IIT JAM

CHEMISTRY

SAMPLE THEORY

* AROMATICITY
* COORDINATION COMPLEXES
* PHASE EQUILIBRIA

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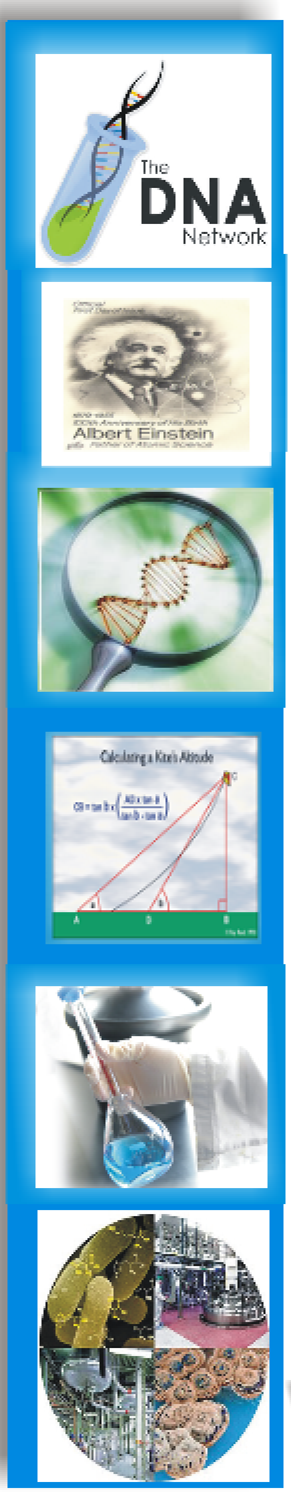

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I Aromaticity

Huckel Rule: The compounds with odd number of pairs of electrons, (which is mathematically written as 4n+2 (n = 0,1,2,3 etc.), show aromaticity. Molecules which do not obey these rules partially fall in the category of anti-aromatic and non aromatic compounds. The p orbital array (A) and delocalization (B) in benzene can be pictorially represented as shown below.

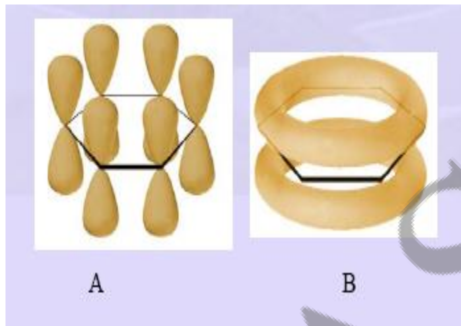

Fig : 1

Molecular orbital description of aromaticity and antiaromaticity

According to molecular orbital theory, the six p orbitals combine to form six molecular orbitals, three of which are bonding and three are anti-bonding. Six π electrons occupy the bonding orbitals, which are lower in energy compared to the un-hybridized p orbitals (atomic orbitals). The relative energies of atomic orbitals and molecular orbitals are shown in Figure.

