(68pm) < Mo^{6+} (73pm) < W^{6+}(73pm) < Nb^{5+}(78pm) < Ta^{5+}(78pm) and is in agreement with the degree of distortion observed. The most common edge shared polyanions are $(V_{10}O_{28}]^{6-}$, $(Mo_7O_{24}]^{6-}$, $(Mo_8O_{26}]^{4-}$, $(W_6O_{19}]^{2-}$, $(W_7O_{24}]^{6-}$, $(Ta_6O_{19}]^{8-}$. To form larger polyanions such as $(W_{12}O_{42}]^{12-}$or $(H_2W_{12}O_{40}]^{6-}$, the edge sharing must give way to apex sharing ie, larger aggregates require some extent of apex sharing in order to reduce cation – cation repulsion.



The structure of regular edge sharing MO_6 octahedra and the distorted edge sharing MO_6 octahedra

As the polymerization increases it becomes more & more difficult to have all the metal ions to distort from their position to reduce the repulsion. Ultimately the sharing of edges ceases, since the requisite distortion become impossible and growth limitation occurs. The stage of saturation of edge sharing of MO_6 Is reached earlier by isopolyanions of relatively bigger metal ions . The edge sharing of MO_6 can occur to a greater extent in the isopoly anions of small sized Mo^{6+} than bigger sized W^{6+} ion. Elements other than V, Nb, Ta, Mo & W do not form isopoly anions. Other ions which have appropriate radii (Al^{3+}, Ga^{3+}, I^{7+}) for discrete poly anion formation , instead form chains , sheets & 3D frameworks. Why polymerization stop for isopoly anions? An O atom in a terminal position in an isopoly anion is strongly π bonded to a transition metal such as Mo or W . These terminal O atoms are never found trans to each other. Instead they are always located opposite to σ bonding bridging O atom . The effect is that the metal is displaced in the direction of terminal O . Metal ions such as Al, Ga are poor π acceptors. Thus their terminal O atoms are not stabilized & can repeatedly attack other units to give continuing polymerization. The terminal O atoms of the transition metal poyanions however are stabilized by π bonding & has less affinity for adjacent metal units.

Isopolytungstate

The formation of isopolytungstate is similar to that of molybdates. But its chemistry is even more difficult. There are three types of polytungstates.
(1) Normal tungstates (2)Paratungstates (3)Metatungstates

Normal tungstates: general formula , $M_m(WO_4)_n$. eg: Na_2WO_4 & $Na_2W_2O_7$ Preparation : by dissolving tungsten trioxide in NaOH & crystallising the solution.

The simple tungstate $\mathbf{WO_4^{2-}}$ exist in strongly basic solution . Acidification results in the formation of polymers built up from WO_6 octahedra. The nature of tungsten species formed depends on pH .

Upon acidification of WO_4^{2-} , **paratungstate A , $\mathbf{(W_6O_{21})^{6-}}$** form rapidly. Its protonated form $(H\ W_6O_{21})^{5-}$ also has been detected. On keeping this solution for some days the salts of dodecameric anion, paratungstate B $(H_2\ W_{12}O_{42})^{10-}$ is formed. Further acidification produces **metatungstates$\mathbf{(H_2\ W_{12}O_{40})^{6-}}$** which are more soluble but will crystallize either on standing for some months or on prolonged heating. Tungsten oxide is precipitated at P^H =1

$(H\ W_6O_{21})^{5}$ --------------------------- $(H_2\ W_{12}O_{42})^{10-}$

paratungstate A paratungstate B $(H\ W_6O_{20})^{3}$ $(H_2\ W_{12}O_{40})^{6-}$

Pseudometatungstate metatungstates

There is greater incidence of corner sharing in the higher poly tungstates than in the poly molybdates. The metatungstate ion $(H_2\ W_{12}O_{40})^{6-}$ is composed of 4 identical tritungstate groups. Each of these tritungstate group is made up of $3WO_6$ octahedra. The 4 tritungstate groups are then attached to each other by corner sharing resulting in a cavity in the centre of the ion.

The isopolytungstate system differs from isopolymolybdate system in that, the equilibrium of the molybdenum species is complete within a matter of minutes, whereas for tungsten, this may take several weeks.

Isopolyvanadate

In strongly alkaline solution the ion present is VO_4^{3-} or $[VO_3(OH)]^{2-}$. As the pH is reduced from 13 to 8 condensation to $[V_2O_7]^{4-}$ takes place. Further reduction pH to 7.2 gives the so called metavanadate. In the solid metavanadate the anion consists of chains of VO_4 tetrahedra linked by sharing corners & the species in solution is almost a trimer $[V_3O_9]^{3-}$ or tetramer $[V_4O_{12}]^{4-}$. As the pH is still reduced further orange decavanadate is produced at about p H =6 $[V_{10}O_{28}]^{6-}$. The ion is protonated to $[HV_{10}O_{28}]^{5-}$ & $[[H_2V_{10}O_{28}]^{4-}$ as the p H is lowered to 3.5 . Many salts of decavanadate ions, for example $[Ca_3\ V_{10}O_{28}]$ occur as minerals . $[V_{10}O_{28}]^{6-}$ are found to be made up of 10 VO_6 octahedra fused together joined by sharing edges.
In very acid solution at a pH =2 , VO_2^+ ions are formed and finally hydrated V_2O_5 separates.

Some of the alkali salts of isopolyvanadates are colourless but others are coloured. The salts with alkali metal to vanadium ratio at least unity are usually colourless, while salts with alkali metal to vanadium ratio less than unity are coloured.

Isopolyniobates & tantalates.

Both niobium & tantalum form condensed oxoanions in aqueous solution . Their hydrated pentoxides are precipitated very rapidly. Hexa niobates & hexatantalates of the type M(Nb /Ta

$)_6 O_{19} .16 H_2O$ may be prepared by pentoxides with KOH & precipitating the salt by means of ethanol. The solutions are stable only at high p H . Under more acidic condition precipitation of the hydrated pentoxide occurs. The tantalum compounds are freely soluble in water & it is found to contain highly symmetrical anion.

Many different techniques have been employed in the study of isopolyanions The important ones are p H measurements , cryoscopy, ion –exchange, uv – viscible spectroscopy & NMR spectroscopy.

HETEROPOLY ACIDS

The principle underlying the formation of hetropoly anions is that the anion of the second acid provides a central group, around which octahedra such as MoO_6 or WO_6 condense by a process of oxygen sharing. It is important to note that the central group $(PO_4)^{3-}$ also share its oxygen atoms with surrounding octahedra.

A variety of elements can act as central atom in hetropoly acids . They include many nonmetals and many transition metals . Salts with smaller cations are soluble in water, while salts of larger cations are usually insoluble.

In these ions , the hetero atoms are situated inside the cavities or baskets formed by MO_6 octahedra of the parent M atoms & are bonded to oxygen atoms of the adjacent MO_6octahedra. The hetero polyacids are classified in terms of the ratio of the number of central atoms to the number of metal atoms associated with the surrounding octahedral. Four major classes are found

(1) **1 : 12 tetrahedral :** → These occur with small hetero atoms such as P^5, As^5, Si^4, Ti^4 which yield tetrahedral oxoanions . Some important members of this class include $[Co W_{12} O_{40}]^{6-}$ and $(NH_4)_3 [P Mo_{12}O_{40}]$.

(2) **2 : 18 tetrahedral :** → If solutions of 1:12 anions $[X^5 M_{12} O_{40}]^{3-}$ are allowed to stand 2:18 $[X_2 M_{18} O_{62}]^{6-}$ ions are generally produced. The ion is best considered to be formed from 1:12 anions each of which loses $3MO_6$ octahedra before fusing together.

(3) **1: 6 octahedral :** → These are formed with larger hetro atoms which coordinate to 6 edge sharing MO_6 octahedra. Eg. $[Te^6 Mo_6 O_{24}]^{6-}$ and $[M^3 Mo_6 O_{24}]^{6-}$ result from a ring of six octahedra about the hetro atom.

(4) **1: 9 octahedral :** → The structures of these ions are based on edge sharing MO_6 octahedra .eg. $[Mn Mo_9 O_{32}]^{6-}$ and $[Ni^4 Mo_9 O_{32}]^{6-}$

Preparation.

These hetero anions can be formed by acidification of solutions containing the requisite simple anions or by introduction of the hetero element after first acidifying the molybdate or tungstate.

$$HPO_4^{2-} + 12 MoO_4^{2-} + 24 H^+ \text{-----------}\rightarrow [P\ Mo_{12} O_{40}]^{3-} + 12 H_2O$$

$$WO_4^{2-} + H^+ \rightarrow Co^{2+} \text{-----------} \rightarrow [Co_2 W_{11} O_{40} H_2]^{8-}$$

A familiar example is the phosphomolybdate test for phosphates. A solution containing phosphate is treated with excess of ammonium molybdate solution , made strongly acidic with nitric acid & warmed , yellow ammonium phosphomolybdate is formed $(NH_4)_3[P\,Mo_{12}O_{40}]$.

During the preparation of hetero polyacids the following precautions must be taken

(1) Exact pH should be maintained.
(2) Exact quantities oftwo types of acid anions must be taken.
(3) These should be prepared at room temperature.

Structures of heteropoly acids 12 – heteropoly acids :

The structure of $[X^n\,Mo_{12}\,O_{40}]^{8-n}$ or $[PW_{12}\,O_{40}]^{3-}$ (12polyacids) is often called **Keggins structure** . The first structural study was made on 12 phospho tungstic acid. The central PO_4 group is surrounded by 12 WO_6 octahedra . Each corner O atom of the PO_4 group is shared with 4 octahedra, each of which also shares one O atom with its two neighbours. The octahedra are further linked together by sharing corners. The same structure is found in a number of hetero polyacids based on elements other than phosphorus (eg: silico tungstates, borotungstates, silico molybdates). (Ref. Emelius & Sharp, page 287)

6 – heteropoly acids:

In 6 – heteropoly acids the central atom is larger (I , Te or Rh) & capable of coordinating with 6 atoms of oxygen. Six MO_6 octahedra are arranged in a hexagonal annulus so as to share two corners with each of two neighbouring octahedral. The central cavity of the resulting $[M_6\,O_{24}]^{12}$ structure is found to be just large enough to accommodate an octahedron corresponding with that of hetero atom. This structure was identified in potassium & ammonium molybdo tellurates which contain $[Te\,Mo_6\,O_{24}]^{6-}$ ion.

-

18– heteropoly acids:

The structure of $[X_2\,M_{18}\,O_{62}]^{6-}$ or $[P_2\,W_{18}\,O_{62}]^{6-}$ sometimes called the **Dawson structure** .

Anions of the Keggins (1:12) & Dawson (2:18) structures can undergo reduction to intense blue mixed valance species without lose of structure known as heteroploy blues. These reduction products are formed rapidly. These heteropoly blues find application in the quantitative determination of Si, Ge, P & As and commercially as dyes and pigments . The reduction evidently occurs on individual M atoms. Transfer of electrons from M^V to M^{VI} ion is then responsible for the intense charge transfer absorption.

Tungsten & Molybdenum bronzes.

These materials owe their name to their metallic lusture and are used in the production of bronze paints. They have good electrical conductivity in which the charge carriers are electrons. Tungsten bronze is prepared by the reduction of sodium tungstate with hydrogen at red heat.

Applications of poly acids

(1) The polyacids and their salts of P,As, Si & B are used in the determination of these & other elements by volumetric, gravimetric & colorimetric methods.
(2) Some polyacids are used for the detection of phosphates and arsenates .
(3) They are used in the preparation of pigments.
(4) The recovery of metals such as V, Mo, W & U from their ores often involve the formation of polyacids.
(5) The heteropolyacids are used for detecting various alkaloids and albumin- they form insoluble precipitates with alkaloids and albumins.
(6) They are used as the starting materials for the manufacture of catalysts particularly for vapour phase oxidation & reduction.
(7) Due to their great solubility , these acids are used for the preparation of solutions of high specific gravity and such solutions are used as liquids for the separation of minerals of different densities.

Suggested Materials

Text Books:

T1: James E. Huheey, Ellen A. Keiter, Richard L. Keiter, Okhil K. Medhi. (2013). *Inorganic Chemistry-Principles of structure and Reactivity* (IV Edition) New Delhi pearson education, India

T2: Cotton, F.A,G.,Murillo,C.A., & Bochmann, M.(2007). *Advanced Inorganic Chemistry* (VI Edition).New York:John Wiley & Sons.

POSSIBLE QUESTIONS

Part A

(1 mark Q.No. 1 to 20)

(Online Examination)

Part B(Each carry two marks)

1. What are clusters?

2. Give an example for inorganic chain. 23.Write down the types of silicates.

3. What are siloxanes.

4. State Wade’s rule.

5. Give examples for sulphur-nitrogen ring compounds.

6. Write down few chemical properties of boron hydrides.

PART C (Each carry 8 marks)

1. Illustrate with suitable examples what are rings, cages and metallic clusters.

2.Explain in detail about the isopoly and heteropoly acids of vanadium and tungsten.

3.Explain the π bonding in phosphazenes

4. Descripe the molecular orbital treatment of bonding in diborane.
5. Why borazine is isoelectronic with benzene? Explain.
6. Discuss the structure of Sulphur and Nitrogen compounds
7. Write notes on organometallic clusters
8. Discuss the preparation, properties and uses of silicone polymers. 36.Explain the heteropoly acids of molybdenum. Give two examples

9. Discuss about carboranes and metallocarboranes.
10. Discuss the structure of isopolymolybdates and tungstates.

19CHP102
Karpagam Academy of Higher Education
Coimbatore-21

(For the candidate admitted on 2019 onwards)
Department of Chemistry
I- semester
INORGANIC CHEMISTRY-I (Nuclear Chemistry and Metalic clusters)

UNIT I- Objective Questions for online examination (Each carry 1 Marks)

S.No	Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers
1	Which one of the following is the organophosphorus compound?	PCl_5	PCl_3	PPh_3	NH_4OH	PPh_3
2	Metals and non metals combine very easily to form	Chains	Rings	Cage	Cluster	Cluster
3	Silicon- silicon bonds are weaker than?	Hydrogen-hydrogen bonds	Carbon-carbon bonds	Nitrogen-nitrogen bonds	Carbon-nitrogen bonds	Carbon-carbon bonds
4	Example for long chain silanes	Si_nH_{2n+2}	Si_n	Si+H	Si_nH_{2n}	Si_nH_{2n+2}
5	Heterocatinated compound are formed by the	Decomposed	Condesation of acid	Dehydration of acid	Addition of acid	Dehydration of acid
6	Silanes are difficult to handle because they are?	Active	Proactive	Reactive	Non-reactive	Reactive
7	Polyphosphates are called	Disodium phosphate	Sodium tetraphosphate	Phospazines	Sodium triphosphate	Sodium triphosphate
8	Sodium triphosphate is main builders of	Detergents	Paints	Lubricants	Pigments	Detergents
9	Ammonium chloride reacts with boron trichloride to give	Phospazene	Borazine	Boron	Carbarane	Borazine
10	Diborane reacts with ammonia to give	Phospazene	Borazine	Boron	Carbarane	Borazine
11	The chemistry of germanes is similsr to that of?	Silicons	Silanes	Phospazene	Borazine	Silanes
12	Physical properties of benzene and borazines are	Same	Slightly same	Slightly different	Different	Same

13	Which One of the following is important framework in aluminosilicates	Boggsite	Pyroxenes	Diopside	Zeolites	Zeolites
14	The open-chain structure becomes increasingly unstable relative to cyclic structures as the	Increases	Decreases	No change	Increases or increase	Increases
15	Low molecular weight silicones will dissolved in	Methanol	Phenol	Benzene	Acetic acid	Benzene
16	Silicone fluids is used for	Solvents	Lubricants	Paints	Degradents	Lubricants
17	Hybridization of Phosphorous is	SP^3	SP^2	SP	dSP^3	SP^3
18	The simplest cage type molecule is	White phosphorus	Phosphorus	Red phosphorus	Green phosphorus	White phosphorus
19	Hittorf's phosphours is	White phosphorus	Phosphorus	Red phosphorus	Green phosphorus	Red phosphorus
20	The chain form for selenium is?	Stable	Most stable	Less stable	Unstable	Most stable
21	Silicone fluids used for	Antifoam agents	Solvents	Detergents	Paints	Antifoam agents
22	The simplest boron hydride is	Boron trifluoride	Diboranes	tri boranes	Boron difluoride	Diboranes
23	Hybridisation of diborane is	SP^2	SP	dSP	SP^3	SP^3
24	Which structure is related to close structure	Tube	Boat	Cup	Chair	Cup
25	Two vertex boron atom are removed from the closo structure to form	Cage structure	Ring structure	Nido structure	Arachno structure	Arachno structure
26	How many terminal bond contain diborane	Three	Two	one	Four	Four
27	Hybridization of boran is	SP^3	SP^2	SP	dSP^3	SP^2
28	Electron frame work for arachno structure is	2n+4	2n+2	2n+6	2n+5	2n+6
29	The simplest heterocatenated compounds are formed by the dehydration of?	Acid	Alkali	Base	Salt	Acid
30	General form of organometallic cluster is	$M_x(CD)_y$	$M_x(CO)_y$	$M_x(CN)_y$	$M_x(CA)_y$	$M_x(CO)_y$
31	Low formal oxidation states of metals are	-1 to +1	-3 to +3	–0 to +0	-2 to +2	-1 to +1
32	Electron frame work for endo structure is	2n+4	2n+2	2n+6	2n+5	2n+2
33	Electron frame work for closo structure is	2n+4	2n+2	2n+6	2n+5	2n+4

34	Borazine on storage	Addition slowly	Polymerize	Decompose slowly	Decompose rapidly	Decompose slowly
35	Phospazene on storage	Addition slowly	Polymerize	Decompose slowly	Decompose rapidly	Decompose slowly
36	Borazine undergo addition reaction with HCl because of	Resonance	Electronegativity	Electronaffinity	Electrochemical reactivity	Electronegativity
37	How many valance electrons present in dinuclear complex	18	17	19	12	18
38	How many valance electrons present in mononuclear complex	17	18	19	12	17
39	Olivine gets its name from which colour?	Red	Blue	Green	Orange	Green
40	Borazine isoelectronic with	Benzene	Naphthalene	Pyridine	Anthracene	Benzene
41	Which one of the following is the example of pyroxenes?	Diopside	PCl_3	PPh_3	NH_4OH	PPh_3
42	Polythiazyl shows some physical properties similar to that of	Metal	Nonmetal	Metalloid	Semiconductor	Metal
43	The isopolyanions are the closest packed array of	Metal ion	Oxides ion	Chloride ion	Sulphide ion	Oxides ion
44	How many terminal hydrogen atom contain diborane	Three	Two	One	Four	Four
45	Which one is non-metal	Nitrogen	Tetrazene	Diphosphine	Distannane	Nitrogen
46	The halogens are known to form reasonably stable chains in?	Polyhalide anions	Polyhalide cations	Anions	Cations	Polyhalide anions
47	The energy of activation of alkanes is very high compared to	Silanes	Polysilanes	Carbene	Nitrene	Silanes
48	Which one is similar to that of silanes	Diphosphine	Distannane	Germanes	Plumbane	Germanes
49	Colour of amosite is	Green asbestos	Grey-brown asbestos	Blue asbestos	Black asbestos	Grey-brown asbestos
50	Colour of crociddite is	Green asbestos	Grey-brown asbestos	Blue asbestos	Black asbestos	Blue asbestos
51	The higher activation energy of alkanes is due to	C-C bond	CH-CH bond	C=C bond	CH=CH bond	C-C bond
52	Oxygen forms no chain longer than?	2 atoms	3atoms	4 atoms	5 atoms	3atoms

53	Silicone resin solution is used in the manufacture of	Soap	Oil	Paints	Detergents	Paints
54	Zeolites also behave as	Acidic catalyst	Basic catalyst	Ordinary catalyst	No catalyst	Acidic catalyst
55	Silicone fluids obtained from	Dibromo dimethylsilane	Dichloro dimethylsilane	Diammino dimethylsilane	Dihydro dimethylsilane	Dichloro dimethylsilane
56	Ultramarine is used for	white pigment	Blue pigment	Green pigment	Yellow pigment	Blue pigment
57	The total number of isomer possible for $N_3P_3Cl_3F_3$ is	1	2	3	4	2
58	Which of the following is known as pseudo proteins	Phosphosulpur	Phospham	Borazine	Phosphonitilic chloride	Phosphonitilic chloride
59	How many bridged hydrogen atom contain diborane	1	2	3	4	2
60	Which one of following have high thermal stability?	Silicone	Nitrogen	Organo silicone	Silicon	Silicone

UNIT II

SYLLABUS

Metallic state-free electron,band and zone theories-non-stoichiometry-point defects in solids-Schottky and Frenkel defects-linear effects-dislocation-effects due to dislocation-electrical properties of solids-insulators-intrinsic semiconductors- n and p type and super conductors-ceramics elementary treatment.
Basic Organometallic Chemistry:Common notation used in organometallic chemistry-Metal-ligand interactions;Basic principles of ligand-field theory;molecular orbital theory-18 electron rule-common organometallic bonding modes-Introduction to metal-centered organometallic reactions.

Free-electron theory of metals

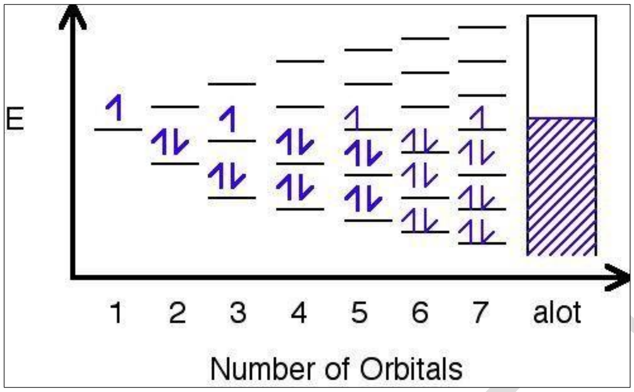
The treatment of a metal as containing a gas of electrons completely free to move within it. The theory was originally proposed in 1900 to describe and correlate the electrical and thermalpropert ies of metals. Later, quantum mechanics became the basis for the theory of most of thegeneral properties of simple metals such as sodium, with one free electron per atom,magnesium with two, and aluminum with three. Transition metals, such as iron, have partiallyfilled electronic d states a nd are not treated by the free-electron model.

Three years after J. J. Thomson's 1897 discovery of the electron, P. Drude suggested that the transport properties of metals might be understood by assuming that their electrons are free and in thermal equilibrium with their atoms. This theory was made more quantitative by H. A.Lorentz. Assuming that the mean free path of electrons was limited by collisions, he was able to derive Ohm's law for the electrical conductivity and obtain the ratio of thermal to electrical conductivity in excellent agreement with experiment. This ratio, divided by the absolute temperature, is called the Wiedemann-Franz ratio and had been observed to be universal 50years earlier.
The theory, however, had two major shortcomings. First, it predicted a large component of the specific heat of a metal, not present in insulators, which was not observed. Second, comparison of the theory with experiment indicated that the mean free path of the electrons became extremely large at low temperatures; the model offered no justification.

In 1928 A. Sommerfeld revised Lorentz's treatment by using quantum statistics, which removed the difficulty of the specific heat without losing the successful description of transport properties. The resulting theory remains the basis for the understanding of most transport properties of metal s and semiconductors. At about the same time, W. V. Houston and F. Bloch solved the quantum-mechanical wave equation for electrons in a regular periodic structure, finding that they could indeed have arbitrarily large mean free paths if there were no defects in the periodicity, thereby putting the free-electron theory on a firm basis.

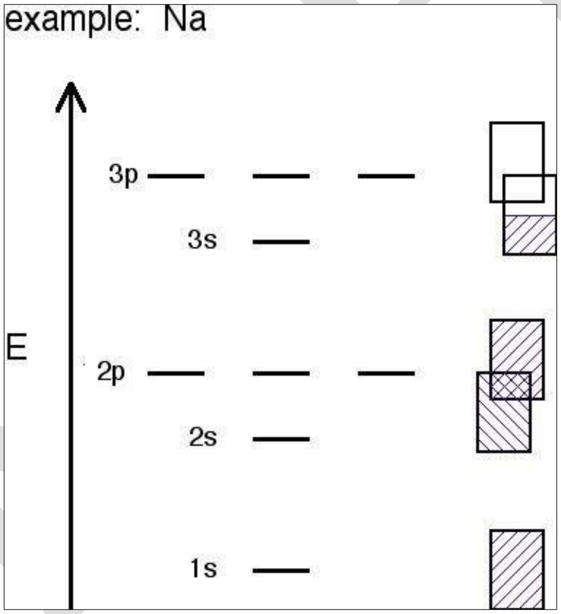
Band theory of metals

Band Theory was developed with some help from the knowledge gained during the quantum revolution in science. In 1928, Felix Bloch had the idea to take the quantum theory and apply it to solids. In 1927, Walter Heitler and Fritz London discovered bands- very closely spaced orbitals with not much difference in energy.



In this image, orbitals are represented by the black horizontal lines, and they are being filled with an increasing number of electrons as their amount increases. Eventually, as more orbitals are added, the space in between them decreases to hardly anything, and as a result, a band is formed where the orbitals have been filled.

Different metals will produce different combinations of filled and half filled bands.



Sodium's bands are shown with the rectangles. Filled bands are colored in blue. As you can see, bands may overlap each other (the bands are shown askew to be able to tell the difference between different bands). The lowest unoccupied band is called the conduction band, and the highest occupied band is called the valence band.

Bands will follow a trend as you go across a period:

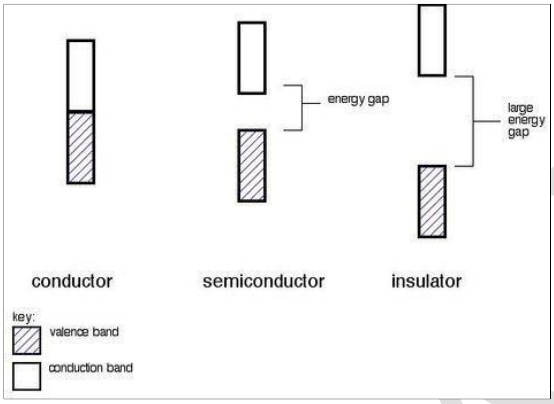
- In Na, the 3s band is 1/2 full.

