AS-2143

M. Sc. (First Semester) Examination 2013

CHEMISTRY

CMT 102: Inorganic Chemistry-I

Time Allowed: Three hours

Maximum Marks: 60

Section- 'A'

(Short Answer Type Questions) 10x2= 20

1. (i) 'Addition of SbF$_5$ enhances the acidity of pure HF while the addition of NaF reduces its acidity'. Why?

SbF5 is fluoride ion acceptor while NaF is fluoride ion donor.

SbF5 reacts with HF as SbF5 + 2HF $\longrightarrow$ SbF6$^-$ + H2F$^+$ H0 value -21.1
NaF reacts with HF as NaF + HF $\longrightarrow$ Na$^+$ + HF2$^-$ H0 value -8.4
Acidity depends on H0 value

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(ii) ***Differentiate between CFT and LFT***.

(a) *Mode of formation of bonding in complexes*: CFT assumes purely ionic or electrostatic attractive force while LFT there is overlap of ligand and metal orbitals.
(b) *Orbital used in bond formation*: CFT- mtal ion d orbitals ignores the behaviour of other metal orbitals such as *s, p* orbitals and also no involvement of ; LFT- metal ion orbitals and also σ- and π-orbitals of the ligands.
(c) Cause of splitting of d-orbitals: CFT-splitting is caused by electrostatic fields exerted by the ligands on central metal ion; LFT-caused by metal-ligand overlap.
(d) *σ- and π-bonding in complexes*: In addition to σ-bonding in complexes, the LFT postulates π-bonding as well as in the complexes.
(e) *Charge-transfer bands*: can be explained by LFT not by CFT.

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(iii) Write down ***major drawbacks of VBT***:

(a) Octahedral, tetrahedral and square planar complexes of d^1, d^2, d^3 and d^9 have the same number of unpaired electron and hence can not be distinguished from each other merely on the basis of number of unpaired electrons.
(b) Spectral properties and quantitative connection between the spectra and magnetic moment could not be explained by this theory.
(c) This theory does not explain the behaviour of complexes having d^8 central ion in forming the expected 5-cordinated complexes.
(d) Too much imphasis has been laid on the metal ion whie the importance of ligand is not properly stressed.
(e) VBT can not explain reaction rates and mechanism of reactions.

(f) VBT can not explain why square planar complexes of Cu2+ ion (d^9) like $[Cu(NH_3)_4]^{2+}$ are not reducing agents like inner orbital complexes of Co^{2+} (d^7).

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(iv) *Which complex will be more coloured either $[Co(NH_3)_6]^{3+}$ or $[Co(NH_3)_5 Cl]^{2+}$. Justify your answer.*

$[Co(NH_3)_5 Cl]^{2+}$ will be more coloured because of non-centrosymmetry of the complex. The unsymmetrical vibrations of an octahedral complex can temporarily destroy its centre of symmetry and allow transitions that wuld otherwise be Laporte forbidden and thus vibronic (vibrational-electronic) transitions will be observable.

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(v) *Differentiate between Orgel and Tanabe-Sugano diagram.*

In Orgel diagrams, the magnitude of the splitting energy exerted by the ligands on d orbitals, as a free ion approach a ligand field, is compared to the electron-repulsion energy, which are both sufficient at providing the placement of electrons. However, if the ligand field splitting energy, 10Dq, is greater than the electron-repulsion energy, then Orgel diagrams fail in determining electron placement. In this case, Orgel diagrams are restricted to only high spin complexes.

Tanabe-Sugano diagrams do not have this restriction, and can be applied to situations when 10Dq is significantly greater than electron repulsion. Thus, Tanabe-Sugano diagrams are utilized in determining electron placements for high spin and low spin metal complexes. Tanabe-Sugano diagrams are useful in interpreting UV-vis spectra and determining the value of 10Dq.

The Orgel diagram and T-S diagram differe in several ways:

1. The ground state is always taken as the abscissa (horizontal axis) and provides a constant reference point. The other energy states are plotted relative to this.
2. Low-spin terms, i.e. states where the spin multiplicity is lower than the ground state, are included in TS diagram.
3. In order to make the diagrams general for different metal ions with the same electronic configuration, and to allow for different ligands, both of which affect *Dq* and *B* (or *B*`) , the axes are plotted in units of energy/*B* and *Dq/B.*

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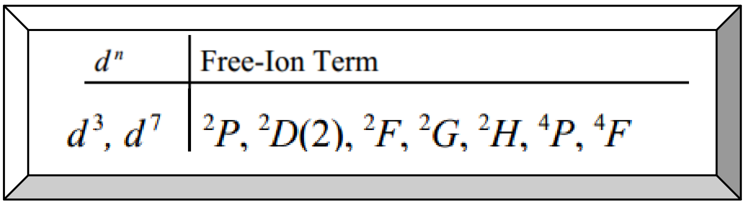
(vi) Write the different spectroscopic term for d^3 configuration.

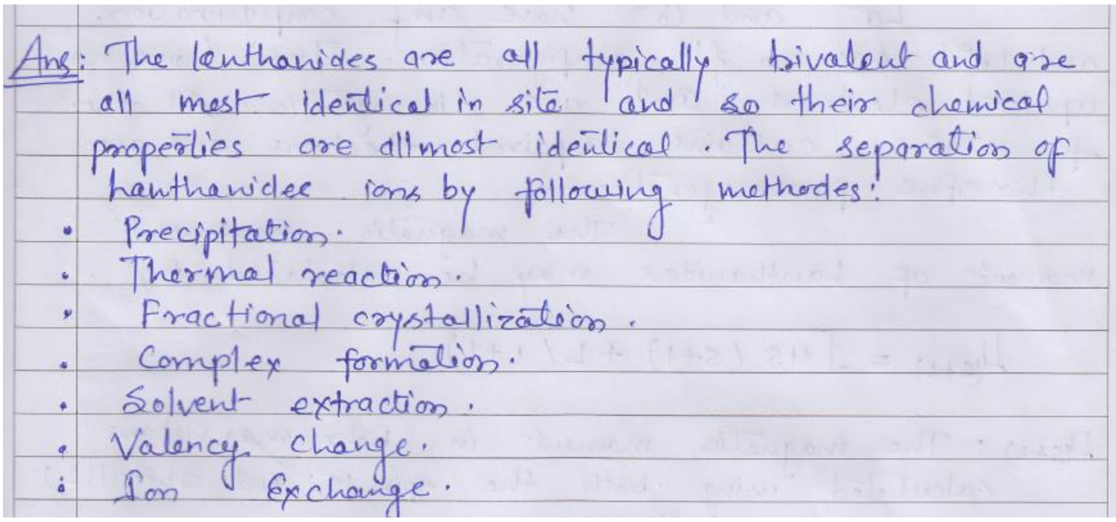
The spectroscopic term is F for which Mulliken symbol in Oh and Td ligand field is as follows:

Spectros. Term	Oh	Td
^4F	$^4A_{2g} + {}^4T_{1g} + {}^4T_{2g}$	$^4A_2 + {}^4T_1 + {}^4T_2$



d^n	Free-Ion Term
d^3, d^7	$^2P, {}^2D(2), {}^2F, {}^2G, {}^2H, {}^4P, {}^4F$

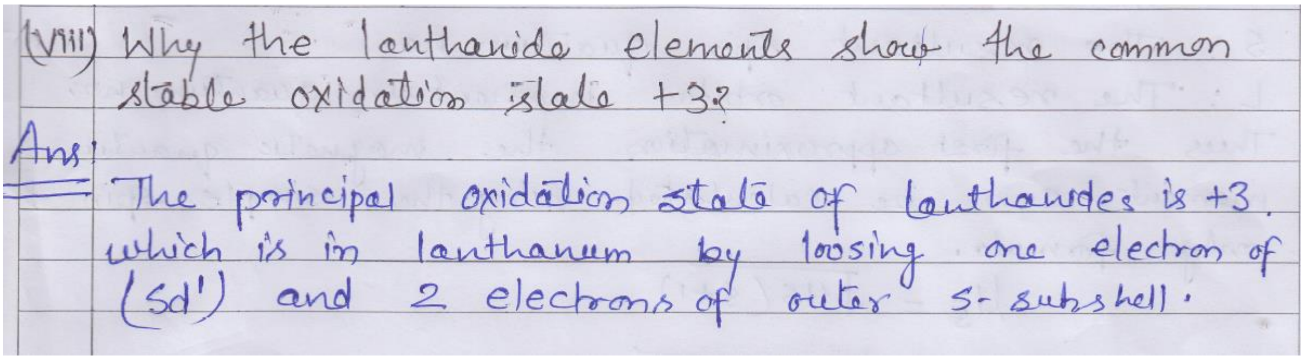
(vii) Write the methods by which lanthanide ions can be separated.



Ans: The lanthanides are all typically trivalent and are all most identical in size and so their chemical properties are allmost identical. The separation of lanthanidee ions by following methodes:

- Precipitation.
- Thermal reaction.
- Fractional crystallization.
- Complex formation.
- Solvent extraction.
- Valency change.
- Ion Exchange.

(viii) Why the lanthanide elements show the common stable oxidation state +3.



(viii) Why the lanthanide elements show the common stable oxidation state +3?

Ans:

The principal oxidation state of lanthanides is +3. which is in lanthanum by loosing one electron of ($5d^1$) and 2 electrons of outer s- subshell.

(ix) Write the applications of donor and acceptor number.

In chemistry a **donor number** or **DN** is a quantitative measure of Lewis basicity. A donor number is defined as the negative enthalpy value for the 1:1 adduct formation between a Lewis base and the standard Lewis acid $SbCl_5$ (antimony pentachloride), in dilute solution in the noncoordinating solvent 1,2-dichloroethane with a zero DN. The units are kilocalories per mole for historical reasons. The donor number is a measure of the ability of a solvent to solvate cations and Lewis acids. The method was developed by V. Gutmann in 1976. Likewise Lewis acids are characterized by acceptor numbers.

The donor numbers provide an interesting comparison of relative donor abilities of various solvents.

Acceptor number measures the electrophilic behaviour of a solvent.

(x) Define spectrochemical series with examples.

It is possible to list the ligands in order of increasing field strength (CFSE or LFSE Δ) in a series and this series is known as spectrochemical series. Although it is not possible to to form a complete series of all igands with a single metal ion, it is possible to construct one from overlapping sequences, each constituting a portion of the series:

Spectrochemical series

$I^- < Br^- < S_2^{2-} < SCN^- < Cl^- < N_3^-$, $F^- <$ urea, OH^- , ox, $O_2^- < H_2O < NCS^- <$ py< $NH_3 <$ en< bpy, phen$< NO_2^- < CH_3^-$, $C_6H_5^- < CN^- <$ CO

Section- 'B'

(Long Answer Type Questions) 5x8= 40

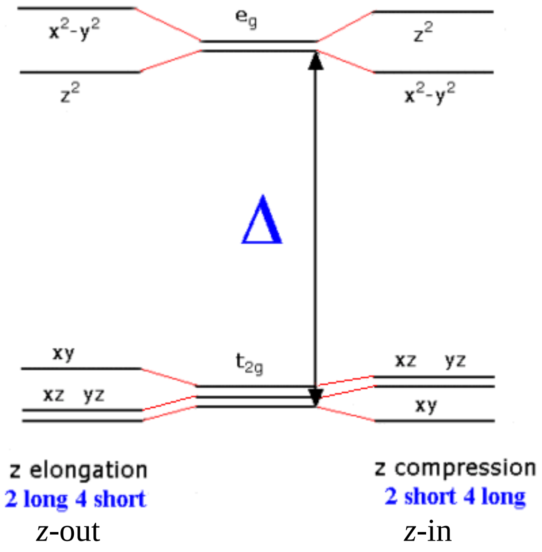
Note: Attempt any five questions. Each question carries 8 marks.

2. What is *John-Teller* distortion? Explain the *z*-out and *z*-in phenomena with examples.

The Jahn–Teller effect, sometimes also known as Jahn–Teller distortion, describes the geometrical distortion of molecules and ions that is associated with certain electron configurations. This electronic effect is named after Hermann Arthur Jahn and Edward Teller, who proved, using group theory, that orbital nonlinear spatially degenerate molecules cannot be stable.*

The Jahn–Teller theorem essentially states that "*"any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy"*".