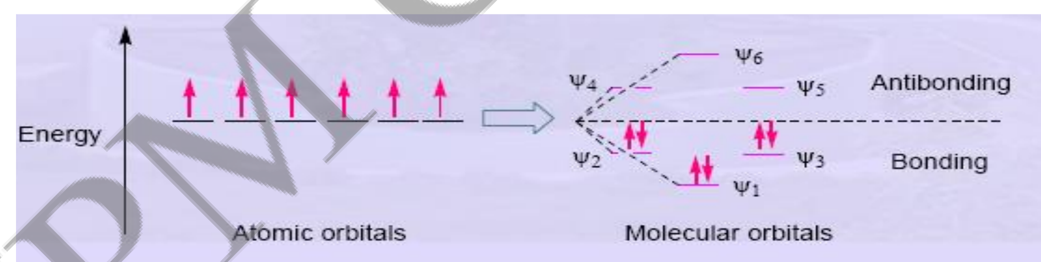

Fig : 2

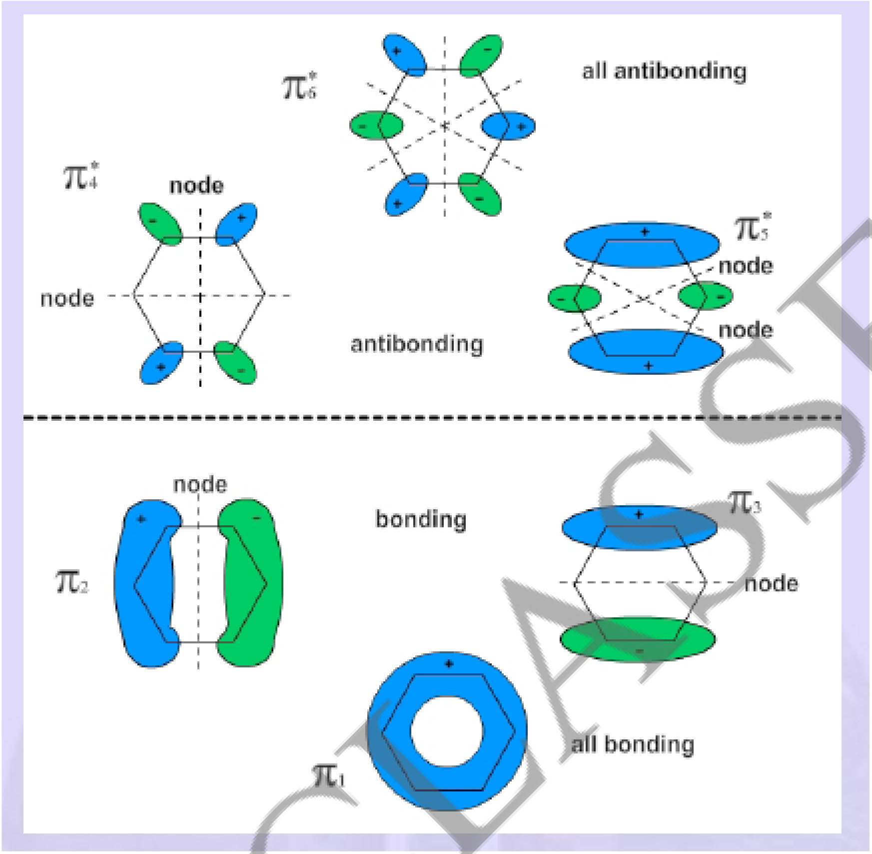

Figure: 3

The relative energies of p molecular orbitals in planar cyclic conjugated systems can be determined by a simplified approach developed by Frost. This involves the following steps:

1)First of all we draw a circle,

2) Then place the ring (polygon representing the compound of interest) in the circle with one of its vertices pointing down. Each point where the polygon touches the circle represents an energy level.

3)Then place the correct number of electrons in the orbitals, starting with the lowest energy orbital first, in accordance with Hund's rule.

If the polygon touches the circle at a horizontal diameter, that point would represent a nonbonding orbital. Energy levels below this line indicate bonding MOs and those above are anti-bonding.

