MAA OMWATI DEGREE COLLEGE, HASSANPUR (PALWAL)

NOTES

SUBJECT : Inorganic Chemistry

CLASS : B.SC 3rd Sem

SESSION : 2021-2022

B. Sc IIIrd Semester

Paper IX (Theory) Inorganic Chemistry **Max. Marks: 29**

CH-301 **Time: 3 Hrs.**

Note: Examiner will set nine questions and the candidates will be required to attempt five questions in all. Question number one will be compulsory containing five short answer type questions covering the entire syllabus and will be of five marks. Further, examiner will set two questions from each section and the candidates will be required to attempt one question from each section which will be o f s ix marks each

Section-A

Chemistry of Elements of Ist transition series:

Definition of transition elements, position in the periodic table, General characteristics & properites of Ist transition elements,. Structures & properties of some compounds of transition elements – TiO_2, $VOCl_2$, $FeCl_3$, $CuCl_2$ and $Ni(CO)_4$

Section-B

Chemistry of Elements of IInd & IIIrd transition series

General characteristics and properties of the IInd and IIIrd trans ition elements Comparison of properties of 3d elements with 4d & 5d elements with reference only to ionic radii, oxidation state, magnetic and Spectral properties and stereochemistry

Section-C

Coordination Compounds

Werner's coordination theory, effective atomic number concept, chelates, nomenclature of coordination compounds, isomerism in coordination compounds, valence bond theory of transition metal complexes

Section-D

Non-aqueous Solvents

Physical properties of a solvent, types of solvents and their general characteristics, reactions in non-aqueous solvents with reference to liquid NH_3 and liquid SO_2

B. Sc. IIIrd Semester

Paper X (Theory) Physical Chemistry **Marks: 30**

CH-302 **Time: 3 Hrs**

Note: Examiner will set nine questions and the candidates will be required to attempt five questions in all. Question number one will be compulsory containing six short answer type questions covering the entire syllabus and will be of six marks. Further,

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Inorganic Chemistry

D- Block Element :-

The d- block elements involves the filling of d- subshell. The penultimate shell in these elements is being expended from eight to eighteen electrons by the addition of ten d- electrons.

In other word it is define as the those elements which either in their elementry form or ion their chemically significant oxidation states, have partly filled d- Sub shell.

Electronic Configuration :-

In the atom of transition elements, the outermost energy level has ns^1 or ns^2 form electronic configuration is

$$(n-1)\,d^{1-10}\;ns^{1-2}.$$

Characteristics Properties :-

1. Physical properties :-

a) Atomic Radii
b) Ionic Radii
Covalent

a) Atomic Radii :-

The variation in atomic radii which transition series in S and P block elements. there the effective atomic no inc. as size dec. from poor Shielding effect.

b) Density :-

The densities of transition elements are very high as compared to metals of group 1 and 2. the densities of the element make close packed Structure of these elements.

c) Ionic Radii :-

Ionic Radii of transition elements are depend upon the oxidation state of transition elements for eG :- Fe^{2+}, Fe^{3+}

The Ionic radii of transition element are Smaller then the rep. of these elements.

d) Melting and Boiling point :-

D- block element has high Boiling and melting point they are held by Strong forces. They are high value of density.

e) Oxidation States :-

One of the most - remarkable features of the Chemistry of d- block metals is the ability of these elements to exhibit a variety of Oxidation states in their Compounds.

2. Chemical properties :-

a) Chemical reactivity :-

Transition metals show less chemical reactivity than S and P- block element due to following reason.

i) They have smaller size then S and P block elements.

ii) They have high ionisation energy.

iii) They have high enthalpy of sublimation.

Transition element :-

Transition element are those element in a modern periodic table, on the left hand side are S-block elements and right hand side are P-block element.

for eg :- Zinc, Mendelevium etc.

→ This genral characterishic properties are Genrally intermediate b/w the elements of S-block on one hand and P-block on other hand. In simple terms we may say that d-block elements represent a change from the most electropositive S-block element to the least electropositive P-block elements. Therefore named Transition elements or Transition metals.

