TDC Part I
Paper I, Group B
Inorganic Chemistry

Department of Chemistry

L.S COLLEGE MUZAFFARPUR

B. R. A. BIHAR UNIVERSITY

Dr. Priyanka

TOPIC:- Group-1,Oxides

Oxides

The oxides of carbon involve рл-рл bonding between carbon and oxygen. The two important oxides of carbon are carbon monoxide (CO) and carbon dioxide (CO_2). Both are colourless and odourless gases. Carbon monoxide is obtained when carbon is burnt in a limited supply of air and by the dehydration of formic acid by concentrated sulphuric acid

$$HCOOH + H_2SO_4 \longrightarrow CO + H_2O$$

It is a neutral oxide of carbon and is highly toxic as it binds to haemoglobin in preference to oxygen. Thus haemoglobin cannot act as an oxygen carrier and oxygen is not available to tissues.

Carbon monoxide evolves a considerable amount of heat on burning and is an important fuel,

$$2CO + O_2 \longrightarrow 2CO_2 + 565\ K\,Jmol^{-1}$$

Producer gas, water gas and coal gas contain carbon monoxide. Carbon monoxide is an important ligand and forms carbonyl complexes with many transition metals in low oxidation states e.g. $V(CO)_6$ $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Fe(CO)_5$, $Fe_2(CO)_9$, $Co_2(CO)_8$, $Ni(CO)_4$ etc. The metal–carbon σ-bond involves donation of an electron pair from CO to the metal, M C≡O. This σ-bond is strengthened by formation of a back bond by overlap of filled orbital of the metal with the vacant л * molecular orbital of carbon monoxide. In carbonyls CO acts as both an electron donor i.e. Lewis base (σ-bond formation) and electron acceptor i.e. Lewis acid (π-bond formation). A schematic representation of the orbital overlaps leading to M – CO bonding is depicted in Fig. 14.

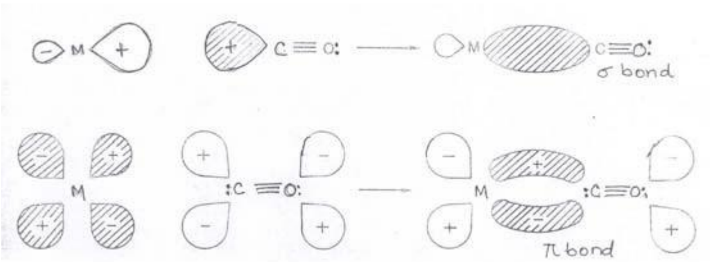

Fig. 14: Schematic representation of Orbital overlaps in metal carbonyls. The σ-bond is formed by overlap of filled orbital on CO with vacant orbital on M. The π-bond involves overlap of filled orbital on M with vacant orbital on CO.

Carbon monoxide acts as a terminal ligand when bonded to only one metal, the M-C≡O bond is linear. It can also act as a bridging ligand and be bonded to two different metal atoms simultaneously. (Fig 15)

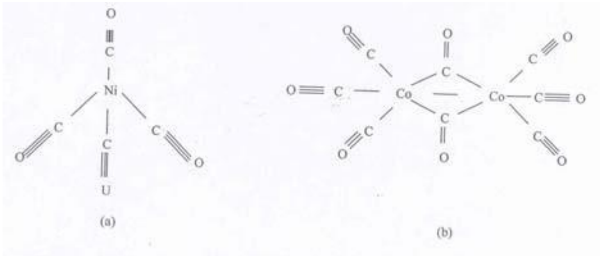

Fig.15: Structures of (a) $Ni(CO)_4$ – only terminal CO groups are present (b) $Co_2(CO)_8$ – having both terminal and bridging CO groups

Carbon dioxide is familiar as a compound in the earth's atmosphere. It has been recognized as a "greenhouse gas", responsible for global warming. It can be liquefied under pressure and the solid form is called "dry ice" which is used as a fire extinguisher. It is an acidic oxide of carbon. Plants to synthesize carbohydrates in the process of photosynthesis use carbon dioxide.

Carbon dioxide exhibits unique properties and behaves as a supercritical fluid above its critical temperature and pressure (31.1ºC and 73 arm respectively). It expands to fill a container like a gas but the density is like that of a liquid. Supercritical carbon dioxide is becoming an important commercial and industrial green solvent as it is non-toxic and is a byproduct of other industrial processes. It is used as a solvent in "dry cleaning" of textiles instead of the toxic tetrachloroethylene. It is also used as an extraction solvent in the perfumery industry. The relatively low supercritical temperature and reactivity of carbon dioxide allows the fragrance compounds to be extracted without denaturing and thereby not affecting their odours. Due to its non- toxicity coffee manufacturers use it as a decaffeinating solvent.

Si, Ge, Sn and Pb all form dioxides (MO_2). Silicon dioxide (silica) exists as an infinite three- dimensional network of silicon and oxygen atoms linked by a single bond. Each silicon atom is tetrahedrally surrounded by four oxygen atoms (fig 16). The network structure of SiO_2 arises due to silicon's inability to form p л-p л bond. Silica is a high-melting solid existing in three crystalline forms – quartz, tridymite and cristobalite.

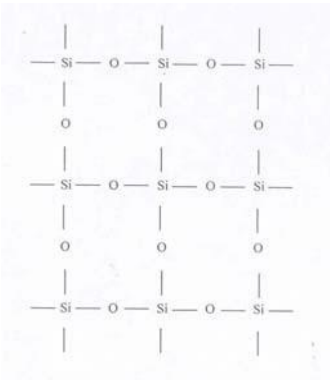

Fig. 16: Two-dimensional structure of SiO_2

Silica is very unreactive. It reacts only with HF and caustic alkali.

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$

$$SiO_2 + NaOH \longrightarrow (Na_2SiO_3)_n + Na_4SiO_4$$

The last reaction illustrates its acidic nature. Quartz is important as a piezo-electric material and is used in gramophone pick-ups, cigarette and gas-lighters and for making crystal oscillators in radios and computers.

The dioxides of Ge, Sn and Pb are solids and the basicity increases on moving down the group. GeO_2 is acidic, SnO_2 amphoteric and PbO_2 basic. PbO_2 contains Pb(IV) and is an oxidizing agent.

The lower oxides GeO, SnO and PbO are more basic and ionic than the higher oxides. Lead also forms a mixed oxide, Pb_3O_4 (red lead). It is represented as 2PbO. PbO_2 and contains Pb
(II) and Pb (IV). The interconversion of various oxides of lead is shown by the following chemical reactions:

$$2PbO_2 \longrightarrow 2PbO + O_2$$

$$6PbO + O_2 \xrightarrow{400-415^0C} 2Pb_3O_4$$

$$2Pb_3O_4 \xrightarrow{500^0C} 6PbO + O_2$$