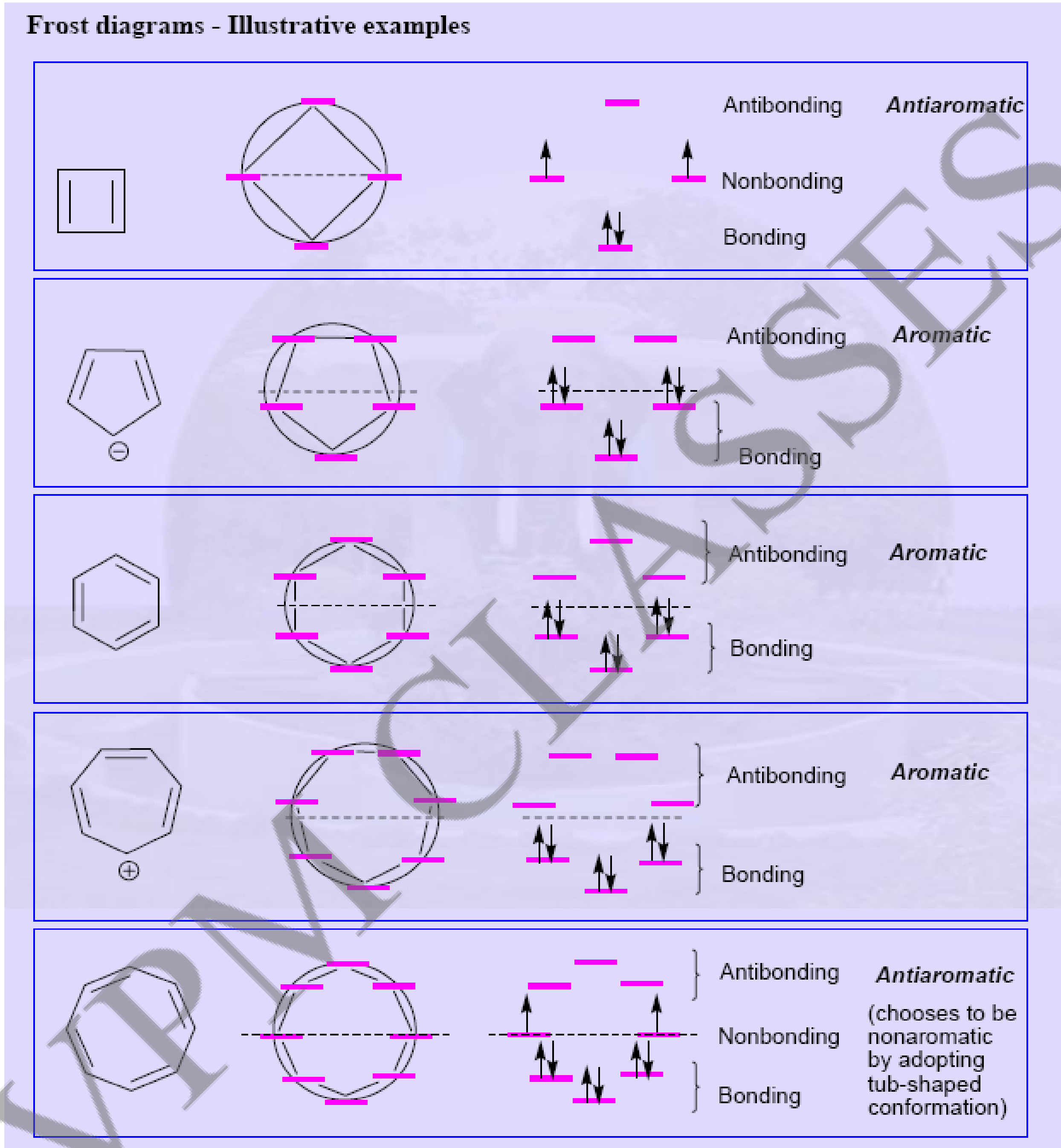

Fig : 4

Points to remember while making predictions on aromaticity using Frost's circle

- Aromatic compounds will have all occupied molecular orbitals completely filled where as antiaromatic compounds would have incompletely filled orbitals.
- If an antiaromatic system (4n electrons) has the freedom to undergo conformational change and become nonaromatic that would do so. Remember that antiaromatic state is less stable than aromatic and nonaromatic forms. A comparison of molecular orbitals in aromatic and antiaromatic systems is presented in figure 5.

