EDO UNIVERSITY IYAMHO

  Department of Chemistry/Physics

Course Code: CHM 212

Course Title: Inorganic Chemistry

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Lectures: Tuesday, 8am – 10 am ,Venue: NLT2; Wednesday, 9 am-10am , NLT1

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Course Description

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.

Prerequisites

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

Assignments: Assignments will be given throughout the course in addition to a Mid-Term Test and a Final Exam. Assignments are due at the beginning of the class on the due date. They 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

Molecular orbital theory is 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

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.
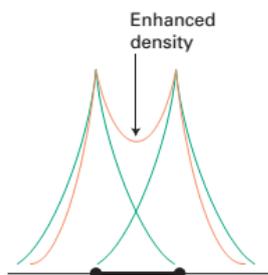

Figure 1: constructive overlapping of atomic orbitals: The enhancement of electron density in the internuclear region arising from the constructive interference between the atomic orbitals on neighbouring atoms.

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
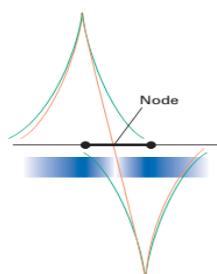

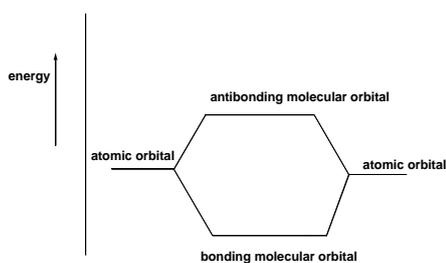Figure 2: destructive overlapping of atomic orbitals

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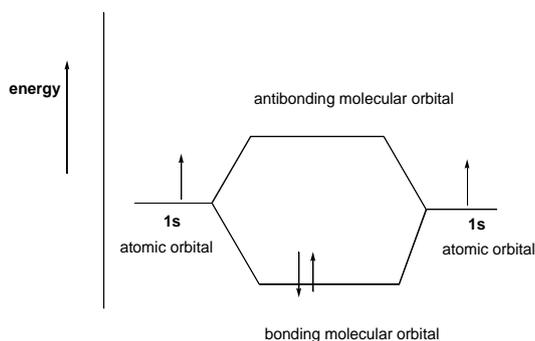
Symmetry around the MO bond axis
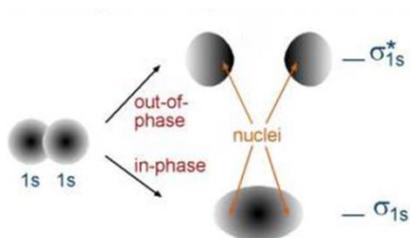
The bonding orbital is sometimes given the notation σ_g, where the *g* stands for *gerade*, or symmetric with respect to a center of inversion

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.

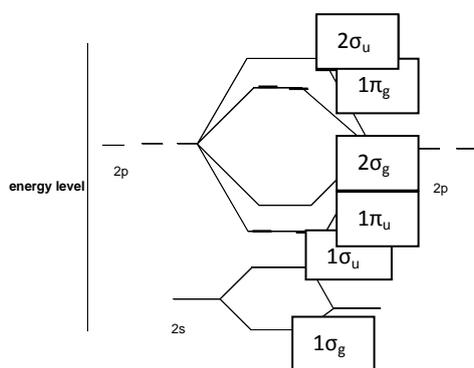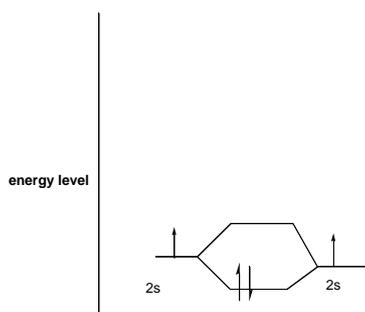**M.Os of period 2 homonuclear diatomic molecules**

Figure 4: Variation of orbital energies for period 2 homonuclear diatomic Li_2 to N_2