*H. Jahn and E. Teller (1937). "Stability of Polyatomic Molecules in Degenerate Electronic States. I. Orbital Degeneracy". Proceedings of the Royal Society A 161 (905): 220–235



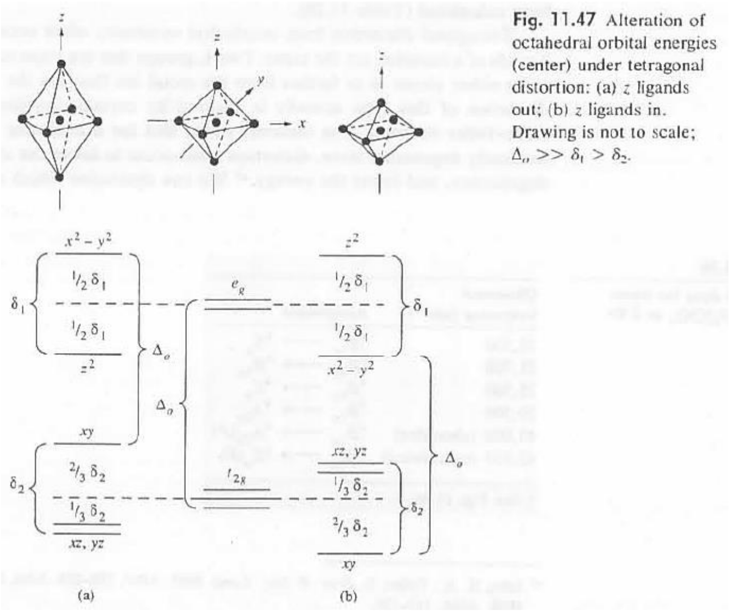


Fig. 11.47 Alteration of octahedral orbital energies (center) under tetragonal distortion: (a) z ligands out; (b) z ligands in. Drawing is not to scale; $\Delta_o >> \delta_1 > \delta_2$.

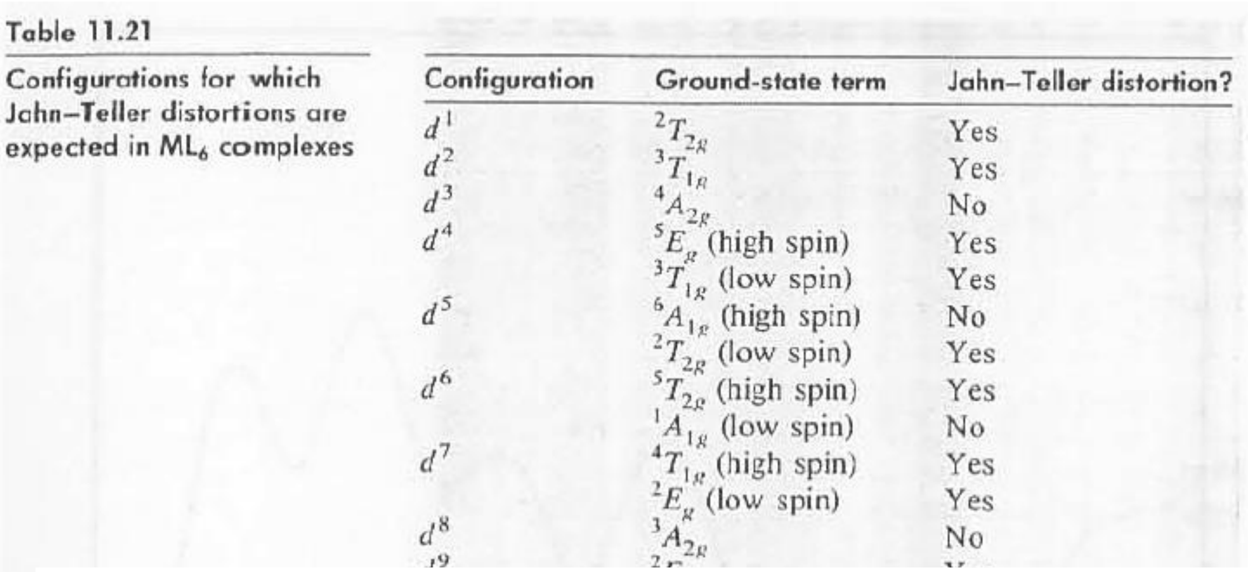


Table 11.21

Configurations for which Jahn–Teller distortions are expected in ML_6 complexes

Configuration	Ground-state term	Jahn–Teller distortion?
d^1	$^2T_{2g}$	Yes
d^2	$^3T_{1g}$	Yes
d^3	$^4A_{2g}$	No
d^4	^5E_g (high spin)	Yes
	$^3T_{1g}$ (low spin)	Yes
d^5	$^6A_{1g}$ (high spin)	No
	$^2T_{2g}$ (low spin)	Yes
d^6	$^5T_{2g}$ (high spin)	Yes
	$^1A_{1g}$ (low spin)	No
d^7	$^4T_{1g}$ (high spin)	Yes
	^2E_g (low spin)	Yes
d^8	$^3A_{2g}$	No

Some examples of Jahn-Teller distorted complexes

$CuBr_2$	4 Br at 240pm 2 Br at 318pm
$CuCl_2$	4 Cl at 230pm 2 Cl at 295pm
$CuCl_2.2H_2O$	2 O at 193pm 2 Cl at 228pm 2 Cl at 295pm
$CsCuCl_3$	4 Cl at 230pm 2 Cl at 265pm
CuF_2	4 F at 193pm 2 F at 227pm
$CuSO_4.4NH_3.H_2O$	4 N at 205pm 1 O at 259pm 1 O at 337pm
K_2CuF_4	4 F at 191pm 2 F at 237pm
$KCuAlF_6$	2 F at 188pm 4 F at 220pm
CrF_2	4 F at 200pm 2 F at 243pm
$KCrF_3$	4 F at 214pm 2 F at 200pm
MnF_3	2 F at 209pm 2 F at 191pm 2 F at 179pm

And other related examples:

Apparent exceptions to the theorem are probably examples of what has been called the *"dynamic Jahn-Teller effect"*. In these cases either the time frame of the measurement does not allow the distortion to be seen because of the molecule randomly undergoing movement or else the distortion is so small as to be negligible.