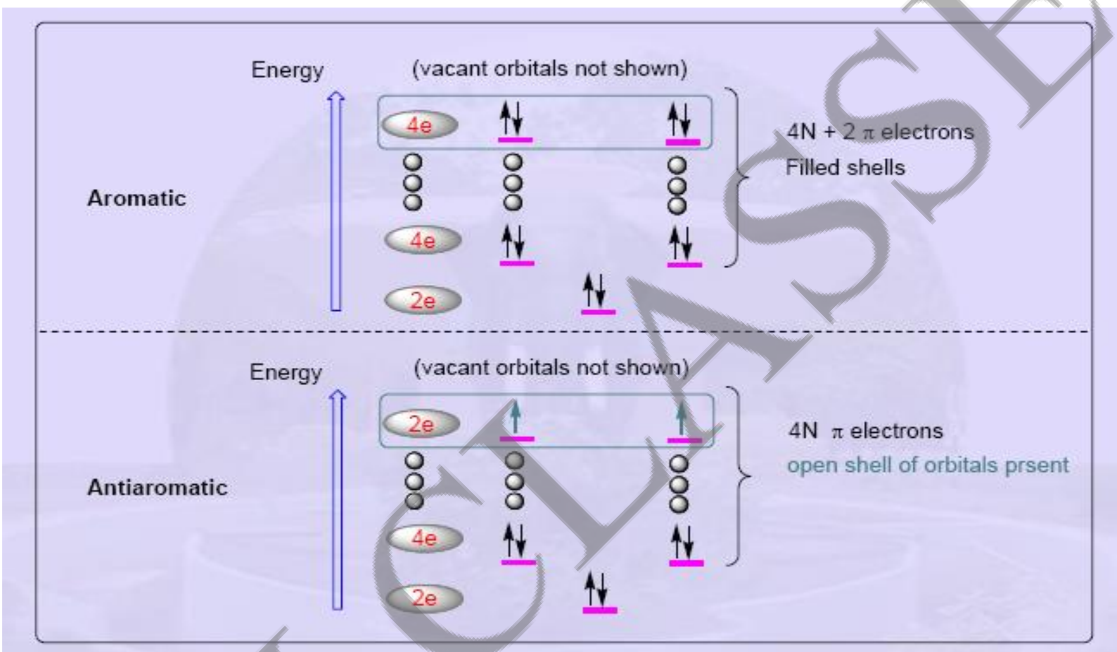

Fig : 5

Aromaticity in higher Annulenes

Completely conjugated monocyclic hydrocarbons are called annulenes.

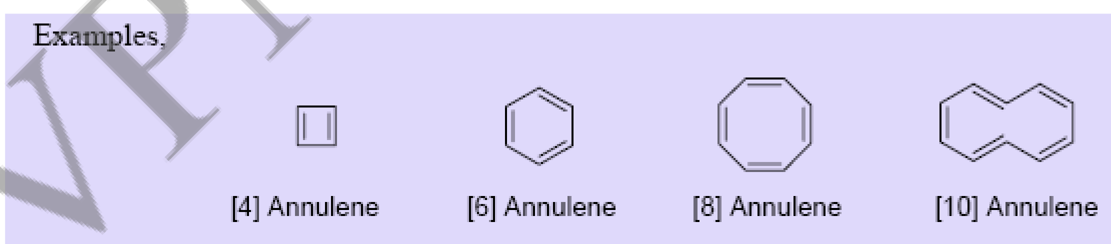

Fig : 6

The criteria for aromaticity that we discussed earlier can be applied to higher annulenes as well. However, achieving planarity is a hurdle for many larger rings due to potential steric clashes or angle strains. If the ring (with 4n+2 π electrons) is sufficiently large such that planarity does not cause steric or angle strains, the system would adopt that conformation, get stabilization through electron delocalization and becomes aromatic. Larger annulenes with 4n π electrons are not antiaromatic because they are flexible enough to become non-planar and become non-aromatic.

In [10]-annulene, there is considerable steric interaction between hydrogens at 1 and 6 positions. Further, a planar form (regular decagon) requires an angle of 144o between carbon atoms which is too large to accommodate in a sp^2 framework. The system prefers a nonplanar conformation and is not aromatic (the fact that angle strain need NOT always be a problem in achieving planarity is evident from examples such as cyclooctatetraenyl dianion, which is stable and aromatic). Bridging C1 and C6 in [10]-annulene leads to the compound VII (Figure) which is reasonably planar with all the bond distances in the range of 1.37-1.42 Å and show aromaticity (In NMR, outer protons are found at 6.9-7.3 ä and the bridgehead methylene at -5.0 ä).

