



EDO UNIVERSITY IYAMHO
Department of Chemistry
CHM 212 Inorganic Chemistry (3 Units)

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Lectures: Wednesday, 1am – 3 pm, LT6, phone: (+234) 8060322740

Office hours: Wednesday, 8.30 to 10.30 PM (before class), Office: Faculty of Science building Rm 7

General overview of lecture: This course is designed to acquaint students with Molecular orbital theory of homonuclear and heteronuclear diatomic molecules; Chemistry of group IVA, VA, Chemistry of noble gases, Transition metals, Concepts of hard and soft acids and bases; Chemistry in aqueous and non-aqueous media; Ionic model and structures of solids.

Prerequisite: Students should have basic knowledge in Atomic theory and Nature of atoms, Properties of periodic table and Electronic configuration; Chemical equilibrium.

Learning outcomes: At the completion of this course, students are expected to:

- i. To be able to construct molecular orbital diagrams for homonuclear and heteronuclear diatomic molecules (neutral and charged molecules)
- ii. Make inferences about molecular orbital diagrams with respect to properties such as stability, diamagnetism, paramagnetism e.t.c.
- iii. Interrelate bond order and bond strength
- iv. to better understand the Chemistry of group IVA, VA, Chemistry of noble gases, Transition metals

Assignments: We expect to have 3 homework assignments throughout the course in addition to a Mid-Term Test and a Final Exam. Term papers are given at the beginning of the class and submission will be on the due date. Home works in the form of individual assignments, and group assignments are organized and structured as preparation for the midterm and final exam, and are meant to be a studying material for both exams.

Grading: 10 % of this class grade to Assignment, 5 % for presentation, 15% for the mid-term test and 70% for the final exam. The Final exam is comprehensive.



Textbook: The recommended textbooks for this course are listed below:

Title: Inorganic chemistry (fifth edition)

Author: Atkins and Shilver.

Publisher: W.H. Freeman & company, New York

ISBN 978-1-42-921820-7

Year: 2010

Title: Inorganic Chemistry (Third Edition)

Author: Missler G.L. & Tarr D.L.

Publisher: Pearson Education International

ISBN- 13: 978-0130354716

Year: 2010

Lectures: Below is a brief description of the course contents

MOLECULAR ORBITAL (M.O.) THEORY

An approach to bonding in which orbitals encompass the entire molecule, rather than being localized or confined between atoms.

- Molecular orbitals are region in space where there is high probability of finding electrons in a molecule

Need for M.O. theory

Valence bond theory fails to explain the bonding in many simple molecules.

Valence bond theory predicts the double bond, but not the paramagnetism of oxygen.



- Molecular orbitals result from the combination of atomic orbitals. Orbitals are wave functions, they can combine either constructively when in phase with each other,

forming a bonding molecular orbital (Figure 1), or destructively when both wavefunctions are out of phase, forming an antibonding molecular orbital (Figure 2).

- The bonding orbital results in increased electron density between the two nuclei, and is of lower energy than the two separate atomic orbitals.

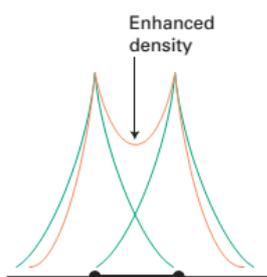


Figure 1: constructive overlapping of atomic orbitals: The enhancement of electron density in the internuclear region arising from the constructive interference between the atomic orbitals on neighbouring atoms.

On the other hand, destructive interference arises if the overlapping orbitals have opposite signs. This interference leads to a nodal surface in an antibonding molecular orbital, which is of greater energy than the two separate atomic orbitals

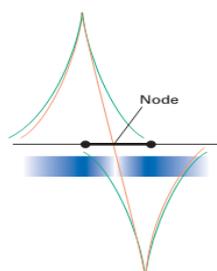


Figure 2: destructive overlapping of atomic orbitals

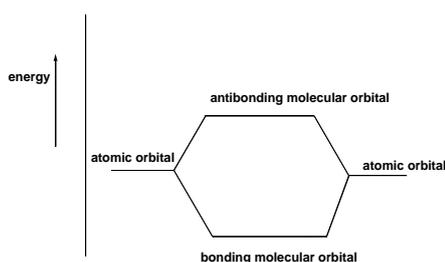




Figure 3: molecular orbital diagram

Approximations of molecular orbital theory

1. Molecular orbitals are constructed as a linear combination of atomic orbitals.
2. There is a high probability of finding electrons in atomic orbitals with large coefficient in the linear combination
3. Only atomic orbitals with similar energy and symmetry can overlap
4. Each M.O can be occupied by up to 2 electrons and they must be of opposite spins (Pauli's exclusion principle)
5. When filling M.O orbitals, orbitals of lower energy level are filled first (Aufbau principle)
6. When electrons are occupying degenerate orbitals, electron occupy separate orbitals with parallel spins before pairing

