Chhatrapati Shahu Ji Maharaj University, Kanpur

Answer Script Details
Barcode 1246442

Roll No.	24063001034	**Exam**	MASTER OF SCIENCE _ODD EXAM-DEC-24
Total Mark	51/75.00	**Subject**	B020701T - INORGANIC CHEMISTRY - I

Question wise Mark Summary

Q.No	Mark	Q.No	Mark	Q.No	Mark	Q.No	Mark
1A	4/5	8	NA/15				
1B	4/5	9A	NA/7				
1C	4/5	9B	NA/7				
1D	3/5	9C	NA/7				
1E	3/5						
1F	3/5						
1G	3/5						
1H	4/5						
1I	3/5						
2	10/15						
3	NA/15						
4	NA/15						
5A	NA/7						
5B	NA/7						
5C	NA/7						
6	10/15						
7	NA/15						

PART-I

Date of Exam: 27/01/25 Shift: 1st Room No. 2406300103

Paper Code: B020701T Subject: Inorganic chemistry Year/Sem.: ✓ 1st

Name of Candidate: Priya Kumari Gupta

Roll No.: 2 4 0 6 3 0 0 1 0 3 4

Signature of Candidate: Priya Kumari Gupta

Signature of Invigilator

COE Facsimile

Chhatrapati Shahu Ji Maharaj University
Kanpur, Uttar Pradesh

PART-II

MARKS OBTAINED

Q.	1	2	3	4	5	6	7	8	9	10
(a)										
(b)										
(c)										
(d)										
(d)										
(f)										
(g)										
(h)										
(i)										
(j)										
Total										

Total Marks in Figures

Max. Marks

Total Marks in Words

B020701T
Paper Code

Signature of Evaluator

PART-III

Course: M.Sc. 1st Semester (Chemistry)

Session: 2024-25 Year/Semester: ✓ 1st

Subject: Inorganic Chemistry

Paper Code

B	0	2	0	7	0	1	T

Exam Date

2	7	-	0	1	-	2	5

Name of Candidate

PRIYA KUMARI
GUPTA

महाविद्यालय का कोड
College Code

U	N	0	1	
Ⓐ	Ⓐ	●	⓪	⓪
Ⓔ	Ⓑ	①	●	①
Ⓕ	Ⓓ	②	②	②
Ⓗ	Ⓙ	③	③	③
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Ⓢ	●	⑦	⑦	⑦
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परीक्षा केन्द्र का कोड
Exam Centre Code

U	N	0	1	
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Ⓔ	Ⓑ	①	●	①
Ⓕ	Ⓓ	②	②	②
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Ⓢ	●	⑦	⑦	⑦
●	Ⓣ	⑧	⑧	⑧
	Ⓤ	⑨	⑨	⑨
	Ⓦ			

परीक्षा का प्रकार
Type of Exam

संस्थागत Regular ● भूतपूर्व छात्र Ex. Student ○
व्यक्तिगत Private ○ बैक पेपर परीक्षा Back paper Exam ○

ANSWER BOOKLET NO.

1246442

B020701T
Paper Code

PART-IV

नामांकन संख्या
Enrollment Number

C	S	J	M	A	2	4	0	0	0	0	6	3	1	7	1

परीक्षार्थी अनुक्रमांक संख्या Candidate's Roll Number

2	4	0	6	3	0	0	1	0	3	4
⓪	⓪	●	⓪	⓪	●	●	⓪	●	⓪	⓪
①	①	①	①	①	①	①	●	①	①	①
●	②	②	②	②	②	②	②	②	②	②
③	③	③	③	●	③	③	③	③	●	③
④	●	④	④	④	④	④	④	④	④	●
⑤	⑤	⑤	⑤	⑤	⑤	⑤	⑤	⑤	⑤	⑤
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⑦	⑦	⑦	⑦	⑦	⑦	⑦	⑦	⑦	⑦	⑦
⑧	⑧	⑧	⑧	⑧	⑧	⑧	⑧	⑧	⑧	⑧
⑨	⑨	⑨	⑨	⑨	⑨	⑨	⑨	⑨	⑨	⑨