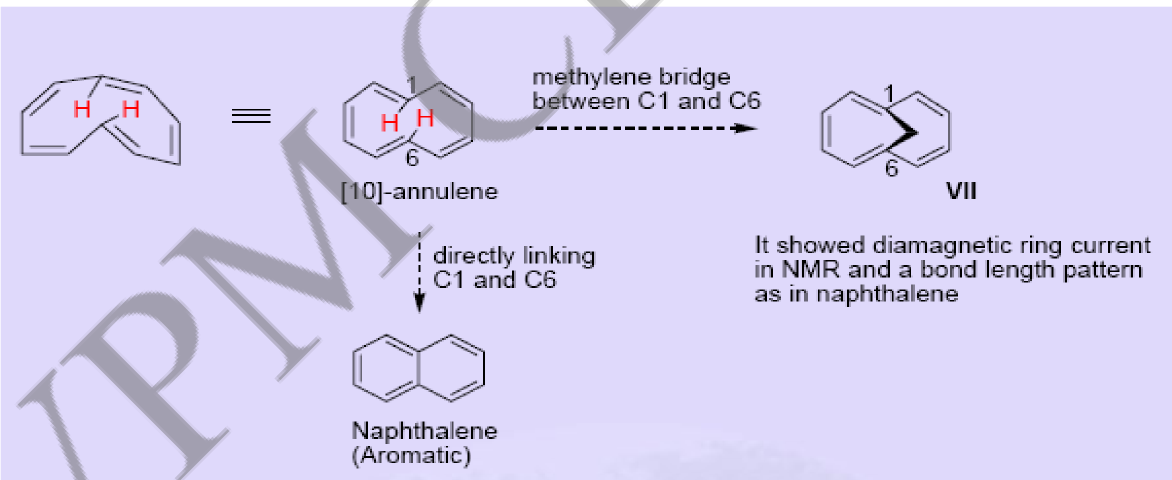

Fig :7

[12]-annulene

[12]-annulene (4n, n = 3) is antiaromatic and hence is not stable above -50oC. Its dianion (4n+2, n = 3) is however stable up to 30oC and is aromatic.

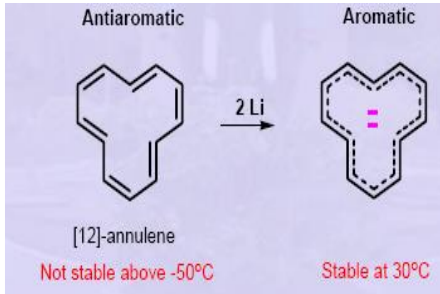

Fig: 8

[14]-annulene

Bond lengths in [14]-annulene range from 1.35-1.41Ao but do not show the alternating pattern of localized polyenes. It is aromatic (except for the isomers that are not planar). NMR shows that it is in conformational equilibrium as shown below Figure. The steric interactions associated with internal hydrogens can be minimized if C3, C6, C10 and C13 positions are locked using suitable bridging units. Thus trans-15,16-dimethyldihydropyrene and its diethyl and dipropyl homologs are aromatic with C-C bond distances between 1.39-1.40 Ao. Conformational flexibility in [14]-annulene can be restricted by inserting triple bond in place of one of the more double bonds. Here, the triple bond contributes only two electrons for delocalization leaving the other two localized.

Homoaromaticity

If a stabilized cyclic conjugated system (4n+2 e s) can be formed by bypassing one saturated atom, that lead to homoaromaticity. Compared to true aromatic systems, the net stabilization here may be low due to poorer overlap of orbitals. Cyclooctatrienyl cation (homotropylium ion) formed when cyclooctatetraene is dissolved in concentrated sulfuric acid is the best example to demonstrate homoaromaticity. Here, six electrons are spread over seven carbon atoms as in Tropylium cation.

II Coordination complexes

CFT: APPLICATIONS

(1) Colour of transition metal complexes

CFT provides an explanation for the observed colours of transition metal complexes. When the light falls on a complex, the following observations may occur:

(i) The complex may absorb the whole of white light. In this case complex appears black.

(ii) The complex may reflect (or transmit) the whole light. In this case it appears white.

(iii) The absorption of light by the coloured complexes takes place in the visible region of the spectrum which extends from 4000 to 7000 in wavelength. The colour of the absorbed light is different from that of the transmitted light

. **EXAMPLES:**

(i) Hydrated cupric sulphate containing $[Cu(H_2O)_4]^{2+}$ ions is blue (colour of the transmitted light) because it absorbs yellow light.

(ii) Cupricammonium sulphate containing $[Cu(NH_3)_4]^{2+}$ ions are violet, because it absorbs yellow green light.

(iii) Anhydrous cupric sulphate is colour less, since it absorbs light in the infra-red region

(iv) $[Cu(CN)_4]^{2-}$ ion absorbs light in the ultra - violet region and hence is colourless.