Electronic configuration of the following

i) Mo ii) Pd iii) W iv) Hg.

i) Mo (Molybdenum) :-

Mo is a Second transition series element. Mo's atomic no is 42

→ The genral electronic configuration of the atoms of the

Second transition series is

$4d^{1-10}\ 5s^{0-2}$

So

Mo :

Atomic no : 42

Electronic Conf. :- $4d^5\ 5s^1$

ii) Pd (Palladium) :-

Pd also Second transition series element.

Elec. Conf. of Second transition Series is

$4d^{1-10}\ 5s^{0-2}$

So

Pd :

Atomic no :- 46

Elec. Conf :- $4d^{10}\ 5s^0$

iii) W (Tungsten) :-

W is a third transition series element

Electronic Confi. of third transition Series are

$4f^0$ or $14 5d^{1-10}\ 6s^{1-2}$

W

atomic no :- 74

Electron Conf. :- $4f^{14}\ 5d^{3}\ 6s^{2}$

iv) Hg (Mercury) :-

Hg also third transition series element its elec conf. is

$4F^{0}$ or $14 5d^{1-10}\ 6s^{1-2}$

5^{0}

Hg

atomic no = 80

Elec Conf. :- $4f^{14}\ 5d^{10}\ 6s^{2}$

→ Why do transition metals

i) Show variable Oxidation.
ii) form a large no of Coordination Compound.
iii) give coloured and paramagnetic Ions.
iv) exhibit good Catalytic properties.

Ans :-

i) Transition element are also called d- block elements. They show Variable Oxidation State because transition have (n-1) d orbitals empty that are closer to the outermost ns orbital in energy levels. These orbitals are never fully filled.

ii) Transition elements form a large no of complex compound due to the comparatively smaller size of the metal ions their high ionic charges and the availability of d- orbitals for bond formation.

iii) Transition metals and their ions are generally paramagnetic due to the presence of unpaired electron and hence show colour. They also act as catalyst.

iv) Transition metals shows catalytic behaviour mainly due to the presence of vacant d- orbitals. They have the ability of exhibit variable valencies and they have a tendency to form to complex Compound.

→ Give reason Zn, Cd, Hg have low melting point other d- block elements.

Ans:- In Zn, Cd, Hg have a filled d- subshell. due to which metallic bond are weak ⊗ than other d- block elements That's why they are soft and have low melting point than other d- block elements

First transition Series:-

The first of the the inner transition series includes the elemen -ts from Cerium (Ce) to lutetium (Lu) these elements are called lanthanoids because the chemistry of each closly resembles that of lanthanum.

Electronic Configuration :-

Elec. Conf. of First transition series are

$3d^{1-10}\ 4s^{1-2}$

Element	Symbol	A.N.	Elec. Conf.
Scandium	Sc	21	$3d^1\ 4s^2$
Titanium	Ti	22	$3d^2\ 4s^2$
vanadium	V	23	$3d^3\ 4s^2$
Chromium	Cr	24	$3d^5\ 4s^1$
manganese	Mn	25	$3d^5\ 4s^2$
Iron	Fe	26	$3d^6\ 4s^2$
Cobalt	Co	27	$3d^7\ 4s^2$
Nickel	Ni	28	$3d^8\ 4s^2$
copper	Cu	29	$3d^{10}\ 4s^1$
zinc	Zn	30	$3d^{10}\ 4s^2$

→ Atomic Radius:-

The atomic radii of the first transition series decrease from Sc to Cr and remain almost constant till Cu and than inc. towards the end. This can be explained based on two effects namely screening and the nuclear Charge effect these two effect oppose each other resulting in an inc. in nuclear charge

→ Cu^{2+} ions are Coloured and paramagnetic while Zn^{2+} ion are Colourless and di- magnetic.

Cu^{2+} ions are coloured and paramagnetic while Zn^{2+} ion are Colourless and di- magnatic due to Cu^{2+} has an unpaired e^- its conf. is $3d^9$ wheres Zn^{2+} has all paired electrons its conf. is $3d^{10}$

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Also, the unpaired e^- in the copper ion allows e^- transition in the visible region to take place, so that ion is coloured.

→ Why are transition element good reducing agents?

Ans:-

Transition elements are good reducing agents because transition element are completely filled d. orbitals.