पेपर कोड Paper Code

B	0	2	0	7	0	1	T
Ⓐ	●	⓪	●	⓪	●	⓪	Ⓝ
●	①	①	①	①	①	●	Ⓟ
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Ⓔ	③	③	③	③	③	③	●
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Ⓖ	⑤	⑤	⑤	⑤	⑤	⑤	
Ⓩ	⑥	⑥	⑥	⑥	⑥	⑥	
Ⓜ	⑦	⑦	⑦	●	⑦	⑦	
Ⓝ	⑧	⑧	⑧	⑧	⑧	⑧	
	⑨	⑨	⑨	⑨	⑨	⑨	

Priya Kumari Gupta
Signature of Candidate

Signature of Invigilator

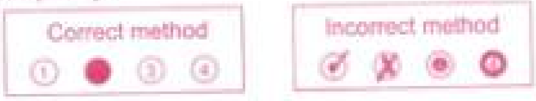
C S Facsimile

INSTRUCTIONS TO THE CANDIDATE FOR FILLING PART-I

1. Read the instructions carefully given on the answer script and admit card.
2. Write Date of Exam, Shift, Paper Code & Name of Subject Correctly.
3. Write Name & Roll No. Correctly.
4. Write Semester & Branch Correctly.

INSTRUCTIONS TO THE CANDIDATE FOR FILLING PART-III

1. Use blue or black ball point pen for writing alphabets & numerals in ☐ Boxes.
2. Carefully study the example before you start marking.
3. As shown in the example below blacken the circles completely.



4. Make no Stray marks on this sheet.
5. **DO NOT WRITE OR MARK ON THE BAR CODE.**

IN ORDER TO AVOID UFM (UNFAIR MEANS) :

1. The Roll No. and Answer Book no. found elsewhere or any other symbol found in the answer book will be treated as unfair means.
2. Any tempering of Bar Code and Booklet no shall be treated as Unfair Means.
3. Do Not bring the materials like slip of paper/mobile/digital diaries/ study material/ revision notes in examination hall. Possession of the mobiles/ digital diaries/ electronic watch and any other electronic gadget except memory less scientific calculator shall be considered as UFM case.
4. Do not keep or paste currency note in answer script it shall be consider as UFM.

अनुचित साधन से बचने हेतु:

1. उत्तर पुस्तिका के निर्देशित स्थान को छोड़कर अनुक्रमांक एवं उत्तरपुस्तिका का क्रमांक कहीं और न लिखें तथा कोई भी चिन्ह न बनायें क्योंकि यह अनुचित साधन प्रयोग की परिधि में आता है।
2. उत्तर पुस्तिका के बारकोड अथवा उत्तर पुस्तिका संख्या पर छेड़ करने पर अनुचित साधन प्रयोग माना जायेगा।
3. परीक्षा कक्ष में निम्न वस्तुएं साथ न लायें, जैसे लिखे हुए कागज के टुकड़े, मोबाईल, डिजिटल डायरी, कॉपी, पुस्तक यह सभी वस्तुएं जो अनुचित साधन के अन्तर्गत आती है। केवल संबंधित प्रश्नपत्र में ही मेमोरी लैस साइंटफिक कैल्कुलेटर ले जाने की अनुमन्यता होगी।
4. उत्तर पुस्तिकाओं में रुपये न रखे न ही उत्तर पुस्तिका में चिपकायें। ऐसा करना अनुचित साधन प्रयोग की परिधि में आता है।

परीक्षार्थी के लिए निर्देश

1. प्रवेश पत्र एवं उत्तर पुस्तिका पर दिये गये निर्देशों को ध्यान से पढ़े।
2. कवर पृष्ठ के दूसरी तरफ कुछ न लिखें।
3. उत्तर पुस्तिका के पृष्ठों पर दोनों तरफ लिखें।
4. प्रश्न पत्र पर अपने अनुक्रमांक के अतिरिक्त कुछ न लिखें।
5. प्रश्न पत्र कोड एवं प्रश्न पत्र कोड सावधानी पूर्वक लिखें।
6. अपनी स्थिति स्पष्ट लिखें।
7. उत्तर पुस्तिका के पृष्ठों की संख्या देखें। अगर उत्तर पुस्तिका में पृष (1–24) से कम है या फटे हुए है, तो परीक्षा शुरू होने के पूर्व दूसरी उत्त पुस्तिका ले ले।
8. प्रश्नपत्र को देख, यदि प्रश्नपत्र के विषय कोड, विषय का नाम तथा प्रश्न में कोई त्रुटि है तो उसके परीक्षा शुरू होने के 30 मिनट के अन्दर कक्ष निरीक्षक को तत्काल सूचित करें, उसके बाद विश्वविद्यालय द्वारा कोई कार्यवाही नहीं की जायेगी।
9. प्रश्नों के उत्तर लिखने के लिये पैंसिल का प्रयोग न करें।
10. B कॉपी या अतिरिक्त ग्राफ नहीं दिया जायेगा।