- In Mg, the 3s band is full.
- In Al, the 3s band is full and the 3p ban is 1/2 full... and so on.The probability of finding an electron in the conduction band is shown by the equation:

$$P=1e\Delta E/RT+1(6.8.1)(6.8.1)P=1e\Delta E/RT+1$$

The ΔE in the equation stands for the change in energy or energy gap. t stands for the temperature, and R is a bonding constant. That equation and this table below show how the bigger difference in energy is, or gap, between the valence band and the conduction band, the less likely electrons are to be found in the conduction band. This is because they cannot be excited enough to make the jump up to the conduction band.

Conductors, Insulators and Semiconductors



A. Conductors

Metals are conductors. There is no band gap between their valence and conduction bands, since they overlap. There is a continuous availability of electrons in these closely spaced orbitals.

B. Insulators

In insulators, the band gap between the valence band the the conduction band is so large that electrons cannot make the energy jump from the valence band to the conduction band.

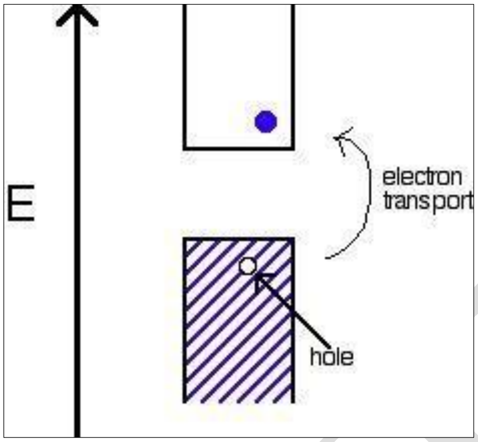
C. Semiconductors

Semiconductors have a small energy gap between the valence band and the conduction band. Electrons can make the jump up to the conduction band, but not with the same ease as they do in conductors.

There are two different kinds of semiconductors: **intrinsic** and **extrinsic**.

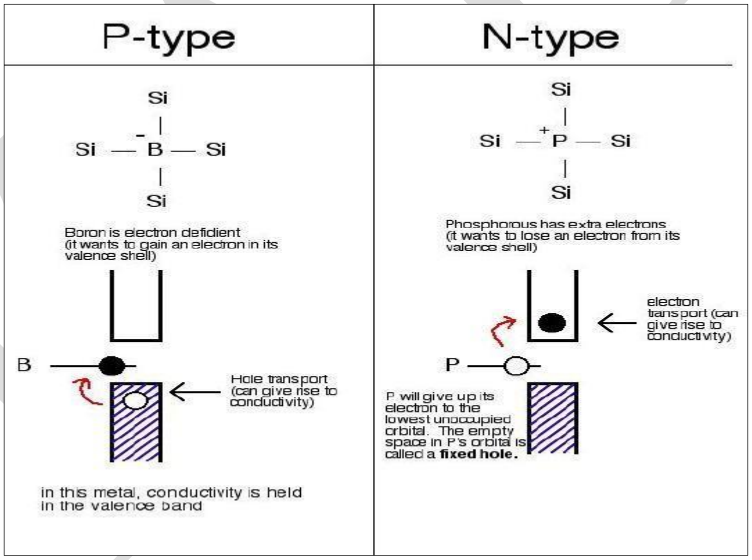
i. Intrinsic Semiconductors

An intrinsic semiconductor is a semiconductor in its pure state. For every electron that jumps into the conduction band, the missing electron will generate a hole that can move freely in the valence band. The number of holes will equal the number of electrons that have jumped.



ii. Extrinsic Semiconductors

In extrinsic semiconductors, the band gap is controlled by purposefully adding small impurities to the material. This process is called **doping**. Doping, or adding impurities to the lattice can change the electrical conductivity of the lattice and therefore vary the efficiency of the semiconductor. In extrinsic semiconductors, the number of holes will not equal the number of electrons jumped. There are two different kinds of extrinsic semiconductors, p-type (positive charge doped) and n-type (negative charge doped).

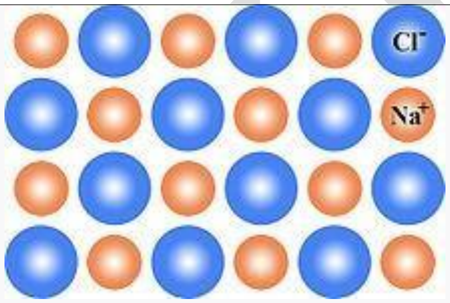


SCHOTTKY AND FRENKEL DEFECTS

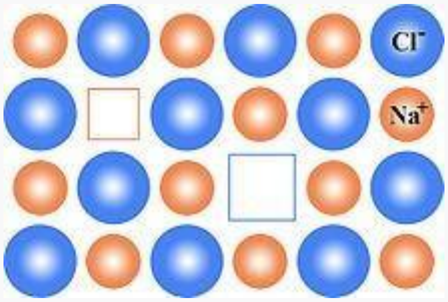
A **Schottky defect** is a type of point defect in a crystal lattice named after Walter H. Schottky. In non-ionic crystals it means a lattice vacancy defect.

In ionic crystals, the defect forms when oppositely charged ions leave their lattice sites, creating vacancies. These vacancies are formed in stoichiometric units, to maintain an overall neutral charge in the ionic solid. The vacancies are then free to move about as their own entities. Normally these defects will lead to a decrease in the density of the crystal. The followings are the chemical equations in Kröger–Vink notation for the formation of Schottky defects in TiO_2 and $BaTiO_3$.

The defect can be illustrated schematically with a two-dimensional diagram of a sodium chloride crystal lattice:



The defect-free NaCl structure



Schottky defects within the NaCl structure

Definition

Schottky defects consists of unoccupied anion and cation sites in a stoichiometric ratio. For a simple ionic crystal of type A^-B^+, a Schottky defect consists of a single anion vacancy (A) and a single cation vacancy (B), or v•A + v′B following Kröger–Vink notation. For a more general crystal with formula A_xB_y, a Schottky cluster is formed of x vacancies of A and y vacancies of B, thus the overall stoichiometry and charge neutrality are conserved.

Schottky defects are observed most frequently when there is a small difference in size between cations and anions. This is produced as the result of the thermal incorporation of unoccupied lattice sites from the exterior of the crystal. The lattice undergoes thermal vibration and thermal expansion when the temperature is raised above 0 K. When it happens the pair of vacancies are incorporated in the crystal.

So electrical neutrality is maintained inside the crystals.

The vacancies that make up the Schottky defects have opposite charge, thus they experience a mutually attractive Coulomb force. If sufficient thermal energy is available the vacancies may migrate through the crystal lattice, and form bound clusters.

The bound clusters are typically less mobile than the dilute counterparts, as multiple species need to move in a concerted motion for the whole cluster to migrate. This has important implications for numerous functional ceramics used in a wide range of applications, including ion conductors, Solid oxide fuel cells and nuclear fuel.

Examples

This type of defect is typically observed in highly ionic compounds, highly coordinated compounds, and where there is only a small difference in sizes of cations and anions of which the compound lattice is composed. Typical salts where Schottky disorder is observed are NaCl, KCl, KBr, CsCl and AgBr. For engineering applications, Schottky defects are important in oxides with Fluorite structure, such as CeO_2, cubic ZrO_2, UO_2, ThO_2 and PuO_2.

Effect on density

Since the total number of ions present in the crystal with this defect is less than the theoretical number of ions for a crystal of its volume, the density of the solid crystal is less than the theoretical density of the material.

Frenkel defect

A Frenkel defect is a type of defect in crystalline solids wherein an atom is displaced from its lattice position to an interstitial site, creating a vacancy at the original site and an interstitial defect at the new location within the same element without any changes in chemical properties.

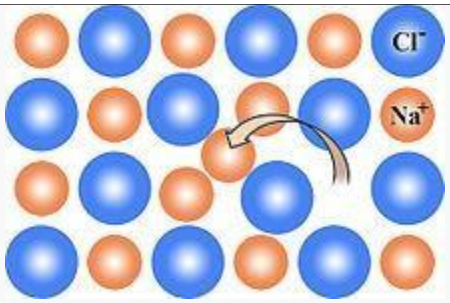
Definition

A **Frenkel defect**, **Frenkel pair**, or **Frenkel disorder** is a type of point defect in a crystal lattice. The defect forms when an atom or smaller ion (usually cation) leaves its place in the lattice, creating a vacancy, and becomes an interstitial by lodging in a nearby location.[2] Their prime mechanism of generation is by particle irradiation, as their equilibrium concentration according to the Ashwath Distribution is much smaller than the pure vacancies distribution, due to the large energy necessary for the creation of the associated interstitial atoms. The phenomenon is named after the Soviet physicist Yakov Frenkel, who discovered it in 1926.

Effect on density

This defect does not have any impact on the density of the solid as it involves only the migration of the ions within the crystal, thus preserving both the volume as well as mass.

Examples



The Frenkel defect within the NaCl structure

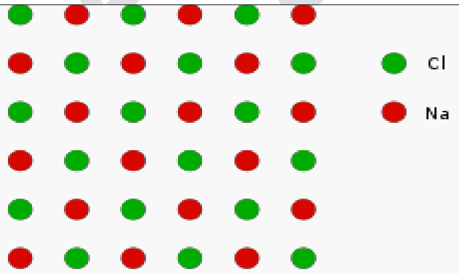
Frenkel defects are exhibited in ionic solids with a large size difference between the anion and cation (with the cation usually smaller due to an increased effective nuclear charge) Some examples of solids which exhibit Frenkel defects:

- zinc sulfide,
- silver(I) chloride,
- silver(I) bromide (also shows Schottky defects),
- silver(I) iodide.

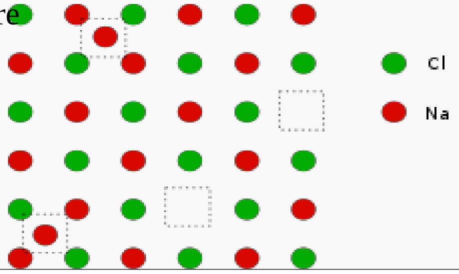
These are due to the comparatively smaller size of Zn^{2+} and Ag^{+} ions.

For example, consider a lattice formed by X^{n+} and M^{n+} ions. Suppose an M ion leaves the M sublattice, leaving the X sublattice unchanged. The number of interstitials formed will equal the number of vacancies formed.

The defect can be illustrated with the example of the sodium chloride crystal structure. The diagrams below are schematic two-dimensional representations.



The defect-free NaCl structure



Two Frenkel defects within the NaCl structure

SUPERCONDUCTORS

High-temperature superconductors (abbreviated **high-T_c** or **HTS**) are materials that behave as superconductors at unusually high temperatures.The first high-T_c superconductor was discovered in 1986 by IBM researchers Georg Bednorz and K. Alex Müller, who were awarded the 1987 Nobel Prize in Physics "for their important break-through in the discovery of superconductivity in ceramic materials".

Whereas "ordinary" or metallic superconductors usually have transition temperatures (temperatures below which they are superconductive) below 30 K (−243.2 °C), and must be cooled using liquid helium in order to achieve superconductivity, HTS have been observed with transition temperatures as high as 138 K (−135 °C), and can be cooled to superconductivity using liquid nitrogen. Until 2008, only certain compounds of copper and oxygen (so-called "cuprates") were believed to have HTS properties, and the term high-temperature superconductor was used interchangeably with cuprate superconductor for compounds such as bismuth strontium calcium copper oxide (BSCCO) and yttrium barium copper oxide (YBCO). Several iron-based compounds (the iron pnictides) are now known to be superconducting at high temperatures.

In 2015, hydrogen sulfide (H_2S) under extremely high pressure (around 150 gigapascals) was found to undergo superconducting transition near 203 K (-70 °C), the highest temperature superconductor known.

For an explanation about T_c (the critical temperature for superconductivity), see Superconductivity § Superconducting phase transitionand the second bullet item of BCS theory § Successes of the BCS theory.

History

The phenomenon of superconductivity was discovered by Kamerlingh Onnes in 1911, in metallic mercury below 4 K (−269.15 °C). Ever since, researchers have attempted to observe superconductivity at increasing temperatures with the goal of finding a room-temperature superconductor. In the late 1970s, superconductivity was observed in certain metal oxides at temperatures as high as 13 K (−260.1 °C), which were much higher than those for elemental metals. In 1986, J. Georg Bednorz and K. Alex Müller, working at the IBM research lab near Zurich, Switzerland were exploring a new class of ceramics for superconductivity. Bednorz encountered a barium-doped compound of lanthanum and copper oxide whose resistance dropped to zero at a temperature around 35 K (−238.2 °C). Their results were soon confirmed by many groups, notably Paul Chu at the University of Houston and Shoji Tanaka at the University of Tokyo.

Shortly after, P. W. Anderson, at Princeton University came up with the first theoretical description of these materials, using the resonating valence bond theory, but a full understanding of these materials is still developing today. These superconductors are now known to possess a d-wave pair symmetry. The first proposal that high-temperature cuprate superconductivity involves d-wave pairing was made in 1987 by Bickers, Scalapino and Scalettar, followed by three subsequent theories in 1988 by Inui, Doniach, Hirschfeld and Ruckenstein, using spin-fluctuation theory, and by Gros, Poilblanc, Rice and Zhang, and by Kotliar and Liu identifying d-wave pairing as a natural consequence of the RVB theory. The confirmation of the d-wave nature of the cuprate superconductors was made by a variety of experiments, including the direct observation of the d-wave nodes in the excitation spectrum through Angle Resolved Photoemission Spectroscopy, the observation of a half-integer flux in tunneling experiments, and indirectly from the temperature dependence of the penetration depth, specific heat and thermal conductivity.

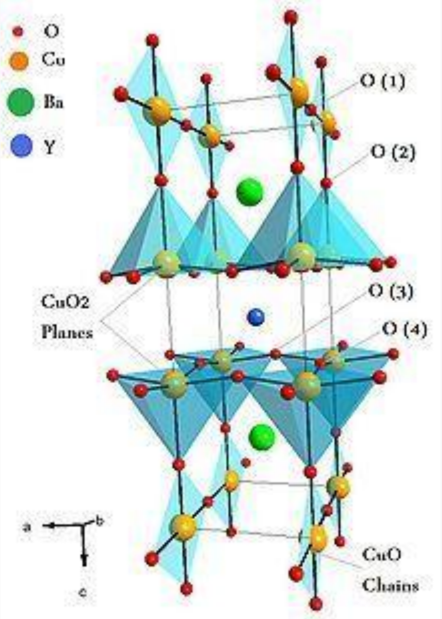
Until 2015 the superconductor with the highest transition temperature that had been confirmed by multiple independent research groups (a prerequisite to be called a discovery, verified by peer review) was mercury barium calcium copper oxide ($HgBa_2Ca_2Cu_3O_8$) at around 133 K.

After more than twenty years of intensive research, the origin of high-temperature superconductivity is still not clear, but it seems that instead of electron-phonon attraction mechanisms, as in conventional superconductivity, one is dealing with genuine electronicmechanisms (e.g. by antiferromagnetic correlations), and instead of conventional, purely s-wave pairing, more exotic pairing symmetries are thought to be involved (d-wave in the case of the cuprates; primarily extended s-wave, but occasionally d-wave, in the case of the iron-based superconductors). In 2014, evidence showing that fractional particles can happen in quasi two-dimensional magnetic materials, was found by EPFL scientists lending support for Anderson's theory of high-temperature superconductivity.

Crystal structures of high-temperature ceramic superconductors

The structure of high-T_c copper oxide or cuprate superconductors are often closely related to perovskite structure, and the structure of these compounds has been described as a distorted, oxygen deficient multi-layered perovskite structure. One of the properties of the crystal structure of oxide superconductors is an alternating multi-layer of CuO_2 planes with superconductivity taking place between these layers. The more layers of CuO_2, the higher T_c. This structure causes a large anisotropy in normal conducting and superconducting properties, since electrical currents are carried by holes induced in the oxygen sites of the CuO_2 sheets. The electrical conduction is highly anisotropic, with a much higher conductivity parallel to the CuO_2 plane than in the perpendicular direction. Generally, critical temperatures depend on the chemical compositions, cations substitutions and oxygen content. They can be classified as super stripes; i.e., particular realizations of super lattices at atomic limit made of superconducting atomic layers, wires, dots separated by spacer layers, that gives multiband and multi gap superconductivity.

YBaCuO superconductors



YBCO unit cell

The first superconductor found with $T_c > 77$ K (liquid nitrogen boiling point) is yttrium barium copper oxide ($YBa_2Cu_3O_{7-x}$); the proportions of the three different metals in the $YBa_2Cu_3O_7$superconductor are in the mole ratio of 1 to 2 to 3 for yttrium to barium to copper, respectively. Thus, this particular superconductor is often referred to as the 123 superconductor.

The unit cell of $YBa_2Cu_3O_7$ consists of three pseudocubic elementary perovskite unit cells. Each perovskite unit cell contains a Y or Ba atom at the center: Ba in the bottom unit cell, Y in the middle one, and Ba in the top unit cell. Thus, Y and Ba are stacked in the sequence [Ba–Y–Ba] along the c-axis. All corner sites of the unit cell are occupied by Cu, which has two different coordinations, Cu(1) and Cu(2), with respect to oxygen. There are four possible crystallographic sites for oxygen: O(1), O(2), O(3) and O(4). The coordination polyhedra of Y and Ba with respect to oxygen are different. The tripling of the perovskite unit cell leads to nine oxygen atoms, whereas $YBa_2Cu_3O_7$ has seven oxygen atoms and, therefore, is referred to as an oxygen- deficient perovskite structure. The structure has a stacking of different layers: (CuO)(BaO)(CuO_2)(Y)(CuO_2)(BaO)(CuO). One of the key feature of the unit cell of $YBa_2Cu_3O_{7-x}$ (YBCO) is the presence of two layers of CuO_2. The role of the Y plane is to serve as a spacer between two CuO_2 planes. In YBCO, the Cu–O chains are known to play an important role for superconductivity. T_c is maximal near 92 K when $x \approx 0.15$ and the structure is orthorhombic. Superconductivity disappears at $x \approx 0.6$, where the structural transformation of YBCO occurs from orthorhombic to tetragonal.

Bi-, Tl- and Hg-based high-T_c superconductors

The crystal structure of Bi-, Tl- and Hg-based high-T_c superconductors are very similar. Like YBCO, the perovskite-type feature and the presence of CuO_2 layers also exist in these superconductors.

However, unlike YBCO, Cu–O chains are not present in these superconductors. The YBCO superconductor has an orthorhombic structure, whereas the other high- T_c superconductors have a tetragonal structure.

The **Bi–Sr–Ca–Cu–O** system has three superconducting phases forming a homologous series as $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+x}$ (n=1, 2 and 3). These three phases are Bi-2201, Bi-2212 and Bi-2223, having transition temperatures of 20, 85 and 110 K, respectively, where the numbering system represent number of atoms for Bi, Sr, Ca and Cu respectively. The two phases have a tetragonal structure which consists of two sheared crystallographic unit cells. The unit cell of these phases has double Bi–O planes which are stacked in a way that the Bi atom of one plane sits below the oxygen atom of the next consecutive plane. The Ca atom forms a layer within the interior of the CuO_2 layers in both Bi-2212 and Bi-2223; there is no Ca layer in the Bi-2201 phase. The three phases differ with each other in the number of CuO_2 planes; Bi-2201, Bi-2212 and Bi-2223 phases have one, two and three CuO_2 planes, respectively. The c axis lattice constants of these phases increases with the number of CuO_2 planes (see table below). The coordination of the Cu atom is different in the three phases. The Cu atom forms an octahedral coordination with respect to oxygen atoms in the 2201 phase, whereas in 2212, the Cu atom is surrounded by five oxygen atoms in a pyramidal arrangement. In the 2223 structure, Cu has two coordinations with respect to oxygen: one Cu atom is bonded with four oxygen atoms in square planar configuration and another Cu atom is coordinated with five oxygen atoms in a pyramidal arrangement.

Tl–Ba–Ca–Cu–O superconductor: The first series of the Tl-based superconductor containing one Tl–O layer has the general formula $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$, whereas the second series containing two Tl–O layers has a formula of $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ with n =1, 2 and 3. In the structure of $Tl_2Ba_2CuO_6$ (Tl-2201), there is one CuO_2 layer with the stacking sequence (Tl–O) (Tl–O) (Ba–O) (Cu–O) (Ba–O) (Tl–O) (Tl–O). In $Tl_2Ba_2CaCu_2O_8$ (Tl-2212), there are two Cu– O layers with a Ca layer in between. Similar to the $Tl_2Ba_2CuO_6$ structure, Tl–O layers are present outside the Ba–O layers. In $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl-2223), there are three CuO2 layers enclosing Ca layers between each of these. In Tl-based superconductors, T_c is found to increase with the increase in CuO_2 layers. However, the value of $T_c$decreases after four CuO_2 layers in $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$, and in the $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ compound, it decreases after three CuO_2layers.

Hg–Ba–Ca–Cu–O superconductor: The crystal structure of $HgBa_2CuO_4$ (Hg- 1201),[30] $HgBa_2CaCu_2O_6$ (Hg-1212) and $HgBa_2Ca_2Cu_3O_8$ (Hg-1223) is similar to that of Tl- 1201, Tl-1212 and Tl-1223, with Hg in place of Tl. It is noteworthy that the T_c of the Hg compound (Hg-1201) containing one CuO_2 layer is much larger as compared to the one-CuO_2- layer compound of thallium (Tl-1201). In the Hg-based superconductor, T_c is also found to increase as the CuO_2 layer increases. For Hg-1201, Hg-1212 and Hg-1223, the values of T_c are 94, 128 and the record value at ambient pressure 134 K, respectively, as shown in table below. The observation that the T_c of Hg-1223 increases to 153 K under high pressure indicates that the T_c of this compound is very sensitive to the structure of the compound.

Critical temperature (T_c), crystal structure and lattice constants of some high- T_c superconductors

Formula	**Notation**	**T_c (K)**	**No. of Cu-O planes in unit cell**	**Crystal structure**
$YBa_2Cu_3O_7$	123	92	2	Orthorhombic
$Bi_2Sr_2CuO_6$	Bi-2201	20	1	Tetragonal
$Bi_2Sr_2CaCu_2O_8$	Bi-2212	85	2	Tetragonal
$Bi_2Sr_2Ca_2Cu_3O_{10}$	Bi-2223	110	3	Tetragonal
$Tl_2Ba_2CuO_6$	Tl-2201	80	1	Tetragonal
$Tl_2Ba_2CaCu_2O_8$	Tl-2212	108	2	Tetragonal
$Tl_2Ba_2Ca_2Cu_3O_{10}$	Tl-2223	125	3	Tetragonal
$TlBa_2Ca_3Cu_4O_{11}$	Tl-1234	122	4	Tetragonal
$HgBa_2CuO_4$	Hg-1201	94	1	Tetragonal
$HgBa_2CaCu_2O_6$	Hg-1212	128	2	Tetragonal

Critical temperature (T_c), crystal structure and lattice constants of some high- T_c superconductors

Formula	**Notation**	**T_c (K)**	**No. of Cu-O planes in unit cell**	**Crystal structure**
$HgBa_2Ca_2Cu_3O_8$	Hg-1223	134	3	Tetragonal

Preparation of high-T_c superconductors

The simplest method for preparing high-T_c superconductors is a solid-state thermo-chemical reaction involving mixing, calcination and sintering. The appropriate amounts of precursor powders, usually oxides and carbonates, are mixed thoroughly using a Ball mill. Solution chemistry processes such as co-precipitation, freeze-drying and sol-gel methods are alternative ways for preparing a homogeneous mixture. These powders are calcined in the temperature range from 800 °C to 950 °C for several hours. The powders are cooled, reground and calcined again. This process is repeated several times to get homogeneous material. The powders are subsequently compacted to pellets and sintered. The sintering environment such as temperature, annealing time, atmosphere and cooling rate play a very important role in getting good high- T_c superconducting materials. The $YBa_2Cu_3O_{7-x}$ compound is prepared by calcination and sintering of a homogeneous mixture of Y_2O_3, $BaCO_3$ and CuO in the appropriate atomic ratio. Calcination is done at 900–950 °C, whereas sintering is done at 950 °C in an oxygen atmosphere. The oxygen stoichiometry in this material is very crucial for obtaining a superconducting $YBa_2Cu_3O_{7-x}$ compound. At the time of sintering, the semiconducting tetragonal $YBa_2Cu_3O_6$ compound is formed, which, on slow cooling in oxygen atmosphere, turns into superconducting $YBa_2Cu_3O_{7-x}$. The uptake and loss of oxygen are reversible in $YBa_2Cu_3O_{7-x}$. A fully oxygenated orthorhombic $YBa_2Cu_3O_{7-x}$ sample can be transformed into tetragonal $YBa_2Cu_3O_6$ by heating in a vacuum at temperature above 700 °C.

The preparation of Bi-, Tl- and Hg-based high-T_c superconductors is difficult compared to YBCO. Problems in these superconductors arise because of the existence of three or more phases having a similar layered structure. Thus, syntactic intergrowth and defects such as stacking faults occur during synthesis and it becomes difficult to isolate a single superconducting phase. For Bi– Sr–Ca–Cu–O, it is relatively simple to prepare the Bi-2212 ($T_c \approx 85$ K) phase, whereas it is very difficult to prepare a single phase of Bi-2223 ($T_c \approx 110$ K). The Bi-2212 phase appears only after few hours of sintering at 860–870 °C, but the larger fraction of the Bi-2223 phase is formed after a long reaction time of more than a week at 870 °C.[27] Although the substitution of Pb in the Bi– Sr–Ca–Cu–O compound has been found to promote the growth of the high-T_c phase, a long sintering time is still required.