For one of the copper complexes above, the bond lengths are apparently identical. If the X-ray structure of the sample is redone at varying temperatures it is sometimes possible to "freeze" a molecule into a static position showing the distortions.

A well documented example includes complexes of the type $M_2PbCu(NO_2)_6$.
For M=Cs, below 285K the molecule shows tetragonal symmetry, for M=K this occurs at below 273K, for M=Rb at less than 276K and for M=Tl at temperatures less than 245K.
Above these temperatures the molecules appear octahedral due to the dynamic Jahn-Teller effect.

The Jahn-Teller Theorem predicts that distortions should occur for any degenerate state, including degeneracy of the t_{2g} level, however distortions in bond lengths are much more distinctive when the degenerate electrons are in the e_g level.

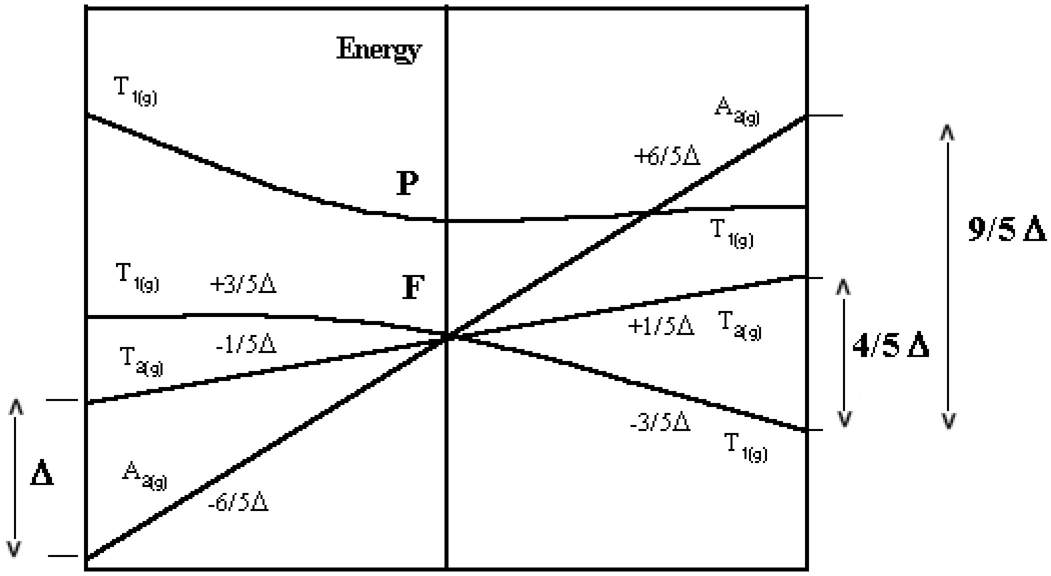
In the electronic spectrum of an aqueous solution of Ti(III), a d^1 octahedral system, the absorption band is not symmetric but rather shows a distinct broad shoulder. This has been interpreted in terms of a lowering of the degeneracy of the t_{2g} level and promotion to the excited state occurring to either of the two orbitals, the d_{z2} and d_{x2-y2}, which will no longer be degenerate. Thus, two transitions are possible but because the energy difference is small, a shoulder appears rather than 2 distinct peaks.

3. ***What is Orgel energy diagram? Draw the combined Orgel energy level diagram for d^3 configuration in octahedral and tetrahedral field.***

It is the energy level diagram where the splitting patterns of the spectroscopic states in weak ligand field or HS transition metal complex can be reflected by graphical presentation, developed by Leslie. E. Orgel since then they are known as *Orgel diagram*. In an Orgel diagram, energy is represented as the vertical dimension, and the vertical line in the center of the diagram represents the gaseous ion where there is no ligand field, $\Delta = 0$. That the splitting for d n is the same as d^{n+5} and the opposite of d^{10-n} is readily seen on an Orgel diagram, both for octahedral and tetrahedral fields. Orgel diagrams are correlation diagrams which show the relative energies of electronic terms in transition metal complexes.

The spectroscopic, optical, and magnetic properties of complexes of transition metals are made clear in such diagrams.

<u>Description of the following diagram</u>



The splitting of free-ion F and P terms in octahedral and tetrahedral fields

d^2,d^7 tet $\quad\longleftarrow\ \Delta\ \longrightarrow\quad$ d^2,d^7 oct

d^3,d^8 oct $\qquad\qquad\qquad$ d^3,d^8 tet

4. Describe the application of LFSE in explaining the heat of hydration of first row transition elements and also calculate their Δo .

Description of the following FIGURE:

Experimental evidence for crystal field stabilization. Consider the heats of hydration ΔH_{hyd} of the high spin first row M^{2+} ions. That is, ΔH for the process

$$M^{2+}(g) + 6\,H_2O \dashrightarrow M(H_2O)_6^{2+}(aq)$$

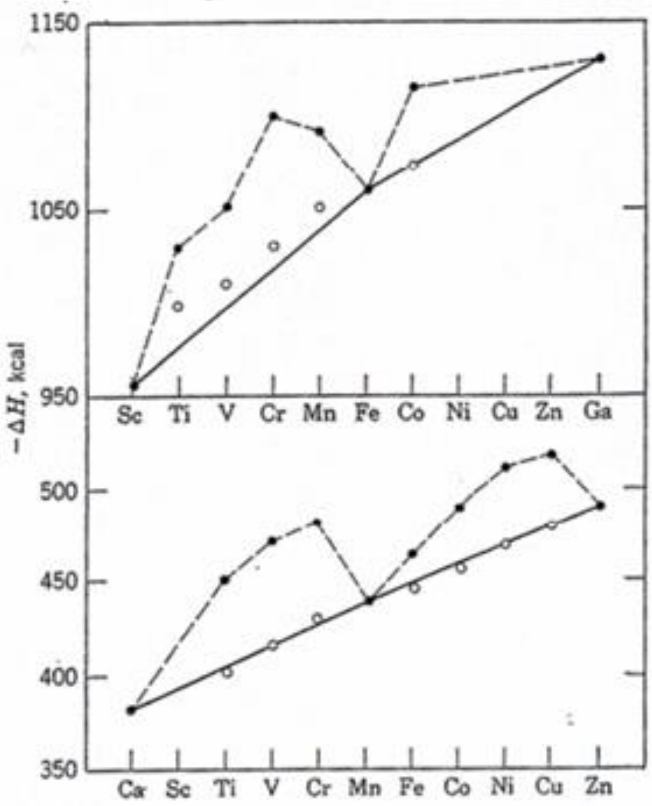


Fig: The uncorrected (dotted line) and crystal field corrected (solid line) hydration Energies of the divalent (lower) and trivalent (upper) ions of the first transition series.