→ Which of the two among Nb, V, Ta are chemically closer and why?

Ans:- Nb, V, Ta are chemically closer and because Nb, and Ta are similar in size his size are cubic face centered.

→ Comment "Cu, Ag, Au" are typical transition element while Zn, Cd and Hg not.

Ans:-

The electronic conf. of "Cu Ag, Au" can be expressed as $(n-1)d^{10}\ ns^1$, and elec. conf of Zn, Cd, Hg are $(n-1)d^{10}\ ns^2$ so there for Zn, Cd, Hg are not classified as transition metals.

→ Chromium and copper have irregular electronic configuration.

Ans:-

$Cu = [Ar]\ 3d^{10}\ 4s^1$

$Cr = [Ar]\ 3d^5\ 4s^1$

Their first ionization energies are low because removal of one electron give a stable $3d^{10}$ or $3d^5$ configuration.

Their second ionization energies are expected to be high because of removal of an electron from stable completely filled orbital $3d^{10}$ for Cu^+ and half filled orbital $3d^5$ for Cr^+.

→ The first ionisation energies of Hg is higher than that of Cd.

Ans:- The presence of 4F orbitals cause poor shielding effect which result in inc. effective nuclear charge on the outer valence electons. This result is higher first ionisation energy of mercury as compared to Cadmium.

→ Magnetic behaviour of transition elements.

Ans:-

Generally, a majority of compounds of transition metal ~~Chemistry~~ are paramagnetic and much of our understanding of transition metal Chemistry has been obtained from the study of magnetic behaviour of their compounds. The magnetic moment of some ions of the first transition series are given in these values have been calculated using the spin only formula as given

$$\mu = \sqrt{n(n+2)}.$$

→ Why Zr and Hf have similar properties?

Ans: Due to lanthanide contraction, Zr & Hf have similar atomic and ionic radii in similarly in their chemical behaviour.

Some compound of d-block elements:-

a). Titanium dioxide TiO_2 (d^0) :-

Preparation:-

(i) from ilmenite:-

The powdered ilmenite is digested with excess of conc. H_2SO_4. when ferrous sulphate, Feric sulphate and titanyl sulphate are formed. the resulting product extracted with water. then the soln is cooled to 10°C to crystallise out ferrous sulphate which are removed by filteration.

Now the soln containg titany sulphate is boild with excess of water which result in its hydrolysis causing precipitation of hydrated titanium di-oxide.

$$TiOSO_4 + H_2O \longrightarrow TiO_2 + H_2SO_4$$

Properties:-

i) It is a white refractory solid which turns yellow on heating like zinc oxide.

ii) It is insoluble in water.

iii) Action with hydrogen :-

on reduction with hydrogen, it forms Ti_2O_3.

$$2TiO_2 + H_2 \rightarrow Ti_2O_3 + H_2O.$$

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Action with acid:-

It is insoluble in HCl, HNO_3, aqua regia. On H_2SO_4 but is soluble in conc. H_2SO_4 to form titanyl sulphate, $TiSO_4$.

$$TiO_2 + H_2SO_4 \rightarrow TiOSO_4 + H_2O$$

Uses:-

i). In enamelling of porcelain goods.
ii). In colouring artificial teeth.
iii) In gas mantless.

Vanadyl Chloride $VOCl_2$ (d') :-

It is prepared by reduction of $VOCl_3$ with hydrogen at a high temp. 400°C.

$$2VOCl_3 + H_2 \rightarrow 2VOCl_2 + 2HCl$$

properties:-

i) The pure compound exist as shiny, greasy-green crystals.

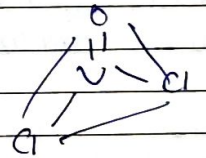
ii) It is a deliquescent solid.

Uses:-

It is used commercially in dyeing under the name of Divandyl Tetrachloride."

d) Structure:-

$VOCl_2$ is a trigonal planar molecule.



Iron (III) Chloride or Ferric Chloride, $FeCl_3$ (d5) :-

Preparation:-

It is prepared by dissolving iron filing in hydrochloric acid. The resulting sol^n contains iron (II) chloride which is oxidised by passing Chroline through it.

$$Fe + 2HCl \rightarrow FeCl_2 + H_2.$$

$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$$

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Properties:-

i) It is a covalent compound which dissolves in organic solvents such as ether and alcohol.

ii) It is a yellow solid which is exceedingly soluble in water.