Figure 5: 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: $1\sigma_g < 1\sigma_u < 2\sigma_g < 1\pi_u < 1\pi_g < 2\sigma_u$
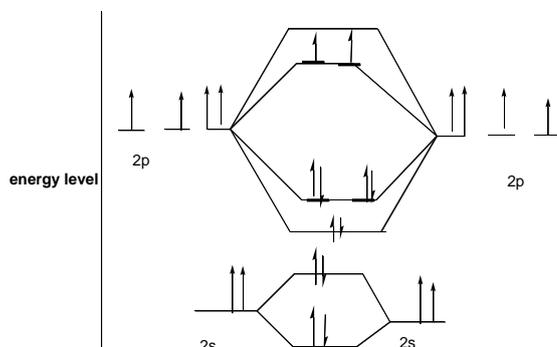

Figure 6: molecular orbital diagram of O$_2$

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 O_2 paramagnetic

- The bond order of O_2 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.

GROUP IV^A ELEMENTS

The lightest member of the group, C, Si is non-metals. Ge is a metalloid while Sn and Pb are metals. This increase in metallic properties as we descend the group can be attributed to increasing atomic radius

Properties

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. 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.

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.

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 CO_2.

Oxides of carbon (CO and CO_2)

Carbon forms oxide more than other elements. Two of these oxides, CO and CO_2 are extremely stable and important. Other less stable oxides include C_3O_2, C_5O_2 e.t.c.

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.

Silicates

Silicates are regarded as salt of silicic acid H_4SiO_4. i.e all silicates consist of $SiO4^{4-}$.

The metal ions generally present in silicate minerals are Li^+, Na^+ Ca^{2+} Mg^{2+} Al^{3+}. 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 $Ca_2(SiO9)$

c. Chain silicates e.g $LiAl(SiO_3)_2$

d. Sheet silicates

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 PbBr4 and PbI4. 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
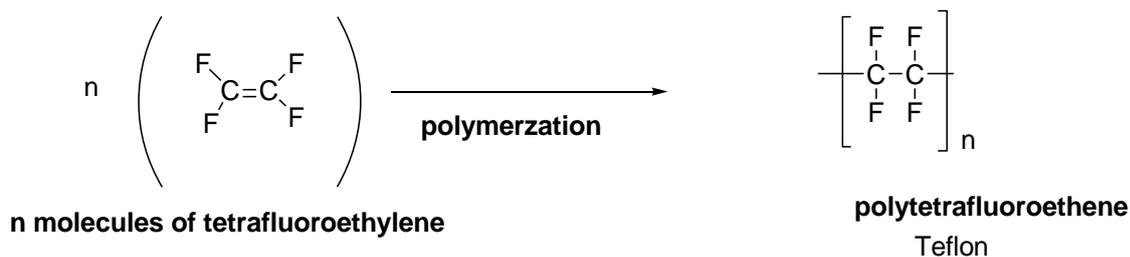
Fluorocarbons (C-F compounds).

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, C2F6, 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

$$C_6H_6 + 6F_2 \longrightarrow C_6F_6 + 6HF$$
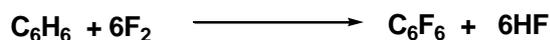
CF4 is the simplest fluorocarbon. It is a colourless gas obtained by the reaction of carbon tetrachloride with silver fluoride at 575 K. Perfluoroethane, C2F6, is analogous to ethane, C2H6. Tetrafluoroethene, C2F4 can be polymerised thermally or in aqueous emulsions to a chemically inert plastic, polytetrafluoroethene (PTFE), commercially known as **Teflon**.

$$n \left(\begin{array}{c} F \\ \diagdown \\ F \end{array} C=C \begin{array}{c} F \\ \diagup \\ F \end{array} \right) \xrightarrow{\textbf{polymerzation}} \left[\begin{array}{cc} F & F \\ | & | \\ -C-C- \\ | & | \\ F & F \end{array} \right]_n$$

n molecules of tetrafluoroethylene

polytetrafluoroethene
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 ultraviolent radiation from the sun and thereby preventing the harmful radiation from reaching the earth. Excessive exposure to UV radiation causes menaloma in humans.