After O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686

Calculation of Δo of first row of transition metals aquo complex $[M^{II}(H_2O)_6]^{2+}$

WEAK FIELD **LIKE H_2O**

		t_{2g}			e_g		CFSE (Dq)
Sc^{2+}	d^1	↑					- 4
Ti^{2+}	d^2	↑	↑				- 8
V^{2+}	d^3	↑	↑	↑			- 12
Cr^{2+}	d^4	↑	↑	↑	↑		- 6
Mn^{2+}	d^5	↑	↑	↑	↑	↑	0
Fe^{2+}	d^6	↑↓	↑	↑	↑	↑	- 4
Co^{2+}	d^7	↑↓	↑↓	↑	↑	↑	- 8
Ni^{2+}	d^8	↑↓	↑↓	↑↓	↑	↑	- 12
Cu^{2+}	d^9	↑↓	↑↓	↑↓	↑↓	↑	- 6
Zn^{2+}	d^{10}	↑↓	↑↓	↑↓	↑↓	↑↓	0

5. Draw the σ-bond MO diagram for a $[CoF_6]^{3-}$.

Description of of LGO symmetry, LCAO and equation etc. along with the following diagram.

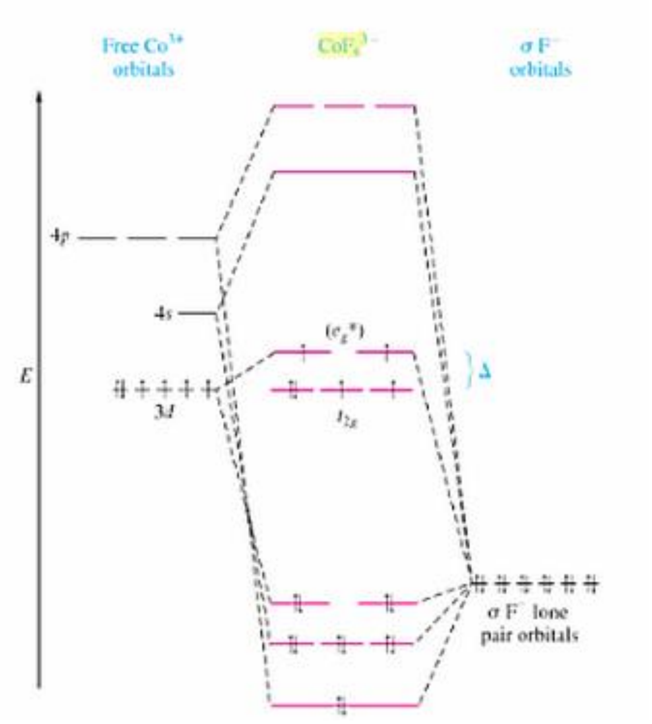


Fig: A σ-bond molecular orbital diagram for a $[CoF_6]^{3-}$

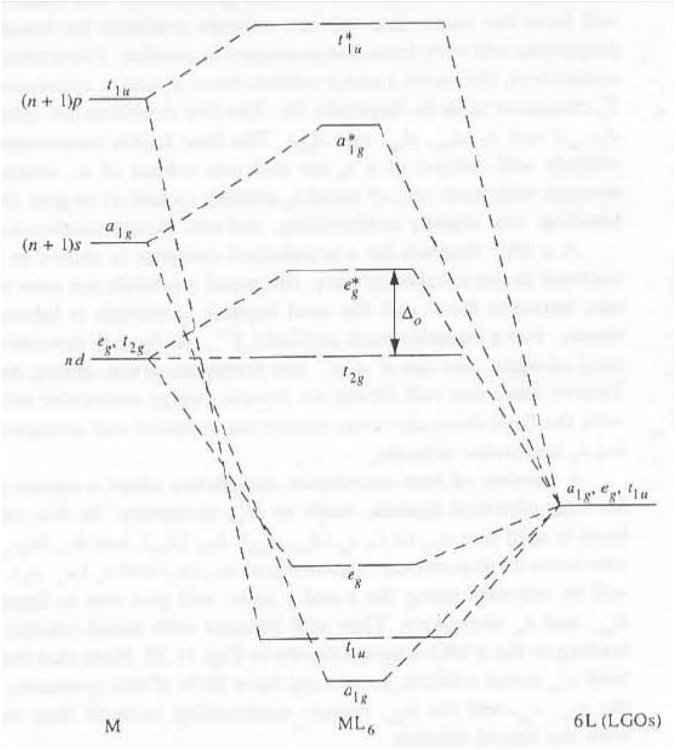


Fig: A σ-bond molecular orbital diagram for a complex of octahedral symmetry.

