Inorganic:- Read Shiver & Atkins.

read pre-requisites:- (pdf)

(I)

Hard Acid - Soft Acid:-

- large positive charge. (hence; less e^-)
- Small size
- Polarization is difficult.
- d-electrons or orbitals are not present; for π-bonding.

Hard base:-

- most electronegative atom ($F^\ominus$) !

i feel. less -ve charge:

- small size.
- difficult to polarize.
- π-bonding is weaker or no π-bonds

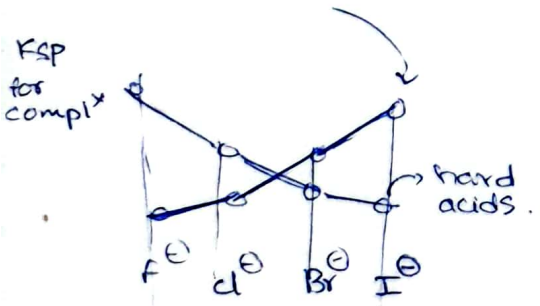
* AgF
  AgCl
  AgBr
  AgI → very less soluble

Soft acid-soft base-covalent
hard - hard - ionic.

Ag^+ Big size
less charge.
∴ soft acid

& $I^\ominus$ soft base.

* Soft metals.



read examples of hard-soft acids/bases.

Soft acids:-

Cu^+, Ag^+, Hg^{+2}, Hg_2^{+2}, Pt^{+2}, Pd^{+2}, Cd^{+2}, Tl^{+1}

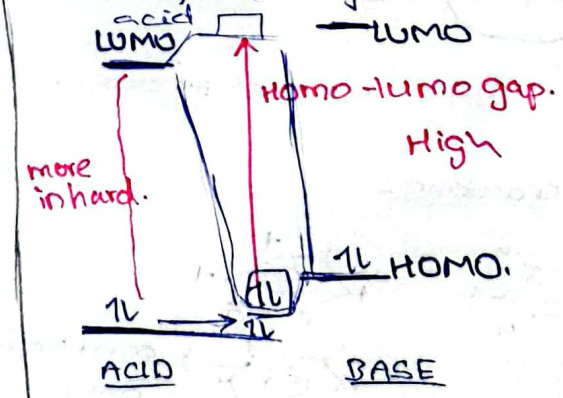
Cu^{+2} borderline.

$AlCl_3$, BH_3.

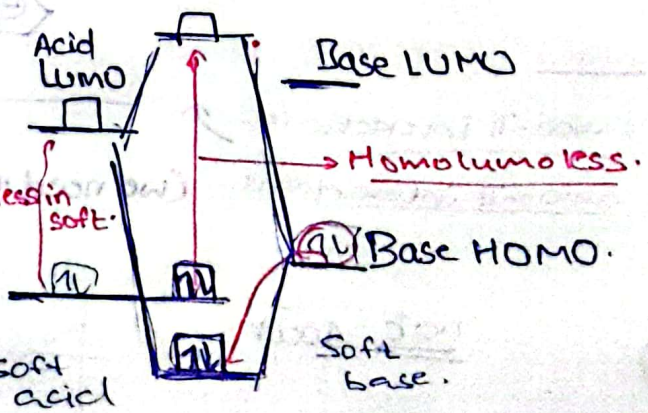
* CO, CN^-, SCN^- are soft bases.
As they give covalent bondings.

why hard likes hard? acid hard base

hard; have large Homo-lumo gap.



soft acid-base:



* Hard-hard is more energitic.
(slide-example).

→ Quantitative measure of hardness (η):- → can be measured; using photoelectron spectroscopy.

$\eta = \frac{IE_{Base} - EA_{Acid}}{2}$; by mulliken;

$\chi = \frac{IE + EA}{2}$

IE = ionization energy of +ve ion. → measures HOMO of base

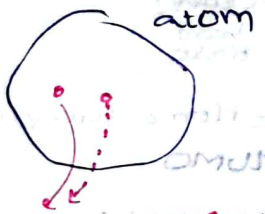
EA = elec Aff. of -ve ion ; ~~verify~~ → measures lumo of acid.
trde.