(v) $[Ti(H_2O)_6]^{3+}$ absorbs green light in the visible region and hence it is purple which is the colour of the transmitted light. $[Ti(H_2O)_6]^{3+}$ ion shows absorption maxima at a wavelength of about 5000 which corresponds to the wave number, = 20000 cm^{-1} as shown below :

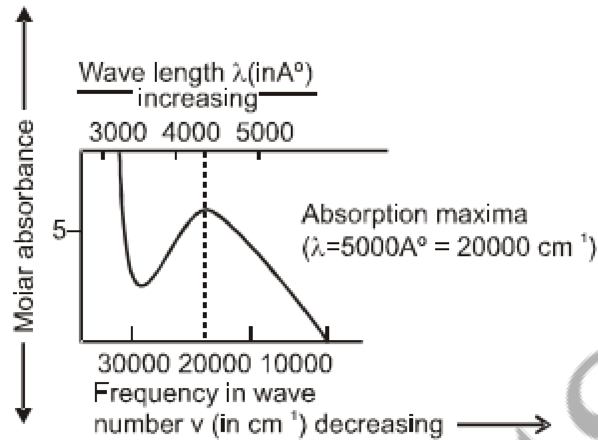

Fig: 9 Visible absorption spectrum of $[Ti^{III}(H_2O)_6]^{3+}$ ion; Peak of the curve shows the maximum absorption

This energy (= 57 Kcalories/ mole) is equal to the energy difference, Δ_0 between t_{2g} and e_g levels and hence is sufficient to excite the single d-electron in t_{2g} orbital to eg orbital. This type of electronic transition from t_{2g} to e_g level is called d-d or ligand field transition. The colour of $[Ti(H_2O)_6]^{3+}$ is attributed to d-d electron transition.

(2) Number of unpaired electrons and magnetic properties of octahedral complexes

CFT is helpful in determining the number of unpaired electrons in a given High Spin- and Low Spin- octahedral complex, and consequently, with the help of "spin only" formula $\mu_S = \sqrt{n(n+2)}BM$.

According to crystal field theory of complex compounds, since the number of unpaired electrons in the central metal ion with d^4 to d^7 configuration in high spin and low spin octahedral complexes is different

their magnetic moments are also different

(3) Distortion of octahedral complexes and Jahn Teller Effect

The six-coordinated complexes in which all the six distances between the ligand electron clouds and central metal ion are the same are said to be regular (i.e., **symmetrical) octahedral complexes.** On the other hand the six - coordinated complexes in which the distances are not equal are said to be **distorted octahedral complexes,** since their shape is changed (i.e distorted). The change in shape is called **distortion.**

Distorted octahedral complexes may be of the following three types.

(i) Diagonally distorted octahedral complexes which are obtained when the distortion of a regular octahedron takes place along a two - fold axis

(ii) Trigonally distorted octahedral complexes in which the distortion takes place along a three-fold axis.

(iii) Tetragonally distorted octahedral complexes which are also known as **tetragonal complexes.** These are obtained when the distortion of a regular octahedron takes place along a four-fold axis.

eg.(i) Most of the square planar complexes of Cu^{2+} ion are distorted octahedral (i.e. tetra-gonal), e.g. the tetrammine Cu(+2) complex, $[Cu(NH_3)_4]^{2+}$ in aquous solution is actually $[Cu(NH_3)_4(H_2O)_2]^{2+}$ in which two water molecules are a larger distance from the central Cu^{2+} ion than the four coplanar NH_3 molecules and consequently the complex has a tetragonal shape rather than square planar.

(ii) Low-spin octahedral complexes of Ni^{2+}, Pd^{2+} and Pt^{2+} (all d^8 ion) undergo strong distortion and assume square planar geometry in which the two ligands along the z-axis are at larger distance and four ligands in the xy-plane are at shorter distance from M^{2+} ion. $M^{III}(diars)_2I_2$ is an example of such complex.

(iii) In $CuCl_2$ crystal each Cu^{2+} ion is surrounded by six Cl^- ions ; four are at a distance of 2.30 Å and the other two are 2.95 Å away.

(iv) In CuF_2 crystal four F^- ions are 1.93 away from Cu^{2+} ion while the two F^- ions are 2.27 Å apart.

Any non-linear molecular system possessing degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy and thus will remove degeneracy.

