

SECOND SEMESTER 2010/2011 ACADEMIC SESSION
CHM 104 LECTURE NOTES PART B

1. HYBRIDISATION OF SHAPES OF SIMPLE MOLECULES INCLUDING CARBON COMPOUNDS.
2. EXTRACTION OF METALS.

PLEASE NOTE:

This note is a guide, explanations, diagrams and other important notations will be discussed in class.

HYBRIDISATION OF SHAPES OF SIMPLE MOLECULES INCLUDING CARBON COMPOUNDS.

DEFINITIONS:

Hybridisation is the process of mixing atomic orbitals. The new orbitals formed from this process are called hybrid orbitals.

The number of hybrid orbitals on an atom equals the number of atomic orbitals that are mixed.

Hybridization is also defined as the arrangement of extra nuclear electrons in atoms such as carbon.

COMMON TYPES OF HYBRIDISATION

1. Hybridisation in Beryllium in BeF_2 : sp hybridisation

The valence shell electron pair repulsion (VSEPR) model predicts BeF_2 is linear

with two identical Be – F bonds



The electronic configuration of F, $1s^2 2s^2 2p^5$ indicates there is unpaired electron in the 2p orbital. The 2p electron in F can be paired with an unpaired electron from Be atom to form a polar covalent bond.

Be electronic configuration is $1s^2 2s^2$ (this shows that there are no unpaired electrons). In this state Be is not capable of forming covalent bonds with the F atom. Be can form two bonds by extra nuclear rearrangement of the 2s electrons by promoting an electron from the 2s orbital to an empty p orbital. Configuration of Be before bonding with F becomes $1s^2 2s^1 2p^1$. With this two unpaired electrons Be can form polar bonds with F atoms.

Sp hybrid orbitals on Be overlaps with a 2p orbital on F to form a bond. The two bonds are equivalent to each other and form an angle of 180° . The arrangement of the orbitals is linear. Thus BeF_2 is a linear molecule. This type of hybridization is called sp because it involves one s and one p orbitals.

Sp^2 Hybridisation

Example is BF_3

Boron electronic configuration is $1s^2 2s^2 2p^1$

Fluorine electronic configuration is $1s^2 2s^2 2p^5$

Electronic configuration of hybridized B is $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^0$, this sp^2 hybrid orbital of boron overlap to form 3 covalent bonds with F. The 3 sp^2 hybrid orbitals are equivalent and arranged in the same plane 120° apart from one another forming a trigonal planar shape.

Hybridisation: involves hybridization of one s, three p and two d orbitals

Examples: SF_6 , SF_4 , BrF_3 . Shape of molecule formed is octahedral

Two of these examples will be explained in class.

Sp^3d ($d Sp^3$) Hybridisation: involves hybridization of one s, three p and one d orbitals Examples: PF_5 , CIF_5 , XeF_4 , PF_6^- : Shape of molecule formed is

trigonal bipyramidal

Two of these examples will be explained in class.

d^3S (Sd^3) Hybridisation: involves hybridization of one s, and three d orbitals

Example MnO_4^- . Shape of molecule formed is tetrahedral

To be explained in class.

Sp^3 Hybridisation: involves hybridization of one s and three p orbitals. Each sp^3 hybrid orbital has a large lobe that points toward a vertex of a tetrahedron at an angle of 109.5° . Example CH_4 , NH_4^+ .

HYBRIDISATION IN CARBON

Electronic configuration of C is $1s^2 2s^2 2p^2$ which indicates that carbon has only two unpaired electron and should be divalent. The quadrivalence (tetravalency) of carbon is accounted for by assuming that the arrangement of electrons in carbon is changed in such a way as to provide unpaired 4 electrons prior to reaction i.e an electron is promoted into an empty 2p orbital from 2s orbital.

Electronic configuration of hybridized C is $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$.

If the four unpaired electrons took part in the formation of 4 covalent bonds with hydrogen for example, the one 2s and three 2p orbitals combine into four different hybrid orbitals to form bonds which are tetrahedrally arranged.

This type of hybridization is sp^3 .

Sp^2 Hybridisation In Carbon.

This leads to the formation of double bond between 2 carbon atoms.

One 2s and two 2p orbitals are hybridized to form a coplanar structure at 120° .