* CN^- → soft base.

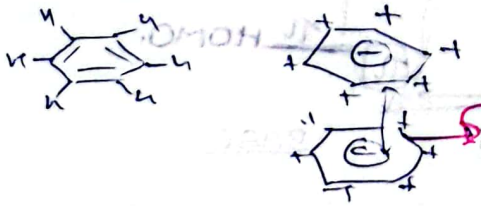
∴ less IE.

→ Intermolecular weak interactions:-

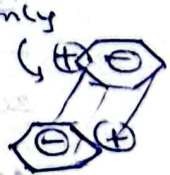
forming instantaneous dipole. * more dispersion forces; when more electrons.



* π-π-interactions:-



can't be headon..
only

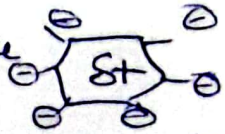


or Tshape

*e clouds on benzene; binds cations

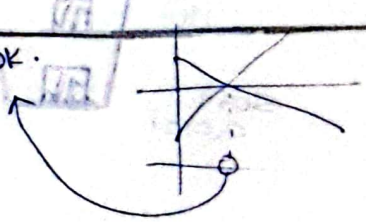
• cation-π interactions:- → Stronger than water. (data)

anion-π interactions:- (we need to make



(II)

710°C 1000K.



* ellingham diagram for metal sulphides:

Slater rules.

* Co_3O_4. $\Delta t = \frac{4}{9}\Delta_o$.

Pairing energy = $0.9\,\Delta_o$.

In tetrahedral; we always see highspins....

since; Δt is always low. & Pairing energy > Δt.

Jahn teller:-

* even organic compounds have Jahn-teller distortion.

(Both sunoj sir & inarg said).

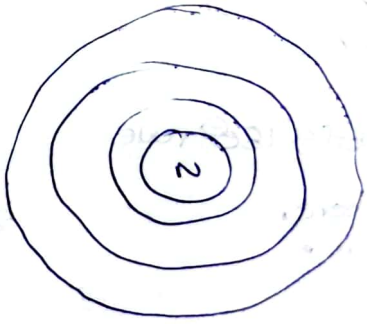
* Co^{+3} Oxide; Strong field.

Co^{+4} oxide; Strong field.

Ni^{+3}
Ni^{+4} oxides } Strong field

* ↑↓ | ↑ | ↑ ↑↓ | ↑

repulsions more here.



Co_3O_4: Co^{+2} Co^{+3}

Spinal — Co^{+2} tetrahedral, Co^{+3} octahedral

Inverse Spinal — Co^{+3} tetrahedral, Co^{+2} octahedral

Co^{+2}: $4s^0\,3d^7$.

Co^{+3}: $4s^0\,3d^6$

↑↑|↑ / ↑↓|↑ (0.3×2Δt)

↑ / ↑↓|↑↓|↑↓ ↓

0.4×6Δo

−2(0.9Δo).

pairing.