Types of overlapping

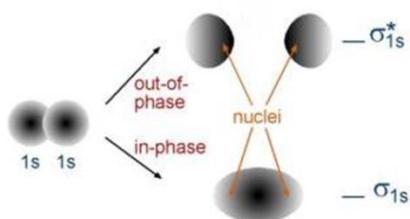
s-s overlapping to give σ bonding

s-p overlapping to give σ bonding

p-p overlapping to give σ bonding

p-p overlapping to give π bonding

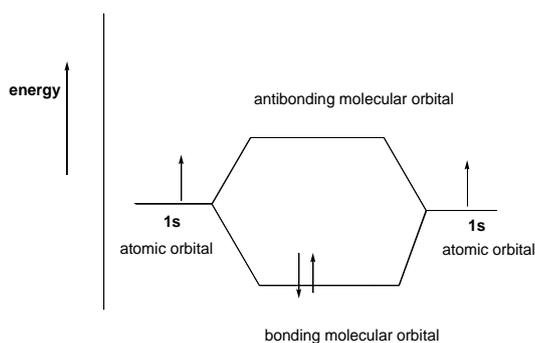
Symmetry around the MO bond axis



The bonding orbital is sometimes given the notation σ_g , where the *g* stands for *gerade*, or symmetric with respect to a center of inversion

MO FOR HOMONUCLEI DIATOMIC MOLECULES

MO for period 1 diatomic molecules such as H_2



Molecular orbital diagram for hydrogen molecule

The result is an energy level diagram with the bonding orbital occupied by a pair of electrons. The filling of the lower molecular orbital indicates that the molecule is stable compared to the two individual atoms.

- **Exercise: Sketch the molecular orbital diagram and predict the stability of the following molecules H_2^+**

M.Os of period 2 homonuclear diatomic molecules



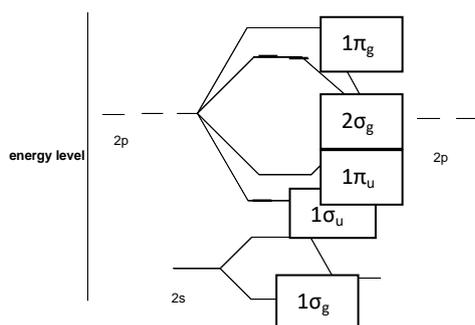


Figure 3: Variation of orbital energies for period 2 homonuclear diatomic Li_2 to N_2

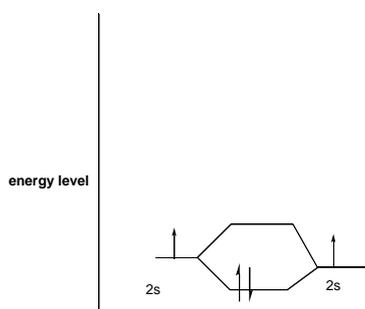


Figure 4: M.O diagram of Li_2 molecule

The ground state electronic configuration is $1\sigma_g^2(2s)$. The two $2s$ electrons are in the bonding m.o

BOND ORDER AND BOND STRENGTH

The bond order assesses the net number of bonds between two atoms in the molecular orbital formalism; the greater the bond order between a given pair of atoms, the greater the bond strength and dissociation energy. Bond order is an indicator of the bond strength and length. A bond order of 1 is equivalent to a single

bond. Fractional bond orders are possible.

The bond order of the molecule = (number of electrons in bonding orbitals - number of electrons in anti-bonding orbitals)/2

N.B: BOND ORDER greater than or equal to one implies that the molecule in question is stable

- Variation of orbital energies for period 2 homonuclear diatomic from O_2 to F_2 is given below: $1\sigma_g < 1\sigma_u < 2\sigma_g < 1\pi_u < 1\pi_g < 2\sigma_u$

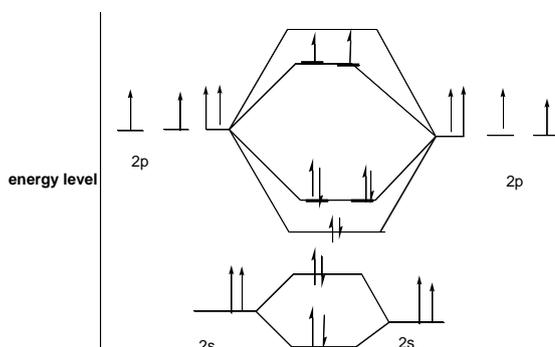


Figure 5: molecular orbital diagram of O₂

The ground state electronic configuration of oxygen molecule is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 1\pi_g^2$

This shows that oxygen molecule has two unpaired electrons in the $1\pi_g$ energy state, hence is O₂ paramagnetic

- The bond order of O₂ is:
- $8-4 / 2 = 2$.

N.B. This is consistent with a double bond

HOMO and LUMO: frontier orbitals

- The highest occupied molecular orbital (HOMO) is the molecular orbital that, according to the building-up principle, is occupied last. The lowest unoccupied molecular orbital (LUMO) is the next higher molecular orbital. These orbitals are referred to as frontier orbitals.