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 1: Electronic configuration of first row transition elements

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Atomic number	21	22	23	24	25	26	27	28	29
Electronic configuration	$[Ar]3d^14s^2$	$[Ar]3d^24s^2$	$[Ar]3d^34s^2$	$[Ar]3d^54s^1$	$[Ar]3d^54s^2$	$[Ar]3d^64s^2$	$[Ar]3d^74s^2$	$[Ar]3d^84s^2$	$[Ar]3d^{10}4s$
M^+	$[Ar]3d^14s^1$	$[Ar]3d^24s^1$	$[Ar]3d^34s^1$	$[Ar]3d^5$	$[Ar]3d^54s^1$	$[Ar]3d^64s^1$	$[Ar]3d^74s^1$	$[Ar]3d^84s^1$	$[Ar]3d^{10}$

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: $[Co(NH_3)_6]^{3+}$, $[Pt(NH_3)_3Br]^+$, $[Fe(CN)_6]^{4-}$

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.

complex ion consist 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: $C_2O_4^{2-}$ (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: $[Co(NH_3)_5Cl]Cl_2$ "chloride" goes last

    $K[Pt(NH_3)Cl_5]$ 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), $C_2O_4^{2-}$ (oxalato) etc.

5. Ligands are named alphabetically without seperation by hyphens.

6. (a) The prefixes mono-, di-, tri-, etc., are used to denote the number of simple ligands. penta ammine e.g: $[Co(NH_3)_5Cl]^{2+}$

6b. Bis, tris, tetrakis for complex ligands such as bidentates e.g $[Co(CH_2NH_2)_2Cl_2]SO_4$

7. The oxidation state of the central metal ion is designated by a (Roman numeral).e.g. $[Co(NH_3)_5Cl]Cl_2$, 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: $K[Pt(NH_3)Cl_5]$, Pt is called platinate in the anionic complex

CONCEPT OF HARD AND SOFT ACIDS AND BASES.

DEFINITIONS OF ACIDS AN D BASES

Arrhenius concept

Arrhenius acids form hydrogen ions (hydronium or oxonium ion, H_3O^+) in aqueous solution. Arrhenius bases form hydroxide ions in aqueous solution. The reaction of hydrogen ions and hydroxide ions to form water is the universal aqueous acid-base reaction.
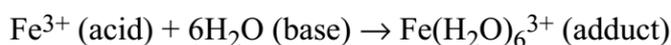
Brønsted-Lowry Model

Acids are hydrogen ion donors and bases are hydrogen ion acceptors

$$H_3O^+ + NO_2^- \longrightarrow H_2O + HNO_2$$
$$\text{acid 1} \quad \text{base 2} \qquad \text{base 1} \quad \text{acid 2}$$

Lewis Model

Acids are electron pair acceptors and bases are electron-pair donors

$$Fe^{3+} (acid) + 6H_2O (base) \rightarrow Fe(H_2O)_6{}^{3+} (adduct)$$

A base has an electron pair in a HOMO of suitable symmetry to interact with the LUMO of the acid. The better the energy match between the base's HOMO and the acid's LUMO, the stronger the interaction.

HARD-SOFT ACID AND BASE (HSAB) Model.

The Hard-Soft Acid-Base concept seeks to understand the reactivity of Lewis acids and bases according to the polarizability of their valence electrons (i.e., their deformability by other molecules/ions).

Hard acids and bases are small and non-polarizable, whereas soft acids and bases are larger and more polarizable. Inaddition, hard acids are any cations with large positive charge (3+ or larger) or those whose d electrons are relatively unavailable for π-bonding (e.g., alkaline earth ions, Al^{3+}) . Other hard acid cations that do not fit this description are Cr^{3+}, Mn^{2+}, Fe^{3+}, and

Co^{3+}. Soft acids are those whose d electrons or orbitals are readily available for π- bonding (+1 cations, heavier + 2 cations).

Examples of hard and soft acids and bases are given below:

Hard acids	Soft acids	Hard bases	Soft bases
H+	Pt^{4+}	F-	I^-
Co^{3+}	I_2	Cl-	S^{2-}
Si^{4+}	Au^+	H_2O	CO
Na^+	Hg^{2+}	O^{2-}	H^-

Interactions between two hard or two soft species are stronger than those between one hard and one soft species.