$-d_{x^2-y^2}$

$-d_{z^2}$

$-d_{xy}$

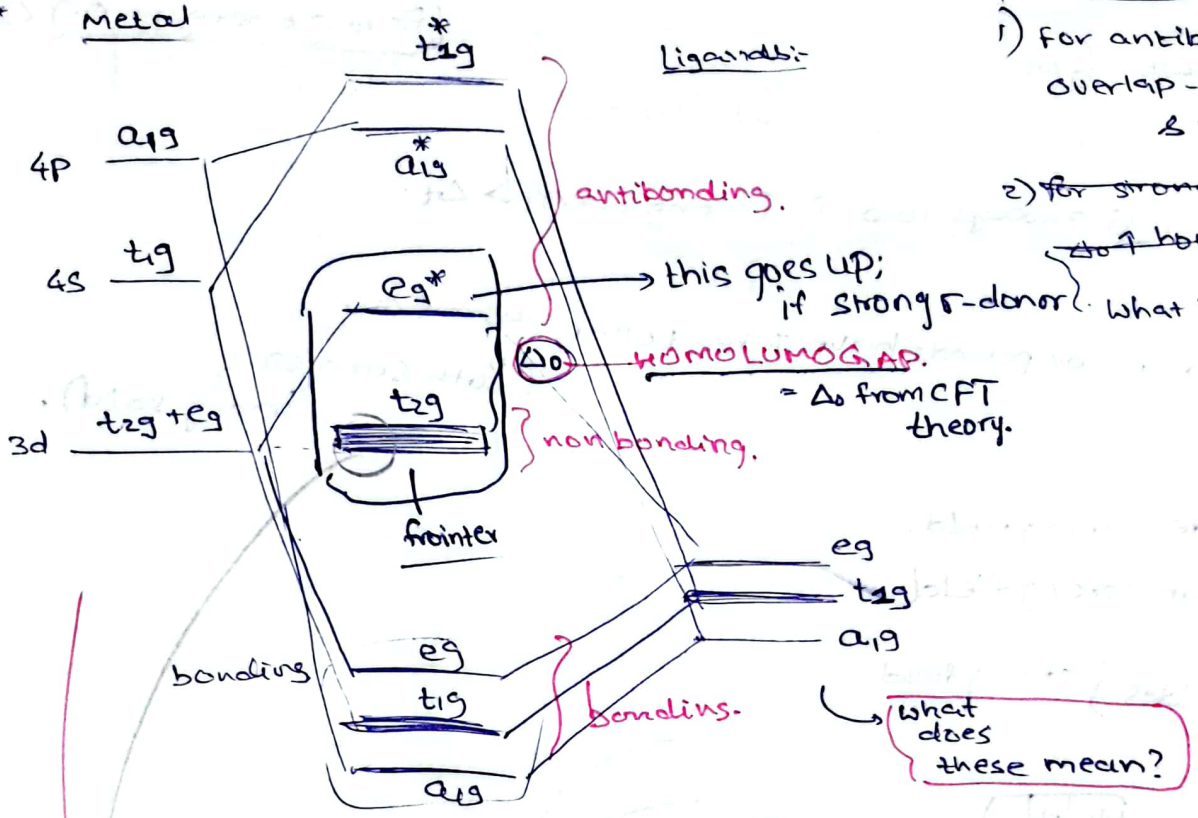
$\overline{d_{zx}}\ \overline{d_{yz}}$

Ligand field theory:- to take covalent character; we draw MO -

covalent bond is directional :- for σ-bond, take axial orbitals

∴ t_{2g} wont involve in bonding.

* Metal



doubt:-

i) For antibonding; overlap-integral $S = ?$

2) ~~for strong π-acceptors, Δ_o ↑ bcoz?~~ What is their energy level in MO diagram.

∴ we can justify 18 e⊖ rule.

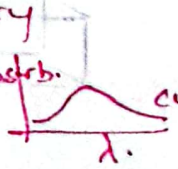
what does these mean?

now, π-donors interact here.
π-acceptors " "

Strong π-acceptor:- matching energy levels.

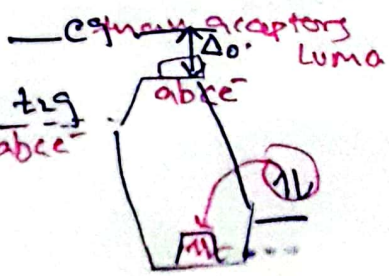
Here, dont initially consider crystal field splitting.

- that is one theory by Ionic rep.
- this is another theory by MO formation.
- But we can always try to justify Δ_o or absorb. curve.



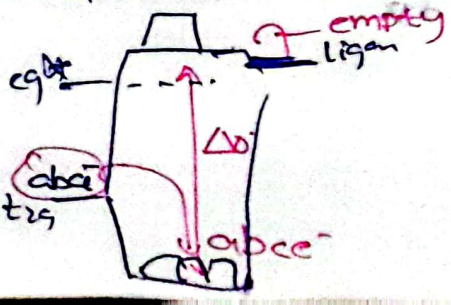
* π donors:-

HOMO always less in energy



* π acceptors:-

donors - lower energy
acceptors - higher energy



Topic-IV:-

Magnetism; transition & Lanthanoide ions & their complexes.