Photoelectron spectroscopy

The result is a spectrum of absorptions which are correlated to the molecular orbitals of the molecule. In addition, electrons ejected from bonding orbitals show more vibrational energy levels than electrons emitted from anti-bonding or non-bonding orbitals.

- **Assignment**

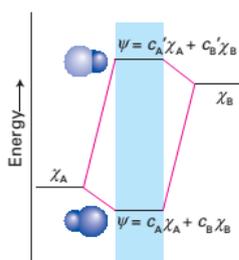
Draw the molecular orbital of F₂ molecule.

- Predict the magnetic property, stability and hence its bond order.

- from the MO diagram of F_2 ,
- I. identify the frontier orbitals
- II. predict the orbitals with highest and lowest ionization energies.
- Compare the ground state electronic configuration of O_2^- and O_2^{2-}

MOLECULAR ORBITAL THEORY OF HETERONUCLEAR DIATOMIC MOLECULES

The more electronegative atom will have orbitals of lower energy, and therefore contribute more to the bonding orbitals. The less electronegative atom has orbitals of higher energy, and contributes more to the antibonding orbitals.

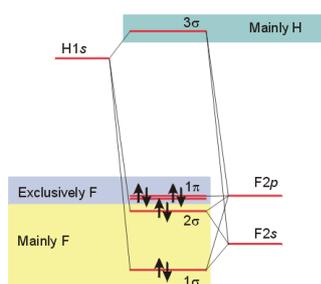


The molecular orbital energy level diagram arising from interaction of two atomic orbitals with different energies. The lower molecular orbital is primarily composed of the lower energy atomic orbital, and vice versa.

For heteronuclear molecules, rules for combining atomic orbitals are

1. The bonding orbital(s) will reside predominantly on the atom of lower orbital energy (the more electronegative atom).
2. The anti-bonding orbital(s) will reside predominantly on the atom with greater orbital energy (the less electronegative atom).

For example, the molecular orbital diagram for HF is given below:





The $2s$ and $2p_x$ orbitals on fluorine interact with the $1s$ orbital on hydrogen. The p_y and p_z orbitals on fluorine lack proper symmetry to interact with hydrogen, and remain as non-bonding orbitals.

Exercise 2:

- Draw the molecular orbital energy diagram and predict the stability of ClO^-
- II. Explain why an electron in the bonding molecular orbital in the H_2 molecule has a lower energy than an electron in the $1s$ atomic orbital of either of the separated hydrogen atoms.
- III. Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond.
 - (a) H_2 , H_2^+ , H_2^-
 - (b) O_2 , O_2^{2+} , O_2^{2-}
- IV. For the first ionization energy for an N_2 molecule, what molecular orbital is the electron removed from?
- V. What charge would be needed on F_2 to generate an ion with a bond order of 2?
- VI. Draw the molecular orbital diagram of ICl . Write out the ground state electronic configuration of the molecule. How many electrons are in the HOMO?

TOPIC 2: GROUP IV^A ELEMENTS

The lightest member of the group, C, Si is non-metals. Ge is a metalloid while S

n and Pb are metals. This increase in metallic properties as we descend the group can be attributed to increasing atomic radius

2.1 Elements, Electronic Configuration And Possible Oxidation States

Element	Atomic number	Electronic configuration	oxidation state
C	6	$1s^2 2s^2 2p^2$	+4
Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$	+4



Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$	+2, +4
Sn	50	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$	+2, +4
Pb	82	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^2$	+2, +4

2.2 Properties

Property	C	Si	Ge	Sn	Pb
Enthalpy of atomization(kJ/mol)	717	456	375	302	195
Melting point (°C)	3823	1687	1211	505	600
Bond energy (M-M)	347	226	118	150	--
First Ionization energy (kJ/mol)	1086	786.5	762	708.6	715.6
Atomic radius (pm)	77	117	112	140	154
Electronegativity	2.5	1.8	1.7	1.7	---

Table 1: selected physical properties of group IV elements.

Atomic radii/covalent radii

Generally, the covalent radii increase with increase in atomic number. Therefore, this trend increases as we descend the group (Table 1). The difference in size between si and Ge is less than might be expected because Ge has full 3d shell which shields the nuclear charge rather ineffectively. Similarly, the small difference between sn and Pb is because of the filling of 4f shell.

Ionization energy



Ionization energy decreases with increase in size. So as we descend the group, the ionization energy decreases from C to Sn, but then change in an irregular way because of the effect of filling d and f shells (Table 1). The amount of energy required to remove M^{4+} is extremely large and hence simple ionic compounds are rare.

Oxidation state and inert pair effect:

As the valence electronic configuration $ns^2 np^2$ suggests, the +4 oxidation state is predominant in the compounds of the elements. The major exception is Pb, for which the most stable oxidation state is +2. Generally, there is a decrease in stability of +4 oxidation state and an increase in the stability of +2 oxidation state as we descend the group due to inert pair effect.