Uses:-

1) It is used as a mordant in dyeing and as an oxidising agent.

2. Its alcoholic soln is used in medicine under the name tinture ferripes chloride.

Copper II Chloride or cupric chloride, $CuCl_2$:

prepration:-

It is a green crystalline solid which is soluble which is soluble in water.

Its aqueous soln is acidic due to hydrolysis as.

$$CuCl_2 + 2H_2O \rightleftharpoons Cu(OH)_2 + 2HCl$$

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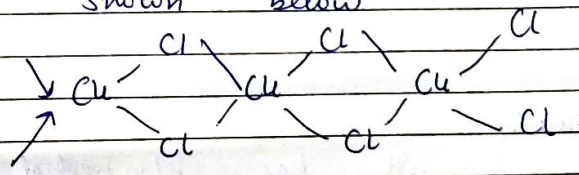
Uses:-

It is used as a crystlyst in deacon process for the manufacture of Chlorine.

It is also used in making green pigments.

Structure:-

Consist of infine halogen bridge chain as shown below



Nickel Carbonyl or Nickel tetracarbonyl (0): $Ni(CO)_4$ (d) :-

prepration:-

It is prepared by passing carbon monoxide gas over finaly divided nickel at about 50° C.

$$Ni + 4CO \xrightarrow{50^\circ C} Ni + 4CO\uparrow$$

properties :-

① It is a colourless volatile liquid which boils at 43°C

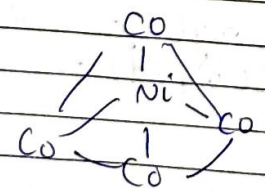
2) It is soluble in alcohol, benzene, and ether.

Uses :-

It has found industrial application in the mond's process for the manufacture of Nickel.

Structure :-

It has tetrahedral shape due to sp^3 hybridization.



Unit - 2.

Coordination Compound.

Werner's coordination theory :-

It was only in 1893 that Werner presented a set of idea which are known as Werner's coordination theory of Valency which could explain all the observable properties of complex compounds. It was werner's theory which laid the foundation of our present-day-knowledge of coordination chemistry.

Postulates of Werner's theory :-

1. Every element exhibits two type of Valency.

a) Primary valency :-

the primary valency of a central metal atom ion is a negative ion.

b). Secondary valency :-

Secondary valency of a central metal ion is other neutral ion which are called legends

2.) Every metal atom has a fixed no of secondary valencies.

3). Every elements wants to satisfy the secondary valency and primary valencies

Application

i). It could predict the exact formulation of each complex.

2.) It could explain the behaviour of each complex.

3.) It could be predict the structure of diff. complexes with coordination no 4 and 6.

Effective Atomic no :-

It is defined as the sum of e^- on central metal in the complex and e^- donate by legends.

E.A.N = e^- central metal in the complex + e^- donate by legends.

for eg. :-

Hexamine cobalt (III) ion

$[Co(NH_3)_6]^{3+}$

Atomic no of Cobalt = 27

$\therefore Co^{3+}$ contains e^- = $24e^-$

6 NH_3 legends donate (6×2) = 12

36

E.A.N of $[Co(NH_3)_6]^{3+}$ is 36.

→ Importance of E.A.N Rule :-

E.A.N rule is obeyed with a high degree of frequency by organometallic Compound especially metal Carbonyls. It also helps us in understanding structure most of the Carbonyls whether they are mohomeric or polymeric.

Chelates :-

If two or more donar atoms coordinate by two or more e^- pair to the same metal ion. The complex thus produce is called Chelates. and this process are called Chelation.

for eg :- $[Co(en)_3]^{3+}$

→ Some special features of Chelates :-

1). Chelate effect :-

The enhanced stability of complex containing chelating legends is known as chelate effect.

2). No of Chelate Rings :-

The larger the no of rings so the larger the stability of complex.

3). Size of Chelate ring :-

The stability of complex is also depend as the size of ring.