Symmetrical and Unsymmetrical t_{2g} - and e_g- orbital

$$t_{2g}\text{orbitals}\begin{cases} t_{2g}^{0}, t_{2g}^{3}, t_{2g}^{6} \rightarrow \text{symmetrical} \\ t_{2g}^{1}, t_{2g}^{2}, t_{2g}^{4}, t_{2g}^{5} \rightarrow \text{unsymmetrical} \end{cases}$$

$$e_g\text{orbitals}\begin{cases} eg^{0}, eg^{4} \rightarrow \text{symmetrical} \\ eg^{1}, eg^{3} \rightarrow \text{unsymmetrical} \\ eg^{2} \begin{cases} \rightarrow \text{symmetrical in HS} - \text{complexes}[(d_{x^2-y^2})^1(d_{z^2})^1] \\ \rightarrow \text{unsymmetrical in LS} - \text{complexes}[(d_{x^2-y^2})^0(d_{z^2})^2] \end{cases} \end{cases}$$

No Distortion Condition

The d-orbitals which have both t_{2g} and e_g^- sets as symmetrical orbitals lead to perfectly symmetrical Conditions for various types of distortions can be summarized as:

t_{2g} (sym) + e_g (sym) $\longrightarrow$ No distortion

t_{2g} (unsym) $\longrightarrow$ Slight distortion

$$\left.\begin{matrix} e_g(\text{unsym}) \\ e_g^{2}[(d_{x^2-y^2})^0(d_{z^2})^2 \text{ in LS} - \text{complexes} \end{matrix}\right\} \longrightarrow \text{Strong distortion}$$

III Phase Equilibria

The phase rule was derived from thermodynamics considerations and is an important tool concerning heterogeneous equilibria. Phase rule gives the relationship between the conditions which must be specified to describe the state of a system at equilibrium. This rule is important for both chemical and physical heterogeneous equilibria.

PHASE RULE

The rule is stated in terms of the number of phases (P), the number of components (C) and the degrees of freedom (F) of a heterogeneous system.

Phase rule states that in a heterogeneous system at equilibrium the number of degrees of freedom plus the number of phases are equal to the number of components plus 2.

Mathematically it is expressed as

$$F = C - P + 2 \qquad \text{...(i)}$$

Explanation of the terms used in Phase Rule

Phase- The homogeneous, physically distinct and mechanical separable parts of the heterogeneous system in equilibrium are called phases.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2\ (g)$$

There are three phases in equilibrium state two solids and one is gas (CO_2), water system can be expressed as

$$H_2O(s) \rightleftharpoons H_2O(l) \rightleftharpoons H_2O(g)$$

Ice water vapours

In this system there are three phases viz solid, liquid and vapours.

Component-

In a heterogeneous system, in equilibrium the minimum number of variables which are necessary to explain the chemical composition of a phase, by a chemical equation, is called component. The meaning of component can be understood by taking following examples:

(a) Ice - Water - Vapours system

$$H_2O\ (s) \rightleftharpoons H_2O\ (l) \rightleftharpoons H_2O(g)$$

This system has three phases i.e. solid (ice), liquid (water) and gas (vapour). Chemical composition of each phase can be expressed by H_2O in the form of chemical equation:

Phase		Component
$H_2O(S)$	=	H_2O
$H_2O(l)$	=	H_2O
$H_2O(g)$	=	H_2O

Thus water system is a one component system.

(b)When solid NH_4Cl heated in a closed vessel, following equilibrium establishes:

$$NH_4C\ell(s) \rightleftharpoons NH_4C\ell(g) \rightleftharpoons NH_3(g) + HC\ell(g)$$

This system has two phases i.e. solid $NH_4C\ell$ and mixture of gases NH_3 and . Here, although system has three components, but chemical composition of both phases can be expressed by a single component i.e. $NH_4C\ell$. Since NH_3 and $HC\ell$ are in equimolar ratio

Phase		Component
$NH_4Cl(s)$	=	$NH_2C\ell$
$NH_3(g) + HCl(g)$	=	$NH_2C\ell$

Thus, this system is also a one component system. If some additional amount of either $NH_3(g)$ or $HCl(g)$ is added in this system at equilibrium then each phase can not be expressed by NH_4Cl, then one more component with be required and number of components with be two in the system.

(c) When solid $CaCO_3$ is heated in a closed vessel, following heterogeneous equilibrium establishes:

$$CaCO_3(s) \rightleftharpoons CaO(s) = CO_2(g)$$

This system consists of three phases i.e. solid $CaCO_3$, solid CaO and gaseous CO_2. Although system has three components but they are not independent of each other. Any of these two can be independently variable. Thus out of three, two components may be selected to express the composition of any phase. Thus number of components in this system are two

(i) When $CaCO_3$ and CaO are taken as components

Phase		Component
$CaCO_3(s)$	=	$CaCO_3 + 0CaO$
$CaO(s)$	=	$CaCO_3 + CaO$
$CO_2(s)$	=	$CaCO_3 - CaO$