Inert pair effect is the unwillingness or reluctance of s-electrons to participate in bonding due to poor screening by d or f electrons. Therefore, the s electrons behave like core electrons rather than valence electrons

The +2 oxidation state does not exist in the case of C and Si, but it does for Sn and Pb, Due to low stability of +4 oxidation state, oxides of Sn and Pb are oxidizing agents. Sn (+2) is a strong reducing agent whereas Sn (+4) ion oxidizing, covalent and stable. Pb (+2) is ionic, stable and more common than Pb (+4) which is oxidizing.

Formation of ionic or covalent compounds

The lower valencies (+2 oxidation state) are more ionic because the ionic radius of M^{2+} is greater than M^{4+} and according to the Fajans rule of bonding, the smaller the cation, the greater the tendency to covalency. Therefore MX_4 compounds are covalent compounds while MX_2 are largely ionic.

Melting point

Melting involves breaking of covalent bonds in lattice and so requires a lot of energy. Melting point decreases down the group because the M-M bond becomes weaker with increase in size

Bond energies(in kJ/mol) of M-M bond are given below:



C	Si	Ge	Sn	Pb
347	226	118	150	---

Multiple bonding and catenation:

Catenation is the tendency for covalent bond formation between atoms of a given element. Catenation can also be described as the tendency of an element to form long chain by single bond or multiple bonds with itself. Carbon shows this tendency to a reasonable extent because of its small size and high bond energy (table 1).

Example of catenation is as seen in hydrocarbons (alkanes, alkenes), catenated halides $-C-Cl$ as in polyvinylchloride.

In group 14, carbon is the only element capable of forming multiple bonding with another carbon, nitrogen or O e.t.c. such as $C-C$, $C=C$, $-C=N-$, $-C=O$.

None of the other elements form stable compounds containing multiple bond. The tendency of multiple bond formation in carbon, is because of high bond energy (bond strength) and a small radius of carbon compared to other elements of the group. So its p-orbital can overlap with p orbital of atoms like N, O, S to form a π -bond.

$P\pi$ - $d\pi$ bonding

A lateral overlap of p and d orbital under favourable condition can lead to the formation of π bond. Such bonds are called $P\pi$ - $d\pi$ bond. In the case of $(SiH_3)_3N$, the orbital of N with a lone pair of electrons overlap with an empty d-orbital of silicon and forms a π bond. This kind of bond is called $P\pi$ - $d\pi$ bond. Since the donation of lone pair is within the molecule, this is called internal π bonding. This type of bonding is possible in Ge, but not in Sn and Pb. Carbon does not have any d-orbital, hence it does not show this type of bonding.