Basic organometallic chemistry:

Ligand field theory

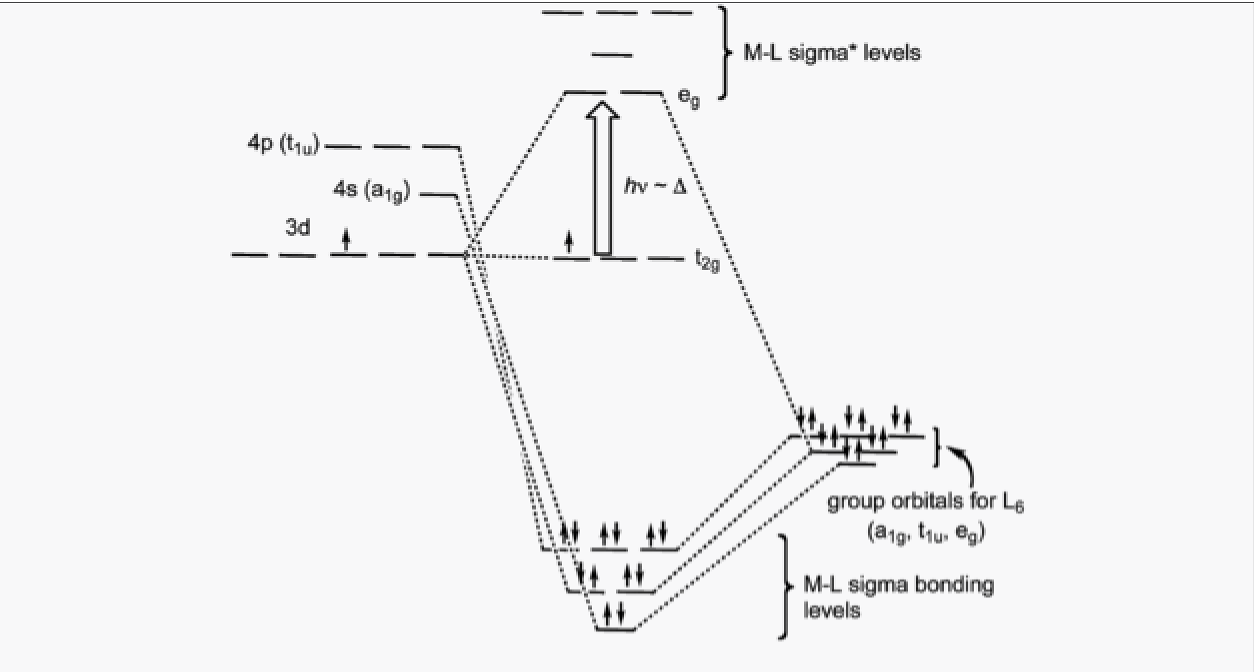
Ligand field theory (**LFT**) describes the bonding, orbital arrangement, and other characteristics of coordination complexes. It represents an application of molecular orbital theory to transition metal complexes. A transition metal ion has nine valence atomic orbitals- consisting of five nd, three (n+1)p, and one (n+1)s orbitals. These orbitals are of appropriate energy to form bonding interaction with ligands. The LFT analysis is highly dependent on the geometry of the complex, but most explanations begin by describing octahedralcomplexes, where six ligands coordinate to the metal. Other complexes can be described by reference to crystal field theory.

Bonding

σ-bonding (sigma bonding)

In an octahedral complex, the molecular orbitals created by coordination can be seen as resulting from the donation of two electrons by each of six σ-donor ligands to the d-orbitals on the metal. In octahedral complexes, ligands approach along the x-, y- and z-axes, so their σ-symmetry orbitals form bonding and anti-bonding combinations with the d_{z^2} and $d_{x^2-y^2}$ orbitals.

The d_{xy}, d_{xz} and d_{yz} orbitals remain non-bonding orbitals. Some weak bonding (and anti-bonding) interactions with the s and p orbitals of the metal also occur, to make a total of 6 bonding (and 6 anti-bonding) molecular orbitals



Ligand-Field scheme summarizing σ-bonding in the octahedral complex $[Ti(H_2O)_6]^{3+}$.

In molecular symmetry terms, the six lone-pair orbitals from the ligands (one from each ligand) form six symmetry adapted linear combinations (SALCs) of orbitals, also sometimes called ligand group orbitals (LGOs). The irreducible representations that these span are a_{1g}, t_{1u} and e_g.

The metal also has six valence orbitals that span these irreducible representations - the s orbital is labeled a_{1g}, a set of three p-orbitals is labeled t_{1u}, and the d_{z^2} and $d_{x^2-y^2}$ orbitals are labeled e_g. The six σ-bonding molecular orbitals result from the combinations of ligand SALC's with metal orbitals of the same symmetry.

π-bonding (pi bonding)

π bonding in octahedral complexes occurs in two ways: via any ligand p-orbitals that are not being used in σ bonding, and via any π or π^* molecular orbitals present on the ligand.

In the usual analysis, the p-orbitals of the metal are used for σ bonding (and have the wrong symmetry to overlap with the ligand p or π or π^* orbitals anyway), so the π interactions take place with the appropriate metal d-orbitals, i.e. d_{xy}, d_{xz} and d_{yz}. These are the orbitals that are non-bonding when only σ bonding takes place.

One important π bonding in coordination complexes is metal-to-ligand π bonding, also called π backbonding. It occurs when the LUMOs(lowest unoccupied molecular orbitals) of the ligand are anti-bonding π^* orbitals. These orbitals are close in energy to the d_{xy}, d_{xz} and d_{yz}orbitals, with which they combine to form bonding orbitals (i.e. orbitals of lower energy than the aforementioned set of d-orbitals). The corresponding anti-bonding orbitals are higher in energy than the anti-bonding orbitals from σ bonding so, after the new π bonding orbitals are filled with electrons from the metal d-orbitals, Δ_O has increased and the bond between the ligand and the metal strengthens. The ligands end up with electrons in their π^* molecular orbital, so the corresponding π bond within the ligand weakens.

The other form of coordination π bonding is ligand-to-metal bonding. This situation arises when the π-symmetry p or π orbitals on the ligands are filled. They combine with the d_{xy}, d_{xz} and d_{yz} orbitals on the metal and donate electrons to the resulting π-symmetry bonding orbital between them and the metal. The metal-ligand bond is somewhat strengthened by this interaction, but the complementary anti-bonding molecular orbital from ligand-to-metal bonding is not higher in energy than the anti-bonding molecular orbital from the σ bonding. It is filled with electrons from the metal d-orbitals, however, becoming the HOMO (highest occupied molecular orbital) of the complex. For that reason, Δ_O decreases when ligand-to-metal bonding occurs.

The greater stabilization that results from metal-to-ligand bonding is caused by the donation of negative charge away from the metal ion, towards the ligands. This allows the metal to accept the σ bonds more easily. The combination of ligand-to-metal σ-bonding and metal-to-ligand π- bonding is a synergic effect, as each enhances the other.

As each of the six ligands has two orbitals of π-symmetry, there are twelve in total. The symmetry adapted linear combinations of these fall into four triply degenerate irreducible representations, one of which is of t_{2g} symmetry. The d_{xy}, d_{xz} and d_{yz} orbitals on the metal also have this symmetry, and so the π-bonds formed between a central metal and six ligands also have it (as these π-bonds are just formed by the overlap of two sets of orbitals with t_{2g} symmetry.)

Role of metal p-orbitals

Current computational findings suggest valence p orbitals on the metal participate in metal- ligand bonding, albeit weakly. Some new theoretical treatments do not count the metal p-orbitals in metal-ligand bonding, although these orbitals are still included as polarization functions. This model has yet to be adopted by the general chemistry community.

High and low spin and the spectrochemical series

The six bonding molecular orbitals that are formed are "filled" with the electrons from the ligands, and electrons from the d-orbitals of the metal ion occupy the non-bonding and, in some cases, anti-bonding MOs. The energy difference between the latter two types of MOs is called Δ_O (O stands for octahedral) and is determined by the nature of the π-interaction between the ligand orbitals with the d-orbitals on the central atom. As described above, π-donor ligands lead to a small Δ_O and are called weak- or low-field ligands, whereas π-acceptor ligands lead to a large value of Δ_O and are called strong- or high-field ligands. Ligands that are neither π-donor nor π-acceptor give a value of Δ_O somewhere in-between.

The size of Δ_O determines the electronic structure of the d^4 - d^7 ions. In complexes of metals with these d-electron configurations, the non-bonding and anti-bonding molecular orbitals can be filled in two ways: one in which as many electrons as possible are put in the non-bonding orbitals before filling the anti-bonding orbitals, and one in which as many unpaired electrons as possible are put in. The former case is called low-spin, while the latter is called high-spin. A small Δ_O can be overcome by the energetic gain from not pairing the electrons, leading to high- spin. When Δ_O is large, however, the spin-pairing energy becomes negligible by comparison and a low-spin state arises.

The spectrochemical series is an empirically-derived list of ligands ordered by the size of the splitting Δ that they produce. It can be seen that the low-field ligands are all π-donors (such as I^-), the high field ligands are π-acceptors (such as CN^- and CO), and ligands such as H_2O and NH_3, which are neither, are in the middle.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < CH_3CN <$ py (pyridine) $< NH_3 <$ en (ethylenediamine) < bipy (2,2'-bipyridine) < phen (1,10-phenanthroline) $< NO_2^- < PPh_3 < CN^- < CO$

Molecular orbital theory

In chemistry, **molecular orbital (MO) theory** is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule. The spatial and energetic properties of electrons within atoms are fixed by quantum mechanics to form orbitals that contain these electrons. While atomic orbitals contain electrons ascribed to a single atom, molecular orbitals, which surround a number of atoms in a molecule, contain valence electrons between atoms. Molecular orbital theory, which was proposed in the early twentieth century, revolutionized the study of bonding by approximating the positions of bonded electrons—the molecular orbitals— as linear combinations of atomic orbitals (LCAO). These approximations are now made by applying the density functional theory(DFT) or Hartree–Fock (HF) models to the Schrödinger equation.

Quantitative applications

In this theory, each molecule has a set of molecular orbitals, in which it is assumed that the molecular orbital wave function ψ_j can be written as a simple weighted sum of the n constituent atomic orbitals χ_i, according to the following equation:

One may determine c_{ij} coefficients numerically by substituting this equation into the Schrödinger equation and applying the variational principle. The variational principle is a mathematical technique used in quantum mechanics to build up the coefficients of each atomic orbital basis. A larger coefficient means that the orbital basis is composed more of that particular contributing atomic orbital—hence, the molecular orbital is best characterized by that type. This method of quantifying orbital contribution as Linear Combinations of Atomic Orbitals is used in computational chemistry. An additional unitary transformation can be applied on the system to accelerate the convergence in some computational schemes. Molecular orbital theory was seen as a competitor to valence bond theory in the 1930s, before it was realized that the two methods are closely related and that when extended they become equivalent.

History

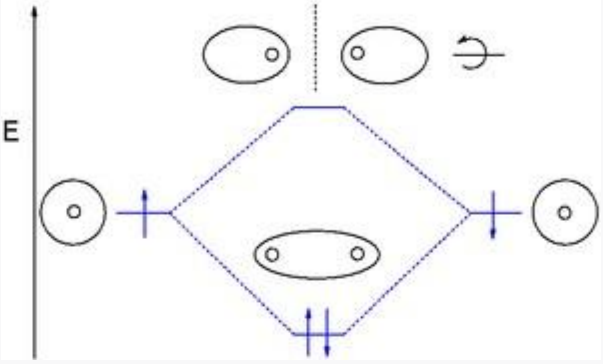
Molecular orbital theory was developed, in the years after valence bond theory had been established (1927), primarily through the efforts of Friedrich Hund, Robert Mulliken, John C. Slater, and John Lennard-Jones. MO theory was originally called the Hund-Mulliken theory. According to German physicist and physical chemist Erich Hückel, the first quantitative use of molecular orbital theory was the 1929 paper of Lennard-Jones. This paper notably predicted a triplet ground state for the dioxygen molecule which explained its paramagnetism before valence bond theory, which came up with its own explanation in 1931. The word orbital was introduced by Mulliken in 1932. By 1933, the molecular orbital theory had been accepted as a valid and useful theory.

Erich Hückel applied molecular orbital theory to unsaturated hydrocarbon molecules starting in 1931 with his Hückel molecular orbital (HMO) method for the determination of MO energies for pi electrons, which he applied to conjugated and aromatic hydrocarbons. This method provided an explanation of the stability of molecules with six pi-electrons such as benzene.

The first accurate calculation of a molecular orbital wavefunction was that made by Charles Coulson in 1938 on the hydrogen molecule. By 1950, molecular orbitals were completely defined as eigenfunctions (wave functions) of the self-consistent field Hamiltonian and it was at this point that molecular orbital theory became fully rigorous and consistent. This rigorous approach is known as the Hartree–Fock method for molecules although it had its origins in calculations on atoms. In calculations on molecules, the molecular orbitals are expanded in terms of an atomic orbital basis set, leading to the Roothaan equations. This led to the development of many ab initio quantum chemistry methods. In parallel, molecular orbital theory was applied in a more approximate manner using some empirically derived parameters in methods now known as semi-empirical quantum chemistry methods.

The success of Molecular Orbital Theory also spawned ligand field theory, which was developed during the 1930s and 1940s as an alternative to crystal field theory.

Types of orbitals



MO diagram showing the formation of molecular orbitals of H_2 (centre) from atomic orbitals of two H atoms. The lower-energy MO is bonding with electron density concentrated between the two H nuclei. The higher-energy MO is anti-bonding with electron density concentrated behind each H nucleus.

Molecular orbital (MO) theory uses a linear combination of atomic orbitals (LCAO) to represent molecular orbitals resulting from bonds between atoms. These are often divided into bonding orbitals, anti-bonding orbitals, and non-bonding orbitals. A bonding orbital concentrates electron density in the region between a given pair of atoms, so that its electron density will tend to attract each of the two nuclei toward the other and hold the two atoms together. An anti-bonding orbital concentrates electron density "behind" each nucleus (i.e. on the side of each atom which is farthest from the other atom), and so tends to pull each of the two nuclei away from the other and actually weaken the bond between the two nuclei. Electrons in non-bonding orbitals tend to be associated with atomic orbitals that do not interact positively or negatively with one another, and electrons in these orbitals neither contribute to nor detract from bond strength.

Molecular orbitals are further divided according to the types of atomic orbitals they are formed from. Chemical substances will form bonding interactions if their orbitals become lower in energy when they interact with each other. Different bonding orbitals are distinguished that differ by electron configuration (electron cloud shape) and by energy levels.

The molecular orbitals of a molecule can be illustrated in molecular orbital diagrams.

Overview

MO theory provides a global, delocalized perspective on chemical bonding. In MO theory, any electron in a molecule may be found anywhere in the molecule, since quantum conditions allow electrons to travel under the influence of an arbitrarily large number of nuclei, as long as they are in eigenstates permitted by certain quantum rules. Thus, when excited with the requisite amount of energy through high-frequency light or other means, electrons can transition to higher-energy molecular orbitals. For instance, in the simple case of a hydrogen diatomic molecule, promotion of a single electron from a bonding orbital to an antibonding orbital can occur under UV radiation. This promotion weakens the bond between the two hydrogen atoms and can lead to photodissociation—the breaking of a chemical bond due to the absorption of light.

Although in MO theory some molecular orbitals may hold electrons that are more localized between specific pairs of molecular atoms, other orbitals may hold electrons that are spread more uniformly over the molecule. Thus, overall, bonding is far more delocalized in MO theory, which makes it more applicable to resonant molecules that have equivalent non-integer bond orders than valence bond (VB) theory. This makes MO theory more useful for the description of extended systems.

An example is the MO description of benzene, C_6H_6, which is an aromatic hexagonal ring of six carbon atoms and three double bonds. In this molecule, 24 of the 30 total valence bonding electrons—24 coming from carbon atoms and 6 coming from hydrogen atoms—are located in 12 σ (sigma) bonding orbitals, which are located mostly between pairs of atoms (C-C or C-H), similarly to the electrons in the valence bond description. However, in benzene the remaining six bonding electrons are located in three π (pi) molecular bonding orbitals that are delocalized around the ring. Two of these electrons are in an MO that has equal orbital contributions from all six atoms. The other four electrons are in orbitals with vertical nodes at right angles to each other. As in the VB theory, all of these six delocalized π electrons reside in a larger space that exists above and below the ring plane. All carbon-carbon bonds in benzene are chemically equivalent. In MO theory this is a direct consequence of the fact that the three molecular π orbitals combine and evenly spread the extra six electrons over six carbon atoms.

Structure of benzene

In molecules such as methane, CH_4, the eight valence electrons are found in four MOs that are spread out over all five atoms. However, it is possible to transform the MOs into four localized sp^3 orbitals. Linus Pauling, in 1931, hybridized the carbon 2s and 2p orbitals so that they pointed directly at the hydrogen 1s basis functions and featured maximal overlap. However, the delocalized MO description is more appropriate for predicting ionization energies and the positions of spectral absorption bands. When methane is ionized, a single electron is taken from the valence MOs, which can come from the s bonding or the triply degenerate p bonding levels, yielding two ionization energies. In comparison, the explanation in VB theory is more complicated. When one electron is removed from an sp^3 orbital, resonance is invoked between four valence bond structures, each of which has a single one-electron bond and three two- electron bonds. Triply degenerate $T_2$and A_1 ionized states (CH_4^+) are produced from different linear combinations of these four structures. The difference in energy between the ionized and ground state gives the two ionization energies.

As in benzene, in substances such as beta carotene, chlorophyll, or heme, some electrons in the π orbitals are spread out in molecular orbitals over long distances in a molecule, resulting in light absorption in lower energies (the visible spectrum), which accounts for the characteristic colours of these substances. This and other spectroscopic data for molecules are well explained in MO theory, with an emphasis on electronic states associated with multicenter orbitals, including mixing of orbitals premised on principles of orbital symmetry matching. The same MO principles also naturally explain some electrical phenomena, such as high electrical conductivity in the planar direction of the hexagonal atomic sheets that exist in graphite. This results from continuous band overlap of half-filled p orbitals and explains electrical conduction.

MO theory recognizes that some electrons in the graphite atomic sheets are completely delocalized over arbitrary distances, and reside in very large molecular orbitals that cover an entire graphite sheet, and some electrons are thus as free to move and therefore conduct electricity in the sheet plane, as if they resided in a metal.

18 ELECTRON RULE

The **18-electron rule** is a rule used primarily for predicting and rationalizing formulae for stable metal complexes, especially organometallic compounds. The rule is based on the fact that the valence shells of transition metals consist of nine valence orbitals (one s orbital, three p orbitals and five d orbitals), which collectively can accommodate 18 electrons as either bonding or nonbonding electron pairs. This means that, the combination of these nine atomic orbitals with ligand orbitals creates nine molecular orbitals that are either metal-ligand bonding or non-bonding. When a metal complex has 18 valence electrons, it is said to have achieved the same electron configuration as the noble gas in the period. The rule and its exceptions are similar to the application of the octet rule to main group elements. The rule is not helpful for complexes of metals that are not transition metals, and interesting or useful transition metal complexes will violate the rule because of the consequences deviating from the rule bears on reactivity. The rule was first proposed by American chemist Irving Langmuir in 1921.

Applicability

The rule usefully predicts the formulae for low-spin complexes of the Cr, Mn, Fe, and Co triads. Well-known examples include ferrocene, iron pentacarbonyl, chromium carbonyl, and nickel carbonyl.

Ligands in a complex determine the applicability of the 18-electron rule. In general, complexes that obey the rule are composed at least partly of π-acceptor ligands (also known as π-acids). This kind of ligand exerts a very strong ligand field, which lowers the energies of the resultant molecular orbitals and thus favorably occupied. Typical ligands include olefins, phosphines, and CO. Complexes of π-acids typically feature metal in a low-oxidation state. The relationship between oxidation state and the nature of the ligands is rationalized within the framework of π backbonding.

Consequences for reactivity

Compounds that obey the 18-electron rule are typically "exchange inert". Examples include $[Co(NH_3)_6]Cl_3$, $Mo(CO)_6$, and $[Fe(CN)_6]^{4-}$. In such cases, in general ligand exchange occurs via dissociative substitution mechanisms, wherein the rate of reaction is determined by the rate of dissociation of a ligand. On the other hand, 18-electron compounds can be highly reactive toward electrophiles such as protons, and such reactions are associative in mechanism, being acid-base reactions.

Complexes with fewer than 18 valence electrons tend to show enhanced reactivity. Thus, the 18-electron rule is often a recipe for non-reactivity in either a stoichiometric or a catalytic sense.

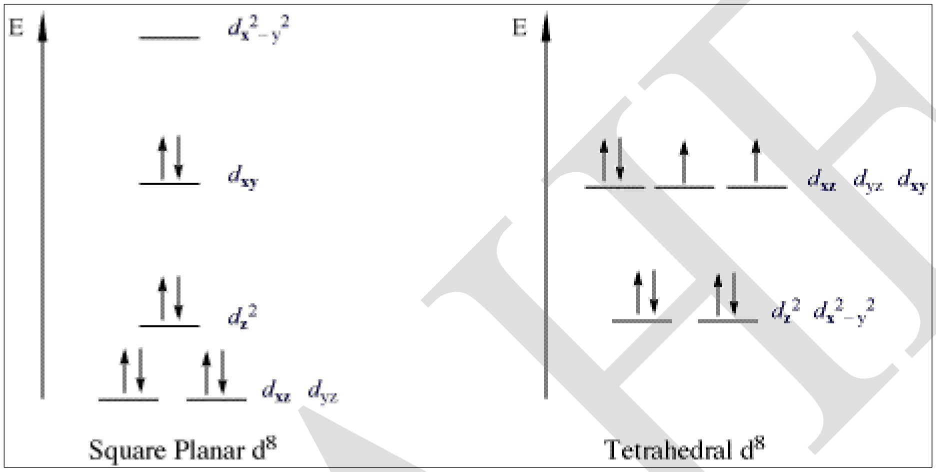
Exceptions

π-donor or σ-donor ligands with small interactions with the metal orbitals lead to a weak ligand field which increases the energies of t_{2g}orbitals. These molecular orbitals become non-bonding or weakly anti-bonding orbitals (small Δ_{oct}). Therefore, addition or removal of electron has little effect on complex stability. In this case, there is no restriction on the number of d-electrons and complexes with 12–22 electrons are possible. Small Δ_{oct} makes filling e_g* possible (>18 e^-) and π-donor ligands can make t_{2g} antibonding (<18 e^-). These types of ligand are located in the low- to-medium part of the spectrochemical series. For example: $[TiF_6]^{2-}$ (Ti(IV), d^0, 12 e^-), $[Co(NH_3)_6]^{3+}$(Co(III), d^6, 18 e^-), $[Cu(OH_2)_6]^{2+}$ (Cu(II), d^9, 21 e^-).

In terms of metal ions, Δ_{oct} increases down a group as well as with increasing oxidation number. Strong ligand fields lead to low-spincomplexes which cause some exceptions to the 18-electron rule.

16- electron complexes

An important class of complexes that violate the 18e rule are the 16-electron complexes with metal d^8 configurations. All high-spin d^8metal ions are octahedral (or tetrahedral), but the low- spin d^8 metal ions are all square planar. Important examples of square-planar low-spin d^8 metal Ions are Rh(I), Ir(I), Ni(II), Pd(II), and Pt(II). At picture below is shown the splitting of the d subshell in low-spin square-planar complexes. Examples are especially prevalent for derivatives of the cobalt and nickel triads. Such compounds are typically square-planar. The most famous example is Vaska's complex ($IrCl(CO)(PPh_3)_2$), $[PtCl_4]^{2-}$, and Zeise's salt $[PtCl_3(\eta^2\text{-}C_2H_4)]^-$. In such complexes, the d ^{2} orbital is doubly occupied and nonbonding.



Many catalytic cycles operate via complexes that alternate between 18-electron and square- planar 16-electron configurations. Examples include Monsanto acetic acid synthesis, hydrogenations, hydroformylations, olefin isomerizations, and some alkene polymerizations.

Other violations can be classified according to the kinds of ligands on the metal center.

Bulky ligands

Bulky ligands can preclude the approach of the full complement of ligands that would allow the metal to achieve the 18 electron configuration. Examples:

- Ti(neopentyl)$_4$ (8 e$^-$)
- Cp*$_2$Ti(C_2H_4) (16 e$^-$)
- $V(CO)_6$ (17 e$^-$)
- Cp*Cr$(CO)_3$ (17 e$^-$)
- Pt(P^{t}Bu3)$_2$ (14 e$^-$)
- Co(norbornyl)$_4$ (13 e$^-$)
- $[FeCp_2]^+$ (17 e$^-$)

Sometimes such complexes engage in agostic interactions with the hydrocarbon framework of the bulky ligand. For example:

- $W(CO)_3[P(C_6H_{11})_3]_2$ has 16 e$^-$ but has a short bonding contact between one C–H bond and the W center.

- $Cp(PMe_3)V(CHCMe_3)$ (14 e^-, diamagnetic) has a short V–H bond with the 'alkylidene- H', so the description of the compound is somewhere between $Cp(PMe_3)V(CHCMe_3)$ and $Cp(PMe_3)V(H)(CCMe_3)$.

High-spin complexes

High-spin metal complexes have singly occupied orbitals and may not have any empty orbitals into which ligands could donate electron density. In general, there are few or no π- acidic ligands in the complex. These singly occupied orbitals can combine with the singly occupied orbitals of radical ligands (e.g., oxygen), or addition of a strong field ligand can cause electron-pairing, thus creating a vacant orbital that it can donate into. Examples:

- $CrCl_3(THF)_3$ (15 e^-)
- $[Mn(H_2O)_6]^{2+}$ (17 e^-)
- $[Cu(H_2O)_6]^{2+}$ (21 e^-, see comments below)

Complexes containing strongly π-donating ligands often violate the 18-electron rule. These ligands include fluoride (F^-), oxide (O^{2-}), nitride (N^{3-}), alkoxides (RO^-), and imides (RN^{2-}). Examples:

- $[CrO_4]^{2-}$ (16 e^-)
- $Mo(=NR)_2Cl_2$ (12 e^-)

In the latter case, there is substantial donation of the nitrogen lone pairs to the Mo (so the compound could also be described as a 16 e^-compound). This can be seen from the short Mo–N bond length, and from the angle Mo–N–C(R), which is nearly 180°. Counter- examples:

- trans-$WO_2(Me_2PCH_2CH_2PMe_2)_2$ (18 e^-)
- Cp^*ReO_3 (18 e^-)

In these cases, the M=O bonds are "pure" double bonds (i.e., no donation of the lone pairs of the oxygen to the metal), as reflected in the relatively long bond distances.

