

Sp-Inorganic Theory - II

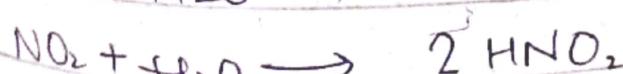
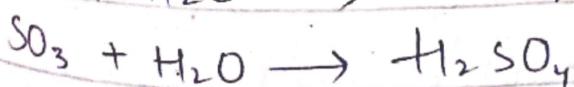
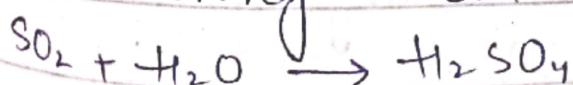
Ch: Oxides

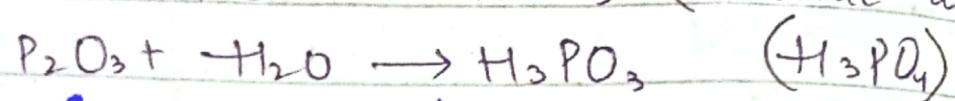
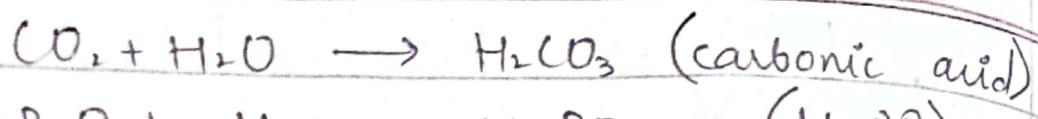
Physical state and structure of oxides, combination of oxygen with other elements produce the compounds which are called oxides. e.g., CO_2 , NO_2 , SO_2 , CaO , SiO_2 , Al_2O_3 , P_2O_5 , Na_2O etc.

These oxides can be solid, liquid or gases depending on nature of oxides and forces of attractions b/w oxide units. Oxides are compounds which can classified according to their acidic or basic nature.

1. Acidic oxides:

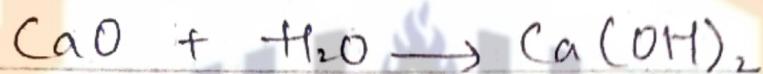
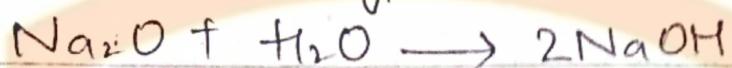
All non-metal oxides are acidic in nature and their solution in water act as strong acid.





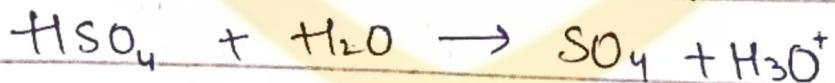
2. Basic oxides:

All metallic oxides are basic in nature and produce basic solution when combine with water. e.g; Na_2O , CaO , K_2O etc.



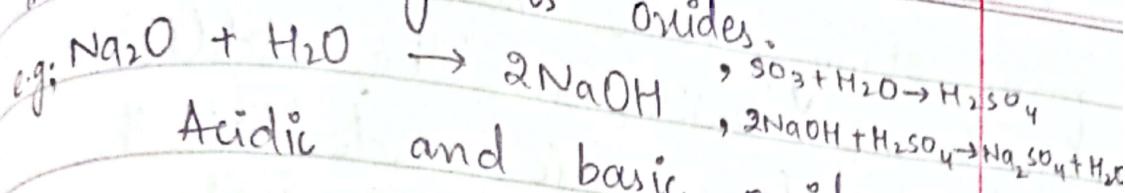
3. Amphoteric Oxides:

Amphoteric oxides can produce acid or base when dissolve in water. e.g; HSO_4^- act as amphoteric oxides and can produce hydronium ion as well as hydroxide ion when dissolve in water.



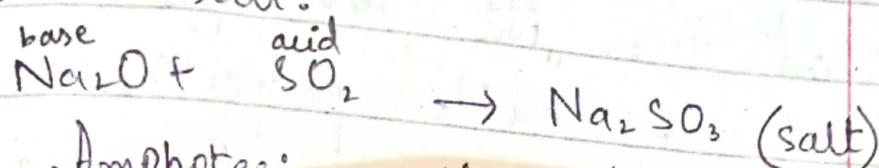
Acidic and Basic oxides are treated as anhydrous oxides but when dissolve in water can produce the oxides and bases. These acids and bases react in

the same way as oxides.