INSTRUCTIONS TO THE CANDIDATE

1. Read the instructions carefully given on the Question Paper, Admit Card & Answer Script.
2. Do not write anything on back side of the cover page.
3. Write on both sides of pages of answer book.
4. Do not write anything on question paper except Roll Number.
5. Write Paper Code & Question Paper Id carefully.
6. CHECK the number of pages (1-32) or any other kind of damage in your answer script. If found than change the answer script immediately before the commencement of examination.
7. CHECK the Question Paper for any kind of discrepancy e.g. Subject Code, Subject Name and Question of the Question Paper during first THIRTY MINUTES of the commencement of the exam, so that it can be corrected in TIME. After that no corrections shall be entertained by the university.
8. Do not use pencil for answering the question.
9. Write status correctly e.g. those appearing in carry over papers should fill in status as Carry Over. Those appearing as Ex-Students should fill in status as ex.
10. No supplementary answer book & graph paper will be provided.

INSTRUCTIONS TO THE CANDIDATE FOR FILLING PART-IV

1. Use blue or black ball point pen for writing alphabets & numberals in ☐ Boxes.
2. Use blue or black ball point pen for filling the circles.

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①	●	①	●	①	①	①	①	●	①	①
②	②	②	②	②	②	②	●	②	②	②
③	③	③	③	③	③	●	③	③	③	③
④	④	④	④	④	●	④	④	④	④	④
⑤	⑤	⑤	⑤	●	⑤	⑤	⑤	⑤	⑤	⑤
⑥	⑥	⑥	⑥	⑥	⑥	⑥	⑥	⑥	●	⑥
⑦	⑦	⑦	⑦	⑦	⑦	⑦	⑦	⑦	⑦	⑦
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Note - If your Roll No. is of 10 digits. Please leave first three columns.

Section-C

6. Bent's Rule is based on the theory of hybridisation. It is the VSEPR theory, which states about the shape and hybridisation of molecule.

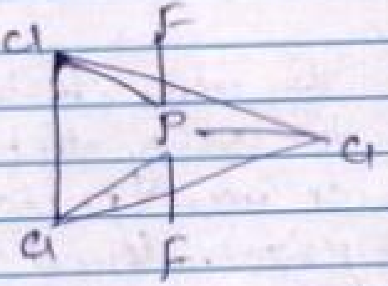
Bent's Rule state that "The more electronegative element or atom or molecule tends to occupy that hybrid orbital which has lesser s-character or more p-character. On the other hand the more electropositive element tends to occupy that hybrid orbital which has more s-character or lesser p-character."

Some of the characteristics of Bent's rule are :-

- The lone-pairs tends to occupy that hybrid orbital which has more s-character or lesser p-character.
- The multiple-bond i.e. double or triple tends to occupy that hybrid orbital which has less p-character or more s-character.
- The electronegative atom tends to occupy that hybrid orbital which has greater p-character.
- The electropositive atom tends to occupy that hybrid orbital which has greater s-character.

In case of sp^3d hybridisation, the shape of the molecule is trigonal ~~bypi~~ bipyramidal. The lp tends to occupy the equitoral position whereas the electropositive element tends to occupy the equitorial position.

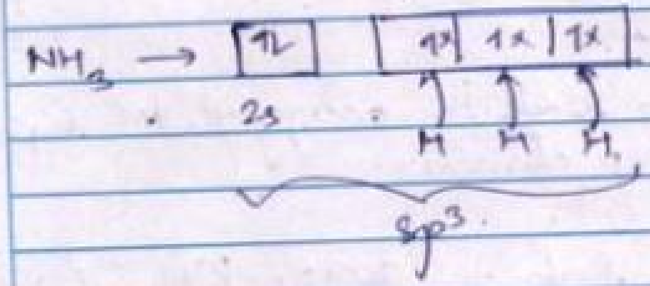
e.g. PCl_3F_2.