π-donating ligands

Ligands where the coordinating atom bear nonbonding lone pairs often stabilize unsaturated complexes. Metal amides and alkoxides often violate the 18e rule.

Combinations of effects

The above factors can sometimes combine. Examples include

- Cp^*VOCl_2 (14 e^-)
- $TiCl_4$ (8 e^-)

Higher electron counts

Some complexes have more than 18 electrons. Examples:

- Cobaltocene (19 e^-)
- Nickelocene (20 e^-)
- The hexaaquacopper(II) ion $[Cu(H_2O)_6]^{2+}$ (21 e^-)

Often, cases where complexes have more than 18 valence electrons are attributed to electrostatic forces – the metal attracts ligands to itself to try to counterbalance its positive charge, and the number of electrons it ends up with is unimportant. In the case of the metallocenes, the chelating nature of the cyclopentadienyl ligand stabilizes its bonding to the metal. Somewhat satisfying are the two following observations: cobaltocene is a strong electron donor, readily forming the 18-electron cobaltocenium cation; and nickelocene tends to react with substrates to give 18-electron complexes, e.g. $CpNiCl(PR_3)$ and free CpH.

In the case of nickelocene, the extra two electrons are in orbitals which are weakly metal- carbon antibonding, this is why it often participates in reactions where the M–C bonds are broken and the electron count of the metal changes to 18.

Suggested Materials

Text Books:

T1: James E. Huheey, Ellen A. Keiter, Richard L. Keiter, Okhil K. Medhi. (2013). *Inorganic Chemistry-Principles of structure and Reactivity* (IV Edition) New Delhi pearson education, India

T2: Cotton, F.A,G.,Murillo,C.A., & Bochmann, M.(2007). *Advanced Inorganic Chemistry* (VI Edition).New York:John Wiley & Sons.

Part A
(1 Mark Q.No.1 to 20)
(Online Examination)

Part B(2 marks)

1. What are conductors?
2. What are semiconductors and insulators?
3. .What is 18 electron rule?Give two examples.
4. Mention basic principles of ligand field theory.
5. Mention basic principles of molecular orbital theory.

Part C(8 marks)

1. Give a detailed account of the Band & Zone theory of metals.
2. Discuss X- ray, neutron and electron diffraction methods.
3. Explain in detail about the various types of crystal defects.
4. Illustrate with an example the catalytic reaction of alkenes, the hydrogenation reaction.
5. Distinguish with the help of sketches between Schottky and Frenkel defects of crystals?
6. Draw and explain the structure of rutile, fluorite and antifluorite.
7. Write notes on neutron and electron diffraction methods.
8. Give a detailed account of the band theory of metals.
9. Explain the structure of CsCl.
10. Give a detailed account on X-ray diffraction method.
11. Discuss insulators, semiconductors and super conductors.
12. Explain briefly about 18 electron rule.
13. Explain molecular orbital theory and ligand field theory.

19CHP102
Karpagam Academy of Higher Education
Coimbatore-21

(For the candidate admitted on 2019 onwards)
Department of Chemistry
I- semester
INORGANIC CHEMISTRY-I (Nuclear Chemistry and Metalic clusters)

UNIT II- Objective Questions for online examination (Each carry 1 Marks)

S.No	Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers
1	A crystal which consist of two or more simple forms is known as a	Form	Combination	edges	Form and edges	Combination
2	Which one of the substance is said to be isotropic.	Semisolid	Crystal	Amorphous solid	Liquid	Semisolid
3	Which one of the following is a process where the catalysts and reactants remain in the same phase	Homogeneous catalysis	Heterogeneous catalysis	Catalysis	No catalyst	Homogeneous catalysis
4	The reaction of dihydrogen with the solvent complex to form?	Cis-dihydride species	Dihydride species	trans-dihydride species	Nin hydrine	Cis-dihydride species
5	In most heterogeneous catalytic systems the catalyst is in the solid phase and the reactants are?	Solid	Liquid	Gas	Liquids or gases	Liquids or gases
6	All the faces corresponding to a crystal are said to constitute a	Form	Combination	Edges	Form and edges	Form
7	Which is have a very sharp melting point?	Semisolid	Crystal	Amorphous solid	Liquid	Crystal
8	Which one of the following is a catalyst precursor?	Wilkinson’s catalyst	Tolman loop	Zieglar-natta catalyst	Carbon dioxide	Wilkinson’s catalyst
9	Which one of the following is a mild lachrymator and can cause skin irritation?	Rhodium (III) chloride hydrate	Triphenylphosphine	Hydrogen	Nitrogen	Triphenylphosphine
10	Which one is a solid with well defined planar surfaces known as faces.	Semisolid	Crystal	Amorphous solid	Liquid	Crystal

11	The reaction of an olefin with CO and H2 in the presence of a metal carbonyl to form ?	Alkenes	Alkynes	Aldehydes	Alcohol	Aldehydes
12	Olefin is oxidized to an aldehyde or ketone in the presence of a soluble ?	Metal carbonyl	CO	Palladium salt	Hydrogen	Palladium salt
13	A line drawn through the center of a crystal in a direction parellel to the edges of a zone is called	Form	Axis of symmetry	Faces	Zone axis	Zone axis
14	In which reaction, the reductive polymerization of CO to form straightchain hydrocarbons, olefins and alcohols?	Fischer-Tropsch	Ziegler Natta reaction	Hydroformylation	Wacker reaction	Fischer-Tropsch
15	Crystals are bounded by a number of surfaces which generally perfect flat are known as	Form	Combination	Edges	Face	Face
16	Higher formal oxidation state of metals are	–0 to +0	-2 to +2	s	+2 to +3	+2 to +3
17	Olefins are polymerized using an organoaluminum-titanium catalyst to form?	Regular polymers	Stereo polymers	Stereoregular polymers	Polymers	Stereoregular polymers
18	Which one of the following is originally a substance that tasted sour and reacted with bases?	Acid	Alkali	Alcohol	Aldehyde	Acid
19	Which one is a solid composed of atoms, molecules or ions arranged in an orderly repetitive array	Crystal	Semisolid	Amorphous solid	Solid	Crystal
20	Which one of the forces occur in solids which consist of polar molecules	Dipole-dipole forces	Vanderwaals forces	Electrostatic forces	Dipole-induced dipole forces	Dipole-dipole forces
21	Frenkel defect is a	Stiochiometric defect	Nonstoichiometric defect	Amorphous defect	Crystal	Stiochiometric defect
22	According to MOT the molecular orbital which has the lower energy is	Non-bonding	Anti bonding	Bonding	Forbidden	Bonding
23	Pt (II) are usually	square planar	tetrahedral	pyramidal	square pyramidal	square planar
24	Pt(II) are	four co-ordinate	three co-ordinate	two co-ordinate	six co-ordinate	four co-ordinate

25	one difficulty with the VB assumption of electron donation from ----------------ions is the buildup of formal negative charge on the metal	metal to ligand	ligand to metal	metal to metal	ligand to ligand	ligand to metal
26	The six ligands in [CoL6]2+ share ---------- electrons with the metal atom	13	12	11	10	12
27	The tendency for zero or low electrical charges on atoms is a rule of thumb known as the ----------- principle	electroneutrality	Electronegativity	electromagnetic	Electrochemical reactivity	electroneutrality
28	CFT was a model based on a purely------------- interaction between the ligands and the metal ion	electroneutrality	electromagnetic	electrostatic	electrochemical	electrostatic
29	The magnitude of Δ increases with -------------- ionic charge on the central metal ion	increasing	decreasing	increasing and decreasing	decreasing and increasing	increasing
30	CFT account magnetic and ---------------properties of complexes	spectral	thermal	electrical	mechanical	spectral
31	d5 have---------CFSE	0	1	2	3	0
32	In aqueous solution Co(III) is unstable with respect to reduction by-------------to form Co(II)	Co(III)	water	ethanol	methanol	water
33	Indirect evidence that electrons are shared betweeen the ligands and the central metal ion comes from the ----------effect	electroneutrality	nephelauxetic	electromagnetic	Electrochemical reactivity	nephelauxetic
34	An organometallic compound is generally defined as one that possesses a metal----------bond	carbon	hydrogen	oxygen	Nitrogen	carbon
35	The bonding interactions as delineated by the organometallics must be ionic or---------	covalent	Vanderwaals forces	metallic	metallic and covalent	covalent
36	Organometallic chemistry can be viewed as a bridge between --------------- and inorganic chemistry	physical	Polymer	organic	material	Polymer

37	Organometallic catalysts will become increasingly important in an age when -----------------------------needs to be minimized in chemical processes	pressure	temperature	volume	concentration	temperature
38	The conditions favoring adherence to the 18 electron rule are an electron--------------central metal	poor and rich	poor	rich	weak	rich
39	The 18 electron rule has remarkable utility for predicting stabilities and ------------------of organometallic compounds	structure	entropy	enthalpy	free energy	structure
40	For Ru the most stable binary carbonyls are the --------------complexes	binuclear	trinuclear	tetranuclear	hexanuclear	trinuclear
41	For Os the most stable binary carbonyls are the --------------complexes	binuclear	trinuclear	tetranuclear	hexanuclear	trinuclear
42	The resemblence of the first row to the heavier elements is ------------------for carbonal complexes than for other classes of coordination compounds	lower	greater	greater and lower	lower and greater	greater
43	Nickel tetracarbonyl is a highly toxic colorless---------------	Solid	Liquid	Gas	semisolid	Liquid
44	Nickel is purified by -----------------process	Vanarkel	mond's	dewar	dewar and vanarkel	mond's
45	18 electron rule breaks down for complexes with more than -------------metal atoms	3	4	5	6	4
46	Anionic carbonyl complexes, also called------------ions	carbonylate	carboxylate	carbocation	carbanion	carbonylate
47	potassium metal is a powerful-----------agent	oxidising	reducing	catalytic agent	supressing	reducing
48	carbonyl hydride complexes may be regarded as------------	acids	bases	donars	acceptors	acids
49	polynuclear carbonyl complex of osmium was referred to as an analague of----------------	cyclohexane	cyclobutane	cyclooctane	cyclopentane	cyclobutane
50	[Mn(CO)5] is a ------------------	nucleophile	electrophile	complex	catalyst	nucleophile
51	Ni(CO)4 is a---------------	octahedral	tetrahedral	squareplanar	pyramidal	tetrahedral

52	Fe(CO)5 is a ------------------	trigonal bipyramidal	tetrahedral	squareplanar	pyramidal	trigonal bipyramidal
53	Mo(CO)6 is a--------------------	tetrahedral	octahedral	squareplanar	pyramidal	octahedral
54	polynuclear carbonyl complexes may be regarded as	carbon monoxide deficient	carbon monoxide rich	carbon dioxide deficient	Carbon dioxide rich	carbon monoxide deficient
55	The molecular structure of the manganese dimer clearly reveals that there is an ----------bond	Mn-Mn	Cu-Cu	Zn-Zn	Re-Re	Mn-Mn
56	Mn2(CO)10 is a --------------species	monomeric	dimeric	trimeric	tetrameric	dimeric
57	--------------a unsaturated organic ligand	(C3H5)	(C2H5)	(CH4)	(C2H6)	(C3H5)
58	If both C5H5 ligands in W are pentahepto, the compound would have----------electrons	18	20	22	24	20
59	V(CO)6 is a ----------	diamagnetic	paramagnetic	polymer	dimer	paramagnetic
60	Ni(CN)5 is a ------------------	4 coordinate	5 coordinate	3 coordinate	6 coordinate	5 coordinate

UNIT III

SYLLABUS

Organometallic Chemistry: Organometallic compounds in homogeneous catalytic reactions- coordinative unsaturation-acid-base behavior reaction-migration of atoms or groups from metal to ligand-insertion reaction –reactions of coordinated ligands-catalytic reactions of alkenes- isomerisation of alkenes-hydrogenation-hydroformylation and hydrosilation of alkenes-alkene polymerization and oligomerisation-fluxional molecules.

ORGANOMETALLIC CHEMISTRY

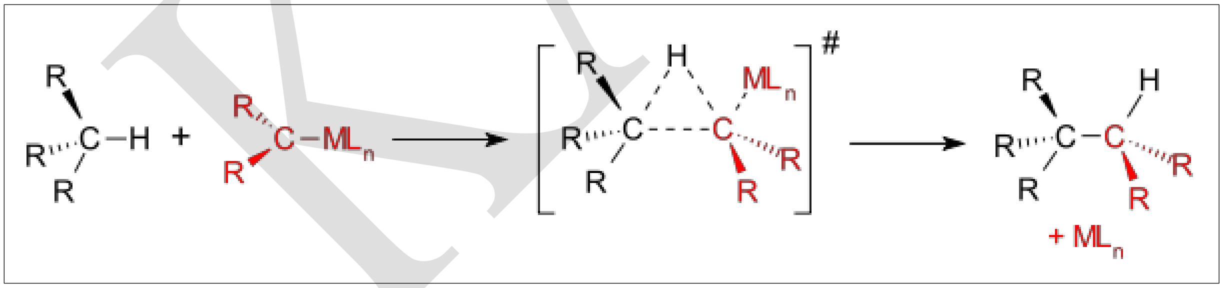
Carbene C−H insertion in organic chemistry concerns the insertion reaction of a carbene into a carbon–hydrogen bond. This organic reaction is of some importance in the synthesis of new organic compounds.

Simple carbenes such as the methylene radical and dichlorocarbene are not regioselective towards insertion. When the carbene is stabilized by a metal the selectivity increases. The compound dirhodium tetraacetate is found to be especially effective. In a typical reaction ethyl diazoacetate (a well-known carbene precursor) and dirhodium tetraacetate react with hexane; the insertion into a C−H bond occurs 1% on one of the methyl groups, 63% on the alpha-methylene unit and 33% on the beta-methylene unit.

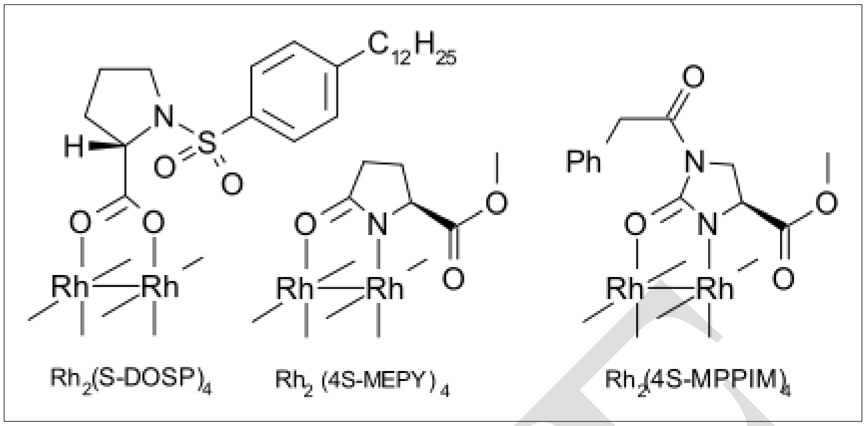
The first such reaction was reported in 1981 by Teyssié

In a general reaction mechanism for this reaction as proposed by Doyle in 1993 the metal that stabilizes the carbene, dissociates at the same time but not to the same degree as carbon–carbon bond formation and hydrogen atom migration. The reaction is distinct from a metal catalyzed C−H activation reaction where the metal actually inserts itself between carbon and hydrogen.

The metal employed as a catalyst in this reaction historically was copper until superseded by rhodium.



Other metals stabilize the carbene too much (e.g. molybdenum as in Fischer carbenes) or result in carbenes too reactive (e.g. gold, silver). Many dirhodium carboxylates and carboxamidates exist, including chiral ones. An effective chiral dirhodium catalyst is $Rh_2(MPPIM)_4$ with MPPIM (**M**ethyl **P**henyl**P**ropyl **IM**idazolidinecarboxylato) asymmetric ligand.

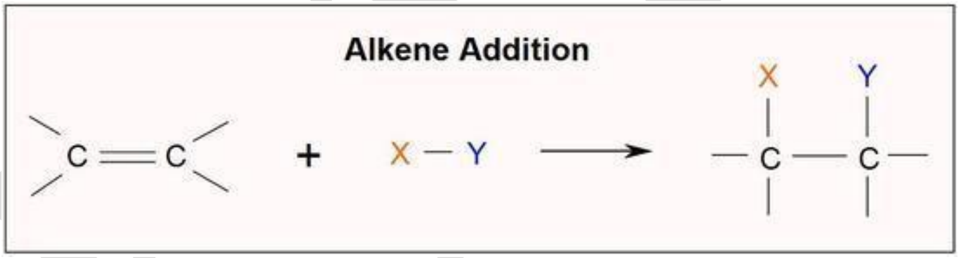


Most successful reactions are intramolecular within geometrically rigid systems, as pioneered by Wenkert (1982) and Taber (1982).

The Wee research group has compared the use of different catalysts:

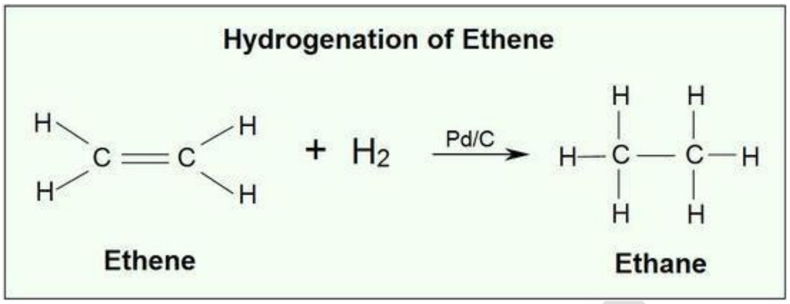
HYDROGENATION OF ALKENES

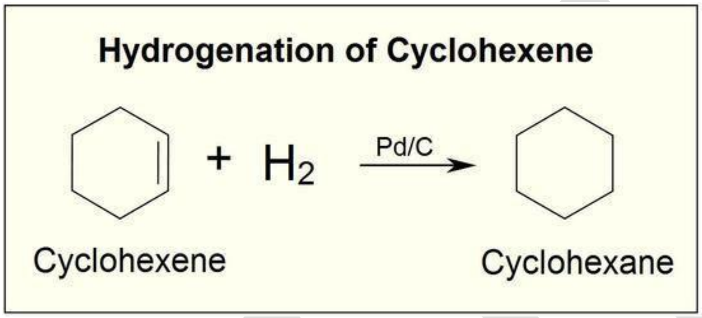
The double bond of an alkene consists of a sigma (σ) bond and a pi (π) bond. Because the carbon-carbon π bond is relatively weak, it is quite reactive and can be easily broken and reagents can be added to carbon. Reagents are added through the formation of single bonds to carbon in an addition reaction.



Introduction

An example of an alkene addition reaction is a process called hydrogenation.In a hydrogenation reaction, two hydrogen atoms are added across the double bond of an alkene, resulting in a saturated alkane. Hydrogenation of a double bond is a thermodynamically favorable reaction because it forms a more stable (lower energy) product. In other words, the energy of the product is lower than the energy of the reactant; thus it is exothermic (heat is released). The heat released is called the heat of hydrogenation, which is an indicator of a molecule’s stability.





Although the hydrogenation of an alkene is a thermodynamically favorable reaction, it will not proceed without the addition of a catalyst.

Common catalysts used are insoluble metals such as palladium in the form Pd-C, platinum in the form PtO2, and nickel in the form Ra-Ni. With the presence of a metal catalyst, the H-H bond in H2 cleaves, and each hydrogen attaches to the metal catalyst surface, forming metal-hydrogen bonds. The metal catalyst also absorbs the alkene onto its surface. A hydrogen atom is then transferred to the alkene, forming a new C-H bond. A second hydrogen atom is transferred forming another C-H bond. At this point, two hydrogens have added to the carbons across the double bond. Because of the physical arrangement of the alkene and the hydrogens on a flat metal catalyst surface, the two hydrogens must add to the same face of the double bond, displaying syn addition

Common Applications

Hydrogenation reactions are extensively used to create commercial goods.Hydrogenation is used in the food industry to make a large variety of manufactured goods, like spreads and shortenings, from liquid oils. This process also increases the chemical stability of products and yields semi- solid products like margarine. Hydrogenation is also used in coal processing. Solid coal is converted to a liquid through the addition of hydrogen. Liquefying coal makes it available to be used as fuel.

HYDROFORMYLATION OF ALKENES

The overall mechanism resembles that for homogeneous hydrogenation with additional steps. The reaction begins with the generation of coordinatively unsaturated metal hydrido carbonyl complex such as $HCo(CO)_3$ and $HRh(CO)(PPh_3)_3$. Such species bind alkenes, and the resulting complex undergoes a migratory insertion reaction to form an alkyl complex.

Selectivity

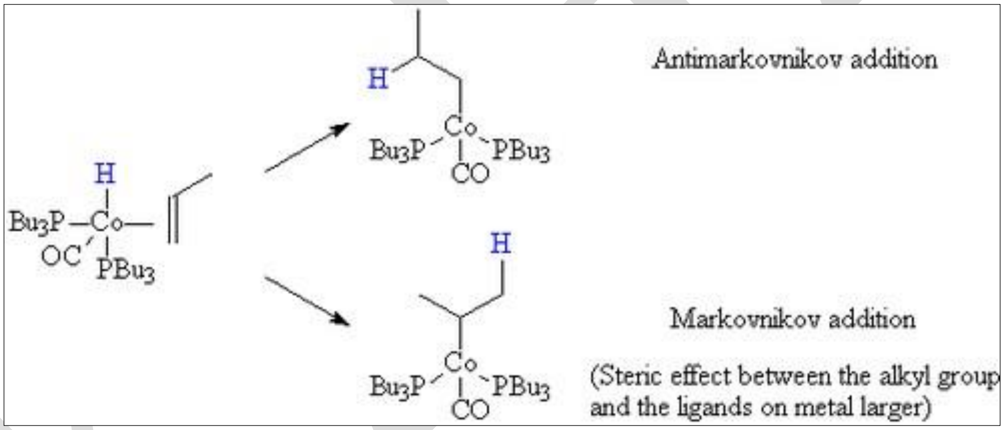
A key consideration of hydroformylation is the "normal" vs. "iso" selectivity. For example, the hydroformylation of propylene can afford
two isomeric products, butyraldehyde or isobutyraldehyde:

$H_2 + CO + CH_3CH{=}CH_2 \rightarrow CH_3CH_2CH_2CHO$ ("normal")
vs.
$H_2 + CO + CH_3CH{=}CH_2 \rightarrow (CH_3)_2CHCHO$ ("iso")

These isomers result from the differing ways of inserting the alkene into the M–H bond. Of course, both products are not equally desirable. Much research was dedicated to the quest for catalyst that favored the normal isomer.

Steric effects

When the hydrogen is transferred to the carbon bearing the most hydrogen atoms (Markovnikov addition) the resulting alkyl group has a larger steric bulk close to the ligands on the cobalt. If the ligands on the cobalt are bulky (such as tributyl phosphine), then this steric effect is greater. Hence, the mixed carbonyl/phosphine complexes offer a greater selectivity toward the straight chain products.

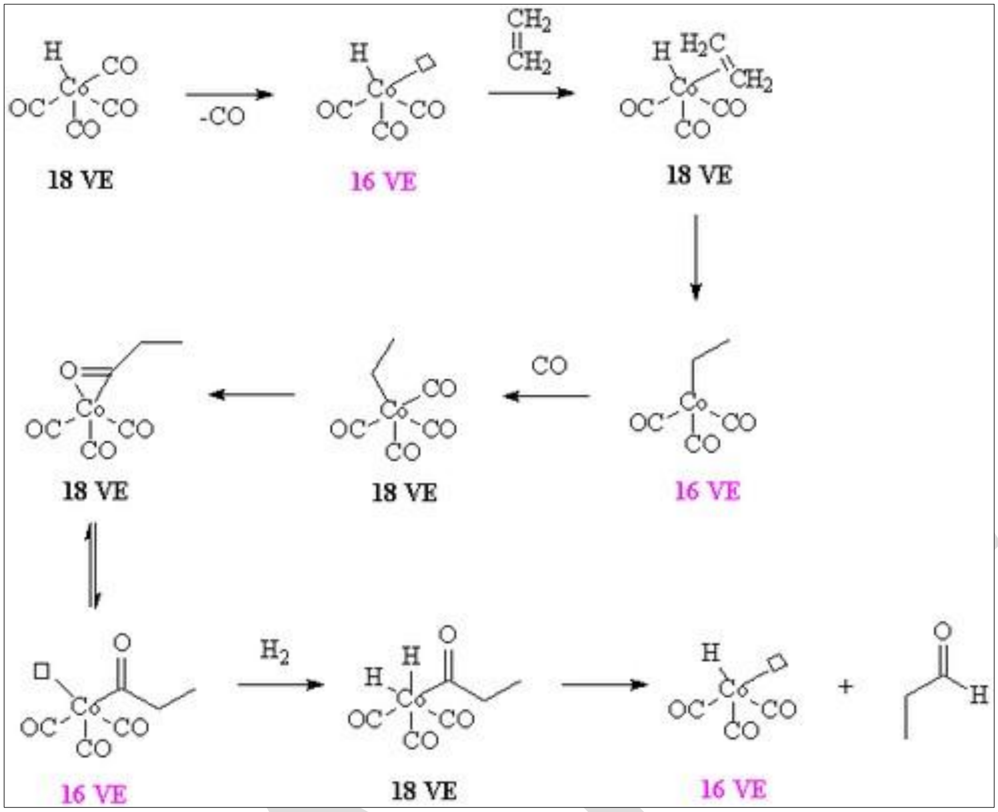


Electronic effects

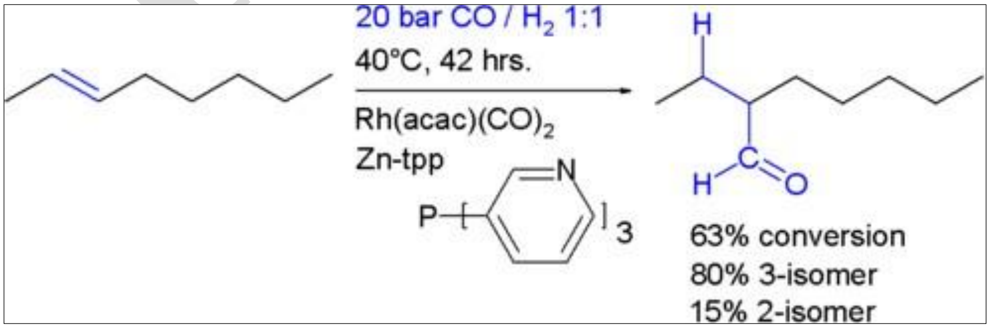
In addition, the more electron-rich the hydride complex is the less proton-like the hydride is. Thus, as a result, the electronic effects that favour the Markovnikov addition to an alkene are less able to direct the hydride to the carbon atom bearing the most hydrogens already. Thus, as a result, as the metal centre becomes more electron-rich, the catalyst becomes more selective for the straight chain compounds.