Acidic and basic oxides
when react together can

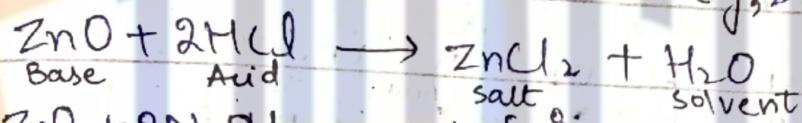
produce salt.



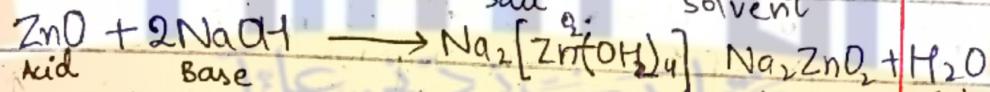
Amphoteric oxides react with acids and behave like a base

and if they react with strong

base, behave like acid. e.g; ZnO , Al_2O_3



Base Acid salt solvent



acid base $\text{Na}_2[\text{Zn}(\text{OH})_4]$ Na_2ZnO_2 H_2O
solvent solvent

While CO and NO are neutral.

Trends in Periodic Table:

In the periodic table, electro +ve elements occur on the very left side and electro -ve on right side. So, on going from left to right along the period, the electro +ve or metallic character of elements decreases and hence the basicity of their oxides decreases accordingly, and acidity of oxides increases. Hence oxides show a change in behaviour as stated

from strong basic oxides, then amphoteric oxides in the middle and strongly acidic oxides at the end of series in each period.

Period III : $\text{Na} \xrightarrow{\text{Strong basic}} \text{Al} \xrightarrow{\text{Amphoteric}} \text{Ar} \xrightarrow{\text{Strong acidic}}$

* Trend of oxide properties

down the group: On moving from top to bottom within a group the metallic character of elements increases and hence the basicity of oxides increases down the group.

* $\begin{array}{c} \text{C} \rightarrow \text{Acidic} \\ \text{Si} \rightarrow \text{Basic} \\ \text{Ge} \rightarrow \text{Amphoteric} \end{array}$ $\begin{array}{c} \text{Sn} \\ \text{Pb} \end{array} \} \text{Basic}$

Li K Cs metallic character ↑
strong basic Rb

1. Stability and acidic behaviour of oxides of metals with multiple oxidation states:

Those metals which have multiple oxidation states show different stability of their oxides. Normally the stability of oxides increases with increase in oxidation state and similarly the oxides of that show higher acidic character in higher oxidation state of metal. e.g; Cr

from multiple oxides with different oxidation state of metal. The oxide with higher O's of Cr show strong acidic character.

Oxide	O.S	Behaviour
CrO	+2	Basic (electro +ve)
Cr_2O_3	+3	Amphoteric
CrO_3	+6	Acidic (electro -ve) (e^- deficient)

Down the column basicity of oxides increases because of increase in electro +ve character of elements, accordingly the solubility of oxides also increases on moving down to column.

2. Melting point of oxides: It depends upon the lattice type of oxides. The packing of lattice is based upon the coordination number of oxides.

Following trends can be observed in the properties of oxides in P.T:

1. Valencies: Valencies of the element with oxygen change from 1-7 along period.

2. Volatility: Oxides becomes more volatile along period.

3. Structure: Structure of oxides changes from ionic to molecular along period.

4. M.P | B.P: M.P and B.P increase from left to right with increase in O.S of metals in metallic oxides along period.

For non-metals oxides, the M.P and B.p depends upon coordination number of the oxides (also in ionic oxides). When coordination number dropped, M.P and B.p will also drop.

→ Solid oxides are found on left side of periodic table and gaseous oxides at right side, On moving from left to right in a period, the coordination number of the more abundant atom (oxygen) decline, when coordination

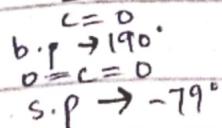
number drop below 2, the M.P drops sharply.

→ Small atoms with high C.N form the oxide with the lowest M.P

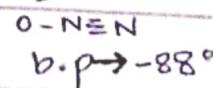
→ Typical trends in m.p.s or b.p.s of oxides in their group O.S as the oxidation and the group number increase as shown below. Monomeric molecules are

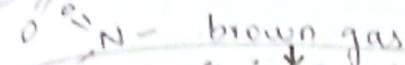
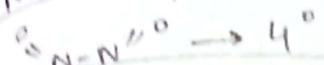
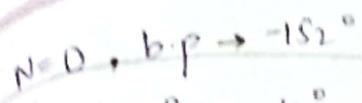
found in the upper right hand portion of the periodic table and also among the d-block elements with O.S of +7 and +8. These species possess relatively weak forces b/w individual units.