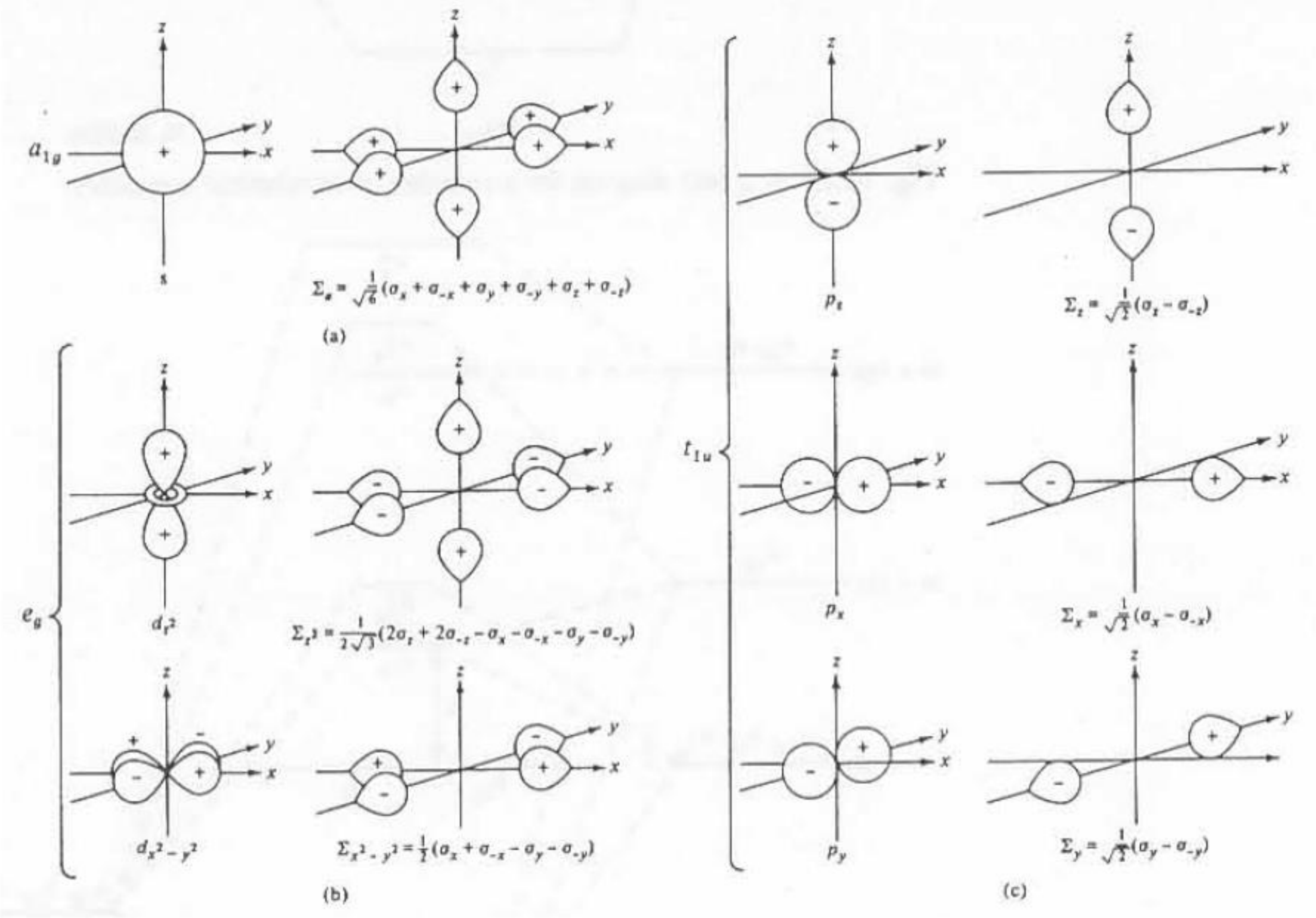
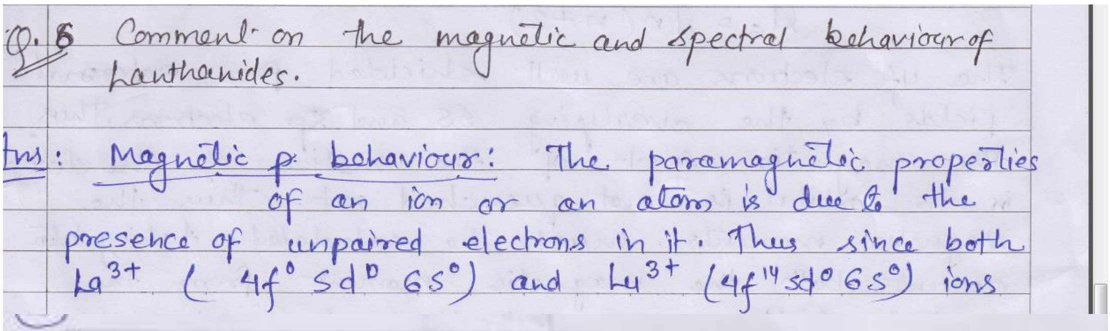