Thus, the bond angle in F—P—Cl is 90° and the bond angle in Cl—P—Cl is 60°.

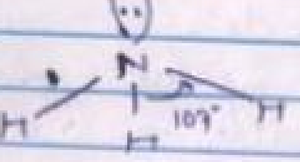
NH$_3$ (ammonia).

N = $1s^2 2s^2 2p^3$.



Thus, the hybridisation of ~~sp~~ NH$_3$ is sp^3.

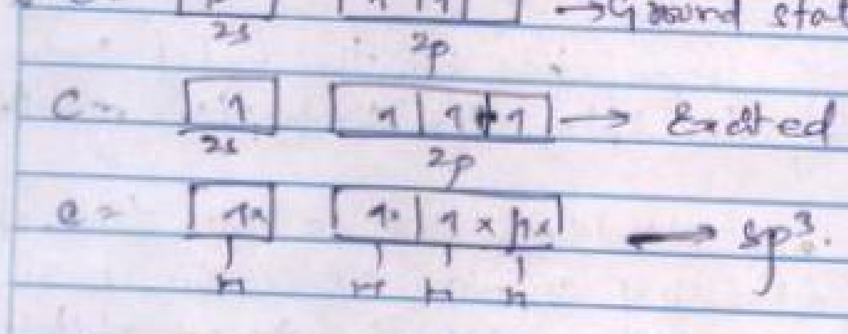
The shape of NH_3 is bent, due to presence of lp-lap repulsion. The standard bond angle for tetrahedral atom is 109.5°. But in NH_3 the bond angle in NH_3 is H-N-H is less than 109.5°.



The lp tends to occupy the maximum space due to its electronic repulsion.

CH_4 (methane).

$C = 1s^2 2s^2 2p^2$.



The hybridisation of CH_4 is tetrahedral. (sp^3). The bond angle in CH_4 is 109.5°. There is no ~~et~~ interelectronic repulsion. So, the shape of the molecule is tetrahedral, The H—C—H bond angle is 109.5°.

Section- B.

2. VBT Theory says about the stability of metal complexes:
In valence bond theory, covalent bonding is explained on the basis of the concentration of electron density between 2 nuclei.
This is the consequence of the sharing of space or overlap of the valence atomic orbital of one atom with the valence atomic orbital of another atom.

VBT Theory predicts many properties better than Lewis Theory.

Some of the features of VBT & CFT provides frame work for understanding the reaction mechanisms and intermediate states, electronic effects involved.

VBT focuses on the bonding between the metal centre and the ligands by describing the overlapping of orbitals

- Bond formation and stability – Acc to VBT the geometry of an octahedral complex arises due to the overlap of metal d-orbitals with the ligand orbitals. Substitution reactions involving breaking of old bonds and formation of new ones.

- Inner vs outer orbital Complexes:

Inner orbital use d^2sp^3 hybridisation (low spin)

These are more stable due to stronger overlap and thus less reactive.

Outer orbital complexes - uses sp^3d^2 hybridisation with outer d orbitals

Kinetics and Thermodynamics:- Stability of the complex affects the ease of substitution. Inner orbital complexes often kinetically inert, whereas outer orbital complexes are more labile.

Crystal Field Theory :-

CFT focuses on the splitting of metal d-orbitals in the ligand's electronic field. Its role in substitution reactions involves :-

- Crystal field splitting Energy (Δ_o) — The larger the CFSE energy, the more stable the complex. Higher Δ_o values are associated with low-spin complexes (strong ligands)
- Ligand Field Stabilisation Energy (LFSE) - LFSE is the energy stabilisation gained due to d-orbital splitting. Complexes with significant LFSE are less likely to undergo substitution reaction.

Key points :-

Inert Complexes :-

- Octahedral complexes with strong-field ligands (e.g. CN^-, CO) are generally substitutionally inert due to high LFSE.

Labile complexes:-

- Complexes with weak-field ligands (e.g. H_2O Cl^-) or $d^0/d^5/d^{10}$ electronic configurations are labile.

E.g. $[Co(H_2O)_6]^{2+}$ labile.

VBT is primarily used to predict the type of hybridisation, bond strength, and inert/labile behaviour based on orbital overlap.