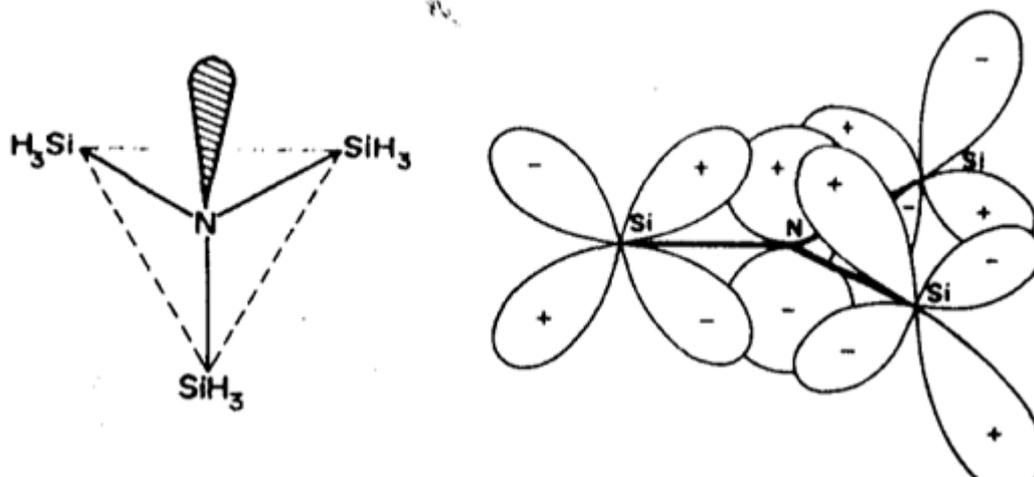


Figure 1: Pπ- dπ bonding between N and Si

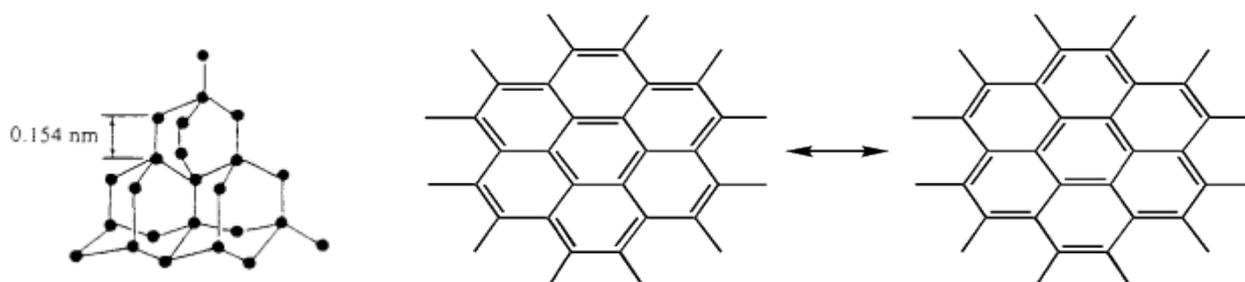
Assignment 1

- How does inert pair effect affect stability of +2 and +4 oxidation states in group IV elements ?
- Why is PbCl_4 less stable than PbCl_2 ?
- Why Sn (IV) covalent and Sn (II) largely ionic?
- Explain why Pb (IV) has oxidizing properties. Give examples of such compounds.
- Discuss briefly why Pb and Sn do not show Pπ- dπ bonding**
- Justify why $(\text{CH}_3)_3\text{N}$ is a good Lewis base and $(\text{SiH}_3)_3\text{N}$ is a weak one**
- Categorise the following compounds into oxidising and reducing agents: CO, GeO, PbO_2 , SnCl_2 and PbCl_4

2.3 ALLOTROPES OF CARBON

Diamond and graphite are not only the allotropes of carbon. The fullerenes (clusters of carbon atoms: C_{35} , C_{60} , C_{70}) often known as bucky balls, were discovered in the 1980s and have given rise to a new field in within the inorganic chemistry of carbon.

In diamond, each c atom is surrounded by four other carbon atoms in a tetrahedral fashion. The result is a rigid 3D framework and the cell unit is cubic. On the other hand, graphite consists of stacks of trigonal planar graphene layers (a 2-D sheet of carbon atoms) in which each carbon atom has three neighbouring carbon atoms (bond length 142 pm). The σ -bond





between neighbours within the sheet are formed from overlap of sp^2 hybridized orbitals and the remaining π bonds result from lateral overlap of p orbitals. The π electrons are delocalized over the sheets and are mobile.

Crystal structure of diamond

Graphite sheet

Figure 2: structural arrangements in graphite and diamond

Both have high m.p. / b.p. giant covalent network with millions of strong C-C bonds between C atoms. Graphite (3700°C) has higher m.p. than diamond (3550°C). the C atoms in graphite & diamond are sp^2 & sp^3 hybridized respectively. C-C bond in graphite has multiple bond character owing to the sideways overlap of unhybridized p -orbital.

Contrasting properties: The difference in the physical properties of these allotropes can be attributed to their structural arrangements (figure 2).

i. Hardness: diamond is the hardest substance known. Strong and directional C-C bonds in diamond restricts the relative motion between C atoms. *Weak* van der Waals' forces between layers of graphite allow the layers to slip over each other. The abrasive impure graphite is slippery and frequently used as lubricant.

ii. Electrical conductivity: diamond is an insulator while graphite is a good conductor of electricity because the π electrons are delocalized. All electrons in diamond are *localized* each C atom has a *delocalized* p -electron to conduct e^- along the same layer.

2.4 ALLOTROPES OF TIN

There are two common allotropes of carbon: α -tin (grey) and β -tin (white). The α -tin is not stable at room temperature. It converts to a more stable white Sn. The two allotropes also interconvert at 13.2°C (transition temperature).



2.5 OCCURRENCE AND USES

a. Carbon



The two almost pure form of carbon (diamond and graphite) are mined. There are also less pure forms such as coke which is made by pyrolysis of coal and carbon black(soot),lamp black, which is the product of incomplete combustion of hydrocarbon (from oil& natural gas).

Graphite is used for making electrodes, in steel making and metal foundries for crucibles, as a lubricant & in pencils, brake lining and brushes for electric motors. Cokes is used in metalling. Carbon black is used in strengthen rubber. About 30% of diamond is used for industrial purposes, mainly for making drills or cutting tools. Synthetic diamond can be by high temperature and pressure treatment of graphite.

b. Silicon: Silicon occurs as silica (in sand, quartz, amethyst, opal and can also be found in asbestos, feldspar, clays and micas. Si is obtained from silica (SiO_2) by reducing it with high purity coke. An excess of SiO_2 is used to prevent the formation of silicon carbide (SiC). Silicon is a shiny blue grey colour & has an almost metal-like lustre.