IV

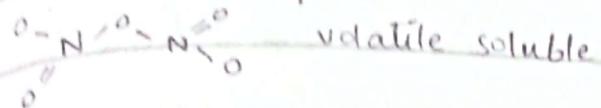


V

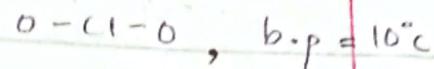
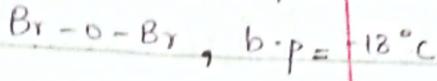
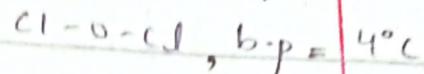
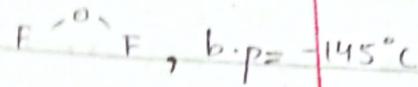




as it is \downarrow gas, its
b.p will be less than
room Temp.



VII



5. Electrical Conductivity: Solid oxides have no free e^- 's and ions. So, they are non-conductors of electricity. However in molten state or in solution from the oxides become electrolyte due to the presence of free ion.

6. Structure: Metallic oxides consisting of Na, Mg and Al have giant structure and strong lattice large amount of energy is required to break this lattice and so there $M.P.s$ are high, these oxides have crystalline structure which resemble to the salts of these metals but in oxides. The -ve ions always include the oxygen with -ve charge.

Silicon dioxide (SiO_2): structure:-

The electronegativity of the elements increases as we go along the period

and in case of silicon oxide, there is not enough difference of electronegativity b/w silicon and oxygen to form an ionic bond. Hence, the silicon dioxide has giant polar structure. There are three different structure of crystal form of silicon dioxide one of these is similar to the diamond structure of carbon. Crystalline silicon has the same structure as diamond, but the difference lies in the fact that silicon include oxygen atoms to built the structure while in diamond only carbon atom can built the 3 dimensional crystalline structure.

Melting and Boiling Points: SiO_2 has varying melting and boiling points depending upon the structure involved. SiO_2 has 3 types of structures but all structures melt around 1700°C . Very strong Si-O covalent bond have to be broken throughout the structure before melting occurs. B.P of SiO_2 is 2230°C .

Electrical conductivity: SiO_2 is non-conductor of electricity due to lack of free ions and free e⁻s in solid as well as liquid states.

On going onward in 3rd period after silicon, non-metal oxides are produced by phosphorus, sulfur and chlorine. These non-metal oxides have different melting and boiling behaviour than metal oxides due to presence of different type of attractive forces among non-metal oxide molecules.

Phosphorous Oxide: Phosphorous has two common oxides:

i) Phosphorous III Oxide P_4O_6

ii) Phosphorous V Oxide P_4O_{10}

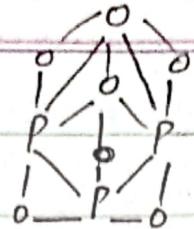
Phosphorous III Oxide (P_4O_6): P_4O_6 is white solid, having M.P 24°C and B.P 173°C .

Structure:- Structure of P_4O_6 is decided by the phosphorous atom which are attached in tetrahedral manner (P_4) and oxygen atoms are attach with these phosphorous atom.



The oxygen atom are present in a bridge form and each oxygen atom link two phosphorous atoms. It has V shape like water. But overall the structure is tetrahedral and not effected by the bridged

oxygen atom.



Phosphorous V Oxide (P_4O_{10}): It is also a white solid having sublimation point around $300^\circ C$. In this oxide, phosphorous shows no inert pair effect and all 5 e⁻'s are used for bonding. Phosphorous V oxide exist in different forms and some of these are polymeric and these polymeric forms sometimes exist in vapour phase as well.

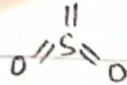
Sulphur Oxides: 'S' has two common oxides: (i) SO_2 (ii) SO_3 .

(i) Sulphur dioxide: It is a colourless gaseous oxide at room temp. it has pungent smell which is easily recognizable. It consist of simple SO_2 molecule having V-shaped structure.