4). Steric effect :-

The metal legends bond becomes weak and leads to reduce stability of complex this effect is known as steric effect.

Application of Chelate formation :-

1. Formation of chelates in Analytical Chemistry :-

Standard EDTA soln are widely use in volumetic analysis to determine the hardness of water. EDTA complex Ca^{2+} and Mg^{2+} ions which are responsible for hardness of water.

2). In living System :-

Hemoglobin impart red colour to human blood. Hemoglobin picks O_2 and form oxyhemoglobic in the lungs.

Nomanclature of Coordination compound. :-

The symbol for central atoms first with ionic and neutral legends. and the whole complex is inclosed in square bracket. In names the central atom should be placed after the legends. the legends are listed in alphabatically order.

for eg.

$[Pt(NH_3)_2Cl_2]$

diamine di Chloro Platinum(II)

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i) When a naming a salt, the cation is named first and then the anion. In the same way the positive is first then negative.

for eg.

$[Cu(NH_3)_4]SO_4$

Tetraamin Copper II Sulphate

2. Non ionic or molecular complex are given one word names with out any separation or hyphenes.

for eg:-

$[Co(NH_3)_3Cl_3]$

Tetra amine tetrachloro Cobalt(III)

iii) Neutral legends are named as molecules.

H_2O aq ua Co Carbonyl

NH_3 ammine No nitrosyl

iv) The prefix di-, tri-, tetra are used.

for eg:-

$[Co(en)_2Cl_2]Cl$

di chloro bis (di ethylene ammine

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Cobalt III Chloride.

Isomerism in Coordination compound:-

It is defined as the substance with the same Chemical formula but differs in structure.

These are two types.

1. Stereoisomerism:-

These are two types.

a) Geometrical isomerism:-

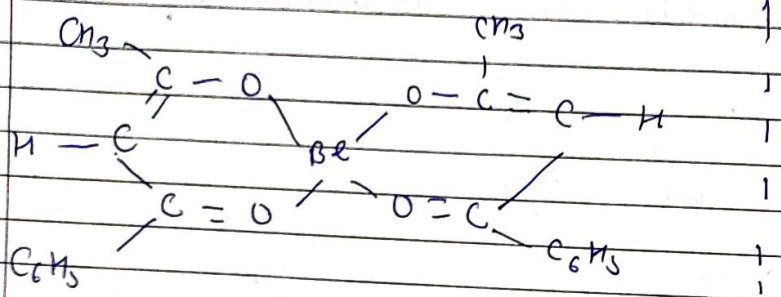
This type of isomerism is not possible with compounds having coordination no 2, 3 is known as Geometrical isomerism.

for eg:- $[Pt(NH_3)_2Cl_2]$

b) Optical Isomerism:-

A molecule is optically active if it cannot superimposed on his mirror image. are known as optical isomerism.

for eg:-



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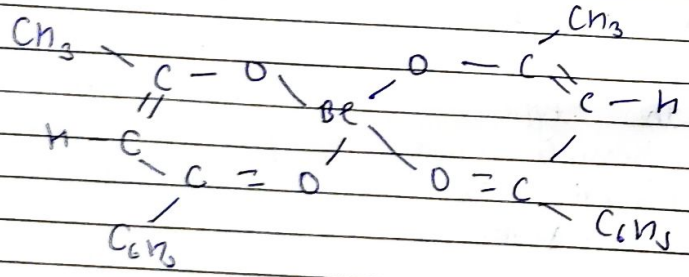


2. Structural Isomerism:-

Same formula but differ in structure are known as structural isomerism. these are five types.

a) Ionisation Isomerism:-

The compound same in formula but differ in ions. are known as ionisation isomerism.

for eg:-

$[Co(NH_3)_5Br]SO_4$

b) Hydrated Isomerism:-

The Compound same formula but differ in hydrated forms.

for eg:-

$[Cr(H_2O)_6]Cl_3$ violet

$[Cr(H_2O)_5Cl_2]Cl\cdot H_2O$ light green.

c) Coordination Isomerism:-

Comound containg both cation and anion species give rise to coordination isomerism due to random distribution of legends.