Silicon materials are insulators when pure but become semiconductors (p- or n-type) when doped with a group 5 or group 3 element respectively. These materials have many applications in integrated circuits, computer chips, solar cells, transistors and other electronic solid state devices. Silica (SiO_2) is a major raw material in the synthesis of glass.

c. Germanium:

This element is of low abundance & occurs naturally in the ore germanite $\text{Cu}_{13}\text{Fe}_2\text{CuS}_{16}$, in Zinc ores and in coal ash. Ge is also used in making transistors & semiconductor.

d. Tin: The most important ore of Sn is SnO_2 (Cassiterite). Sn is resistant to corrosion & it is used to electroplate steel to make tin plate and alloys. Tin-plate is extensively used for making cans for food and drinks

e. Lead: The main ore is galena (PbS). This is black, shiny and very dense (heavy). Galena is mined & separated from other materials by froth flotation. About 55% of Pb produced is used to make lead acid storage batteries. PbH_4 is used as an additive to petrol for internal combustion engines. Abt 10% is used in paint & pigment. Their use has declined because lead is toxic. Lead salts are extremely toxic. The ingestion of a soluble lead salt can cause acute poisoning, and long-term exposure to a source of the metal (e.g. old water pipes, Pb-based paints) may result in chronic poisoning. The softness & malleability of Pb has resulted



in its use in plumbing although the application is not illegal in some countries due to concerns over lead poisoning in materials. Pb is used in ammunition due to its high density (11.34 g/cm³).

2.6. OXIDES OF GROUP IV

All the elements in the group form mainly mono and dioxides. The dioxides are all stable except for PbO₂, the reason being an increase in stability of +2 oxidation state down the group (see sub-section 3.2.1). Acidic character of the dioxides decreases down the group; CO₂ and SiO₂ are acidic oxides, while GeO₂, SnO₂ and PbO₂ are amphoteric. Carbon is exceptional in forming gaseous mono and dioxides, CO and CO₂.

Oxides of carbon (CO and CO₂)

Carbon forms oxide more than other elements. Two of these oxides, CO and CO₂ are extremely stable and important. Other less stable oxides include C₃O₂, C₅O₂ e.t.c.

CO (carbon monoxide)

CO is a colourless, odourless, reactive and poisonous gas. It is formed when carbon is burned in limited supply of air.



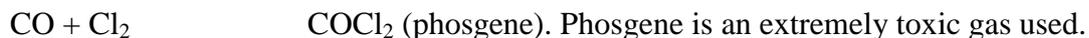
CO is prepared in the laboratory by dehydrating formic acid with concentrated H₂SO₄.



Mixture of CO, H₂ (water gas) is an important industrial fuel. Coal gas (CO, CH₄, CO₂ and H₂) is used in domestic cooking and heating, but this has been replaced by natural gas (CH₄).

CO is an important ligand. It can donate electron pair to many transition metals, forming carbonyl compounds. e.g.: Cr(CO)₆, the metal donates electron to π antibonding orbital of CO, while CO uses the electron in its LUMO σ orbital to form σ bond with the metal. M=C=O.

CO is quite reactive and can readily combine with X, S, and O.



Reaction of phosgene with NH_3 gives urea and HCl

CO_2 (carbon iv oxide)

CO_2 is a colourless and odourless gas. CO_2 is always present in air but the burning of fossil fuels is increasing the amount of CO_2 in the air which is then in-turn leading to global warming (Greenhouse effect). The main industrial source is as a by-product in the fermentation of carbohydrate in the presence of yeast gives ethanol and CO_2 . Small scale uses of CO_2 includes use in extinguisher, blasting in coal mines, as an aerosol propellant and for inflating life-rafts

CO_2 can easily be liquefied by application of pressure at ordinary ambient temperatures. If liquid CO_2 is allowed to expand rapidly, solid CO_2 is obtained. Solid CO_2 is known as **dry ice**. When it is used as a refrigerant, it does not pass through the liquid phase. Solid carbon dioxide is also used as a freezing mixture in organic solvents like acetone or methanol.

CO_2 is an acid anhydride of carbonic acid. Carbonated beverages have high partial pressures of CO_2 to drive the equilibrium to H_2CO_3 when the beverage is opened the equilibrium shifts to produce CO_2



Oxides of Si (silica, silicates and silicones)

Silica

The earth's crust is largely composed of silica and silicates, which are the principal constituents of all rocks and the sands, clays and soils that are the breakdown products of rocks. Most inorganic building materials are based on silicate minerals. These include natural silicates such as sandstone, granite and slate, and manufactured materials such as cement, concrete and ordinary glass.



Figure : structure of SiO₂

Silicon dioxide, SiO₂, is commonly known as silica. Its amorphous as well as crystalline forms are known. Flint is the amorphous form of silica. The crystalline forms are quartz, tridymite and cristobalite which have different structures. SiO₂ differs from CO₂ in an important respect, that it is solid at room temperature, whereas CO₂ is a gas. CO₂ is a simple linear molecule where the oxygen atoms are doubly bonded to carbon. On the other hand, SiO₂ forms a giant macromolecular structure in which each silicon atom is surrounded by four covalently bonded oxygen atoms in a tetrahedral fashion; each oxygen atom is surrounded by two silicon atoms. However, the overall ratio of Si-O remains the same SiO₂.

These reactions are used in analytical chemistry. Silica is acidic in nature and gives silicates when fused with alkalis.