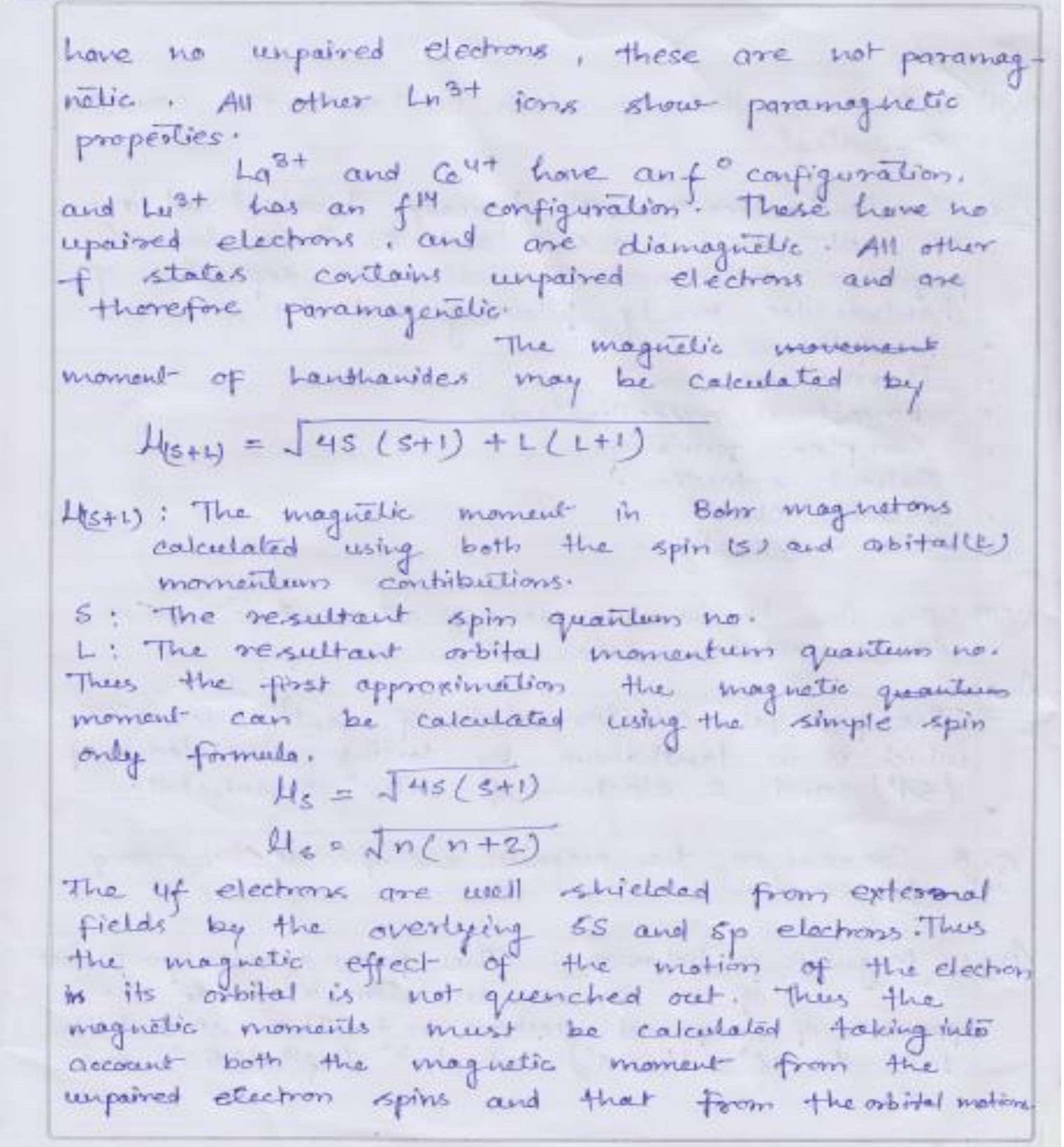
Fig: Ligand Group Orbitals (LGOs) and symmetry matched metal atomic orbitals appropriate for a sigma bonding in a octahedral ML$_6$ complex.

6. Comment on the magnetic and spectral behaviour of Lanthanides.



Q. 6 Comment on the magnetic and spectral behaviour of Lanthanides.

Ans: Magnetic p. behaviour: The paramagnetic properties of an ion or an atom is due to the presence of unpaired electrons in it. Thus since both La^{3+} ($4f^0 5d^0 6s^0$) and Lu^{3+} ($4f^{14} 5d^0 6s^0$) ions



have no unpaired electrons, these are not paramagnetic. All other Ln^{3+} ions show paramagnetic properties.

La^{3+} and Ce^{4+} have an f^0 configuration, and Lu^{3+} has an f^{14} configuration. These have no upaired electrons, and are diamagnetic. All other f states contains unpaired electrons and are therefore paramagenetic.

The magnetic ~~movement~~ moment of Lanthanides may be calculated by

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

$\mu_{(S+L)}$: The magnetic moment in Bohr magnetons calculated using both the spin (S) and orbital(L) momentum contibutions.

S : The resultant spin quantum no.

L : The resultant orbital momentum quantum no.

Thus the first approximation the magnetic ~~quantum~~ moment can be calculated using the simple spin only formula.

$$\mu_S = \sqrt{4S(S+1)}$$

$$\mu_s = \sqrt{n(n+2)}$$

The 4f electrons are well shielded from external fields by the overlying 5S and 5p electrons. Thus the magnetic effect of the motion of the electron ~~in~~ its orbital is not quenched out. Thus the magnetic moments must be calculated taking into account both the magnetic moment from the unpaired electron spins and that from the orbital motion.

This also happens with the second and third row transition elements. However the magnetic properties of the lanthanides are fundamentally different from those of the transition elements. In the lanthanides the spin contribution S and orbital contribution L couple together to give a new quantum number J.

$J = L - S$ when the shell is less than half full
$J = L + S$ when the shell is more than half full

The magnetic moment μ is calculated in Bohr magnetons (BM) by:

$$\mu = g\sqrt{J(J+1)}$$

where $g = 1\frac{1}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$

Spectral behaviour: Colour arises because light of a particular wavelength is absorbed in the visible regions. The wavelength absorbed corresponds to the energy required to promote an electron to a higher energy level. In the lanthanides spin orbit coupling is more important than crystal field splitting. In thispetra of transition metals, crystal field splitting is of major importance. All but one of the lanthanide ions show absorptions in the visible or near UV regions of the spectrum. The exception is Lu^{3+} ~~has~~ which has a full f shall. These colours arise from f-f transition. Strictly these transition are Laporte transition forbidden. Thus the colours are pale becauses they depend on relaxation of the rules. The f orbitals are deep inside the atom. Thus they are largely shieled from enviromental factors such as the nature and number of ligands which from the complexes, and from vibrational of the ligands. Thus the position of the absorption band. does not change with different ligands. Vibration of the ligands changes the external fields.

Absorption spectra of lanthanide ions are useful both for the qualitative detection and the quantitative estimation of lanthanides. Lanthanides elements are sometimes used as biological tracers for drugs in humans and animals. this is because lanthanide elements can quite easily be followed in the body by spectroscopy, because their peaks are narrow and very characteristic.

Ce^{3+} and Yb^{3+} are colourless because they do not absorb in the visible region. However they show exceptionally strong absorption in the UV region. because of transition from 4f to 5d. Absorption is very strong for two ~~region~~ regions. Since $\Delta l = 1$ this is an allowed transition and so gives stronger electron absorption than forbidden f-f. transitions. furthermore promotion of e^- in these ions is easier than for other ions. The electronic configuration of Ce^{3+} is f^1 and Yb^{3+} is f^8. Loss of one electron gives the extra stability of an empty or half full shell. f-d peaks are broad in contrast to the narrow f-f peaks.