(ii) When CaO and CO_2 are taken as components

Phase		Component
$CaCO_3(s)$	=	$CaO + CO_2$
$CaO(s)$	=	$CaO + 0CO_2$
CO_2 (g)	=	$0CaO + CO_2$

(iii) When $CaCO_3$ and CO_2 are taken as components

Phase		Component
$CaCO_3(s)$	=	$CaCO_3 + 0CO_2$
$CaO(s)$	=	$CaCO_3 - CO_2$

$CO_2(s)$ = $0CaCO_3 + CO_2$

Therefore, minimum number of components which are required to express any phase is two and the system is bi-component system

(d) Sodium Sulphate - water system may have different 'phases as Na_2SO_4, $7H_2O$, Na_2SO_4, $10H_2O$, Na_2SO_4 solution, Ice, vapours etc. Any phase can be expressed by chemical formulae Na_2SO_4 and H_2O.

Therefore, it is also a two component system.

(e) In $CuSO_4.5H_2O$ (s) ⇌ $CuSO_4.3H_2O(s) + 2H_2O(g)$ system also the number of components are two.

Number of components may also be calculated by the following formula

(1) For components which do not ionize

The number of components can be calculated by the following formula.

$C = C' - m$

where C = number of components

C' = total number of undissociated components

m = number of chemical equations which correlate undissociated species with each other.

(2) For ionised species

The number of components can be calculated by the following formula.

$C = C'' - (n + 1)$

C = number of components

C" = total number of species (including ions)

n = total number of equilibria (equilibrium states)

Ex.1 Find out the number of components in the following systems:

(i) $CaCO_3(s)$ ⇌ $CaO(s) + CO_2(g)$

(ii) $NH_4C\ell(s)$ ⇌ $NH_3(g)$ + {where the partial pressures of NH_3 and are equal)

(iii) $KC\ell$ – $NaC\ell$ – $H_2O(l)$ system

(iv) KCl - NaBr - $H_2O(l)$ system

(v) Aqueous solution of

Sol.1 (i) $CaCO_3$ (s) ⇌ $CaO(s) + CO_2(g)$

C' = 3 ($CaCO_3$, CaO, (CO_2)

m = 1 [$CaCO_3(s)$ ⇌ $CaO(s) + CO_2$ (g)]

C = 3 – 1 = 2

(ii) NH_4C $NH_4C\ell(s)$ ⇌ $NH_3(g)$ + $HC\ell(g)$

C' = 3 [$NH_4Cl(s)$, $NH_3(g)$, HCl(g)]

m = 2 [$NH_4Cl(s)$ ⇌ $NH_3(g)$ + HCl(g)] and [$P_{NH3} = P_{HCl}$]

C = 3 – 2 = 1

(iii) KCl – $NaCl$ - $H_2O(l)$ system

C' = 3 [KCl, $NaCl$, $H_2O(l)$]

m = 0

C = 3 – 0 = 3

(iv) KCl, NaBr, $H_2O(l)$ system

C = 5[KCl, NaBr, KBr, NaCl, H_2O (l)]

m = 1[KCl + NaBr ⇌ KBr + NaCl]

C = 5 – 1 = 4

(v) Aqueous solution of $NaCl$

C' = 2 [NaC*l*, H_2O]

m = O

C = 2 – 0 = 2

This can be illustrated by following examples.

Ex.2 Find out the number of components in the following systems.

(i) KCl – NaCl – H_2O (*l*) system

(ii) KCl – NaBr – H_2O (*l*) system

(iii) Aqueous solution of NaC*l*

(iv) Aqueous solution of acetic acid

(v) Aqueous solution of sulphuric acid.

Sol.2 (i) KC*l* – NaC*l* – H_2O (*l*) system

C = C" – (n + 1)

C" = 6 [KC*l*, NaC*l*, K^+, Na^+, Cl^-, H_2O]

$$\begin{bmatrix} \text{NaCl(s)} \rightleftharpoons \text{Na}^+\text{(aq)} + \text{Cl}^-\text{(aq)} \\ \text{KCl(s)} \rightleftharpoons \text{K}^+\text{(aq)} + \text{Cl}^-\text{(aq)} \end{bmatrix}$$

C = 6 – (2 + 1) = 3