One of the 2p orbital remain unchanged, each carbon atom is linked by bond has three equivalent sp^2 orbitals. Two of the orbitals from each carbon forms a sigma bond with hydrogen atoms, the remaining sp^2 orbitals of each carbon atoms forms a sigma bond between the 2 carbon atoms. The 2 carbon atoms and four hydrogen atoms are all in the same plane. At right angles to this plane there remain the unchanged 2p orbitals of each carbon atom and these

two 2p orbitals interact to form a pi- bond between the 2 carbon atoms. A double bond in carbon consists of one sigma bond and one pi bond. A sigma bond is stronger than a pi- bond. Two atoms linked by a sigma bond can rotate freely about the bond unless there is steric interference. Free rotation is prevented when two atoms are linked by a pi- bond. Sp Hybridization in Carbon. Formation of carbon – carbon triple bond.

One 2s and one 2p orbitals are hybridized to form two equivalent orbitals which are collinear. The two 2p orbital which are unchanged on each carbon atom interact to form two pi- bonds between the carbon atoms, the two bonds being placed at right angles to each other. In ethyne, one of the sp orbital from each carbon forms a sigma bond with hydrogen atoms and the remaining sp orbital of each carbon atoms forms a sigma bond between the 2 carbon atoms two. A triple bond in carbon consists of one sigma bond and two pi bonds.

EXRACTION OF METALS

There are four ways in which metals are extracted from their ores.

1. Mining of the pure metals, e.g. noble metals like gold, silver, platinum
2. Reduction of the oxide ore, e.g. some transition metals, most especially, Iron.
3. Roasting the sulphide ore and the reduction of the oxide, e.g. Pb, Ni, Zn, Hg, Cu
4. Electrolysis of the molten solid, e.g. reactive elements of group I, II and III – Na, Mg, Al.

REDUCTION OF THE OXIDE

Extraction of Iron from its ore, Haematite – Fe_2O_3 .and magnetite – Fe_3O_4 Reduction of the ore is carried out in a blast furnace. [Picture of a blast furnace to be shown in class]. The furnace is charged with a mixture of limestone, coke, and iron ore. Air is passed through the bottom of furnace. At the bottom of the furnace, coke combines with oxygen to form carbonmonoxide. This reaction releases energy that keeps the furnace going. The reduction of the ore takes place at the top of the furnace and the carbonmonoxide generated is employed in the reduction of the ores.

Limestone is decomposed to give calcium oxide which reacts with part of the ore that contains silica to give calcium silicate. The silicate is the chief component of the molten slag that is tapped off near the bottom of the furnace. The liquid iron is run off at the bottom and this can be cast into pigs {pig iron}. The bulk of the molten iron can be turned into steel by blasting oxygen through the impure iron. This oxidizes impurities like carbon, phosphorus.

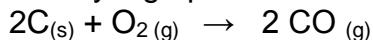
There are different grades and qualities of steel, each having a different set of characteristics. The amount of carbon mixed with iron determines the nature

of the steel like tensile strength, malleability. Small amounts of magnesium can be added to give desirable qualities.

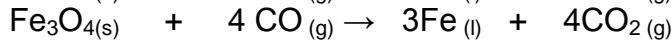
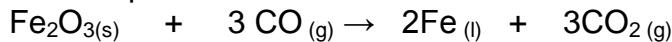
Equation of the major reactions at the furnace:

Bottom of the furnace,

At very high pressure

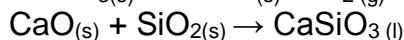


At the top of the furnace



Temperature at the furnace = 1500 – 2000 °C

Formation of slag



REDUCTION OF SULPHIDE ORES

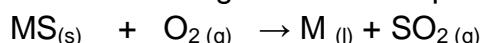
The sulphide ores are treated by

- Crushing to fine particles

Froth flotation – This technique takes advantage of the fact that metal sulphides are relatively non polar and are attracted to oil. Water, light weight oil and some chemicals are added to the crushed ore. The mixture is shaken vigorously. Froths are formed by bubbling air through the mixture. The chemicals added to the water act as an interface between the mineral particles, water and air (surfactants)

Roasting in air converts the sulphide into oxide

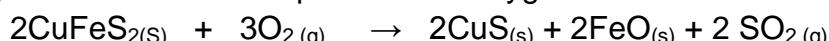
General equation for roasting of metal sulphides is written as



Examples

The isolation of copper from its most common ore Chalcopyrite requires several additional steps:

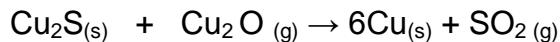
The chalcopyrite is roasted in the presence of oxygen



Copper sulphide and iron oxide from the reaction above are mixed with limestone and sand in a blast furnace, CuS is converted to Cu₂S. The limestone and sand form the molten slag CaSiO₃ in which the Fe dissolves. The copper sulphide melts and sinks to the bottom of the furnace. The less dense iron containing slag floats above the molten copper sulphide and is drained off.

The isolated copper sulphide is roasted in air to give the copper metal. The copper obtained is known as blister copper and is purified by electrolysis using the blister copper as the anode and copper sulphate solution as the electrolyte.

Equation of reaction:

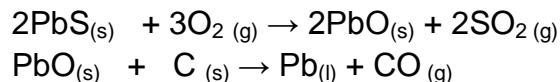


Lead from impure galena PbS is obtained by

Mixing the ore with limestone and roasting in air to produce lead (II) oxide – PbO. PbO lumps are mixed with more limestone and reduced with coke at about 900°C in a blast furnace.

The molten lead run off at the bottom of the furnace can be further purified.

Equations of reaction:



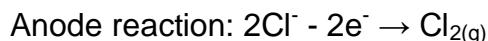
ELECTROLYTIC METHODS

This method is useful in recovering reactive metals from their ores.

The Downs process for the extraction of sodium from sodium chloride.

Electrolysis of molten sodium chloride is carried out in a Downs cell. Calcium chloride is added to lower the melting point of the molten sodium chloride (ratio 2 to 3) from the normal melting point of 804°C to about 600°C. Sodium is discharged at the cathode which is made of steel and Chlorine is released at the anode which is made of graphite. The sodium collects in inverted troughs above the cathode ring.

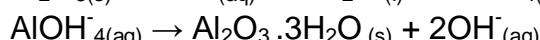
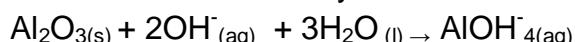
Equations at the electrodes:



Extraction of Aluminium from Bauxite - Bayer process:

Bauxite contains 60% alumina (Al_2O_3)

The ore is concentrated by dissolving in sodium hydroxide solution at 250°C and 40 atmospheres to form aluminium hydroxide



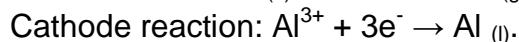
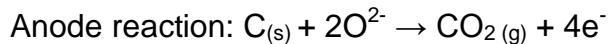
The hydrated aluminium oxide produced in equation ii is dried at approximately 1000°C to obtain the anhydrous aluminium oxide.

The electrolytic process for aluminium is known as the Hall – Heroult process (smelting).

Smelting is a melting process in which pure alumina is dissolved in a mixture of molten cryolite (Na_2AlF_6) and fluorspar (CaF_2), melting point 950°C . Conducts electric current effectively.

The anode is made of graphite and it is consumed in electrolysis because oxygen is liberated at the anode. Al is deposited at the cathode.

Reaction at the electrodes:



Molten Al is tapped from the smelter and kept in a reverberatory furnace until it is cast into ingots.

Electro refining of Copper

Slabs of crude copper serve as the anode in the cell and thin sheets of copper as the

cathode. The electrolyte consists of acidic copper sulphate solution. When a suitable

voltage is applied to the electrodes, copper metal is oxidized at the anode and Cu^{2+} is

reduced to copper at the cathode. Metallic impurities that are more active than copper are readily oxidized at the anode but do not plate out at the cathode because their reduction potentials are more negative than that of Cu^{2+} . Less active metals will not be oxidized at the anode; they will be collected below the anode as a sludge that can be processed to recover the valuable metals.

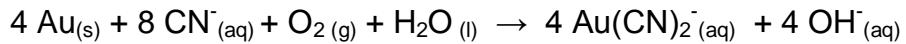
MINING THE PURE METALS

Mining of Gold

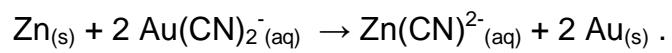
Method involves digging a hole and collecting tiny fragments of impure lumps of metals. Gold is recovered from the lump obtained from the mine by flotation method or panning method.

Panning method: the mixture of earth and rock containing gold is swirled with water; because gold is denser it tends to lie at the bottom of the pan while the other solid particles are washed away.

Chemically, gold obtained from the mine can be purified by treating crushed samples of the gold with sodium cyanide solution and oxygen to form the stable AuCN^{-2} ion, which is soluble in water;



Gold is precipitated from the cyanide complex by reduction with zinc powder.



References/ further reading

- Introduction to Physical Chemistry by G.I. Brown
S I Edition, Publ Longman
- Chemistry. The central Science by T.L. Brown et.al
11th Edition, (Pearson International Edition)
- Advanced chemistry by Philip Matthews
Cambridge edition.