Acetyl formation

After the alkyl formation a second migatory insertion converts the alkyl into an acetyl ligand (this is when the alkyl carbon forms a bond with the carbon of a carbonyl ligand). The vacant site on the metal is filled by two hydrogens (from the oxidative insertion of a hydrogen molecule.
One of these hydrides then takes part in a reductive elimination to form the molecule of the aldehyde and the complex $[HCo(CO)_3]$.



It is important that the rate of migatory insertion of the carbonyl into the carbon-metal bond of the alkyl is fast; in systems where the migatory insertion does not occur (such as nickel hydride tristriphenyl phosphite), the reaction of the hydride with the alkene is reversible. This results in the isomerisation of the alkene, in this way oct-2-ene could be converted into a mixture of both oct-1-ene and oct-2-ene by a beta hydride elimination from the alkyl. In the system below, the rate of insertion of the carbonyl carbon into the C-M bond is likely to be greater than the rate of beta-hydride elimination. If the converse was true then some n-C_8H_{17}CHO would have been formed. Hydroformylation of 2-octene: the rhodium catalyst is coordinated to acac and carbon monoxide and encapsulated in a molecular self-assembly process by zinc tetraphenylporphyrin or Zn-tpp and the pyridine analogue of triphenylphosphine. In this process very much like the way enzymes work encapsulation of the catalytic site explains the observed regioselectivity:

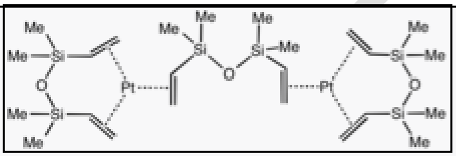


HYDORSILILYATION

The overall mechanism resembles that for homogeneous hydrogenation with additional steps. The reaction begins with the generation of coordinatively unsaturated metal hydrido carbonyl complex such as $HCo(CO)_3$ and $HRh(CO)(PPh_3)_3$. Such species bind alkenes, and the resulting complex undergoes a migratory insertion reaction to form an alkyl complex.

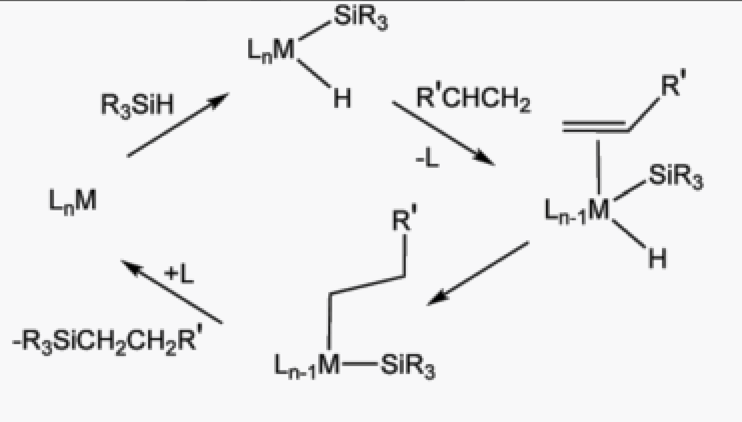
The catalytic transformation represents an important method for preparing organosilicon compounds. An idealized transformation is the addition of triethylsilane to diphenylacetylene:

$Et_3SiH + PhC{\equiv}CPh \rightarrow Et_3Si(Ph)C{=}CH(Ph)$



Kartstedt's catalyst is often used in hydrosilylation.

Hydrosilylation is related to hydrogenation, and similar catalysts are sometimes employed for the two catalytic processes. Popular industrial catalysts are "Speier's catalyst," H_2PtCl_6,
and Karstedt's catalyst, an alkene-stabilized platinum(0) catalyst. One prevalent mechanism, called the **Chalk-Harrod mechanism**, assumes an intermediate metal complex that contains a hydride, a silyl ligand (R_3Si), and the alkene substrate. The reaction usually produces anti- Markovnikov addition alkane, i.e., silicon on the terminal carbon. Variations of the Chalk- Harrod mechanism. Some cases involve insertion of alkene into M-Si bond followed by reductive elimination, the opposite of the sequence in the Chalk-Harrod mechanism. In certain
cases, hydrosilylation results in vinyl or allylic silanes resulting from beta-hydride elimination.



Idealized mechanism for metal-catalysed hydrosilylation of an alkene.

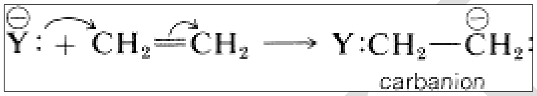
These reactions can also be catalyzed using nanomaterial-based catalysts.

ALKENE POLYMERIZATION

Most technically important polymerizations of alkenes occur by chain mechanisms and may be classed as anion, cation, or radical reactions, depending upon the character of the chain-carrying species. In each case, the key steps involve successive additions to molecules of the alkene, the differences being in the number of electrons that are supplied by the attacking agent for formation of the new carbon-carbon bond. For simplicity, these steps will be illustrated by using ethene, even though it does not polymerize very easily by any of them:

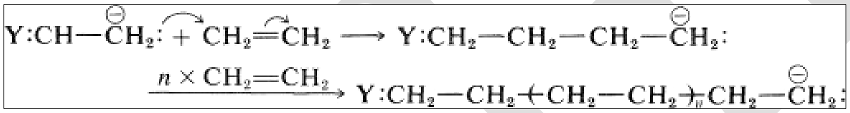
ANIONIC POLYMERIZATION

Initiation of alkene polymerization by the anion-chain mechanism may be formulated as involving an attack by a nucleophilic reagent Y⊖Y⊖ on one end of the double bond and formation of a carbanion:



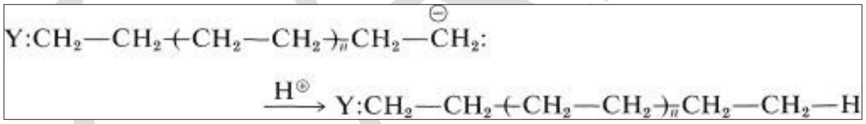
$$\overset{\ominus}{Y}{:} + CH_2{=}CH_2 \longrightarrow \underset{\text{carbanion}}{Y{:}CH_2-\overset{\ominus}{C}H_2{:}}$$

Attack by the carbanion on another alkene molecule would give a four-carbon carbanion, and subsequent additions to further alkene molecules would lead to a high-molecular-weight anion:



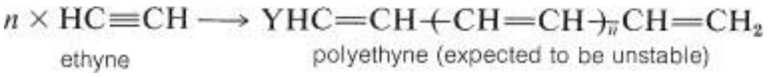
$$Y{:}CH-\overset{\ominus}{C}H_2{:} + CH_2{=}CH_2 \longrightarrow Y{:}CH_2-CH_2-CH_2-\overset{\ominus}{C}H_2{:}$$
$$\xrightarrow{n \times CH_2=CH_2} Y{:}CH_2-CH_2(CH_2-CH_2)_n CH_2-\overset{\ominus}{C}H_2{:}$$

The growing chain can be terminated by any reaction (such as the addition of a proton) that would destroy the carbanion on the end of the chain:



$$Y{:}CH_2-CH_2(CH_2-CH_2)_n CH_2-\overset{\ominus}{C}H_2{:} \xrightarrow{H^{\oplus}} Y{:}CH_2-CH_2(CH_2-CH_2)_n CH_2-CH_2-H$$

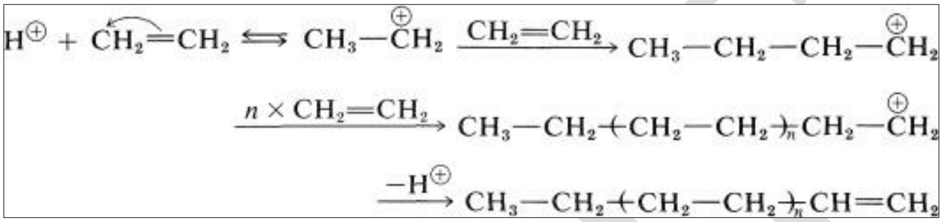
Anionic polymerization of alkenes is quite difficult to achieve because few anions (or nucleophiles) are able to add readily to alkene double bonds (see Section 10-6). Anionic polymerization occurs readily only with alkenes substituted with sufficiently powerful electron- attracting groups to expedite nucleophilic attack. By this reasoning, alkynes should polymerize more readily than alkenes under anionic conditions, but there appear to be no technically important alkyne polymerizations in operation by this or any other mechanism. Perhaps this is because the resultant polymer would be highly conjugated, and therefore highly reactive, and may not survive the experimental conditions:



$$n \times \underset{\text{ethyne}}{HC{\equiv}CH} \longrightarrow \underset{\text{polyethyne (expected to be unstable)}}{YHC{=}CH(CH{=}CH)_n CH{=}CH_2}$$

CATIONIC POLYMERIZATION

Polymerization of an alkene by acidic reagents can be formulated by a mechanism similar to the addition of hydrogen halides to alkene linkages. First, a proton from a suitable acid adds to an alkene to yield a carbocation. Then, in the absence of any other reasonably strong nucleophilic reagent, another alkene molecule donates an electron pair and forms a longer-chain cation. Continuation of this process can lead to a high-molecular-weight cation. Termination can occur by loss of a proton. The following equations represent the overall reaction sequence:

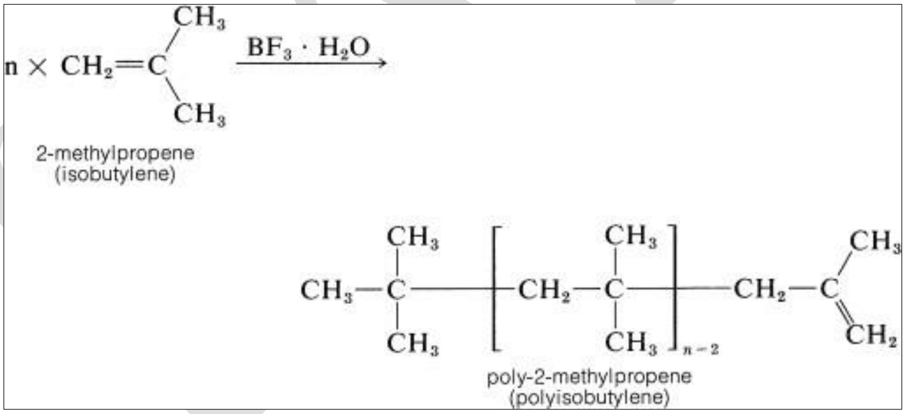


$$H^{\oplus} + CH_2{=}CH_2 \rightleftharpoons CH_3{-}\overset{\oplus}{C}H_2 \xrightarrow{CH_2=CH_2} CH_3{-}CH_2{-}CH_2{-}\overset{\oplus}{C}H_2$$

$$\xrightarrow{n \times CH_2=CH_2} CH_3{-}CH_2{-}(CH_2{-}CH_2)_n{-}CH_2{-}\overset{\oplus}{C}H_2$$

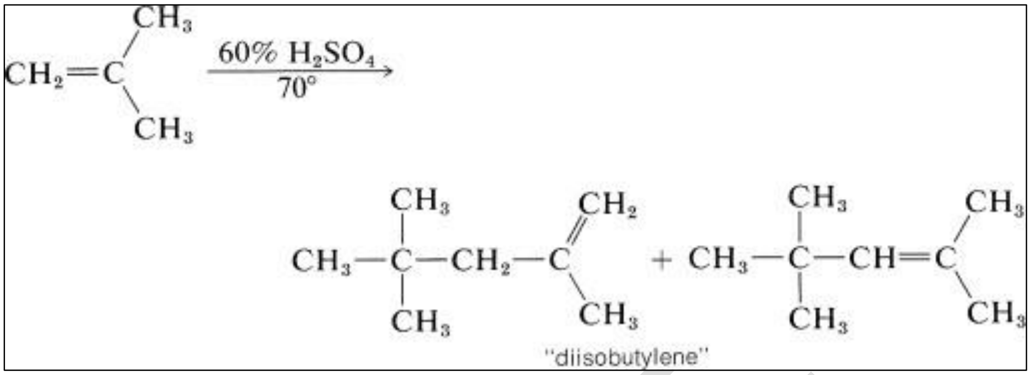
$$\xrightarrow{-H^{\oplus}} CH_3{-}CH_2{-}(CH_2{-}CH_2)_n{-}CH{=}CH_2$$

Ethene does not polymerize by the cationic mechanism because it does not have sufficiently electron-donating groups to permit easy formation of the intermediate growing-chain cation. 2- Methylpropene has electron-donating alkyl groups and polymerizes much more easily than ethene by this type of mechanism. The usual catalysts for cationic polymerization of 2- methylpropene are sulfuric acid, hydrogen fluoride, or a complex of boron trifluoride and water. Under nearly anhydrous conditions a very long chain polymer called polyisobutylene is formed.



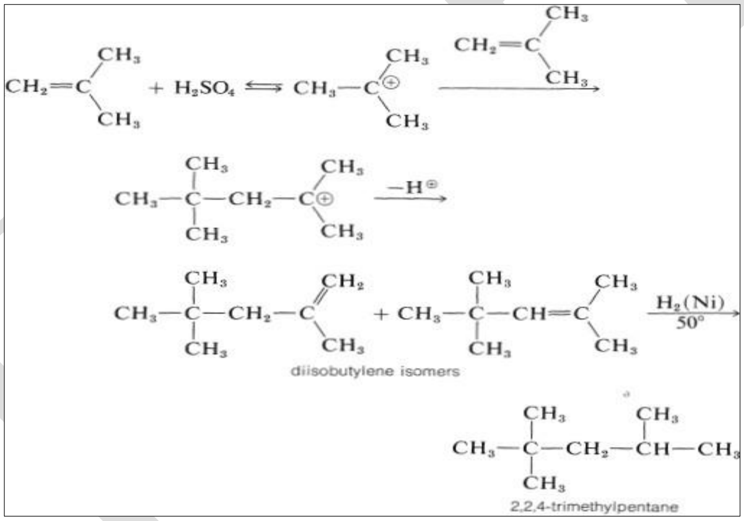
Polyisobutylene fractions of particular molecular weights are very tacky and are used as adhesives for pressure-sealing tapes.

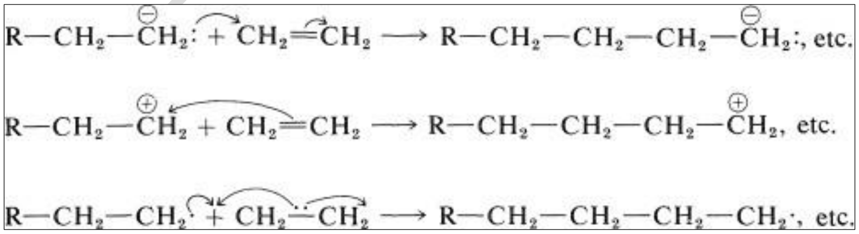
In the presence of 60%60% sulfuric acid, 2-methylpropene is *not* converted to a long-chain polymer, but to a mixture of eight-carbon alkenes. The mechanism is like that of the polymerization of 2-methylpropene under nearly anhydrous conditions, except that chain termination occurs after only one 2-methylpropene molecule has been added:



The short chain length is due to the *high water concentration*; the intermediate carbocation loses a proton to water *before* it can react with another alkene molecule.

The proton can be lost in two different ways, and a mixture of alkene isomers is obtained. The alkene mixture is known as "diisobutylene" and has a number of commercial uses. Hydrogenation yields 2,2,4-trimethylpentane (often erroneously called "isooctane"), which is used as the standard "100 antiknock rating" fuel for internal-combustion gasoline engines:

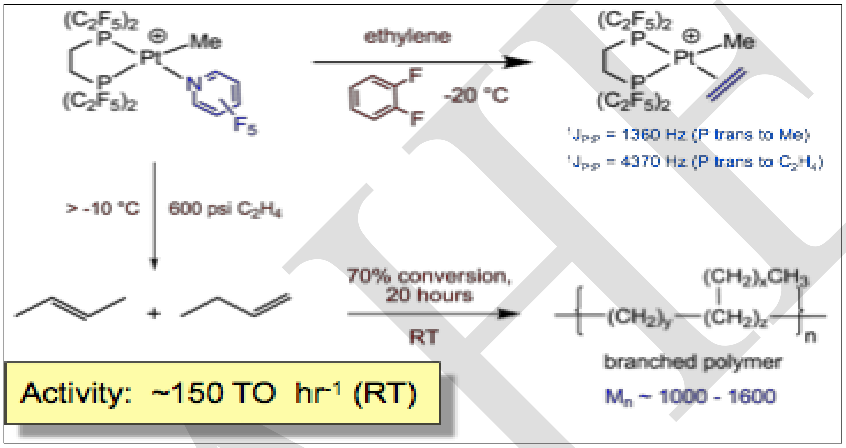




ALKENE OLIGOMERISATION

A major advance in alkene oligomerization catalysis was Brookhart's 1995 report of highly active group 10 metal diimine systems. In contrast to nickel and palladium catalysts, the corresponding platinum diimine system has very limited activity towards ethylene dimerization. In 1999 we reported a related PFAP system which, though somewhat more active, was limited by slow anion dissociation (White & Bennett, Organometallics 1999):

We have more recently reported the synthesis of a labile platinum PFAP system which is considerably more active (Basu, Organmetallics 2008). Production of 2-butenes occurs at subambient temperatures and is followed by proton-mediated oligomerization initiated by highly acidic platinum hydride intermediates:



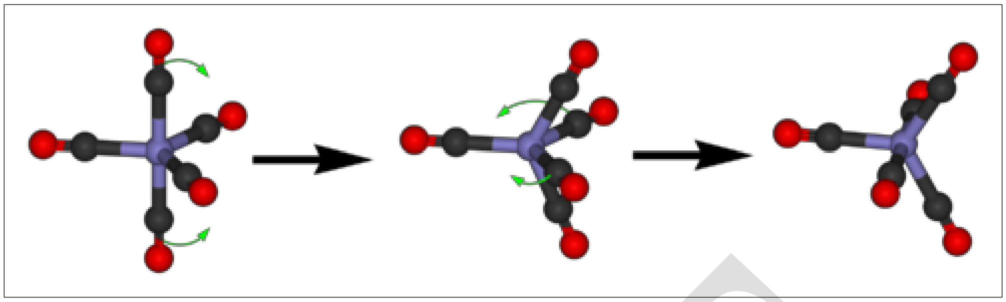
The dimerization activity of electron-poor (dfepe)Pt(Me)(C2H4)$^{+}$ is orders of magnitude greaterthan the corresponding diimine system: subsequent kinetic studies have determined the ethylene insertion barrier for (dfepe)Pt(Et)(C2H4)$^{+}$ to be 17.3 kcal mol^{-1}, nearly 13 kcal mol^{-1}lower than that reported for the diimine analog (29.6 kcal mol^{-1}) and comparable to palladium diimine catalysts (17 - 19 kcal mol^{-1})

Why are PFAP systems so much more reactive than conventional diimine analogs? DFT calculations as well as a current program of developing a wide range of alkylphosphine analogs indicate that lower alkene insertion barriers are due to a combination of high phosphine trans influence (i.e., a weakening of the trans metal-alkyl bond) and a reduction of metal electron density imparted by PFAP ligands. We are currently exploring these ideas with the aim of establishing a new class of highly-active oligomerization catalysts.

FLUXIONAL MOLECULES

Fluxional molecules are molecules that undergo dynamics such that some or all of their atoms interchange between symmetry-equivalent positions. Because virtually all molecules are fluxional in some respects, e.g. bond rotations in most organic compounds, the term fluxional depends on the context and the method used to assess the dynamics. Often, a molecule is considered fluxional if its spectroscopic signature exhibits line-broadening (beyond that dictatedby the Heisenberg uncertainty principle) due to chemical exchange. In some cases, where the rates are slow, fluxionality is not detected spectroscopically, but by isotopic labeling.

BERRY PSEUDOROTATION



Pentacoordinate molecules of trigonal pyramidal geometry typically exhibit a particular kind of low energy fluxional behavior called Berry pseudorotation. Famous examples of such molecules are iron pentacarbonyl ($Fe(CO)_5$) and phosphorus pentafluoride (PF_5). At higher temperatures, only one signal is observed for the ligands (e.g., by ^{13}C or ^{19}F NMR) whereas at low temperatures, two signals in a 2:3 ratio can be resolved. Molecules that are not strictly pentacoordinate are also subject to this process, such as SF_4.

Suggested Materials

Text Books:

T1: James E. Huheey, Ellen A. Keiter, Richard L. Keiter, Okhil K. Medhi. (2013). *Inorganic Chemistry-Principles of structure and Reactivity* (IV Edition) New Delhi pearson education, India

T2: Cotton, F.A,G.,Murillo,C.A., & Bochmann, M.(2007). *Advanced Inorganic Chemistry* (VI Edition).New York:John Wiley & Sons.

POSSIBLE QUESTIONS

Part A
(1 Mark Q.No 1 to 20)
(Online Examination)

Part B (2marks)

1. What are fluxional molecules?
2. Give an example for hydroformylation reaction.
3. What is known as hydrogenation reaction.Give an example.
4. What is co-oridinative unsaturation?
5. Mention few reactions of alkene polymerization.
6. Mention few reactions of alkene oligomerisation.