CFT is more quantitative and is used to analyse splitting energy ~~splitt~~ LFSE and how ligand effects influence substitution reactivity.

Sec-A.

5(a) The main postulate of VSEPR theory are as follows:-

- The shape of a molecule depends upon the number of valence shell electron pairs around the central atom.
- Pairs of electrons in the valence shell repel one another since their orbitals are negatively charged.
- These pairs of electrons tend to occupy such positions in space that ~~man~~ minimises repulsion and maximises the distance between them.
- The valence shell is taken as a sphere with the electrons localising on the spherical surface at maximum distance from one another.
- A multiple bond is treated as a ~~sphere~~ single electron pair and two or three electron pairs of a multiple bond are treated as a single super pair.
- The repulsive interaction of electron pairs decreases in order: lp-lp > lp-bp > bp-bp.

The lp occupies more space so, the inter-electronic repulsion is high compared to bp-bp repulsion.
These repulsion effects result in deviation from idealised shapes and alteration in bond angles in molecules.

e.g. NH_3 has bond angle 107.5°. and CH_4 has a bond angle of 109.5°.

b) Redox reaction plays a significant role in chemistry of transition metal complexes, both in nature and in synthetic chemistry.

• Variable Oxidation state – Transition metals can exist in multiple oxidation states enabling redox reactions where the metal ion either loses or gain e^-. e.g. The Fe^{2+}/Fe^{3+} redox couple in hemoglobin facilitates oxygen transport in living beings.

• Catalysis – Some of the catalytic reactions are: Homogeneous Catalysis – Many of catalysts rely on the ability of the metal centre to cycle through oxidation states.
e.g. Wilkinson's catalyst involves oxidative addition and reductive elimination steps in $[RhCl(PPh_3)_3]$.

• Electron Transfer in Biological System – Transition metal complexes are crucial in biochemical redox reactions: Photosynthesis – The Mn cluster in Photosystem II catalyzes water splitting, involving multiple bond.

• Industrial Applications – Redox transition metal complexes are used in various industries:- Batteries – Transition metals like Mn and Co batteries are undergoes redox reactions.

Redox reactions in transition metal complexes are significant due to their versatility, enabling vital biological processes, catalytic applications and in cuttable technologies.

c) Inner Complexes – Complexes that undergo ligand substitution reaction slowly, requiring a high activation energy. They are kinetically stable.

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

• Liable Complexes – Complexes that undergo ligand substitution reactions quickly, with a low activation energy.

e.g. $[Ni(H_2O)_6]^{2+}$

• CFSE – Inner Complexes have high CFSE, which stabilises the complex and make ligand substitution energetically. On the other hand, liable complexes have no CFSE, so the energy barrier for substitution is low.

• Oxidation State of metal – In Inner Complexes higher oxidation states lead to stronger metal-ligand bonds making the complex less reactive. On the other hand, labile complexes have a lower oxidation states results in weaker metal-ligand bonds.

• Nature of ligand – Inner complexes have strong field ligands forming strong bonds on the other hand weak field ligands form weaker bonds allowing faster substitution

d) Principles of pH metry in metal ligand Equilibria –

When a ~~ligand~~ metal ion reacts with a ligand they form a complexes such as ML, ML_2, etc. These reactions often involve changes in pH due to the release of H^+.

$$M^{n+} + HL \longrightarrow ML + H^+$$

Calculation of pH-metry ~~of~~ in metal-ligands:-

- Protonation Constants of the ligand - The protonation equilibria of the ligand are determined as:-

$$HL \rightleftharpoons H^+ + L^-$$

$$K_a = \frac{[H^+][L^-]}{[HL]}$$

- Formation Constants of Complexes:- is represented as

$$M^{n+} + L^- \longrightarrow ML^{(n-1)+}$$

$$K_f = \frac{[ML]}{[M^{n+}][L^-]}$$

Stability Constant - overall stability constants (β_n) for complexes are calculated:-

$$M^{n+} + nL^- \longrightarrow ML_n^{(n-1)+}$$

$$\beta_n = \frac{[ML_n]}{[M^{n+}][L^-]^n}$$

e) The primary purpose of Walsh diagram are:-

- Predicting Molecular Orbital Geometry:- By analyzing the energy of (HOMO) and LUMO at different geometries one can determine the most stable geometry of a molecule.