1 _ _

↳ this $\bar{e}$ can rotate around nucleus.

2. contribution due to orbital ang. momentum + intrinsic spin.

1 1 1 _

↳ Here orbital ang. momentum → zero contribut^{n}. only spin contribt^{n}.

Zeeman effect:-

Splitting leads to (2S+1)ms levels in presence of external magnetic field.

---

*

also

1 _ _ _ _

x^2-y^2 z^2

1 1 1 _ _

} here, no orbital contribution. to μ.

as x^2-y^2 to z^2 is NA by symmetry operations.

_ _ _ _ _

1 _

↳ No orbital movement contribution..

* spin multiplicity = 2S+1.

(2S+1) — orbital angm. — J — term symbols.

total spin ang. mom.. — Spin-orbital coupling.

Eg: Ni^{+2}

d^8

J: -2 -1 0 1 2

↑↓ ↑↓ ↑↓ ↑ ↑

$S_{max} = 1$

$L_{max} = 1+2 = 3$

these are possible places; to which $\bar{e}$ jump.

$J = |S-L|$ to $S+L$.

2 to 4

$J = 2, 3, 4$.

→ Rules for least energy:-

1) S_{max} → least energy.

2) L_{max} → least energy.

3) a) if $\bar{e}$ < half filled; J_{min} → least energy.

b) if $\bar{e}$ > half filled; J_{max} → least energy.

Concept.

Tut-IV!

Q2) $\mu_{S.O} = \sqrt{n(n+2)} = \sqrt{4S(S+1)}$

$\mu_{L+S} = \sqrt{4S(S+1) + l(l+1)}$ } good for transition.

$\mu_{eff} = g \cdot \sqrt{J(J+1)}$

$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$ } for Lanthanoids.

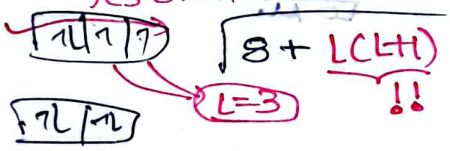
Q4) $CoCl_4^{-2}$ CoI_4^{2-}

more μ.

Here Δ_0 is more; Excited State is tough.

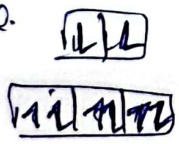
Q7) $(Ni(NH_3)_x(H_2O)_4)Cl_2$.

if tetrahedral Yes orbital cont.



$\sqrt{8 + L(L+1)}$!!

if Octahedral. Here, no orbital contⁿ.



No of micro states is; for $\begin{bmatrix} 2S+1 \\ - \\ L \end{bmatrix}$.

$(2S+1)(2L+1)$

$S = 1/2$

$L = 2$ → max. → farey aaur

$\therefore$ = 10 microstates.

m_S = S ka 2 component.

m_L = L ka 2 component.

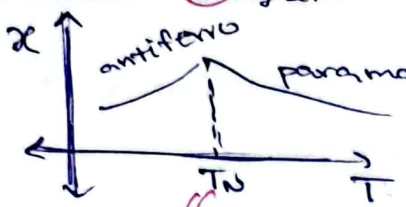
* m_S varies from $-S$ to S.
* m_L varies from $-L$ to L.

Topic-IV:

$(2S+1)L_J$ → spin angular momentum.

* paramagnetism: no interaction between spins.

Antiferro: J → net ang. momentum. negative.



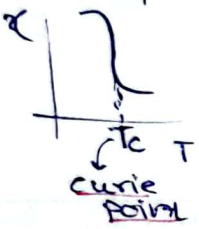
↳ temp. prevents interactions: Neel temp.

in a domain: ↑↓ ↑↓ ✓

→ ferro coupled.

Antiferro coupled.