Part C (8 marks)

1. Write notes on
    a. hydrogenation reactions (ii)fluxional molecules
2. Write notes on
    a. hydroformylation reactions (ii)insertion reactions of alkenes.
3. Illustrate with an example the catalytic reaction of alkenes, the hydrogenation reaction.
4. Explain alkene polymerization and oligomerisation.
5. Discuss Insertion reactions of alkenes and hydrogenation reactions
6. Explain hydrosilation and isomerisation of alkenes in detail.
7. Explain hydrogenation reactions in organometallic compounds.
8. Write a note on fluxional molecules
9. Discuss alkene polymerization in organometallic compounds.
10. Explain hydroformylation reactions in organometallic compounds

19CHP102
Karpagam Academy of Higher Education
Coimbatore-21

(For the candidate admitted on 2019 onwards)
Department of Chemistry
I- semester
INORGANIC CHEMISTRY-I (Nuclear Chemistry and Metalic clusters)

UNITIII- Objective Questions for online examination (Each carry 1 Marks)

S.No	Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers
1	The reaction of an alkene with carbon monoxide and hydrogen,catalysed by cobalt or rhodium salts, to form an aldehyde is called-------------	hydroformylation	hydrosilation	hydrogenation	oxylation	hydroformylation
2	Hydroformylation was discovered by	einstein	charles	boyles	roelen	roelen
3	Hydroformylation was discovered in-----------	1948	1938	1928	1918	1938
4	About 5 million tons of aldehyde and----------- derivatives are produced annually	aldehydes	ketones	acids	esters	aldehydes
5	The name hydroformylation arises from the fact that a hydrogen atom and a ---------group are added across a double bond	formyl	aldehydes	ketones	acids	formyl
6	The net result of hydroformylation is extension of the ------------------chain by one and introduction of oxygen into the molecule	carbon	boron	nitrogen	halogen	carbon
7	HCo(CO)4 is a --------------species	17	16	18	15	18
8	HCo(CO)3 is a ----------species	16	17	18	19	16
9	In hydroformylation the aldehydes products are reduced to give-------------	acids	alcohols	esters	ketones	alcohols

10	In hydroformylation, some disadvantages are associated with the cobalt carbonyl catalyst when it is used to converst propylene to ---------	butyraldehyde	alcohols	esters	ketones	butyraldehyde
11	The reaction of hydrogen gas with ethylene is thermodynamically favourable, it does not take place at room temperature and ------------	pressure	concentration	volume	composition	pressure
12	In hydrogenation, presence of metallic nickel, copper, the reaction is -----------	fast and incomplete	fast and complete	slow and complete	slow and incomplete	fast and complete
13	In hydrogenation an inert solid support such as-----------is used	alumina	silica	oxygen	carbon dioxide	alumina
14	The first effective homogeneous catalyst to be discovered for hydrogenation was the---------- 16 electron d8 complex	square planar	pyramidal	tetrahedral	triagonal pyramidal	square planar
15	(Ph3P)3RhCl is a ---------catalyst	Wilkinson’s	dewar	albert	alexander	Wilkinson’s catalyst
16	An alkene can coordinate and react with a coordinated hydrogen ligand to form an ----- group	alkyl	aryl	keto	acid	alkyl
17	----------------is commonly chosen to illustrate homogeneous hydrogenation with wilkinsons catalyst	propylene	ethylene	butylene	methylene	ethylene
18	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
19	Oxidative addition reactions lead to products that appear to have had a --------atom inserted into a bond	metal	atom	molecule	proton	metal

20	Insertion reactions are enormously important in ----- ---------------cylces	catalytic	polymeric	material	dimeric	catalytic
21	A classic example of a CO insertion reaction is found in the work of ------------and calderazzo	einstein	albert	noack	clausius	noack
22	The reverse of insertion is called -------------	decarbonylation	carbonylation	oxidation	reduction	decarbonylation
23	The CO of the acetyl ligand has a choice of --------------cis positions	3	4	5	6	3
24	Insertion involves ligands which are------------------to one another	cis	trans	exo	endo	cis
25	The reverse reaction in isertion cannot occur unless a -------------------is first eliminated	acid	base	ligand	keto	ligand
26	Inversion of configuration is expected for-------------migration	ethyl	methyl	propyl	pentyl	ethyl
27	Retention is expected for ------------insertion	carbonyl	keto	acids	aldehyde	carbonyl
28	--------------of configuration is observed in nitromethane	retention	inversion	insertion	elimination	inversion
29	β elimination represents the chief pathway for decompositionof a --------------metal alkyl complexs	s block	p block	transition	inner transition	transition
30	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
31	Coordinatively saturated catalyst precursors become activated by -------------loss	electron	ligand	metal	proton	ligand
32	Ligand dissociation is most commonly induced by --------------and is assisted by the solvent	cooling	heating	polymerising	condensing	heating

33	At higher temperature the red mononuclear complex is converted to the ------------halide bridged species	orange	red	white	Yellow	orange
34	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
35	Thermal subsititution reactions of --------- electron species are highly reactive	16	17	18	19	17
36	Coordinatively unsaturated compounds whether transition metal or main group element are capable of -----electron donor ligands	accepting	donating	accepting and donating	donating and accepting	accepting
37	Oxidative addition can also occur with metal-metal----------bonds	multiple	single	double	triple	multiple
38	Olefin isomerizations can follow ------------- different mechanisms	two	three	four	five	two
39	In zieglar natta polymerisation ---------is reduced by AlEt3 to polymeric TiCl3	TiCl4	TiCl5	TiCl3	TiCl2	TiCl4
40	Among organometallic compounds the molecules in which the M-C bond exchanges sites by choosing different carbon atoms at different times is called ----------------molecule	fluxional	polymer	dimer	monomer	fluxional
41	Fluxionality is seen characteristically in organometallic compounds containing ----------cyclic polyolefins	conjugated	unconjugated	saturated	unsaturated	conjugated
42	Insertion involves ligands which are------------------to one another	cis	trans	exo	endo	cis
43	The reverse reaction in isertion cannot occur unless a --------------------is first eliminated	acid	base	ligand	keto	ligand
44	Inversion of configuration is expected for-------------migration	ethyl	methyl	propyl	pentyl	ethyl

45	Retention is expected for -------------insertion	carbonyl	keto	acids	aldehyde	carbonyl
46	---------------of configuration is observed in nitromethane	retention	inversion	insertion	elimination	inversion
47	HCo(CO)4 is a ---------------species	17	16	18	15	18
48	HCo(CO)3 is a -----------species	16	17	18	19	16
49	In hydroformylation the aldehydes products are reduced to give--------------	acids	alcohols	esters	ketones	alcohols
50	In hydroformylation, some disadvantages are associated with the cobalt carbonyl catalyst when it is used to converst propylene to ---------	butyraldehyde	alcohols	esters	ketones	butyraldehyde
51	The reaction of hydrogen gas with ethylene is thermodynamically favourable, it does not take place at room temperature and ------------	pressure	concentration	volume	composition	pressure
52	In hydrogenation, presence of metallic nickel, copper, the reaction is -----------	fast and incomplete	fast and complete	slow and complete	slow and incomplete	fast and complete
53	Coordinatively saturated catalyst precursors become activated by --------------loss	electron	ligand	metal	proton	ligand
54	Ligand dissociation is most commonly induced by ---------------and is assisted by the solvent	cooling	heating	polymerising	condensing	heating
55	At higher temperature the red mononuclear complex is converted to the ------------halide bridged species	orange	red	white	Yellow	orange
56	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
57	Thermal subsititution reactions of --------- electron species are highly reactive	16	17	18	19	17

58	In hydroformylation, some disadvantages are associated with the cobalt carbonyl catalyst when it is used to converst propylene to ---------	butyraldehyde	alcohols	esters	ketones	butyraldehyde
59	The reaction of hydrogen gas with ethylene is thermodynamically favourable, it does not take place at room temperature and ------------	pressure	concentration	volume	composition	pressure
60	In hydrogenation, presence of metallic nickel, copper, the reaction is -----------	fast and incomplete	fast and complete	slow and complete	slow and incomplete	fast and complete

UNIT IV

SYLLABUS

Nuclear Chemistry: The nucleus-subatomic particles and their properties, binding energy. N/P ratios in stable and meta stable nuclei-different type of nuclear forces-liquid model-shell model. Modes of radioactive decay-α,β and γ decay radiation, electron capture, nuclear isomerism and internal conversion

NUCLEAR CHEMISTRY

Any subatomic particle, like any particle in the 3-dimensional space that obeys laws of quantum mechanics, can be either a boson (an integer spin) or a fermion (a half-integer spin).

By composition

The elementary particles of the Standard Model include:

- Six "flavors" of quarks: up, down, bottom, top, strange, and charm;
- Six types of leptons: electron, electron neutrino, muon, muon neutrino, tau, tau neutrino;
- Twelve gauge bosons (force carriers): the photon of electromagnetism, the three W and Z bosons of the weak force, and the eight gluons of the strong force;
- The Higgs boson.

Various extensions of the Standard Model predict the existence of an elementary graviton particle and many other elementary particles.

Composite subatomic particles (such as protons or atomic nuclei) are bound states of two or more elementary particles. For example, a proton is made of two up quarks and one down quark, while the atomic nucleus of helium-4 is composed of two protons and two neutrons. The neutron is made of two down quarks and one up quark. Composite particles include all hadrons: these include baryons (such as protons and neutrons) and mesons (such as pions and kaons).

By mass

In special relativity, the energy of a particle at rest equals its mass times the speed of light squared, $E = mc^2$. That is, mass can be expressed in terms of energy and vice versa. If a particle has a frame of reference where it lies at rest, then it has a positive rest mass and is referred to as *massive*.

All composite particles are massive. Baryons (meaning "heavy") tend to have greater mass than mesons (meaning "intermediate"), which in turn tend to be heavier than leptons (meaning "lightweight"), but the heaviest lepton (the tau particle) is heavier than the two lightest flavours of baryons (nucleons). It is also certain that any particle with an electric charge is massive.

All massless particles (particles whose invariant mass is zero) are elementary. These include the photon and gluon, although the latter cannot be isolated.

Other properties

Through the work of Albert Einstein, Satyendra Nath Bose, Louis de Broglie, and many others, current scientific theory holds that *all* particles also have a wave nature. This has been verified not only for elementary particles but also for compound particles like atoms and even molecules. In fact, according to traditional formulations of non-relativistic quantum mechanics, wave– particle duality applies to all objects, even macroscopic ones; although the wave properties of macroscopic objects cannot be detected due to their small wavelengths.

Interactions between particles have been scrutinized for many centuries, and a few simple laws underpin how particles behave in collisions and interactions. The most fundamental of these are the laws of conservation of energy and conservation of momentum, which let us make calculations of particle interactions on scales of magnitude that range from stars to quarks. These are the prerequisite basics of Newtonian mechanics, a series of statements and equations in *Philosophiae Naturalis Principia Mathematica*, originally published in 1687.

Dividing an atom

The negatively charged electron has a mass equal to $^1⁄_{1837 \text{ or } 1836}$ of that of a hydrogen atom. The remainder of the hydrogen atom's mass comes from the positively charged proton. The atomic number of an element is the number of protons in its nucleus. Neutrons are neutral particles having a mass slightly greater than that of the proton. Different isotopes of the same element contain the same number of protons but differing numbers of neutrons. The mass number of an isotope is the total number of nucleons (neutrons and protons collectively).

Chemistry concerns itself with how electron sharing binds atoms into structures such as crystals and molecules. Nuclear physics deals with how protons and neutrons arrange themselves in nuclei. The study of subatomic particles, atoms and molecules, and their structure and interactions, requires quantum mechanics. Analyzing processes that change the numbers and types of particles requires quantum field theory. The study of subatomic particles *per se* is called particle physics. The term *high-energy physics* is nearly synonymous to "particle physics" since creation of particles requires high energies: it occurs only as a result of cosmic rays, or in particle accelerators. Particle phenomenology systematizes the knowledge about subatomic particles obtained from these experiments. Total known Isotopes of Hydrogen - Deuterium and tritium – 2

BINDING ENERGY

In general, binding energy represents the mechanical work that must be done against the forces which hold an object together, disassembling the object into component parts separated by sufficient distance that further separation requires negligible additional work.

In bound systems, if the binding energy is removed from the system, it must be subtracted from the mass of the unbound system, simply because this energy *has* mass. Thus, if energy is removed (or emitted) from the system at the time it is bound, the loss of energy from the system will also result in the loss of the mass of the energy from the system.[1]System mass is not conserved in this process because the system is "open" (i.e., is not an isolated system to mass or energy input or loss) during the binding process.

There are several types of binding energy, each operating over a different distance and energy scale. The smaller the scale of a bound system, the higher its associated binding energy.

Types of binding energy

In astrophysics, the gravitational binding energy of an object, such as a celestial body, is the energy required to expand the material to infinity. Solely for the purpose of comparison with the other types of binding energy, if a body with the mass and radius of the Earth were made purely of hydrogen-1, then the gravitational binding energy of that body would be about 0.391658 eV per atom. If a hydrogen-1 body had the mass and radius of the Sun, its gravitational binding energy would be about 1,195.586 eV per atom.

At the molecular level, bond energy and bond-dissociation energy are measures of the binding energy between the atoms in a chemical bond. It is the energy required to disassemble a molecule into its constituent atoms. This energy appears as chemical energy, such as that released in chemical explosions, the burning of chemical fuel and biological processes. Bond energies and bond-dissociation energies are typically in the range of few eV per bond. For example, the bond-dissociation energy of a carbon-carbon bond is about 3.6 eV.

At the atomic level, the *atomic binding energy* of the atom derives from electromagnetic interaction, mediated by photons. It is the energy required to disassemble an atom into free electrons and a nucleus.[2] Electron binding energy is a measure of the energy required to free electrons from their atomic orbits. This is more commonly known as ionization energy. Among the chemical elements, the range of ionization energies is from 3.8939 eV for the first electron in an atom of caesium to 11.567617 keV for the 29th electron in an atom of copper.

At the nuclear level, nuclear binding energy is the energy required to disassemble a nucleus into the free, unbound neutrons and protons it is composed of. It is the energy equivalent of the mass defect, the difference between the mass number of a nucleus and its true measured mass. Nuclear binding energy derives from the nuclear force or residual strong force, which is mediated by three types of mesons. The average nuclear binding energy per nucleon ranges from 2.22452 MeV for hydrogen-2 to 8.7945 MeV for nickel-62.

At a yet more fundamental level, quantum chromodynamics binding energy is the energy which binds the various quarks together inside a hadron. This energy derives from the strong interaction, which is mediated by gluons. The chromodynamic binding energy inside a nucleon, for example, amounts to approximately 99% of the nucleon's mass. The chromodynamic binding energy of a proton is about 928.9 MeV, while that of a neutron is about 927.7 MeV.

DIFFERENT TYPES OF NUCLEAR FORCES

The **nuclear force** (or **nucleon–nucleon interaction** or **residual strong force**) is a force that acts between the protons and neutrons of atoms. Neutrons and protons, both nucleons, are affected by the nuclear force almost identically. Since protons have charge +1 *e*, they experience an electric force that tends to push them apart, but at short range the attractive nuclear force is strong enough to overcome the electromagnetic force. The nuclear force binds nucleons into atomic nuclei.

The nuclear force is powerfully attractive between nucleons at distances of about 1 femtometre (fm, or 1.0×10^{-15} metres), but it rapidly decreases to insignificance at distances beyond about 2.5 fm. At distances less than 0.7 fm, the nuclear force becomes repulsive. This repulsive component is responsible for the physical size of nuclei, since the nucleons can come no closer than the force allows. By comparison, the size of an atom, measured in angstroms (Å, or 1.0×10^{-10} m), is five orders of magnitude larger. The nuclear force is not simple, however, since it depends on the nucleon spins, has a tensor component, and may depend on the relative momentum of the nucleons. The nuclear force is not one of the fundamental forces of nature.

The nuclear force plays an essential role in storing energy that is used in nuclear power and nuclear weapons. Work (energy) is required to bring charged protons together against their electric repulsion. This energy is stored when the protons and neutrons are bound together by the nuclear force to form a nucleus. The mass of a nucleus is less than the sum total of the individual masses of the protons and neutrons. The difference in masses is known as the mass defect, which can be expressed as an energy equivalent. Energy is released when a heavy nucleus breaks apart into two or more lighter nuclei. This energy is the electromagnetic potential energy that is released when the nuclear force no longer holds the charged nuclear fragments together.

A quantitative description of the nuclear force relies on equations that are partly empirical. These equations model the internucleon potential energies, or potentials. (Generally, forces within a system of particles can be more simply modeled by describing the system's potential energy; the negative gradient of a potential is equal to the vector force.) The constants for the equations are phenomenological, that is, determined by fitting the equations to experimental data. The internucleon potentials attempt to describe the properties of nucleon–nucleon interaction. Once determined, any given potential can be used in, e.g., the Schrödinger equation to determine the quantum mechanical properties of the nucleon system.

The discovery of the neutron in 1932 revealed that atomic nuclei were made of protons and neutrons, held together by an attractive force. By 1935 the nuclear force was conceived to be transmitted by particles called mesons. This theoretical development included a description of the Yukawa potential, an early example of a nuclear potential. Mesons, predicted by theory, were discovered experimentally in 1947. By the 1970s, the quark model had been developed, by which the mesons and nucleons were viewed as composed of quarks and gluons. By this new model, the nuclear force, resulting from the exchange of mesons between neighboring nucleons, is a residual effect of the strong force.

THE LIQUID-DROP MODEL

One of the first models which could describe very well the behavior of the nuclear binding energies and therefore of nuclear masses was the mass formula of **von Weizsaecker** (also called **the semi-empirical mass formula – SEMF**), that was published in 1935 by German physicist **Carl Friedrich von Weizsäcker**. This theory is based on **the liquid drop model**proposed by **George Gamow**.

According to this model, the atomic nucleus behaves **like the molecules in a drop** of liquid. But in this nuclear scale, the fluid is made of nucleons (protons and neutrons), which are held together by **the strong nuclear force**. The liquid drop model of the nucleus takes into account the fact that the nuclear forces on the nucleons on the surface are different from those on nucleons in the interior of the nucleus. The **interior nucleons are completely surrounded** by other attracting nucleons. Here is the analogy with the forces that form a drop of liquid.

In the ground state the nucleus is **spherical**. If the sufficient kinetic or binding energy is added, this spherical nucleus may be distorted into a **dumbbell shape** and then may be splitted into **two fragments**. Since these fragments are a more stable configuration, the splitting of such heavy nuclei must be accompanied by **energy release**. This model does not explain all the properties of the atomic nucleus, but does explain the predicted nuclear binding energies.

The nuclear binding energy as a function of the mass number A and the number ofprotons Z based on **the liquid drop model** can be written as:

$$E_b(MeV) = a_V A - a_S A^{\frac{2}{3}} - a_C \frac{Z^2}{A^{\frac{1}{3}}} - a_A \frac{(A-2Z)^2}{A} \pm \delta(A,Z)$$

$$\delta(A,Z) = \begin{array}{c} +\delta_0 \; for \; Z,N \; even \\ 0 \\ -\delta_0 \; for \; Z,N \; odd \end{array}$$

The above formula is called **the Weizsaecker Formula** (or **the semi-empirical mass formula**). The physical meaning of this equation can be discussed term by term.

SHELL MODEL

In nuclear physics and nuclear chemistry, the **nuclear shell model** is a model of the atomic nucleus which uses the Pauli exclusion principle to describe the structure of the nucleus in terms of energy levels.[1] The first shell model was proposed by Dmitry Ivanenko (together with E. Gapon) in 1932. The model was developed in 1949 following independent work by several physicists, most notably Eugene Paul Wigner, Maria Goeppert Mayer and J. Hans D. Jensen, who shared the 1963 Nobel Prize in Physics for their contributions.

The shell model is partly analogous to the atomic shell model which describes the arrangement of electrons in an atom, in that a filled shell results in greater stability. When adding nucleons (protons or neutrons) to a nucleus, there are certain points where the binding energy of the next nucleon is significantly less than the last one. This observation, that there are certain magic numbers of nucleons: 2, 8, 20, 28, 50, 82, 126 which are more tightly bound than the next higher number, is the origin of the shell model.

The shells for protons and for neutrons are independent of each other. Therefore, one can have "magic nuclei" where one nucleon type or the other is at a magic number, and "doubly magic nuclei", where both are. Due to some variations in orbital filling, the upper magic numbers are 126 and, speculatively, 184 for neutrons but only 114 for protons, playing a role in the search for the so-called island of stability. Some semimagic numbers have been found, notably Z=40 giving nuclear shell filling for the various elements; 16 may also be a magic number.[2]

In order to get these numbers, the nuclear shell model starts from an average potential with a shape something between the square well and the harmonic oscillator. To this potential a spin orbit term is added. Even so, the total perturbation does not coincide with experiment, and an empirical spin orbit coupling must be added with at least two or three different values of its coupling constant, depending on the nuclei being studied.

Nevertheless, the magic numbers of nucleons, as well as other properties, can be arrived at by approximating the model with a three-dimensional harmonic oscillator plus a spin-orbit interaction. A more realistic but also complicated potential is known as Woods–Saxon potential.

Together with the spin-orbit interaction, and for appropriate magnitudes of both effects, one is led to the following qualitative picture: At all levels, the highest *j* states have their energies shifted downwards, especially for high *n*(where the highest *j* is high). This is both due to the negative spin-orbit interaction energy and to the reduction in energy resulting from deforming the potential to a more realistic one. The second-to-highest *j* states, on the contrary, have their energy shifted up by the first effect and down by the second effect, leading to a small overall shift. The shifts in the energy of the highest *j* states can thus bring the energy of states of one level to be closer to the energy of states of a lower level. The "shells" of the shell model are then no longer identical to the levels denoted by *n*, and the magic numbers are changed.

We may then suppose that the highest *j* states for $n = 3$ have an intermediate energy between the average energies of $n = 2$ and $n = 3$, and suppose that the highest *j* states for larger *n* (at least up to $n = 7$) have an energy closer to the average energy of $n-1$.

Note that the numbers of states after the 4th shell are doubled triangular numbers plus two. Spin-orbit coupling causes so-called 'intruder levels' to drop down from the next higher shell into the structure of the previous shell. The sizes of the intruders are such that the resulting shell sizes are themselves increased to the very next higher doubled triangular numbers from those of the harmonic oscillator.

MODES OF RADIOACTIVE DECAY

Radioactive decay occurs when an unstable atomic nucleus loses energy by emitting energy in the form of emitted particles or electromagnetic waves, called radiation. Isotopes are atoms of the same element (thereby having the same number of protons) which differ in the number of neutrons in their nucleus. Some isotopes of a given element are more unstable than others, causing a nuclear reaction which releases energy to achieve a more stable nuclear configuration. Such isotopes are radioactive, and are referred to as "radioisotopes."

Types of Decay

There are many types of emitted particles and radiation that radioisotopes produce when they decay. The types we will discuss here are: alpha, beta, and gamma (listed in increasing ability to penetrate matter). Alpha decay is seen only in heavier elements greater than atomic number 52, tellurium. The other two types of decay are seen in all of the elements.

Alpha Decay

Alpha decay is usually restricted to the heavier elements in the periodic table. (Only a handful of nuclides with atomic numbers less than 83 emit an α-particle.) The product of α-decay is easy to predict if we assume that both mass and charge are conserved in nuclear reactions. Alpha decay of the ^{238}U "parent" nuclide, for example, produces ^{234}Th as the "daughter" nuclide.

$$^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He \qquad (\alpha\text{-decay})$$

The sum of the mass numbers of the products (234 + 4) is equal to the mass number of the parent nuclide (238), and the sum of the charges on the products (90 + 2) is equal to the charge on the parent nuclide.

Beta Decay

Here are three different modes of beta decay:

- electron emission
- electron capture
- positron emission

Electron emission is literally the process in which an electron is ejected or emitted from the nucleus. When this happens, the charge on the nucleus increases by one. Electron emitters are found throughout the periodic table, from the lightest elements (^{3}H) to the heaviest (^{255}Es). The product of emission can be predicted by assuming that both mass number and charge are conserved in nuclear reactions. If ^{40}K is a emitter, for example, the product of this reaction must be ^{40}Ca.

$$^{40}_{19}K \rightarrow {}^{40}_{20}Ca + {}^{0}_{-1}e \qquad [\text{electron } (\beta^{-}) \text{ emission}]$$

Once again the sum of the mass numbers of the products is equal to the mass number of the parent nuclide and the sum of the charge on the products is equal to the charge on the parent nuclide.

Nuclei can also decay by capturing one of the electrons that surround the nucleus. **Electron capture** leads to a decrease of one in the charge on the nucleus. The energy given off in this reaction is carried by an x- ray photon, which is represented by the symbol hv, where h is Planck's constant and v is the frequency of the x-ray. The product of this reaction can be predicted, once again, by assuming that mass and charge are conserved.

$$^{40}_{19}K + {}^{0}_{-1}e \rightarrow {}^{40}_{18}Ar + h\nu \qquad (\text{electron capture})$$

The electron captured by the nucleus in this reaction is usually a 1s electron because electrons in this orbital are the closest to the nucleus.

A third form of beta decay is called **positron emission**. The positron is the antimatter equivalent of an electron. It has the same mass as an electron, but the opposite charge. Positron decay produces a daughter nuclide with one less positive charge on the nucleus than the parent.

$$ {}^{40}_{19}K \rightarrow {}^{40}_{18}Ar + {}^{0}_{+1}e \qquad [\text{positron } (\beta^{+}) \text{ emission}] $$

Positrons have a very short life-time. They rapidly lose their kinetic energy as they pass through matter. As soon as they come to rest, they combine with an electron to form two γ-ray photons in a matter- antimatter annihilation reaction.

$$ {}^{0}_{+1}e + {}^{0}_{-1}e \rightarrow 2\,\gamma $$

Thus, although it is theoretically possible to observe a fourth mode of beta decay corresponding to the capture of a positron, this reaction does not occur in nature.

Note that in all three forms of decay for the ^{40}K nuclide the mass number of the parent and daughter nuclides are the same for electron emission, electron capture, and position emission. All three forms of decay therefore interconvert isobars.

Gamma Decay

The daughter nuclides produced by α-decay are often obtained in an excited state. The excess energy associated with this excited state is released when the nucleus emits a photon in the γ-ray portion of the electromagnetic spectrum. Most of the time, the γ-ray is emitted within 10^{-12} seconds after the α-particle or particle. In some cases, gamma decay is delayed, and a short- lived, or **metastable**, nuclide is formed, which is identified by a small letter m written after the mass number. ^{60m}Co, for example, is produced by the electron emission of ^{60}Fe.

$$ {}^{60}_{26}Fe \rightarrow {}^{60m}_{27}Co + {}^{0}_{-1}e $$

The metastable ^{60m}Co nuclide has a half-life of 10.5 minutes. Since electromagnetic radiation carries neither charge nor mass, the product of -ray emission by ^{60m}Co is ^{60}Co.

$$ {}^{60m}_{27}Co \rightarrow {}^{60}_{27}Co + \gamma \qquad (\gamma\text{-ray emission}) $$

NUCLEAR ISOMERISM AND INTERNAL CONVERSION

A **nuclear isomer** is a metastable state of an atomic nucleus caused by the excitation of one or more of its nucleons (protons or neutrons). "Metastable" refers to the property of these nuclei that these excited states have half-lives more than 100 to 1000 times the half-lives of the excited nuclear states that decay with a "prompt" half life (ordinarily on the order of 10^{-12} seconds). As a result, the term "metastable" is usually restricted to refer to isomers with half-lives of 10^{-9} seconds or longer. Some sources recommend 5×10^{-9} seconds to distinguish the metastable half life from the normal "prompt" gamma emission half life.[1]Occasionally the half-lives are far longer than this, and can last minutes, hours, or years. In the case of 180m 73Ta
, a nuclear isomer has survived so long that it has never been observed to decay (at least 10^{15} years).

Sometimes, the gamma decay from a metastable state is given the special name of an isomeric transition, but with the exception of the long-lived nature of the meta-stable parent nuclear isomer, this process resembles shorter-lived gamma decays in all external aspects. The longer lives of nuclear isomers (metastable states) are often due to the larger degree of nuclear spin change which must be involved in their gamma emission to reach the ground state. This high spin change causes these decays to be forbidden transitions, and delayed. Delays in emission are also caused by low or high available decay energy.

The first nuclear isomer and decay-daughter system (uranium X_2/uranium Z, now known as 234m.

Internal conversion

While most metastable isomers decay through gamma ray emission, they can also decay by internal conversion, a process in which the energy of nuclear de-excitation is not emitted as a gamma ray, but instead used to accelerate one of the inner electrons of the atom, so that it leaves at high speed and energy. This result occurs because inner atomic electrons penetrate the nucleus, where they are subject to the intense electric fields which result when the protons of the nucleus re-arrange in a different way. In nuclei which are far from stability in energy, still other decay modes are known.

Metastable isomers

Metastable isomers can be produced through nuclear fusion or other nuclear reactions. A nucleus thus produced generally starts its existence in an excited state that relaxes through the emission of one or more gamma rays or conversion electrons. Sometimes it happens that the de- excitation does not proceed rapidly all the way to the nuclear ground state. This usually occurs because of the formation of an intermediate excited state with a spin far different from that of the ground state. Gamma-ray emission is far slower (is "hindered") if the spin of the post-emission state is very different from that of the emitting state, particularly if the excitation energy is low.

The excited state in this situation is therefore a good candidate to be metastable if there are no other states of intermediate spin with excitation energies less than that of the metastable state.

Metastable isomers of a particular isotope are usually designated with an "m" (or, in the case of isotopes with more than one isomer, m1, m2, m3, and so on). This designation is placed after the mass number of the atom; for example, cobalt-58m (abbreviated 58m 27Co, where

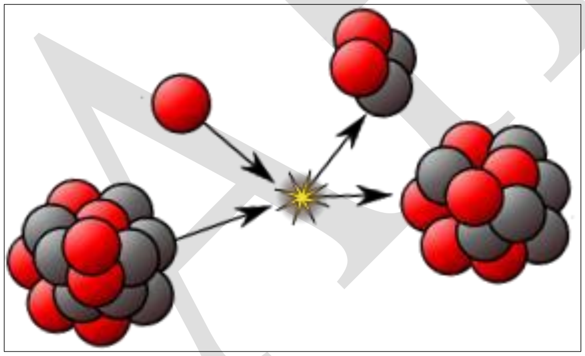
27 is the atomic number of cobalt). Increasing indices, m1, m2, etc., correlate with increasing levels of excitation energy stored in each of the isomeric states (e.g., hafnium- 178m2).

A different kind of metastable nuclear state (isomer) is the fission **isomer** or **shape isomer**. Most actinide nuclei, in their ground states, are not spherical, but rather spheroidal—specifically, prolate, with an axis of symmetry longer than the other axes (similar to an American football or rugby ball). In some of these, quantum-mechanical states can exist in which the distribution of protons and neutrons is farther yet from spherical (about as non-spherical as an American football), so much so that de-excitation to the nuclear ground state is strongly hindered. In general, these states either de-excite to the ground state (albeit far more slowly than a "usual" excited state) or undergo spontaneous fission with half-lives of the order of nanoseconds or microseconds—a very short time, but many orders of magnitude longer than the half-life of a more usual nuclear excited state. Fission isomers are usually denoted with a postscript or superscript "f" rather than "m", so that a fission isomer in, e.g., plutonium 240 is denoted plutonium-240f or 240f, 94Pu.

NUCLEAR FORCES

Definition:

Nuclear force is one of the four fundamental forces of nature, the others being gravitational and electromagnetic forces. In fact, being 10 million times stronger than the chemical binding forces, they are also known as the strong forces. In this section, we will discuss this force in detail.



Nuclear force is the force that binds the neutrons and protons in a nucleus together. This force can exist between neutrons and neutrons, neutrons and protons or protons and protons. This force is what holds the nucleus together. The charge of protons, which is +1*e*, tends to push them away from each other with a strong electric field repulsive force, following Coulomb's law. But nuclear force is strong enough to overcome that resistance at short range and keep them together. **Properties**

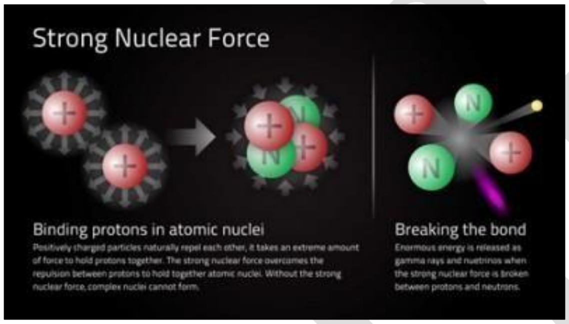
- It is attractive in nature but with a repulsive core. That is the reason that the nucleus is held together without collapsing in itself.
- The **range of nuclear force** is very short. At 1 Fermi, the distance between particles in a nucleus is extremely small. At this range, the nuclear force is much stronger than the repulsive

Coulomb's force that pushes the particles away. However, if the distance is anything more than 2.5 Fermi, nuclear force is practically non-existent.

- Nuclear force is identical for all nucleons. It does not matter if it is a neutron or proton, once the Coulomb resistance is taken into consideration, nuclear force affects everything in the same way.
- At a distance less than 0.7 Fermi, this force becomes repulsive. It is one of the most interesting **properties of nuclear force**, as this repulsive component of the force is what decides the size of the nucleus. The nucleons come closer to each other till the point that the force allows, after which they cannot come any closer because of the repulsive property of the force.

Examples

The most obvious **example of Nuclear Force,** as discussed earlier, is the binding of protons, which are repulsive in nature because of their positive charge.



Positively charged particles naturally repel each other, it takes an extreme amount of force to hold protons together. The strong nuclear force overcomes the repulsion between protons to hold together atomic nuclei. Without the strong nuclear force, complex nuclei cannot form.

Enormous energy is released as gamma rays and nuetrinos when the strong nuclear force is broken between protons and neutrons.

On a larger scale, this force is responsible for the immense destructive power of nuclear weapons. It is also used in Nuclear power plants to generate heat for the purpose of generating energy, such as electricity.

Suggested Materials

Text Books:

T1: James E. Huheey, Ellen A. Keiter, Richard L. Keiter, Okhil K. Medhi. (2013). *Inorganic Chemistry-Principles of structure and Reactivity* (IV Edition) New Delhi pearson education, India

T2: Cotton, F.A,G.,Murillo,C.A., & Bochmann, M.(2007). *Advanced Inorganic Chemistry* (VI Edition).New York:John Wiley & Sons.

POSSIBLE QUESTIONS

Part A
(1 Mark Q.No. 1 to 20)
(Online Examination)

PART B (2 Marks)

1. What is known as binding energy.
2. What are sub atomic particles.
3. Mention few examples for electron capture.
4. What is nuclear isomerism and internal conversion.
5. Define Nuclear force
6. List out the subatomic particles?

PART C (8 Marks)

1. Write a note on subatomic particles and their properties
2. Explain different type of nuclear forces.
3. What is the significance of n-p ratio in deciding the stability of nucleus.
4. Illustrate using an example electron capture process.
5. Explain nuclear isomerism and isomeric transition.
6. Discuss the stability of radioactive nuclei in different aspects.
7. Explain the properties of α, β and γ radiations in detail.
8. Write notes on shell model of nucleus.
9. Write a brief account of the liquid drop model of nucleus and its advantages and disadvantages.
10. Write a brief account of the liquid-drop model of nucleus and the N/P ratios in metastable nuclei.

19CHP102
Karpagam Academy of Higher Education
Coimbatore-21

(For the candidate admitted on 2019 onwards)
Department of Chemistry
I- semester

INORGANIC CHEMISTRY-I (Nuclear Chemistry and Metalic clusters)

UNIT IV- Objective Questions for online examination (Each carry 1 Marks)

S.No	Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers
1	Radioactive disintegration rate is affected by	Temperature	Pressure	Electric field	Mechanical fied	Temperature
2	Alpha emission mans	Emission of positron	Emission of helium nucleus	Emission of electron from nucleus	Emission of neutron	Emission of helium nucleus
3	Which one of the following is an electromagnetic radiation?	α-rays	β-rays	γ-rays	α and β-rays	γ-rays
4	β-emission takes place	When neutrons is converted to proton	When positron is converted to neutron	When neutrons is converted to positron	When proton is converted to positron	When neutrons is converted to proton
5	The nuclear reaction involving the positron emission $_{29}Cu^{64}$ will lead to	$_{29}Cu^{63}$	$_{28}Ni^{63}$	$_{30}Zn^{64}$	$_{30}Zn^{63}$	28Ni63
6	Then energy equivalent of 1 amu is	931.5 MeV	1 MeV	1.607x10-19J	1.66x10-27	931.5 MeV
7	Mass defect of l g gives energy equal to	9×10^{13} J	9×10^{10} J	9×10^{12} J	9×10^{15} J	9 x 1013 J
8	After the emission of β-particle followed by α-particle from $^{214}Bi_{83}$, the number of neutrons in the atom is	127	129	128	125	128
9	A nucleus whose n/p ratio lies below the stability belt an	α-rays	β-rays	γ-rays	Visible light	γ-rays

10	$_{26}Fe^{55} + e \rightarrow {}_{25}Mn^{55} + v$ is an example for	Isobars	Electron capture	Nuclear isomerism	Internal conversion	Nuclear isomerism
11	Water used as moderator in nuclear reactor is called	Heavy water	Nuclear water	Critical water	Hard water	Heavy water
12	Hydrogen atom has no	Protons	Electrons	Neutrons	Positrons	Positrons
13	The instability of a nucleus is due to	High p-e ratio	High p-n ratio	Low p-e ratio	Low p-n ratio	High p-n ratio
14	In half life period is 100 yr, average life is nearly	70 yr	85 yr	144 yr	100 yr	144 yr
15	The type of radiation that has the greatest penetrating power through matter is	α-rays	β-rays	γ-rays	Visible light	γ-rays
16	Binding energy per nucleon of intermediate element is	Low	High	Zero	Very low	High
17	Antiparticle differs from its particle by	Mass and velocity	Charge and spin	Mass and charge	Spin and density	Charge and spin
18	The radiation that produces the greatest number of ions as it passes through matter is	α-rays	β-rays	γ-rays	Visible light	α-rays
19	A process that produces a one-unit increase in atomic number is	α-emission	β-emission	γ- emission	Electron capture	β-emission
20	$^{AM}X_{z\rightarrow} {}^{A}X_{z} + \gamma$ is an example of	Auger effect	Electron capture	Nuclear fission	Isometric transition	Isometric transition
21	$_{10}Ne^{22} \rightarrow ? + \beta+$	$_{10}Ne^{22}$	$_{10}Na^{22}$	$_{11}Na^{23}$	$_{12}Na^{23}$	10Ne22
22	The proportion of atoms of an isotope decaying per second is called	Half life	Mass defect	Decay constant	Average life	Half life
23	Which one of the following types of radiations, the only one to be deflected in a magnetic field is	α-rays	β-rays	γ-rays	Neutrons	β-rays
24	The heaviest stable nuclide with 126 neutron and protons in nature is	$_{83}Bi^{209}$	$_{83}Pb^{206}$	$_{83}Bi^{210}$	$_{84}Bi^{210}$	83 Bi 209
25	Which of the following is able to predict the total angular momenta of nuclei?	Hund’s rule	Pauli exclusion principle	Aufbau principle	Hund's and pauli rule	Aufbau principle

26	The number of α and β particles lost when $_{92}U^{238}$ changes to $_{82}Pb^{206}$ are	6α , 6β	6α , 8β	8α , 6β	8α , 8β	8α , 6β
27	$_{13}Al^{27}$ is a stable isotope. $_{13}Al^{29}$ is expected to disintegrate by	α-emission	β-emission	γ- emission	Neutron emission	β-emission
28	$_{7}N^{15}$ is an example of	Isotopes	Isotones	Isobar	Isochore	Isotones
29	Neutrino theory of β - decay explains the continous energy spectrum in	α-rays	β-rays	γ-rays	Neutrons	α-rays
30	Which of the following is an example for isotones?	Auger effect	Compton effect	Tunnel effect	Shielding effect	Tunnel effect
31	What is the average binding energy per nucleon, of helium nucleus, if it's true mass defect is 0.030377 md?	22.65 x 10 $^{-13}$ J	28.28 x 10 $^{-13}$ J	38.38 x 10 $^{-13}$ J	11.32 x 10 $^{-13}$ J	11.32 x 10 -13 J
32	Which radioactive emanations have a charge of -1?	Neutrons	Gamma rays	Alpha particles	Beta particles	Beta particles
33	What kind of radiation will travel through an electric field on a pathway that remains	A proton	A gamma ray	An electron	An alpha particle	A gamma ray
34	Which radioactive isotope is used in geological dating?	Uranium-238	Iodine-131	Cobalt-60	Technetium-99	Uranium-238
35	Which particle cannot be accelerated in a magnetic field?	Alpha particle	Beta particle	Neutron	Proton	Neutron
36	In the reaction 4Be9 + X -> 6C12 + 0n1, the X represents	Alpha particle	Beta particle	Electron	Proton	Alpha particle
37	The missing particle is [3Li16 + {?} --> 2He4 + 1H3]	Electron	Proton	Neutron	Deutron	Neutron
38	A deutron contains	Neutron and positron	Neutron and Proton	Proton and two neutron	Positron and two neutron	Neutron and Proton
39	Which of the following does not contain material particles	α-rays	β-rays	γ-rays	Neutrons	γ-rays
40	Radio-activity was discovered by	Henry Becquerel	Rutherford	Curie	Thomson	Henry Becquerel

41	γ-rays are	High energy protons	High energy electron	Low energy protons	High energy electromagnetic waves	High energy electromagnetic waves
42	The nucleus of radioactive element possesses	High binding energy	Lowbinding energy	High potential energy	Lowpotential energy	Lowbinding energy
43	Which nuclear decay emission consist of energy only?	α-particles	β- particles	γ- radiations	Neutrons	γ- radiations
44	The radioisotope I-131 is used to	Control nuclear reactors	Diagnose thyroid disorders	Fission reactors	Fission reactors	Diagnose thyroid disorders
45	An α-particle has the same composition as a	Helium nucleus	Hydrogen nucleus	Berllium nucleus	Positron	Helium nucleus
46	When unstable nuclei undergo radioactive decay, they emit three types of radioactivity.	Alpha	Beta	Gamma	Delta	Delta
47	Which type of radioactive decay doesn't change the atomic number?	Alpha	Beta	Gamma	Delta	Delta
48	The ratio of the nuclear radii of the α-particle and the proton is	1.59	1.28	1.41	1.82	1.59
49	The barrier height for an α-particle inside the $_{88}Ra^{226}$ nucleus	931 MeV	31 MeV	500 MeV	32 MeV	31 MeV
50	N^{13} decays by β^+ emission. The maximum kinetic energy of β^+ is 1.20 MeV. The nuclidic	13.005874	14.0078	13.7859	13	13.0059
51	ThE binding energy per nucleus of O^{16} is 7.79 MeV and that of O^{17} is 7.75 meV. Calculate the	2.43 MeV	4.23 MeV	8.25 MeV	5.51 MeV	4.23 MeV
52	Volume of H_2 produced per minute in the above reactor is	28 L	18 L	35 L	140 L	28 L
53	The total binding energy of an atom is given by B=	$Zm_n+(A-Z)m_H$	$Zm_H+(A-Z)m_n$	$Zm_H+(A-Z)M_H$	ZmH+(A+Z)M H	ZmH+(A-Z)MH

54	A β-particle is just an	Electron	Proton	Neutron	Anti neutron	Electron
55	Antiparticle differs from its particle by charge and	Mass	Density	Spin	Velocity	Spin
56	Which of the following exhibits nuclear isomerism	$_{25}Mn^{55}$	$_{35}Br^{80}$	$_{26}Fe^{55}$	$_{36}Br^{80}$	35Br80
57	Meson is a quantum of	α-decay	β-decay	γ-decay	Neutrons	γ-decay
58	Which of the following exhibits nuclear isomerism	$_{25}Mn^{55}$	$_{35}Br^{80}$	$_{26}Fe^{55}$	$_{36}Br^{80}$	35Br80
59	Pauli's exclusion principle limits the number of nucleons in	Orbit	Orbital	Shell	Nucleus	Shell
60	Which atom has no neutrons?	Helium	Hydrogen	Neon	Argon	Hydrogen

UNIT V

SYLLABUS

Nuclear reaction-Bethes's notation, Q-value, columbic barrier, cross section, different types of nuclear reactions-projectiles capture-particle emission, spallation, fission, fusion, theories of fission, use of fission products, nuclear reactors-fissile and fertile isotopes-U^{233}, U^{235}, $Pu^{239,}$ Th^{232}-atomic power projects in India, stellar energy, synthetic elements-application of radio isotopes-Hot atom chemistry

BETHES'S NOTATION

A nuclear reaction is generally represented as

$$^{A1}X_{Z1}+{}^{A2}a_{Z2}\rightarrow{}^{A3}b_{Z3}+{}^{A4}Y_{Z4}$$

Where X stands for parent nuclei, a stands for projectile, b stands for ejectile and Y stands for daughter nuclei

A shorter form of writing nuclear reaction was given by Bethe and is known as Bethes notation.

$$^{A1}X(a,b)^{A4}Y$$

Q VALUE

Considering the energy conservation of the simple reaction, enables the general definition of Q based on mass-energy equivalence, where K is kinetic energy and m is mass:

A reaction with a positive Q value is exothermic, i.e. has a net release of energy, since the kinetic energy of the final state is greater than the kinetic energy of the initial state. A reaction with a negative Q value is endothermic, i.e. requires a net energy input, since the kinetic energy of the final state is less than the kinetic energy of the initial state.

Applications

Chemical Q values are measurement in calorimetry. Exothermic chemical reactions tend to be more spontaneous and can emit light or heat, resulting in runaway feedback(i.e. explosions).

Q values are also featured in particle physics. For example, Sargent's rule states that weak reaction rates are proportional to Q^5. The Q value is the kinetic energy released in the decay at rest. For neutron decay, some mass disappears as neutrons convert to a proton, electron and antineutrino.

where m_n is the mass of the neutron, m_p is the mass of the proton, m_v is the mass ofthe electron antineutrino and m_e is the mass of the electron; and the K are the corresponding kinetic energies. The neutron has no initial kinetic energy since it is at rest. In beta decay, a typical Q is around 1 MeV.

The decay energy is divided among the products in a continuous distribution for more than 2 products. Measuring this spectrum allows one to find the mass of a product. Experiments are studying emission spectrums to search for neutrinoless decay and neutrino mass; this is the principle of the upcoming KATRIN experiment.

COLUMBIC BARRIER

The **Coulomb barrier**, named after Coulomb's law, which is in turn named after physicist Charles-Augustin de Coulomb, is the energy barrier due to electrostatic interaction that two nuclei need to overcome so they can get close enough to undergo a nuclear reaction. This energy barrier is given by the electrostatic potential energy:

where
k is the Coulomb's constant = 8.9876×10^{9} N m^2 C^{-2};
ε_0 is the permittivity of free space;
q_1, q_2 are the charges of the interacting particles;
r is the interaction radius.

A positive value of U is due to a repulsive force, so interacting particles are at higher energy levels as they get closer. A negative potential energy indicates a bound state (due to an attractive force).

The Coulomb barrier increases with the atomic numbers (i.e. the number of protons) of the colliding nuclei:

where e is the elementary charge, $1.602\ 176\ 53\times10^{-19}$ C, and Z_i the corresponding atomic numbers.

To overcome this barrier, nuclei have to collide at high velocities, so their kinetic energies drive them close enough for the strong interaction to take place and bind them together.

According to the kinetic theory of gases, the temperature of a gas is just a measure of the average kinetic energy of the particles in that gas. For classical ideal gases the velocity distribution of the gas particles is given by Maxwell Boltzmann. From this distribution, the fraction of particles with a velocity high enough to overcome the Coulomb barrier can be determined.

In practice, temperatures needed to overcome the Coulomb barrier turn out to be smaller than expected due to quantum-mechanical tunnelling, as established by Gamow. The consideration of barrier-penetration through tunnelling and the speed distribution gives rise to a limited range of conditions where the fusion can take place, known as the Gamow window.

The absence of the Coulomb barrier enabled the neutron's discovery by James Chadwick in 1932.

TYPES OF NUCLEAR REACTIONS

Although the number of possible **nuclear reactions** is enormous, nuclear reactions can be sorted by types. Most of nuclear reactions are accompanied by gamma emission. Some examples are:

- **Elastic scattering**. Occurs, when no energy is transferred between the target nucleus and the incident particle.

208Pb (n, n) 208Pb

- **Inelastic scattering**. Occurs, when energy is transferred. The difference of kinetic energies is saved in excited nuclide.

40Ca (α, α') 40mCa

- **Capture reactions**. Both charged and neutral particles can be captured by nuclei. This is accompanied by the emission of ˠ-rays. Neutron capture reaction produces radioactive nuclides (induced radioactivity).

238U (n, ˠ) 239U

- **Transfer Reactions**. The absorption of a particle accompanied by the emission of one or more particles is called the transfer reaction.

4He (α, p) 7Li

- **Fission reactions**. Nuclear fission is a nuclear reaction in which the nucleus of an atom splits into smaller parts (lighter nuclei). The fission process often produces free neutrons and photons (in the form of gamma rays), and releases a large amount of energy.

235U (n, 3 n) *fission products*

- **Fusion reactions**. Occur when, two or more atomic nuclei collide at a very high speed and join to form a new type of atomic nucleus.The fusion reaction of deuterium and tritium is particularly interesting because of its potential of providing energy for the future.

3T (d, n) 4He

- **Spallation reactions**. Occur, when a nucleus is hit by a particle with sufficient energy and momentum to knock out several small fragments or, smash it into many fragments.

NUCLEAR FISSION AND FUSION

Definition

Fission is the splitting of a large atom into two or more smaller ones.

Fusion is the fusing of two or more lighter atoms into a larger one.

Natural occurrence of the process

Fission reaction does not normally occur in nature.

Fusion occurs in stars, such as the sun.

Byproducts of the reaction

Fission produces many highly radioactive particles.

Few radioactive particles are produced by fusion reaction, but if a fission "trigger" is used, radioactive particles will result from that.

Conditions

Critical mass of the substance and high-speed neutrons are required.

High density, high temperature environment is required.

Energy Requirement

Takes little energy to split two atoms in a fission reaction.

Extremely high energy is required to bring two or more protons close enough that nuclear forces overcome their electrostatic repulsion.

Energy Released

The energy released by fission is a million times greater than that released in chemical reactions, but lower than the energy released by nuclear fusion.

The energy released by fusion is three to four times greater than the energy released by fission.

Nuclear weapon

One class of nuclear weapon is a

One class of fission bomb, also known as an atomic bomb or atom bomb. Nuclear weapon is the hydrogen bomb, which uses a fission reaction to "trigger" a fusion reaction.

Energy production

Fission is used in nuclear power plants.

Fusion is an experimental technology for producing power.

Fuel

Uranium is the primary fuel used in power plants.

Hydrogen isotopes (Deuterium and Tritium) are the primary fuel used in experimental fusion power plants.

ATOMIC POWER PROJECTS IN INDIA

Nuclear power is the fourth-largest source of electricity in India after thermal, hydroelectric and renewable sources of electricity. As of 2016, India has 22 nuclear reactors in operation in 8 nuclear power plants, having an installed capacity of 6780 MW and producing a total of 30,292.91 GWh of electricity while 6 more reactors are under construction and are expected to generate an additional 4,300 MW.

In October 2010, India drew up "an ambitious project plan to reach a nuclear power capacity of 63,000 MW in 2032",but, after the 2011 Fukushima nuclear disaster in Japan, "populations around proposed Indian NPP sites have launched protests, raising questions about atomic energy as a clean and safe alternative to fossil fuels". There have been mass protests against the French- backed 9900 MW Jaitapur Nuclear Power Project in Maharashtra and the Russian-backed 2000 MW Kudankulam Nuclear Power Plant in Tamil Nadu. The state government of West Bengal state has also refused permission to a proposed 6000 MW facility near the town of Haripur that intended to host six Russian reactors. A Public Interest Litigation (PIL) has also been filed against the government’s civil nuclear programme at the Supreme Court.

India's and Asia's first nuclear reactor was the Apsara research reactor. Designed and built in India, with assistance and fuel from the United Kingdom, Apsara reached criticality on August 4, 1956 and was inaugurated on January 20, 1957. A further research nuclear reactor and its first nuclear power plant were built with assistance from Canada. The 40 MW research reactor agreement was signed in 1956, and CIRUS achieved first criticality in 1960. This reactor was supplied to India on the assurance that it would not be used for military purposes, but without effective safeguards against such use. The agreement for India's first nuclear power plant at Rajasthan, RAPP-1, was signed in 1963, followed by RAPP-2 in 1966. These reactors contained rigid safeguards to ensure they would not be used for a military programme. The 200 MWe RAPP-1 reactor was based on the CANDU reactor at Douglas Point and began operation in 1972. Due to technical problems the reactor had to be downrated from 200 MW to 100 MW The technical and design information were given free of charge by AECL to India. The United States and Canada terminated their assistance after the detonation of India's first nuclear explosion in 1974.

India's domestic uranium reserves are small and the country is dependent on uranium imports to fuel its nuclear power industry. Since early 1990s, Russia has been a major supplier of nuclear fuel to India. Due to dwindling domestic uranium reserves, electricity generation from nuclear power in India declined by 12.83% from 2006 to 2008.] Following a waiver from the Nuclear Suppliers Group (NSG) in September 2008 which allowed it to commence international nuclear trade, India has signed bilateral deals on civilian nuclear energy technology cooperation with several other countries, including France, the United States, the United Kingdom, Canada. and South Korea. India has also uranium supply agreements with Russia, Mongolia, Kazakhstan Argentina] and Namibia. An Indian private company won a uranium exploration contract in Niger

Since March 2011, large deposits of uranium, has been discovered in the Tummalapalle belt and in the Bhima basin at Gogi in Karnataka by the Atomic Minerals Directorate for Exploration and Research (AMD) of India. The Tummalapalle belt uranium reserves promises to be one of the top 20 uranium reserves discovery of the world. So far 44,000 tonnes of natural uranium has been discovered in the belt, which is estimated to have three times that amount. The natural uranium deposits of the Bhima basin has better grade of natural uranium ore, even though it is smaller than the Tummalapalle belt.

In recent years, India has shown increased interest in thorium fuels and fuel cycles because of large deposits of thorium (518,000 tonnes) in the form of monazite in beach sands as compared to very modest reserves of low-grade uranium (92,000 tonnes)

STELLAR ENERGY

It was soon realised that the energy of the stars was produced by nuclear fusion, the temperatures required in the stars being lower than those needed in the laboratory because of the enormous pressures in the stellar interiors.

One such reaction that occurs in the Sun is the so called PP chain shown below.

$$\begin{array}{lllllllll} {}^{1}_{1}H & + & {}^{1}_{1}H & \rightarrow & {}^{2}_{1}H & + & e^{+} & + & \text{energy} \\ {}^{2}_{1}H & + & {}^{1}_{1}H & \rightarrow & {}^{3}_{2}He & + & \text{energy} & & \\ {}^{3}_{2}He & + & {}^{3}_{2}He & \rightarrow & {}^{4}_{2}He & + & 2{}^{1}_{1}H & + & \text{energy} \end{array}$$

Part of the energy in the first reaction is high-speed neutrinos and these can be detected on the Earth.

The apparent imbalance between particles in these equations can be understood if we look at the first of these. On the left we have two protons and no neutrons. On the right we have one proton and one neutron and a positron. One of the protons has been converted into a neutron and a positron. Similar reasoning will explain the other equations.

Other reactions may then occur such as:

$$\boxed{{}^{3}_{2}He + {}^{4}_{2}He \longrightarrow {}^{7}_{4}Be + \gamma}$$

Heavier and heavier nuclei can be produced by successive fusion reactions. The types of reaction taking place in the Sun are shown below:

$$\begin{array}{lllllll} {}^{12}_{6}C & + & {}^{1}_{1}H & \rightarrow & {}^{13}_{7}N & + & \text{energy} \\ & & {}^{13}_{7}N & \rightarrow & {}^{13}_{6}C & + & e^{+} \\ {}^{13}_{6}C & + & {}^{1}_{1}H & \rightarrow & {}^{14}_{7}N & + & \text{energy} \\ {}^{14}_{7}N & + & {}^{1}_{1}H & \rightarrow & {}^{15}_{8}O & + & \text{energy} \\ & & {}^{15}_{8}O & \rightarrow & {}^{15}_{7}N & + & e^{+} \\ {}^{15}_{7}N & + & {}^{1}_{1}H & \rightarrow & {}^{14}_{6}C & + & {}^{4}_{2}He \end{array}$$

The net result of this series of reactions is:

$$4{}^{1}_{1}H \rightarrow 4{}^{4}_{2}He + 2e^{+} \quad \text{energy}$$

In other words, 564 million tonnes of hydrogen are being converted into 560 million tonnes of helium every second, producing a staggering output of 3.90x10^{20} MW - equivalent to some million million million large power stations!

Although the Sun is converting four million tonnes of mass into energy every second it is thought that it will continue to last for a further 10^9 years.

At higher temperatures (around 10^8 K) the fusion of helium starts the building of heavier elements.

The reaction is:

$$
\begin{array}{l}
{}^{4}_{2}\mathrm{He} + {}^{4}_{2}\mathrm{He} \rightleftharpoons {}^{8}_{4}\mathrm{Be} + \gamma \\
{}^{8}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{12}_{6}\mathrm{C} + \gamma
\end{array}
$$

This is known as the **triple alpha process** and is the first stage of 'helium burning'. Beryllium 8 is very unstable and so can revert to two alpha particles but eventually an equilibrium is set up and maintained.

SYNTHETIC ELEMENTS

In chemistry, a **synthetic element** is a chemical element that does not occur naturally on Earth, and can only be created artificially. So far, 24 synthetic elements have been created (those with atomic numbers 95–118). All are unstable, decaying with half-lives ranging from 15.6 million years to a few hundred microseconds.

Seven other elements were first created artificially and thus considered synthetic, but later discovered to exist naturally (in trace quantities) as well; among them plutonium—first synthesized in 1940—the one best known to laypeople, because of its use in atomic bombs and nuclear reactors.

Synthetic elements are radioactive and decay rapidly into lighter elements—possessing half-lives so short, relative to the age of Earth (which formed approximately 4.6 billion years ago), that any atoms of these elements that may have existed when the Earth formed have long since decayed. Atoms of synthetic elements only occur on Earth as the product of atomic bombs or experiments that involve nuclear reactors or particle accelerators, via nuclear fusion or neutron absorption.

Atomic mass for natural elements is based on weighted average abundance of natural isotopes that occur in Earth's crust and atmosphere. For *synthetic* elements, the isotope depends on the means of synthesis, so the concept of natural isotope abundance has no meaning. Therefore, for synthetic elements the total nucleon count (protons plus neutrons) of the most stable isotope, i.e. the isotope with the longest half-life—is listed in brackets as the atomic mass.

List of synthetic elements

The following elements do not occur naturally on Earth. All are transuranium elements and have atomic numbers of 95 and higher.

Element name	Chemical Symbol	Atomic Number	First definite synthesis
Americium	Am	95	1944
Curium	Cm	96	1944
Berkelium	Bk	97	1949
Californium	Cf	98	1950
Einsteinium	Es	99	1952
Fermium	Fm	100	1952
Mendelevium	Md	101	1955
Nobelium	No	102	1966
Lawrencium	Lr	103	1971
Rutherfordium	Rf	104	1966 (USSR), 1969 (U.S.) *
Dubnium	Db	105	1968 (USSR), 1970 (U.S.) *
Seaborgium	Sg	106	1974

Element name	Chemical Symbol	Atomic Number	First definite synthesis
Bohrium	Bh	107	1981
Hassium	Hs	108	1984
Meitnerium	Mt	109	1982
Darmstadtium	Ds	110	1994
Roentgenium	Rg	111	1994
Copernicium	Cn	112	1996
Nihonium	Nh	113	2004
Flerovium	Fl	114	2004
Moscovium	Mc	115	2010
Livermorium	Lv	116	2004
Tennessine	Ts	117	2010
Oganesson	Og	118	2006

HOT ATOM CHEMISTRY

In physical chemistry, a **hot atom** is an atom that has a high translational energy.

When molecule AB adsorbs on a surface dissociatively,

1. both A and B adsorb on the surface, or
2. only A adsorbs on the surface, and B desorbs from the surface.

In case 2, B gains a high translational energy from the adsorption energy of A, and hot atom B is generated. For example, the hydrogenmolecule, because of its light mass, gets a high translational energy. Such a hot atom does not fly into vacuum but is trapped on the surface, where it diffuses with high energy.

Hot atoms are expected to play important roles in catalytic reactions. For example, a reaction of a hydrogen atom with hydrogen atoms on a silicon surface and a reaction of an oxygen atom with oxygen molecules on Pt(111) have been reported. Hot atoms can also be generated by degenerating molecules on a metal surface with UV light. It has been reported that the reactivity of an oxygen atom generated in such a way on a platinum surface is different from that of chemisorbed oxygen atoms. Elucidating the role of hot atoms on surfaces will lead to a deeper understanding of the mechanism of reaction.

FERTILE AND FISSILE ISOTOPES

Fertile material is a material that, although not itself fissionable by thermal neutrons, can be converted into a fissile material by neutron absorption and subsequent nuclei conversions.

Naturally occurring fertile materials

Naturally occurring fertile materials that can be converted into a fissile material by irradiation in a reactor include:

- thorium-232 which converts into uranium-233
- uranium-234 which converts into uranium-235
- uranium-238 which converts into plutonium-239

FISSILE MATERIAL

In nuclear engineering, **fissile material** is material capable of sustaining a nuclear fissionchain reaction. By definition, fissile material can sustain a chain reaction with neutrons of any energy. The predominant neutron energy may be typified by either slow neutrons (i.e., a thermal system) or fast neutrons. Fissile material can be used to fuel thermal-neutron reactors, fast-neutron reactors and nuclear explosives.

APPLICATIONS OF RADIOISOTOPES

Applications of Radioisotopes in Different Fields
Some radioisotopes exist naturally. For example 3H1, 17O8, 40K19. While other radioisotopes are produced artificially by transmutation in a nuclear reactor by this processes:

i. A stable nucleus is bombarded by high speed alpha particles, neutrons or protons to produce artificial radioisotopes.
ii. The bombarding particles are trapped in the nucleus creating a radioactive isotopes.

Among the properties of radioisotopes are:

i. Emits radioactive radiation.
ii. Radioactive radiations can kill cells.
iii. Radioactive radiations have different penetrating ability with materials of different thickness and densities.
iv. Radioactive radiations can cause cell mutation.
v. Radioactive radiations can ionise molecules.
vi. Its activity decreases with time.
vii. Radioisotopes have the same chemical properties as non-radioactive isotopes of the same element.

Applications of radioisotopes in Medicine

1. To diagnose of thyroid disease using iodine-123.
2. To treat an overactive thyroid gland and certain kinds of thyroid cancer by using sodium iodide labelled with radioactive iodine.
3. To detect position of blood clots or thrombosis using Sodium-24 injected in the bloodstream.

4. To detect and treat brain tumor using phosphorus-32
5. To study the circulation of iron in the blood using iron-59
6. To sterilise medical equipments and to destroy cancer cells in radiotherapy radioisotope cobalt-60 is used.

Applications of radioisotopes in Industries

1. The thickness of paper, plastics, clothes and metal sheets need to be standardised and this is done by placing a raioactive source at one side of the material and a detector on the other side.
2. For sheets of metal, gamma ray is used. For plastics, clothes and paper, beta particles are used.
3. The detector will register a higher count if the material is too thin and lower register if too thick. The computer will make adjustments according to the thickness of the material.
4. This mechanism is also used to ensure that containers such as cans and food packages are filled to the specified amount.
5. Radioisotope is added to engine oil so that its level of wear and tear can be determined.
6. In order to kill germs that cause food to spoil quickly, gamma rays are used.
7. If exposed to gamma ray, latex becomes harder without the need for adding sulphur.

Applications of radioisotopes in Agriculture

1. Pests can be killed using radioactive rays esp using gamma rays.
2. To stop pests from reproducing, induced mutation by using gamma rays can be employed. But this has the probability of producing GMO and resistant pests.
3. To be used as tracers in the effectiveness of fertilisers using nitrogen-15 and phosphorus -32.
4. To induce genetic mutation in a plant in order to produce a better strain which has higher resistance against pest and diseases.

Applications of radioisotopes in Archaeology

To determine the age of artifacts, the carbon dating method is used.

Suggested Materials

Text Books:

T1: James E. Huheey, Ellen A. Keiter, Richard L. Keiter, Okhil K. Medhi. (2013). *Inorganic Chemistry-Principles of structure and Reactivity* (IV Edition) New Delhi pearson education, India

T2: Cotton, F.A,G.,Murillo,C.A., & Bochmann, M.(2007). *Advanced Inorganic*

Chemistry (VI Edition).New York:John Wiley & Sons.

POSSIBLE QUESTIONS

Part A
(1 Mark Q.No. 1 to 20)
(Online Examination)

Part B (2 Marks)

1. What is Q-Value?
2. What is projectile capture?
3. What is known as particle emission and spallation.
4. Define nuclear fission and fusion.
5. What are fissile and fertile isotopes.
6. Mention few applications of radio isotopes.
7. What is known as breeder reactor?

Part C(8 Marks)

1. Briefly explain the significance of the following
   (i) Hot atom chemistry
   (ii) Stellar Energy
2. Distinguish between fissile and fertile isotopes. Explain with an example.
3. Briefly explain the significant of the following
   (i) Hot atom chemistry
   (ii) Bethe's notation
4. Discuss any eight important applications of radio isotopes.
5. What is a nuclear fusion and its application?
6. Describe the use of radioactive isotopes in agriculture and medicine
7. How is plutonium formed in the nuclear reactor and how it is separated from the fission products of uranium? .

8. Describe the use of radioactive isotopes in agriculture and medicin

9. Write notes on stellar energy.

10. Describe the fusion reactions taking place in Sun and Stars.

11. Describe the theories of fission.

12. Explain Nuclear fission and nuclear fusion in detail.

13. Discuss in detail about fissile and fertile isotopes

19CHP102
Karpagam Academy of Higher Education
Coimbatore-21

(For the candidate admitted on 2019 onwards)
Department of Chemistry
I- semester

INORGANIC CHEMISTRY-I (Nuclear Chemistry and Metalic clusters)

UNIT V- Objective Questions for online examination (Each carry 1 Marks)

S.No	Questions	Opt-1	Opt-2	Opt-3	Opt-4	Answers
1	$_{92}U^{238}$ (IIIB) emits two a-particles, new element will be placed in	IIA	IIB	VIIA	VIIB	IIA
2	Thorium is found in	Uranite	Monazite	Pitchblende	Malachite green	Monazite
3	The half life of ^{99}Tc is 6 h. Hence average life is	3 hr	4.17 hr	8 hr	8.66 hr	8.66 hr
4	The proportion of atoms of an isotope decaying per second is called	Half life	Mass defect	Decay constant	Average life	Half life
5	The heaviest stable nuclide with 126 neutron and protons in nature is	$_{83}Bi^{212}$	$_{83}Bi^{210}$	$_{83}Bi^{209}$	$_{83}Pb^{206}$	$_{83}Pb^{206}$
6	Which of the following is application of Nuclear fission	Atom bomb	Nuclear reactor	Atom bomb,nuclear reactor	Coolant reactor	Atom bomb,nuclear reactor
7	Which of the following size is safe in atom bomb	Sub critical	Critical	Super critical	Noncritical	Sub critical
8	Uranium is used in kalpakkam nuclear plant as	Fuel	Moderators	Coolant	Cladding	Fuel
9	Which one of the following is used as a coolant in nuclear reators	Boron 10	Heavy water	Hard water	Neutron	Heavy water
10	The most radioactive of the isotopes of an element is the one with the largest value of its	Atomic number	Half-life	Decay constant	Neutron number	Decay constant
11	C + H2 → B +He . It is an example of	α,n	d, α	d,p	p,γ	α,n
12	Among the following nuclides, the highest binding energy per nucleon is found for	$^{3}H_{1}$	$^{16}O_{8}$	$^{56}Fe_{26}$	$^{235}U_{92}$	$^{56}Fe_{26}$

13	Spontaneous fission is highly probable in	U-238	Pu-239	U-235	Fe-56	U-235
14	Atom bomb is an application for	Nuclear fission	Nuclear fusion	Nuclear transition	Nuclear effect	Nuclear fission
15	A negative Q value indicates the reaction is	Exothermic	Endothermic	No reaction	fast reaction	Exothermic
16	The isotope of carbon encountered in carbon-dating studies is	C-11	C-13	C-12	C-14	C-14
17	$^{AM}X_{z\rightarrow}{}^{A}X_{z}+\gamma$ is an example of	Auger effect	Electron capture	Nuclear fission	Isometric transition	Auger effect
18	α-emission means	Emission of electron from nucleus	Emission of positron only	Emission of helium nucleus	Emission of beta particles	Emission of electron from nucleus
19	Which one of the following is an electromagnetic radiation?	Neutron	α-rays	β-rays	γ-rays	γ-rays
20	One of the elements has eight –naturally occurring stable isotopes.	Cd	Br	Ra	Au	Cd
21	A nucleus whose n/p ratio lies below the stability belt (in the plot of n versus p)	α-rays	β-rays	α and β-rays	No particles	No particles
22	One of the following nuclides, the one most likely to be radioactive is	$^{14}N_{7}$	$^{16}O_{8}$	$^{56}Fe_{26}$	$^{235}U_{92}$	$^{14}N_{7}$
23	The nuclear reaction involving the positron emission $_{29}Cu^{64}$ will lead to	$_{29}Cu^{63}$	$_{30}Zn^{64}$	$_{30}Zn^{63}$	$_{28}Ni^{63}$	$_{30}Zn^{63}$
24	Which of the following act as source of neutron atom bomb?	Ra-Be	Ba-Kr	Ba-Ca	Ra-Ba	Ra-Be
25	If binding energy high means the nuclei stability	Low	High	Zero	Very low	High
26	In a nuclear reactor, oxides of which of the following metals are not used as fuel material?	Thorium	Uranium	Actinium	Plutonium	Thorium
27	How much amount of energy produced during fission of U-235?	100	200	300	400	200
28	Which of the following is not a fissile isotope?	U-233	U-235	U-238	U-239	U-235
29	APSARA REACTOR was established at	Tormbay	Calcutta	Madras	Delhi	Tormbay
30	Which one is used in diagnosis of thyroid disorder	Na-24	Iodine-131	CO -50	O-18	Iodine-131

31	The fissionable material used in the reactor is called	Control rods	Fuel	Coolant	Moderator	Fuel
32	Which one of the following is a good moderator	Diamond	Graphide	Heavy water	Graphide and Heavy water	Graphide and Heavy water
33	Which One of the nuclear process occurring in star	Nuclear fusion	Orbital electron capture	Nuclear fission	Hydrogen burning	Nuclear fission
34	Which of the following referred to as Oppenheimer-phillips reactions	Fission	Fragmentation	Transfer reaction	Fusion	Transfer reaction
35	Kinetic energy of projectile conserved in	Spallation	Elastic scattering	Inelastic scattering	Nuclear fission	Elastic scattering
36	The nuclear reaction involving the positron emission $_{29}Cu^{64}$ will lead to	Calcium	Copper	Nickel	Zinc	Nickel
37	Ra-A has an atomic number 84 and mass number 218. If it emits an α-particle, the resulting	81	**82**	83	84	82
38	The main part of the nuclear reactor is	Nuclear reactor	Nuclear core	Core and moderator	Moderator	Nuclear core
39	A positive Q value indicates the reaction is	Slow reaction	Exothermic	Endothermic	No reaction	Exothermic
40	Which one is resembles liquid drop model	Atomic nucleus	Electron	Proton	Neutron	Atomic nucleus
41	How many neutron produced in the fission of U-235	1	2	3	4	3
42	Which of the following can be used as control rods	Cadmium	Boron steel	Cadmium and boron steel	Heavy water	Cadmium and boron steel
43	Chain reaction is uncontrolled in	Atom bomb	Nuclear reactor	Nuclear core	Fertile isotope	Atom bomb
44	Two longer nuclei combine to produce heavier nucleus is known as	Fusion reaction	Fission reaction	Nuclear reaction	Projectile capturer	Fusion reaction
45	The Q-value is generally separated in	MeV	K_{cal}	KJ	MeV , K_{cal} and KJ	MeV , K_{cal} and KJ
46	Nuclear power station is situated in	Kalpakkam	Chennai	Punjab	Mumbai	Kalpakkam
47	Nuclear power station is situated in	Tarapur	Chennai	Punjab	Mumbai	Tarapur

48	The spontaneous conversion of one nuclear isomer in to another is known as	Isomeric transition	Internal transition	External transition	Nuclear transition	Isomeric transition
49	${}_{92}U^{235}$ + ${}_{0}n^{1}$→${}_{56}Ba^{141}$ + ${}_{36}Kr^{92}$ +3 ${}_{0}n^{1}$, the reaction is an example for	Moderator	Nuclear fission	Nuclear fusion	Spallation reaction	Nuclear fission
50	Atom bomb is an application for	Nuclear fission	Nuclear fusion	Nuclear transition	Nuclear effect	Nuclear fission
51	Special photographic emulsion used as track detectors are known as a	Gel	Optical emulation	Nuclear emulation	Delta particle	Nuclear emulation
52	Example of nuclear fission reaction	Atom bomb	Hydrogen bomb	Alpha particle	Beta particle	Atom bomb
53	India’s first nuclear plant was constructed at	Kalpakkam	Kolkatta	Tarapur	Chennai	Tarapur
54	${}_{5}B^{10}$ + ${}_{2}He^{4}$ →${}_{7}N^{13}$ + ${}_{0}n^{1}$ is an example of	a,n	d, n	d, p	d, g	a,n
55	Kinetic energy of projectile not conserved in	elastc scattering	Inelastic scattering	Spallation	Fragmentation	Inelastic scattering
56	Boron + He →Nitrogen + neutron is an example of	a,n	d, n	d, p	d, g	a,n
57	${}_{6}C^{12}$ + ${}_{1}H^{2}$ → ${}_{5}B^{10}$ +${}_{2}He^{4}$ is an example of	a,n	d, a	d, p	d, g	d, a
58	Given the masses H=1.0078 amu, n=1.008 amu and 4He=4.0026 amu. The mean binding energy of helium is	7.08 MeV	7.98 MeV	6 MeV	10,08 MeV	6 MeV
59	An atomic nucleus undergoes electron capture to give a nucleus which is	One place to the right	One place to the left	Two places to the left	Two places to the right	Two places to the left
60	Q-value is otherwise called as	Exothermic reaction	Endothermic reaction	Nclear reaction energy	Fission reaction	Nuclear reaction energy

Reg. No…………………………….

[17CHP102]

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COIMBATORE – 641 021
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M.Sc., DEGREE EXAMINATION, NOVEMBER 2017
First Semester

CHEMISTRY

INORGANIC CHEMISTRY – I:
(Nuclear Chemistry and Metallic Cluster)

Time: 3 hours Maximum : 60 marks

PART – A (20 x 1 = 20 Marks) (30 Minutes)
(Question Nos. 1 to 20 Online Examinations)

(PART - B & C 2 ½ Hours)

PART B (5 x 6 = 30 Marks)
Answer ALL the Questions

21. a. Give an account of structures of silicates.

Or

b. Discuss the structure and properties of inorganic benzene.

22. a. Describe electron gas theory regarding the binding of the metal atoms in metallic crystals.

Or

b. State and explain 18 electron rule with two suitable examples.

23. a. What is an isomerization reaction? How is isomerization of alkenes brought about using rhodium complex as catalyst.

Or

b. Discuss the mechanism of hydroformylation of alkenes.

24. a. Explain the nuclear shell structure theory of nucleus.

Or

b. Give a sketch of the curve showing the variation of binding energy per nucleus with mass number.

25. a. With respect to nuclear reactions explain the terms
i. coulombic barrier and ii. nuclear cross section.

Or

b. Explain the principle and various components of nuclear reactor.

PART C (1 x 10 = 10 Marks)
(Compulsory)

26. Describe the environmental impacts of atomic power plant in India.

Reg. No.................................

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M.Sc., DEGREE EXAMINATION, NOVEMBER 2016

First Semester

CHEMISTRY

INORGANIC CHEMISTRY I
(Nuclear Chemistry and Metallic Clusters)

Time: 3 hours
Maximum : 60 marks

PART – A (20 x 1 = 20 Marks) (30 Minutes)
(Question Nos. 1 to 20 Online Examinations)

(Part - B & C 2 ½ Hours)

PART B (5 x 6 = 30 Marks)

Answer ALL the Questions

21. a. Write a note on organometallic clusters

Or

b. Briefly explain the sulphur- nitrogen ring compounds

22. a. Write a note on Non-stoichiometric defects

Or

b. Write a brief note on hydrogenation of alkenes

23. a. Write a note on binding energies and stability of nuclei

Or

b. Explain the shell model nuclear energy reaction

24. a. Explain (i) Wilson colud chamber (ii) Bubble chamber

Or

b. Write a note on particle accelerator

25. a. Explain the different types of nuclear reactions

Or

b. Explain the Isotopes of U^{233}, U^{235} and its nuclear reaction

PART C (1 x 10 = 10 Marks)
(Compulsory)

26. Explain (i) Semi conductors (ii) Super conductors

Reg. No..................................

[15CHP102]

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COIMBATORE – 641 021
(For the candidates admitted from 2015 onwards)

M.Sc., DEGREE EXAMINATION, NOVEMBER 2015

First Semester

CHEMISTRY

INORGANIC CHEMISTRY I
(NUCLEAR CHEMISTRY AND METALLIC CLUSTERS)

Time: 3 hours Maximum : 60 marks

PART – A (20 x 1 = 20 Marks) (30 Minutes)
(Question Nos. 1 to 20 Online Examinations)

(Part - B & C 2 ½ Hours)

PART B (5 x 6 = 30 Marks)
Answer ALL the Questions

21. a. Explain the structure and bonding in $Re_2Cl_8^{2-}$

Or

b. How diboranes are prepared? With neat Sketch explain its structure and bonding.

22. a. Give a comparative account of the structures of zinc blende and rutile.

Or

b. Write the mechanism of hydroformylation propene.

23. a. Establish the liquid drop model of nucleus and discuss its features.

Or

b. Explain the term mass defect and binding energy of a nucleus

24. a. Write short notes on linear particle accelerators.

Or

b. Write notes on Geiger muller counter.

25. a. Highlight the uses of radioisotopes in agriculture, explain the pı involved

Or

b. Write a note on Q-values of nuclear reactions

PART C (1 x 10 = 10 Marks)
(Compulsory)

26. What is Wilkinson catalyst? Discuss the mechanism of hydrogenation of alkenes using this catalyst and explain each step in the mechanism.

Reg. No................................

[14CHP102]

KARPAGAM UNIVERSITY
(Under Section 3 of UGC Act 1956)
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M.Sc. DEGREE EXAMINATION, NOVEMBER 2014
First Semester

CHEMISTRY

INORGANIC CHEMISTRY – I
(Nuclear Chemistry and Metallic Clusters)

Time: 3 hours Maximum : 60 marks

PART – A (10 x 2 = 20 Marks)
Answer any TEN Questions

1. What is heterocatenation?
2. Give four examples for tetra nuclear cluster.
3. What is meant by isoelectronic structure?
4. Define crystallography.
5. What is point defect in solids?
6. Write the NaCl & KCl structure.
7. Define nuclear isomerism?
8. What is β decay radiation?
9. How can you calculate the total binding energy of an atom?
10. Define gamma ray photon?
11. What is a tracer technique?
12. Describe the basic principles of bevatron
13. Discuss radio isotopes with an example.
14. What are the types of nuclear reactions?
15. List out the atomic power projects in India.

PART B (5 X 8= 40 Marks)
Answer ALL the Questions

16. a. Give a detailed account of the Band & Zone theory of metals.

Or

b. Discuss X- ray, neutron and electron diffraction methods.

17. a. (i) Write a note on subatomic particles and their properties
(ii) Explain different type of nuclear forces.

Or

b. (i) What is the significance of n-p ratio in deciding the stability of nucleus.
(ii) Illustrate using an example electron capture process.

18. a. What are particle accelerators? How do they function?

Or

b. (i) Explain the major differences between Proportional counter and Geiger Muller counter.
(ii) Write short notes on a) Bubble chamber b) Scintillation Counter

19. a. Briefly explain the significant of the following
(i)Hot atom chemistry (ii) Stellar Energy

Or

b. Distinguish between fissile and fertile isotopes. Explain with an example.

20. **Compulsory : -**

(i) Explain how Keggin type of heteropoly anions undergo reversible redox reactions.
(ii) Why the metal dissolved in liquefied ammonia gives a characteristic color, explain with a suitable example.