The geometry where the bonding orbitals are lowest in energy and antibonding orbitals are higher in energy is most stable configuration.

- It explains why certain molecule deviated from ideal bond angles based on their electronic structure. e.g. H_2O has a bond angle of [illegible]5°. due to interaction of lp & bp.

- The diagram provides insight into electronic transitions between molecular orbitals, which is useful in spectroscopy and photochemistry.

Eg. of Walsh Diagram:-
It is applicable for Triatomic molecules e.g. H_2O, diatomic molecule BeH_2 as well as to electron-rich systems.

Walsh diagram bridges the gap between MOT ~~abd~~ and molecular geometry by showing the direct relationship between electronic structure.

They provide theoretical basis for VSEPR theory.

b) Acid hydrolysis of metal complexes involves the replacement of a ligand in a metal complex by water or another ligand, facilitated by the presence of H^+ ions. The mechanism of acid hydrolysis depend on the nature of the complex, the coordination environment, and the experimental condition.

- Dissociative Mechanism:-

A ligand dissociates from the complex to generate a lower-coordination intermediate, which is then attacked by water.

- Rate-determining step - The dissociation of the ligand from the complex.

Steps:-

1. $[ML_n]^{2+} \xrightarrow{slow} [ML_{n-1}]^{(2-1)} + L$

2. $[ML_{n-1}]^{(2-1)} + H_2O \xrightarrow{fast} [ML_{n-1}(H_2O)]^{2+}$

Conditions favouring this mechanism

- High charge density on the metal center.
- Weakly bound ligands, such as halides or neutral ligands.

e.g.

$[CoCl(NH_3)_5]^{2+} \longrightarrow + H_2O \quad [Co(H_2O)(NH_3)_5]^{3+} + Cl^-$

g) Marcus-Hush theory is a fondamental theory in electron transfer process, which are crucial in fields like chemistry, biological.

- Electron Transfer as a Chemical reaction - The theory treats electron transfer as a quantum mechanical process occuring within the framework of classical reaction dynamics.

The transfer of an electron from a donor to an acceptor is written as

$$D + A \longrightarrow D^+ + A^-$$

2. Reorganisation Energy (λ) – The reorganisation energy represents the energy required to reorganise the molecular and solvent environment for the electron transfer to occur.
λ consists of –

- Inner reorganisation energy – (λ_{in}) – Changes in bond length and bond angles.

3. Free Energy of Reaction ($\Delta G°$) – The driving force of electron transfer is $\Delta G°$. $\Delta G°$ determines the favourable reaction.

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It is applicable in photosynthesis, biological system, electrochemistry, etc.

b) The oxidation state of the metal ion plays a vital role in determining the stability of metal complexes. This arises due to effect of the oxidation state on the metal ion's size, charge, and ability to interact with ligands.

- Charge density and Coulombic Attraction – A higher oxidation state leads to a higher positive charge on the metal ion. This increases the charge density, enhancing the electrostatic attraction between the metal ion and the negatively charged ligands.

- LFSE – The oxidation state affects the splitting of d-orbitals in the presence of ligands. Higher oxidation states generally leads to strong field ligands, increasing LFSE.

- Ionic Radius and Steric Effects – Higher oxidation state reduces the ionic radius of the metal ion due to increased effective nuclear charge, and vice versa.

- Hard and Soft Acid-Base (HSAB) Principle – metal ions in higher oxidation states are hard acids, preferring to bind with hard ligands. e.g. O^{2-}, F^-.

- Solvent and Outer Space – Higher oxidation states often involve stronger interactions with the solvent further stabilizing the [illegible].

ii) π-bonding plays a crucial role in many areas. It determines the structure, stability, reactivity and properties of molecules and complexes.

- ~~Stur~~ Structural role – ~~Kt~~ π-bond in addition to a σ bond form double and triple bonds. (e.g. C=C, C≡C).

- Rigid Geometry – π-bonding restricts free rotation around the bond axis, resulting in planar or linear structures.

- Bond Strength – π bonds contribute additional strength to multiple bonds, although they are weaker than σ-bond. The combination of σ and [illegible] bonds in double and triple bond significantly [illegible] bond energy.

- Reactivity – π bonds are electron rich and more exposed than σ bond, making them reactive in nature.

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