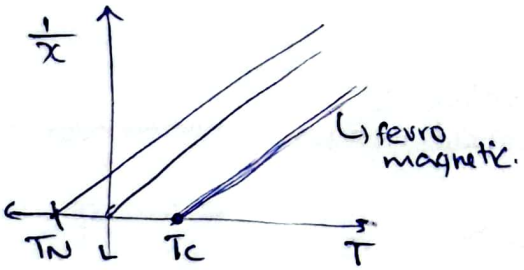
ferro: J positive



• Curie-Weiss law:-

$$\chi = \frac{C}{T-\theta}$$

$$\theta = \frac{2ZJS(S+1)}{3k}$$ +ve for ferro. -ve for antiferro.



In transition metals; J is absent in μ_{net}.

$$\mu_{S+L} = \sqrt{4 \cdot S(S+1) + L(L+1)}\ BM.$$

transition metals!

magnetic moment — Angular momentum.

→ Orbital contribution:- Ang. momentum. only t_{2g} mei possible. not possible among e_g.

i) degenerated t_{2g} orbitals can be interconverted by 90° rotations.

Hence; yes orbital contribution.

ii) a) degeneracy b) symmetry operations should be there to convert one into other.

Hence:

↑ _ _	↑ ↑ _	_ _ _	↑ _ _
		↑ ↑ ↑	↑ ↑ ↑ *
$S = 1/2$.	Yes contb^n	NO contb. as ↑↑ dont exist.	NO as x^2-y^2 ↓ z^2 no symmetry
$L = \_\_\_ \ldots$			
Yes contb			

* ↑↓ ↑

↑↓ ↑↓ ↑↓

Beware

NO orbital contribution!! as $x^2-y^2 \not\equiv z^2$.

* orbital contribution due to excited states:- Ang. momentum.

↑↓ ↑ → ↑↓ ↑↓

↑↓ ↑↓ ↑↓ → ↑ ↑↓ ↑↓

No contribution — Yes contribution!

$\mu_{expt} > \mu_S$ for Oct-Ni^{+2} — only spin. as no L in G.S.

Sometimes given. takecare.

→ Term symbols:- J = total angular momentum quantum number

gotta do some $\sqrt{J(J+1)}$ if magnetic moment is asked.

Determination of ground state:-

$J = L+S, L+S-1, \ldots |L-S|$ → except d^5: J = — (not applicable).

d8: -2 -1 0 1 2 — ↑↓ | ↑↓ | ↑↓ | ↑ | ↑

L = total Σ orbital ang. mom.

$S_{max} = 1$.

$L_{max} = 1+2 = 3$ → see, which contribute to orbital magnetic moment.

? but question.

either calculate electrons or calculate holes.... means?

L: 0 1 2 3 4 5 6

Symbol: S P D F G H I

Now: J: from |3-1| to 3+1

2 to 4.

more than half-filled:

so J = 4.

$^3F_4$ → 2S+1 value...

Angular momentum pointers

↑ term symbol of the most stable state i.e ground state.

Magnetic p. of lanthanoids:-

"spin-orbit coupling"

Δ_o transition : 30000 cm^{-1}

but Δ_o lanthanoides : 100 cm^{-1}. (not much) } ligands don't much effect f-electrons....

spin-orbit coupling:

→ In transition metals; L is less. so; didn't have 'J' in μ_{net}.

* But in lanthanoids; we need J in μ_{net}.

as spin orbit coupling constant is high.

Lande calculation:

$$\mu_{net} = g_J \cdot \sqrt{J(J+1)}\,\mu_B .$$

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

J value: minimum value |L-S|
→ upto half filled.

maximum value L+S
→ Above half filled.

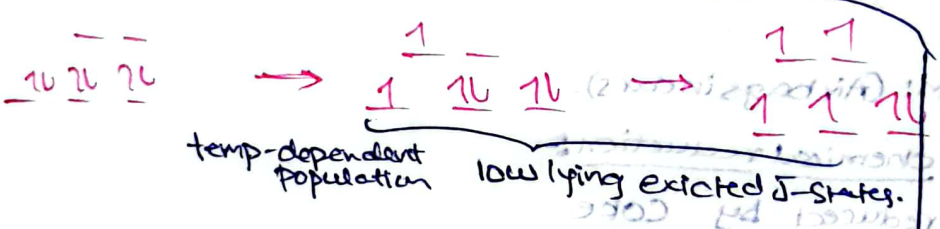
* for f^0, f^7, f^{14}
L=0.
∴ J=S & subsequently

μ_{net} Lanthanoids = μ_S

darn logical!