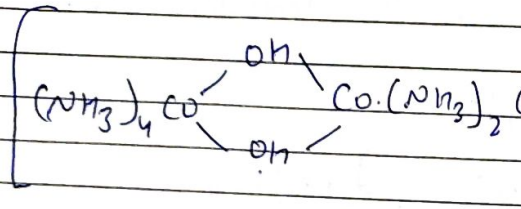
for eg:-

$[Co(NH_3)_6]$

d) coordination position Isomerism:-

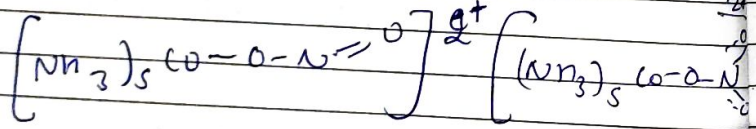
Compound which have same formula but differ in arrangement of legends.

for eg:-



e) Linkage Isomerism :-

This type of Isomerism is exhibited by complex containg monodentate legends with more than one donar atom.
for eg :-



Valence Bond theory [V.B.T] :-

This theory is the simplest of the three theories and is easy to apply. It gives fairly accurate explation of the structure and magnetic properties of a large no of Coordination Compound.

→ Silent features of this theory :-

1) The atomic orbitals of metal hybrid hybridised to form a new set of equivalent hybridised orbital.

2). The non bonding metal e⁻ occupy the inner d-orbitals which do not participate in the hybridisation

3). Each legends must contain a lone pair.

→ Limitation of V.B.T :-

1). It is limited to qualitive explanation only.

2) It does not explain predict of spectra of complex.

3). It does not predict the relative stability of diff. legends.

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Unit-3.

Non-aqueous Solvents.

Physical properties of Solvents:-

1. Liquid range.

Boiling and melting point :-

Since chemists often study rxn in liquid phase the liquid range b/w melting and point determine the useful of a Solvent for eg water freez at 0°C and rxn are highly exothemic.

2. Heat of fusion and Heat of Vaporization :-

Heat of fusion :-

The amount of heat absorved by one mole of substance to change from solid to liquid.

Heat of Vaporization :-

The amount of heat absorved by one mole of substance to change from liquid to Vappor.

3. Polar nature :-

Polar molecule introduce polarity in a solvent because of the tendency to orient diff. molecules.

4. Dielectric Constant :-

It is property of solvent which determines the amount of force operating b/w diff. ion of a solute in that solvent.

$$\epsilon = \frac{q^+ q^-}{q\pi r\varepsilon}$$

5. Viscosity :-

The viscosity of a solvent is an important criteria in evaluating the usefulness of a solvent for a synthetic Chemist. Viscosity refers to the rate of flow.

Type of Solvent :-

There are two types.

1. Ionizing solvent :-

It is defined as thus solvents which are highly

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polar in nature are known as ionizing solvent.

General Characterishics :-

i) They Generally dissolve a large no of inorganic Compounds.

2.) These solvents are generally Contain ionizable proton like as HF, H_2SO_4 etc.

Non-Ionizing solvents :-

It is defined as thus solvents are non polar and very weekly polar in nature are known as Non-Ionizing Solvents.

General Characterishics :-

1). They are generally considered as inert solvents.

2.) Inorganic Compound are often in soluble in these solvents.

Rxn in Non-aqueous solvents :-

i) precipitation rxn :-

Rxn bpw two reactant which lead to the precipitation of one of the product are called precipitation or metathetic rxn.

$$BaCl_2 + 2AgNO_3 \xrightarrow{H_2O} Ba(NO_3)_2 + 2AgCl\downarrow$$

2. Salt formation :-

Salt formation takes place by reacting an appropriate acid and a base which are sufficiently acidic or basic respectivly, to react completly.

$$Na^+(H_2NCONH^-) + H_2O \rightarrow NaOH + H_2NCONH_2.$$

3. Solvolysis :-

In a Solvatic rxn the Solvent molecule reacts with the solute in a manner that the solvent is split into two parts.

$$SO_2Cl_2 + 4H_2O \xrightarrow{H_2O} SO_2(OH)_2 + 2H_3O^+ + 2Cl^-$$

4. Solvation :-

In a Solvation rxn, Solvent molecules attach themselves to a solute species.