7. Describe HSAB principle with example. Discuss Lewis acid-base reactivity approximation.

The **HSAB concept** is an initialism for "hard and soft (Lewis) acids and bases". Also known as the **Pearson acid base concept**, HSAB is widely used in chemistry for explaining stability ofcompounds, reaction mechanisms and pathways. It assigns the terms 'hard' or 'soft', and 'acid' or 'base' to chemical species. 'Hard' applies to species which are small, have high charge states (the charge criterion applies mainly to acids, to a lesser extent to bases), and are weakly polarizable. 'Soft' applies to species which are big, have low charge states and are strongly polarizable. The concept is a way of applying the notion of orbital overlap to specific chemical cases.

The theory is used in contexts where a qualitative, rather than quantitative, description would help in understanding the predominant factors which drive chemical properties and reactions. This is especially so in transition metal chemistry, where numerous experiments have been done to determine the relative ordering of ligands and transition metal ions in terms of their hardness and softness.

HSAB theory is also useful in predicting the products of metathesis reactions. Quite recently it has been shown that even the sensitivity and performance of explosive materials can be explained on basis of HSAB theory.

Ralph Pearson introduced the HSAB principle in the early 1960 as an attempt to unify inorganic and organic reaction chemistry

The gist of this theory is that *soft* acids react faster and form stronger bonds with *soft* bases, whereas *hard* acids react faster and form stronger bonds with *hard* bases, all other factors being equal.[7] The classification in the original work was mostly based on equilibrium constants for reaction of two Lewis bases competing for a Lewis acid.

Hard acids and **hard bases** tend to have the following characteristics:

- small atomic/ionic radius
- high oxidation state
- low polarizability
- high electronegativity (bases)
- hard bases have highest-occupied molecular orbitals (HOMO) of low energy, and hard acids have lowest-unoccupied molecular orbitals (LUMO) of high energy.

Examples of hard acids are: H^+, light alkali ions (Li through K all have small ionic radius), Ti^{4+}, Cr^{3+}, Cr^{6+}, BF_3. Examples of hard bases are: OH^-, F^-, Cl^-, NH_3, CH_3COO^-, CO_3^{2-}. The affinity of hard acids and hard bases for each other is mainly ionic in nature.

Soft acids and **soft bases** tend to have the following characteristics:

- large atomic/ionic radius
- low or zero oxidation state bonding
- high polarizability
- low electronegativity

- soft bases have HOMO of higher energy than hard bases, and soft acids have LUMO of lower energy than hard acids. (However the soft-base HOMO energies are still lower than the soft-acid LUMO energies.)

Examples of soft acids are: CH_3Hg^+, Pt^{2+}, Pd^{2+}, Ag^+, Au^+, Hg^{2+}, Hg_2^{2+}, Cd^{2+}, BH_3. Examples of soft bases are: H^-, R_3P, SCN^-, I^-. The affinity of soft acids and bases for each other is mainlycovalent in nature.

8. Write short notes on
   (a) Donor and acceptor numbers

In chemistry a **donor number** or **DN** is a quantitative measure of Lewis basicity. A donor number is defined as the negative enthalpy value for the 1:1 adduct formation between a Lewis base and the standard Lewis acid $SbCl_5$ (antimony pentachloride), in dilute solution in the noncoordinating solvent 1,2-dichloroethane with a zero DN. The units are kilocalories per mole for historical reasons. The donor number is a measure of the ability of a solvent to solvate cations and Lewis acids. The method was developed by V. Gutmann in 1976. Likewise Lewis acids are characterized by acceptor numbers.

The donor numbers provide an interesting comparison of relative donor abilities of various solvents.

Acceptor number measures the electrophilic behaviour of a solvent.

(b) E and C equation

Systematics of Lewis Acid Base Interactions : ①

Drago and coworkers proposed many equations to related enthalpies of reactions with acid, base parameters.

$$-\Delta H = E_A E_B + C_A C_B \longrightarrow (i)$$

ΔH = enthalpy of formation of Lewis Acid Base adduct

E_A and C_A parameters are characteristics of acids.

E_B and C_B parameters are characteristics of bases.

E parameters — susceptibility of the species to undergo electrostatic interactions, C parameters — susceptibility to form covalent bonds.

Those acids which bond well electrostatically to form the most stable adduct with those bases which bond well electrostatically. (since the product $E_A \cdot E_B$ is high.

Conversely those acids that bond well covalently will tend to form most stable adducts with bases that bond well covalently.

Example: Reaction between pyridine and iodine.

$$-\Delta H_{cal} = E_A E_B + C_A C_B$$

For pyridine E = 1.78 C = 3.54

For iodine E = 0.50 C = 2.00

$$= 0.50 \times 1.78 + 2.00 \times 3.54$$

$$= 7.97 \text{ Kcal/mole} = 33.3 \text{ KJmol}^{-1}$$

(~~1Kcal =~~ 1 K cal/mole = 4.18 KJmol^{-1})

Applications of E-C equations

① Prediction of enthalpies of reactions that have not been studied.

Example $(CH_3)_3N + SO_2 \rightarrow (CH_3)_3NSO_2$

$$-\Delta H = 0.56 \times 1.21 + 1.52 \times 5.6$$

$$= 9.19 \text{ Kcal/mole}$$

$$= 38.5 \text{ KJ/mol}$$

From table

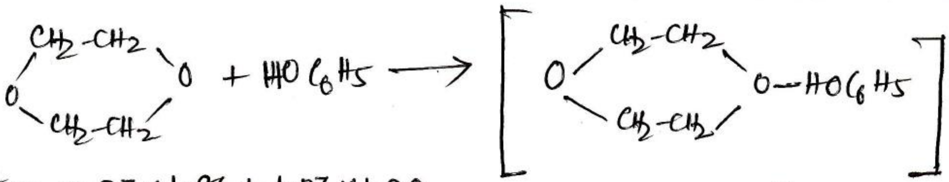
Kcal/mole

E → $(CH_3)_3N$ 1.21

C → $(CH_3)_3N$ 5.6 Kcal/mol

E → SO_2 0.56

C - SO_2 1.52



$$-\Delta H = 2.27 \times 1.86 + 1.07 \times 1.29$$

$$= 5.6 \text{ Kcal mol}^{-1} = 23.4 \text{ KJ mol}^{-1}.$$

	E	C	Kcal/mole
ether	1.86	1.29	
phenol	2.27	1.07	