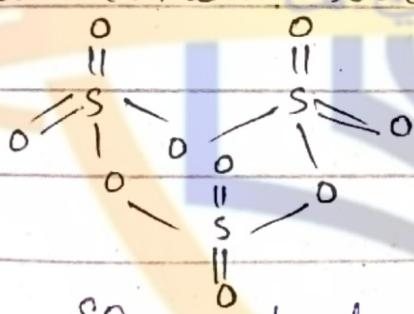
In this molecule sulphur used 4 out of its 6 valence electron to generate bonding with oxygen atom and one electron pair remain inert and appear as lone pair on sulphur in its molecule. The bent/V-shaped structure is produced as a result of 4 + 2 = 6

Sulphur Trioxide: Pure SO_3 is a white solid with low M.P and B.P. Its solubility in water is so high that it reacts with water even in vapour form to produce H_2SO_4 .

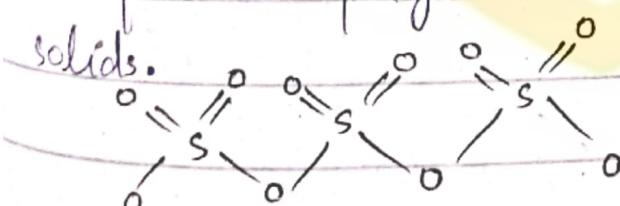
The structure of SO_3 consists of simple molecule in which sulphur uses all of its valence e⁻s to bond with oxygen atom and generate trigonal planar geometry.



In solid state, SO_3 exists in the form of trimer having formula S_3O_9 . In this trimer, SO_3 molecule joint in a ring and trimeric solid having molecular S_3O_9 .



SO_3 molecules can sometimes also arrange in the form of long chains to produce polymeric open chain SO_3 solids.



Chlorine Oxides: 'Cl' can produce several oxides, but the important oxides includes

(i) Chlorine I oxide

(ii) Chlorine VII oxide

(i) Chlorine I oxide: It is a yellowish red gas at room T (Cl_2O). It consists of simple bent structure molecule. $\text{Cl}-\ddot{\text{O}}-\text{Cl}$

(ii) Chlorine VII oxide: In this oxide, chlorine uses all of its seven valence shell e⁻'s to generate bonding with oxygen atoms. Structure of Cl_2O_7 consist of following molecule

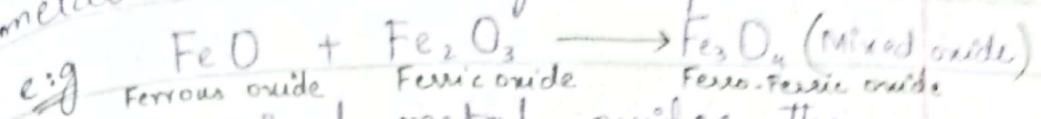


Each chlorine consists of tetrahedral structure and bridged oxygen between two chlorine atoms form a V-shape.

* Cl_2O_7 has higher m.ps and b.ps than Cl_2O .

Mix Metal Oxides: Mix metal oxides are produced by calcination (heat at ↑ temp. so that substance react each other in solid state & it is irreversible process), or simple

metal oxides at high temperature

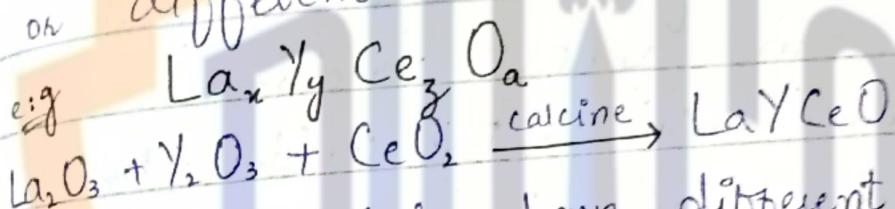


In mixed metal oxides the cations (metal ions) may be similar or different types.

e.g. In general representation

$M_x M_y O_z$, contain M_x and M_y metal atom which may be similar

or different.



Different metals have different ratios. These mixed metal oxide have

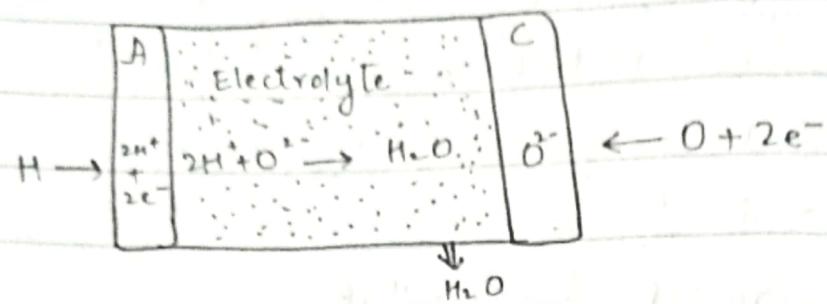
attracted much interest due to their wide range of applications in many critical areas of modern

technology, such as solar energy (solar plates have mix metal oxides on their photoemissive surface),

catalysis, organic synthesis, oil recovery, and in environmental pollutants screening (control).

→ These mix metal oxides are also used in the space for the generation of electricity to drive laboratories

and for uptake of water.



→ This H_2O is used for drinking purpose in space.

→ Electrodes of fuel cells are made up of mix metal oxides.

→ These mix metal oxides also used for doping.

Perovskites: The name perovskite is applied to the class of compounds which have specific structure like that of calcium titanium oxide ($CaTiO_3$). Perovskite structure of $CaTiO_3$ having IIA^{2+} and VII B^{4+} and O^{2-} is basic for the minerals of other mix metal oxides. Many metal cations can be dopped in this structure to produce diverse engineered materials.

The mineral having perovskite structure was first discovered by Lev perovskite. "After the name, it is the reason of name perovskite." OR

"And it is the reason of name perovskite after the name of scientist who discovered the mineral for the first time."

Perovskite is often found in contact with carbonate skarns at Magnet Cove, in altered blocks of lime stone produce from Mount Vesuvius, in chlorite and talc in Urals and in Switzerland etc.

Perovskite is a common mineral material in the Ca, Al rich inclusions found in some chondritic meteorites.

A rare earth (Ca, Na, Ce)(Ti, Fe)O₃ are found in alkali intrusive rock. Similarly other varieties exist in different areas of earth crust.

Structure: Perovskites of the general formula ABX₃ may be regarded as derived from the structure of ReO₃ as shown below. The BX₃ framework in perovskite is similar to that in ReO₃ structure consisting of corner-shared BX₆ octahedra.

Perovskite have almost cubic

structure with general formula $\text{ABO}_3 \cdot \text{In}$. In this structure, A site ion is usually an alkaline earth or rare earth element & is accommodated in the centre of lattice while B-site ions on the corners of the lattice are 3d, 4d, 5d transition element. The A-site cations are in 12-folds coordination with anions and B-site are in 6-folds coordination. A large number of metallic elements are stable in perovskite structure with the range of tolerance factor from 0.7 to 1.

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}$$

Tolerance factor is the stability factor which depends upon the ionic radii of different ions.

If the value of tolerance factor is < 0.71 then different trigonal type perovskite structure is produced like that of FeTiO_3 .

	Structure	Explanation	Example
0.71	Trigonal different structure	A & B have similar radii	FeTiO_3
0.7-0.9	Orthorhombic / Rhombohedral	A ion too small to fit into B-ion interstices <small>(empty spaces)</small>	GdFeO_3 (orthorhombic) CaTiO_3 (orthorhombic)
0.9-1	cubic	A and B have SrTiO_3 ideally similar size.	
>1	Hexagonal / Tetragonal	A ion too big & B ion small	BaNiO_3 / BaTiO_3

Spinel:- It is a type of mineral and have linked with MgAl_2O_4 and exist in cubic crystal system. Spinel has different colors and formed Gem like stones.

Silica + Fe minerals \rightarrow Dark colour \rightarrow mafic igneous rocks. $(\text{Mg}, \text{Fe})\text{Al}_2\text{O}_4$ and (CaAl_3) inclusions are found in mantle of earth.

General Formula: AB_2X_4 . A and B are cations while X is anion.

Aluminium spinel groups

Iron spinel groups

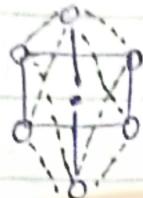
Cr_2O_4 Chromium spinel groups

Cobalt spinel groups

Vanadium spinels group
 Structure: Cubic closed packed crystal
 structure (Diamond) $MgAl_2O_4$



A atom



B atom

A B O atoms

INVERSE SPINEL: cubic closed packed

A.U A] → octahedral
 half B]

remaining half B → Tetrahedral

- * Cation distribution is different in both spinel and inverse spinel.



Fe^{2+} , Fe^{3+}
 d^6 , d^5

high spin, high spin

- * Crystal field stabilization energy also play important role in it and cause crystal field splitting.

- * Ferrites spinels used in circuits, permanent magnets, magnetic recording.

Bioimaging, photocatalysis, gas sensing, semiconductor, tunable optoelectronic properties, Photo Fenton and Solar fuel Production:-

OH^- → disinfectant of water radical

CO_2 reduction

H_2O → splitting

$\text{H}_2\text{O} \longrightarrow \text{Hydrogen} + \text{oxygen}$