Silica is the chief constituent of glass. **Silica gel** is an amorphous form of SiO₂ with a porous structure. It is used as a dehydrating agent as well as a catalyst. Silica gel is being increasingly used as an adsorbent in chromatography.

Silicates

Silicates are regarded as salt of silicic acid H₄SiO₄. i.e all silicates consist of SiO₄⁴⁻. The tetrahedral structure of SiO₄⁴⁻ can be represented in 3 ways:

The metal ions generally present in silicate minerals are Li⁺, Na⁺, Ca²⁺, Mg²⁺, Al³⁺. Depending on the way the silicate units are linked, different structures and complexity are obtained



- a. Pyrosilicates e.g. ScSiO_7
- b. Cyclic silicate e.g. $\text{Ca}_2(\text{SiO}_9)$
- c. Chain silicates e.g. $\text{LiAl}(\text{SiO}_3)_2$
- d. Sheet silicates

2.7 HYDRIDES OF GROUP IV

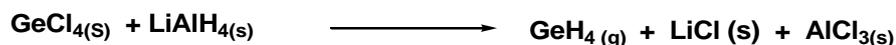
All the elements in the group form tetravalent covalent hydrides, MX_4 . Carbon and silicon form catenated molecular halides. The stability of the hydrides decreases down the group, because of decreasing M-H bond energies. Thus while CH_4 and other alkanes are stable compounds, PbH_4 has not even been properly characterised, so far.

- a. Carbon catenates to form hydrocarbons such as alkenes, alkanes, benzenes due to strong C-C bond
- b. Silicon forms silanes ($\text{Si}_n\text{H}_{2n+2}$). Silanes are commercially prepared by reacting silica with Al under a high pressure of H_2 in a molten salt



Silanes are different from alkanes due to the following:

- i. Difference in electronegativity of Si-H and C-H
 - ii. The larger size of Si makes it easier to attack
 - iii. Si has low energy d orbital which can be used to form intermediate compounds with nucleophiles (via $p\pi$ - $d\pi$ bonding)
- c. Germanes: several germanes are known, up to $n=5$. Germanes can be prepared as follows:



Stannes and plumbanes are less stable and are difficult to prepare.

2.8 HALIDES OF GROUP IV

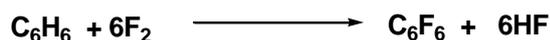
All the elements of the group form dihalides (except carbon) and tetrahalides. All the four tetrahalides, namely, fluorides, chlorides, bromides and iodides are known for all the elements of the group, except PbBr_4 and PbI_4 . MX_4 are typically covalent and are volatile. The C-X bonds are weaker than M-X bond of other members of the group. This is because other elements below C have available d orbitals for donation of electrons from the halogens

Fluorocarbons (C-F compounds).

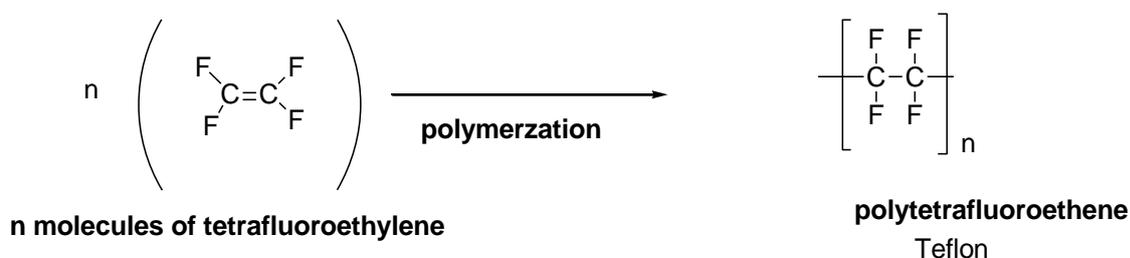


Fluorocarbons are the synthetic equivalents of hydrocarbons in which some or all of the hydrogens have been replaced by fluorine atoms, e.g. CF_4 , C_2F_4 , C_2F_6 , etc.

It is possible to synthesise a number of fluorocarbons and their derivatives by reacting hydrocarbons with fluorine either directly or in the presence of catalyst, or by using other fluorinating agents, like CoF_3 , AgF_2 and MnF_3



CF_4 is the simplest fluorocarbon. It is a colourless gas obtained by the reaction of carbon tetrachloride with silver fluoride at 575 K. Perfluoroethane, C_2F_6 , is analogous to ethane, C_2H_6 . Tetrafluoroethene, C_2F_4 can be polymerised thermally or in aqueous emulsions to a chemically inert plastic, polytetrafluoroethene (PTFE), commercially known as **Teflon**.



Teflon has an extremely low coefficient of friction. It is used as a protective coating in non-stick kitchen utensils, razor blades, bearings, etc.