Spin-crossover:-

When Δ_o, Pairing energy are close.



temp-dependent population — low lying excited J-states.

* examples for Ln^{+3} : $[Xe]f^{(?)}$.

- works for all Ln^{+3} except Sm^{+3} Eu^{+3}

experimentally, higher value is observed.

Term symbols example:-

one low lying energy level of C: $1s^2 2s^2 2p^2\ {}^3P_2$

ground state of C: $1s^2 2s^2 2p^2\ {}^3P_0$.

Multiplicity: {wikipedia}

in chem; multiplicity of an energy level is (2S+1) where S = total spin angular momentum.

Hence J = L+S to L-S (2S+1)

* the multiplicity is often equal to the possible orientations of total spin; relative to total orbital ang. mom. (L).
(ang. mom.)

& therefore to the no. of near-degenerate levels; that differ only in their spin-orbit interaction energy.

→ However; when S ≤ L; only 2L+1 states are possible....

Zeemaneffect:-

Has to do with an atom in a magnetic field.

- $\vec{B} \Longrightarrow \vec{e}$

two μ.

- orbital motion → $\vec{\mu_L} = \frac{-e}{2m_e}\vec{L}$
- Spin. $\vec{\mu_S} = \frac{-e}{m_e}\vec{S}$

Topic-II:-

Abundance in earth: oxygen
Silicon
Aluminium

Marsh test:
Separation by decomposition

As, Sb + salts $\xrightarrow{Zn, H^+}$ AsH_3, SbH_3 $\xrightarrow{\Delta}$ silver mirror of metal.

* Azide decomposition: (Airbags in cars).

→ **High temperature chemical reduction:-**

oxide ores → reduced by Coke
Al
Si
H_2

Monds;

$NiO + H_2 \rightarrow Ni + H_2O$

↓ contd.

Krolls;

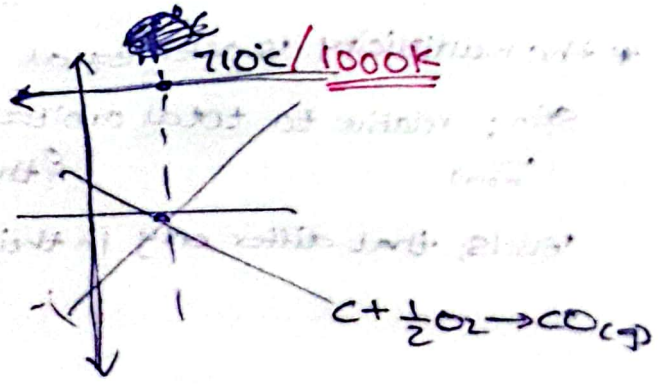
$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$

van-Arkel:

TiI_4
ZrI_4.

electrolytic redⁿ; expensive.

IA group halides.



Thermite process:- sacrifical method.

$\frac{4}{3}Al + \frac{2}{3}Cr_2O_3 \rightarrow \frac{4}{3}Cr + \frac{2}{3}Al_2O_3$. ΔG_0 = -ve at all temperatures.

However; Activation energy is high. (kinetic)

$Mg + BaO_2 \rightarrow MgO + BaO$

H_2: poor reductant. limited uses.

* soft metals; occur in sulphides. FeS, ZnS → borderline.
Cu_2S, HgS → soft metals.

Purification:-

1) Fusion, distillation of volatile metal | Crystallization.
- Fusion → removes adsorbed gases (SO_2, P_4O_{10})
- distillation of volatile metal
- Crystallization → fractional crystn of Pt as $(NH_4)_2MCl_6$.

2) Oxidative refining:-
impurities have more affinity to oxygen than metal.

* pig irons C, Si, P, Mn removed like this.

$CO, SiO_2, P_4O_{10}, MnO \xrightarrow[CaO]{} Slag$

3) thermal decomp.:
marsh test $AsH_3, SbH_3 \triangleq$ silver mirror.