Mixed chlorofluorocarbons CFCs:

CFCs such as CCl_2F_2 , CFCl_3 and CF_3Cl are known as '**Freons**'. They are volatile, thermally stable and chemically inert compounds with low viscosity. Therefore, they are used in refrigeration, in aerosol propellants and for washing computer boards. CF_3CHBrCl is a safe anaesthetic. Freons can penetrate the upper atmosphere (5-20 miles high) and can cause damage to the ozone layer. Ozone layer helps to filter the ultraviolet radiation from the sun and thereby preventing the harmful radiation from reaching the earth. Excessive exposure to UV radiation causes melanoma in humans.

ASSIGNMENT 2

- i. Diamond and graphite both are allotropic forms of carbon; still only graphite is used as a lubricant. Why?



- ii. Justify the following observations:
- iiia. carbon (graphite), a non-metal, has melting point of 3730°C and the melting point of Pb is 237°C . iib. Graphite conducts electricity while diamond is an insulator.
- iii. What are the properties responsible for the anomalous behaviour of carbon?
- iv. Why are tin and lead incapable of showing the property of catenation?
- v. Why is trisilylamine a very weak and trimethylamine a good Lewis base?
- vi. Give reactions to show that CO_2 is an acidic oxide and SnO_2 is an amphoteric oxide.

TOPIC 3: TRANSITION METAL CHEMISTRY

Transition elements have incompletely filled d-orbitals or incompletely filled f-orbitals next to the outermost shell. Transition metals are divided into d-block elements and f-block elements (inner transition elements: actinide and Lanthanides)

Table 2: First row transition elements

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Electronic configuration	$[\text{Ar}]3d^14s^2$	$[\text{Ar}]3d^24s^2$	$[\text{Ar}]3d^34s^2$	$[\text{Ar}]3d^54s^1$	$[\text{Ar}]3d^54s^2$	$[\text{Ar}]3d^64s^2$				$[\text{Ar}]3d^{10}4s^2$
M^+										

Properties of transition metals

1. Atomic/ ionic radius: In the transition metal series, the atomic and ionic radii decreases with increasing atomic number across a row.
2. Metallic character: In the d-block elements, the penultimate shell of electrons is expanding. Thus, they have many physical and chemical properties in common. All transition elements are metals. They are good conductors of heat and electricity. They have are hard, ductile and strong
3. They exhibit variable oxidation state
4. The transition metals have high tendency to form complex ions with ligands e.g: $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Pt}(\text{NH}_3)_3\text{Br}]^+$, $[\text{Fe}(\text{CN})_6]^{4-}$



5. Most transition metal compounds are coloured due to d-d transitions in the transition metal.
6. Many transition metals compounds are paramagnetic due to the presence of unpaired electrons. Ferromagnetism (a special form of paramagnetism). Elements such as Fe, Co, Ni are ferromagnetic.
7. Catalytic properties: Transition metals and compounds are known for their homogenous and heterogeneous catalytic activity.

COORDINATION COMPOUNDS

A coordination compound typically consists of a complex ion and a counter ion. A complex ion consists of a transition metal ion with its attached ligand, while counter ions are anions or cations needed to produce a neutral compound).

Ligand: A neutral molecule or ion having a lone electron pair (Lewis base) that can be used to form a bond to a metal ion (Lewis acid).

Coordinate covalent bond: metal-ligand bond formed because of the interaction of Lewis base and Lewis acid.

Types of Ligands

1. Monodentate ligand: bind to metal ion through one atom. E.g. NH_3
2. Bidentate ligands: bind to the metal ion using two points of attachments (2 atoms) e.g: $\text{C}_2\text{O}_4^{2-}$ (oxalate ion), ethylenediamine (en)
3. Polydentate ligand (chelates): can form more than two bonds to a metal ion. E.g EDTA

Rules for naming coordination complexes

1. Cationic complex is named before the anion. e.g: $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ "chloride" goes last
 $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$ anionic complex is named last
2. Ligands are named before the metal ion. ammine, chlorine named before cobalt
3. Neutral ligands are named as the molecule. However, there are few exceptions e.g water is called aqua; NH_3 is called ammine, CO as carbonyl and NO is called nitrosyl.
4. The name of negatively charged ligands end with an "o" F^- (fluoro), bromo (Br^-), CN- (cyano), H- (hydrido), $\text{C}_2\text{O}_4^{2-}$ (oxalato) etc.
5. Ligands are named alphabetically without separation by hyphens.
6. (a) The prefixes mono-, di-, tri-, etc., are used to denote the number of simple ligands. penta ammine e.g: $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$
- 6b. Bis, tris, tetrakis for complex ligands such as bidentates e.g $[\text{Co}(\text{CH}_2\text{NH}_2)_2\text{Cl}_2]\text{SO}_4$



7. The oxidation state of the central metal ion is designated by a (Roman numeral).e.g. $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, the oxidation state of Co is (III)

8. If the complex ion has a negative charge, the suffix “ate” is added to the name of the metal. E.g: $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$, Pt is called platinate in the anionic complex

Exercise

1. Give the molecular formulae of the following compounds:

Hexaammineiron(III) nitrate

Ammonium tetrachlorocuprate(II)

Potassium hexafluorocobaltate(III)

2. Name the following coordination compounds:

