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"I don't love studying. I hate studying. I like learning. Learning is beautiful."

"An investment in knowledge pays the best interest."

Hi, My Name is

Chemical Science for CSIR NET *Career Endeavour*

Coordination Chemistry

6 July

- Coordination compound → Metal cation + Ligands
- Metal cation/atom → Lewis acid
  → Electophile
- Ligand → Any species (molecule or ion) having at least one electron pair and that can be donated to a metal cation.

Example:

An atom can donate electron only when its octet is complete otherwise not. So, molecule/Ion can donate, act as ligand.

More e⁻ → large attraction → less energy → ↑ stable → ↑ donation

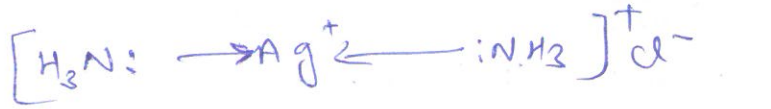
After completion or making of covalent bond, we don think about donation of e⁻.

Coordination compound:

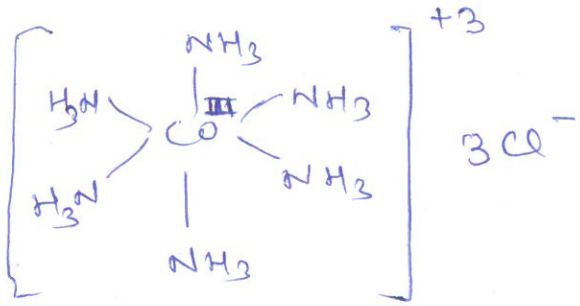
The compound in which a group of ligands is attached to a metal cation/atom through coordinate covalent bonds is called a coordination comp.

Ex:-

$[Ag(NH_3)_2]Cl$



$[Co(NH_3)_6]Cl_3$



Classification of complexes:-

1) Complexes having no complex ion.

Ex: i) $[Pt^{II}(NH_3)_2Cl_2]$ → Neutral, having no charge

↓

• It does not give any ion in aq. Sol.

ii) $[Co^{III}(NH_3)_3Cl_3]$

2) Complexes containing complex cation.

$[Co^{III}(NH_3)_6]^{+3}Cl_3$ — $[Co(NH_3)_6]^{+3}$ complex cation

$[Ag(NH_3)_2]^{+}Cl^{-}$ — $[Ag(NH_3)_2]^{+}$ complex cation

3) Complexes containing complex anion.

i) $Fe^{II} \cdot 6CN^{-} \rightarrow 4K^{+}[Fe(CN)_6]^{4-} \rightarrow K_4[Fe(CN)_6]^{4-}$

$[Fe(CN)_6]^{4-}$ complex anion

ii) $Co^{2+}\ 4Cl^{-} \rightarrow (NH_4)_2[CoCl_4]^{2-}$

4) complexes containing both complex cation and complex anion:-

Ex:- $[Pt^{+2}(NH_3)_4][Pt^{+2}Cl_4]$

$[Pt^{+2}(NH_3)_4]$ complex cation; $[Pt^{+2}Cl_4]$ complex anion.

$[Pt(NH_3)_4Cl_2][PtCl_4]$

★ To learn for both cation & anion complexes ★

Pt^{2+} → C.N 4 & Sq. Planar

Pt^{+4} → C.N 6 Octahedral

4) Complexes containing bridging ligands:
(Bridged complexes)

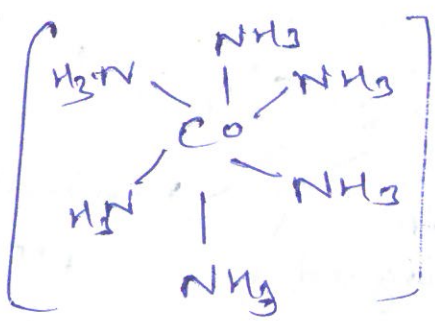
Ex- $\left[(H_3N)_4 Co(OH)(NH_2)Co(NH_3)_4\right]Cl_4$

$2x - 2 + 0 - 4 = 0$
$x = +3$

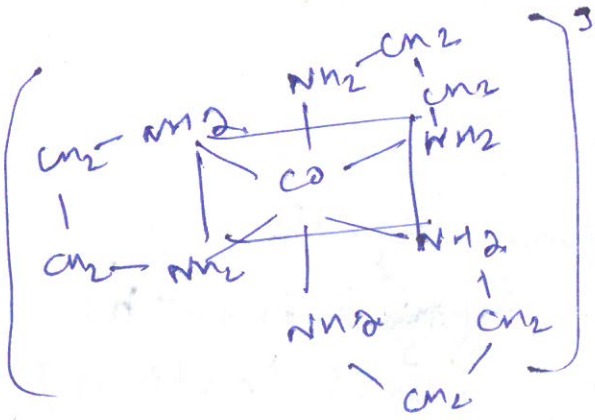
Coordination Number:

Number of donar atoms attached to a metal cation. (No. of coordinate bonds)

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



2) $[Co(en)_3]^{3+}$



→ No. of donar atoms → 6
No. of ligands → 3

3) en → $NH_2-CH_2-CH_2-NH_2$
(C, N)

Coordination sphere:

The square bracket [ ] in which a complex ion is enclosed.

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

Counter ion OR Ionization Sphere:

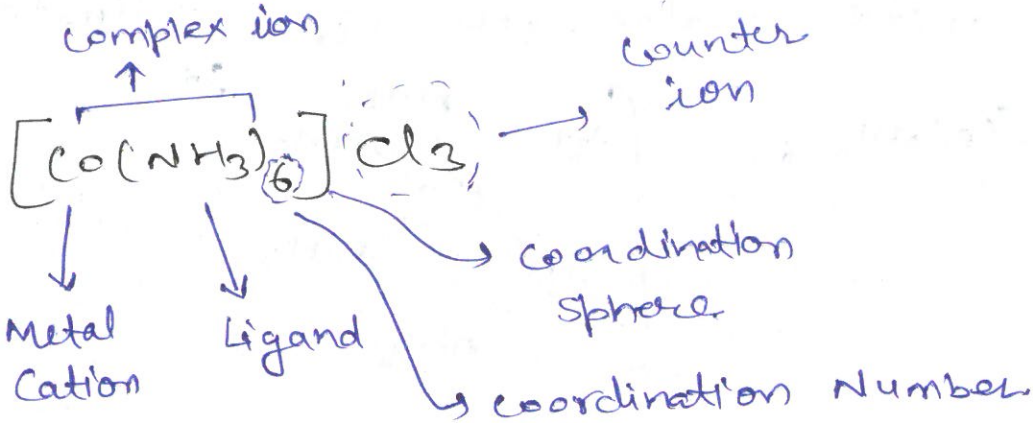
The ion (cation or anion) outside the coordination sphere.

$[Co(NH_3)_6]Cl_3$, $K_4[Fe(CN)_6]$

↘ ↙

counter ion

⇒



Classification of Ligands:-

i) Monodentate Ligands:-

Mono → single

dentate → comes from dentis (teeth or tooth)

A ligand can bite a metal cation/atom by one donar atom is called monodentate ligand.

OR

A ligand that can donate one e⁻ pair from its donar atom to a metal cation/atom is called monodentate ligand.

Anglo Saxon

Beowulf :- early and greatest epic, or heroic poem in literature. It begins with a prologue. Writer is unknown

* Beowulf fights with three dragons :-
  1) with the danger of the sea
  2) the conquering of the sea itself and
  3) the conflict with the hostile forces of nature.

Widsith :- author and date of composition are unknown.

Deor's Lament* :-

The Seafarer* :- seems to be in two distinct parts :-
  1) shows the hardships of ~~life~~ the ocean life.
  2) 2nd part is an allegory

* Both are first recorded speech, which the Anglo-Saxons may have brought with them when the first conquered Britain.

ALL MATERIAL AVAILABLE HERE

Hand Written Class Notes

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MATHS, CHY, PHY, LIFE SCI .

NET for UGC

ENG , ECO , HIS , GEO , PSCY , COM ENV,.... Etc.

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IAS , JEE , NEET(PMT).

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The Fight at Finnsburgh and Waldere :- a war song of fifty lines discovered on the inside of a piece of parchment, describing with sixty warriors, against the attack of Finn and his army.

* Anglo-Saxon denotes two of the three Germanic tribes — Jutes, Angles and Saxons.

Caedmon :- 'Paraphrase' the book opens with a hymn of praise, and then tells of the fall of Satan and his rebel angel from heaven,

Cynewulf :- Greatest of the Anglo Saxon poets, excepting only the unknown poet of Beowulf.
* The Christ, Juliana, The Fates of the Apostles and Elene.
↳ a didactic poem in three parts, first celebrating the Nativity, Second the Ascension and the third "Doomsday"

Alfred (848-901) :- Alfred is known chiefly as a translator. His important translations are four in number :-
1) Orosius's Universal History and Geography'
2) Bede's History (1st great historical work written on English soil)
3) Pope Gregory's Shepherds' Book and
4) Boethius's Consolations of Philosophy.

* Last known poem of the Anglo-Saxon period, 'The Battle of Malden', otherwise called 'Byrhtnoth's Death.'

ANGLO-NORMAN PERIOD (1066-1350)

* Battle of Hastings – 1066.
* Harold – last of the Saxon king.
* In the Norman period literature was in the hands of the clergy and Nobles; that the common people could not read, and had only a few songs and ballads for their literary portion.
* There was of Oriental tales called 'The Seven Wise Masters'. There are legends of the Virgin and the Saints, a paraphrase of Scripture, a treatise on the seven deadly sins.

* All the scholarly works of the period, like William of Malmesbury's History and Anselm's Cur Deus Homo and Roger Bacon's Opus Majus, the beginning of modern experimental science, were written in Latin. While nearly all other works were written in French, or else were English copies or translations of French original.

Geoffrey of Monmouth (d. 1154) :- His work is 'Historia Regum Britannia' is noteworthy, not as literature, but rather as a source book from which many later writers drew their literary materials.

14th Century

Age of Chaucer (1340 - 1400)

Chief features of 14th Century or the Age of Chaucer

The age of Chaucer is one of the most active, complicated, vexed and entangled transitional periods in the history of England. This age faced dramatic change from old to new, there were drastic changes in society, religion etc.

Social Changes :- It was a great social, political, relegious and literary activities. Politicaly it was a period of 100 year's war (1338 - 1453) which released and stranthened the feeling of national consciousness and patriotism both in England and France.

* Two battle during the 100 years war :-
  i) Battle of Crecy (1346) - Black prince.
  ii) Battle of Poitiers (1356)

Black Death :- (1348) An epedemic called Black Death devasted 1/3 population and reoccured in 1362, 1367 and 1370. It led discontent supply of labours and demand of grosseries in England. It gave rise to the labour, lower class.

Major Writers and Their Works

(1340-1400)

1. Geoffrey Chaucer - Father John Chaucer,
   Mother Agnes Chaucer

Born in the reign of Edward III 1327-77
lived through that of Richard II 1377 99
died in the reign of Henry IV 1399-1413

* When Chaucer was still in his teen, (19 year) (17 yr) he was appointed in the service Lionel, afterward duke of Clarence 3rd son of Edward III

* He also went with Duke travel of 100 years war, seige of reigh

* Chaucer was ransomed in 16 £ from the royal purse.

* Married with Phillippa Roet sister of IIIrd wife of Duke John of Gaunt, influencial Duke of Lancaster.

* English was introduced in court in 1362. and 1363 in Parliament.

* Died in 1400, and was buried in that part of Westminster Abbey which afterwards came to be known as the Poet's Corner. 1st poet was burried in W. A..

* ~~He marrie with the~~ Geoffrey Chaucer was also known as :-

a) Father of English poetry.
b) Grandfather of English novel.
c) Father of English language.
d) "Morning star of Renaissance."

*

*

Important Comments and Quotations :-

1) "Chaucer is the first great painter of character."
— A.C. Ward.

2) "He found English a dialect and left it a language."
— Lowel

3) "The well of English undefiled"
— Ed. Spenser.

4) "Under his influence rhyme gradually displaced allitration in English poetry."
— W.H. Hudson

5) "Specially charming feature of his poetry is its fresh out of doors atmosphere."
— W.H. Hudson.

6) W.J. Long has called his "prologue to the Canterbury Tales" — "Prologue to the modern fiction."

7) "Had Chaucer written in prose, it is possible that his 'Troilus and Cressyed' and not Richardson's 'Pamela' would be celebrated as the first English novel."
— S. D. Neil

8) "I see all the pilgrims, their humours, features and their very dress as distinctly as if I has supper with them at the Tabbard Inn in South work."
— Dryden.

Works of Chaucer :-

Chaucer passed through the three period of his carrier a) The French b) The Italian and c) The English, of which the last is the most important and original.

a) The French Period :-

* Followed two French writers DeLorries and DeMeung

1) * Translated their lengthy romance "The Romaunt of the Rose" into English. It consists of 8000 lines.

* It depicts the drawbacks of marriage and the deceitfulness of women.

2) * "The Book of the Duchess" (1369) a long allegory on the death of Blanche the ~~dead~~ wife of his powerful patron.
Hadow remarked on this poem "Chaucer shows that truth to life and impatience of artificiality which are to become two of his most striking features."
⇒ The Parliament of Fowls. Rhyme - Royal

3) * "Complaint unto Pity" a shorter poem remarkable for its skillful use of the French seven lined stanza or "Rime Royal".

"An ABC"
The Compleynt of Mars"

(1370-84)

b) The Italian Period :- * Visited Italy in 1372 and came in contact with Dante, Petrach and Bocaccio.

*- 1) " Troylus and Cryseyde" poem of ~~8002~~ 8200 lines adopted from Boccaccio's - 'Il Filostrato'. → (Mid 1380's)

* Written in Rime Royle and considered first novel ~~in~~ of English in verse. → ab ab b c c (7 lines stanza)

* He dedicated this poem to John Gower.

* 2) "The House of the Fame" :- It is a dream allegory type poem written in Octo syllabic couplet.

"Written ful of names
Of folk that hudden grate fames."
(The House of Fame)

* 3) "Legende of Good Women" - incomplete.

* Ist attempt to use the Heroic Couplet in English.

* Originally planed to narrate 19 ~~viz~~ tales of virtuous women of antiquity, remarkable for their chestity sincerity and devotion to love. but he could compose only 8 legends.

* 4) "Anelida and Arcite"

* 5) Parliament of Fouls" :- Characterization of

ORGANOMETALLIC CHEMISTRY

19/9/19

Edward Frankland: Father of oreganometallic chemis

Difference btw organometallic & coordition compound

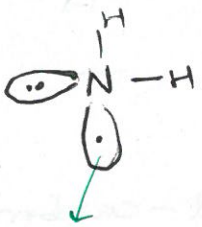
1) In coordination, wecner complexes

$[Fe(H_2O)_6]^{2+}$, $[Co(NH_3)_6]^{2+}$ ⇒ only simple ligands like H_2O, NH_3, Cl (inorganic comp.)

But in organometallic, most of cases oreganic ligands are used (ligands formed by H & C)

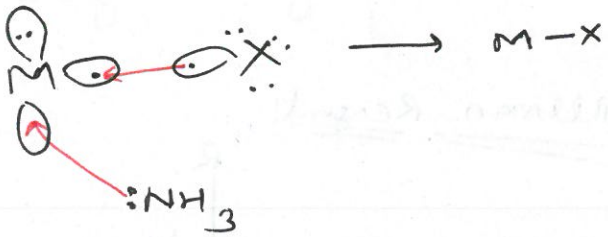
2) Coordination: Fe^{2+}, F^{3+}, F^{+4} → High O.S

organometallic: Fe(-2), 0 → Low O.S



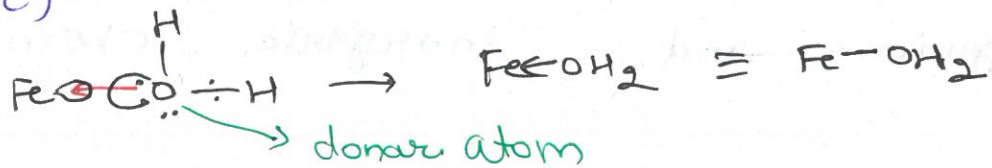
→ Jb tk odd e⁻ h, even e⁻ donate nhi krega.

This will donate



Metal don't used any e⁻ to make bond with NH_3.

Ligand: all properties are similar as donar (σ OC)

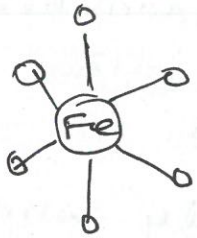


- Central atom is head of family.
- Transistion metal have filled & empty orbitals both.

even Zn also have vacant orbital.

$3d^{10}4s^2$ → filled, 4p, 4d ↦ empty

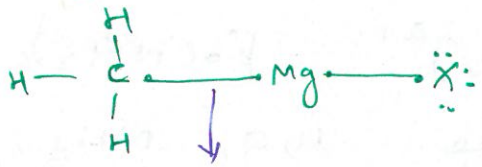
3)



Grignard reagent ($RMgX$)

I

Mg:- 2.8.2 — 1

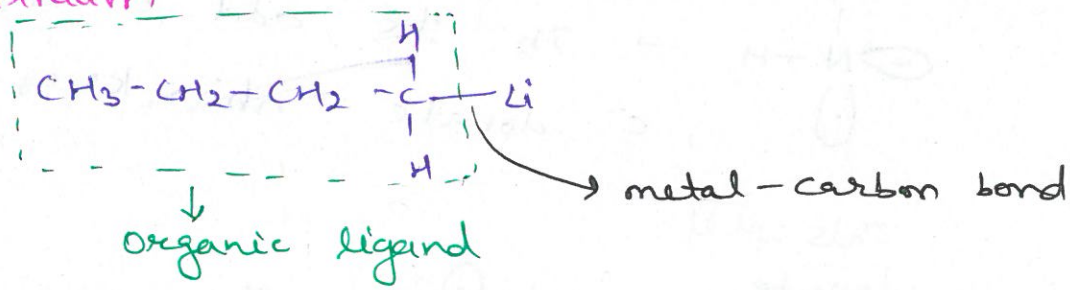


one metal-carbon bond

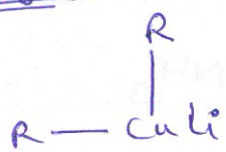
* For a compound said to be organometallic, there must be atleast one metal-carbon bond. For eg: Grignard reagents

Li - $1s^2 2s^1$

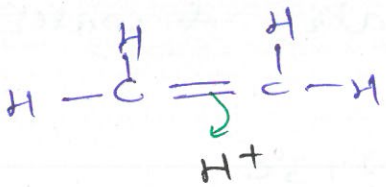
methyl lithium

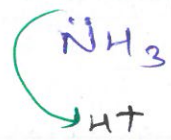


Gilliman Reagent:



Organometallic chemistry is a bridge btw Oreganic and inorganic chemistry.





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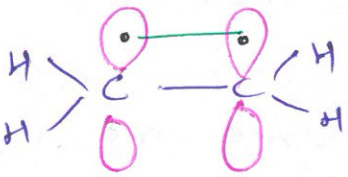
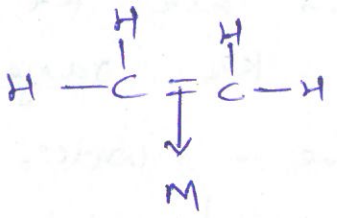
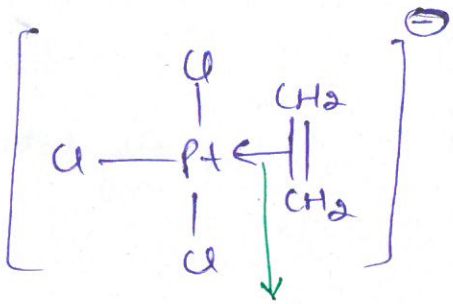




→ Organometallic compound

Zeise's Salt:

It uses only 3e⁻ to make this complex.



Pt – d^{10} system
10 valence e⁻

Organometallic comp.
(M – C bond)

→ In coordination: Low & High spin complexes depends on metal & ligand both.

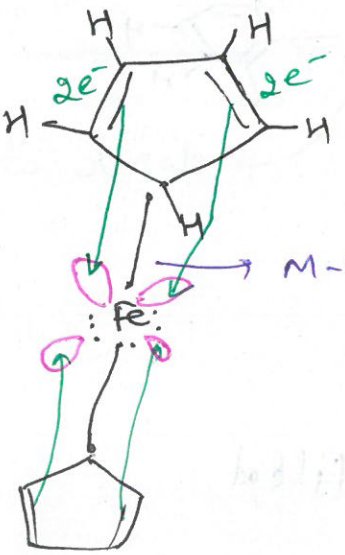
3d – $[Fe(H_2O)_6]^{2+}$ – H.S 4d – $[Ru(H_2O)_6]^{2+}$ L.S

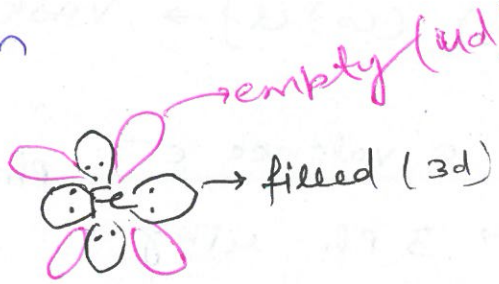
→ In organometallic, ligand is always strong & forms LS complexes.

Co – $3d^7 4s^2$

Co – $3d^9$ system

*





Cp_2Fe

Ferrocene

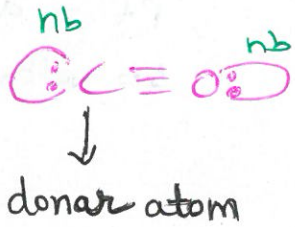
Organometallic compl

- Organometallic compounds are air & water sensitive.

Ferrocene: M.P greater than 273°C

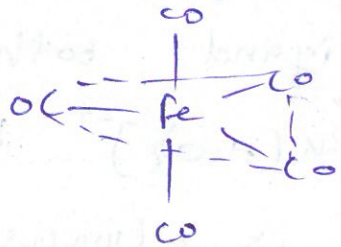
Air sensitive → air ki presence me oxidation ho jayega.

water sensitive – water ke presence me breakdown ho jayenge.



Lewis dot: St

OMC → $[Fe(CO)_5]$ ⇒ TBP geometry

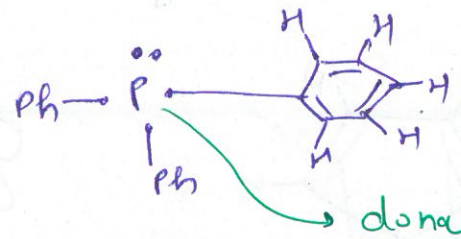


CO is not organic ligand (not H present)
But then also $[Fe(CO)_5]$ is omc.

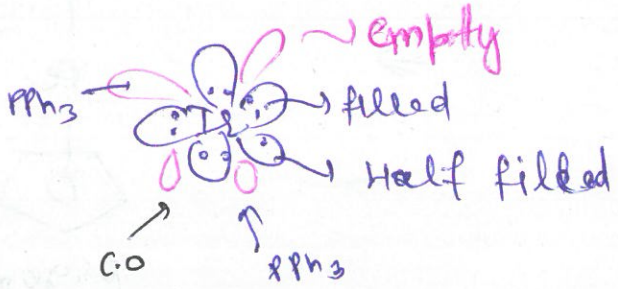
$[Fe(CO)_4]^{2-}$ → collman's reagent

$[Ir(PPh_3)_2(CO)Cl]$ → Vaska's complex

P → 5 valence e⁻
→ 3 Ph ring



Ir → $d^7 s^2$

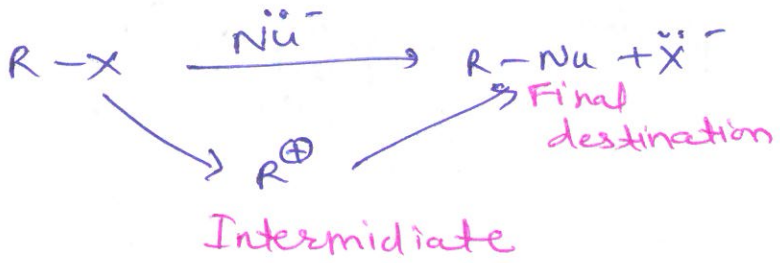


Reactive Intermidiate

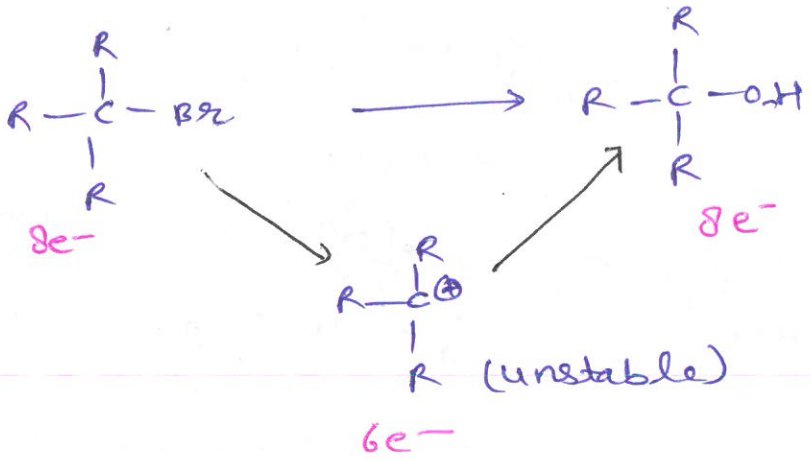
10/8/19

→ They are highly unstable

→ They are very short lived species.



→ Intermidiates is not final destination. It is the ~~state~~ b/w reactant & product.

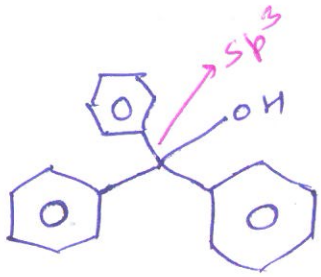


→ Intermediates are high unstable because their octet is not complete & these are not charged species.

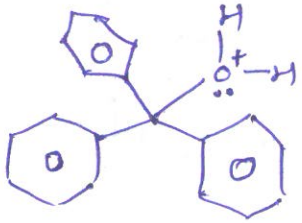
→ All are unstable & we find stability in unstability.

→ Intermediates are transient they formed during rxn & dissappears.

Carbocation :— [1902] (accidental Invention)

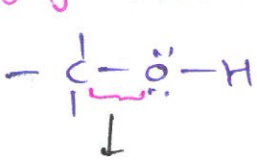


$H_2SO_4 \rightarrow H^+$
(fall on floor)

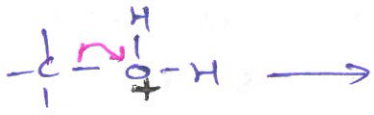


Colourless
(No conjugation)

Coloured



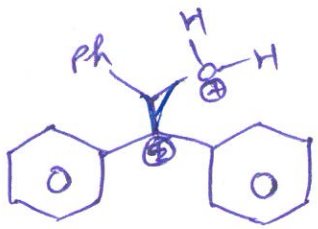
H^+



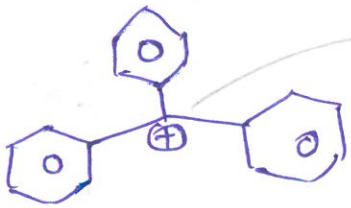
$\longrightarrow$ $+H_2O$

Polar bond
due to E.N diff.
(unhappy)

Very unstable
due to +ve charge on O.
(break)



$-H_2O$



1st charge in organic chemistry

conjugation, extent of delocalisation → coloured

(carbonium ion)

(+vely charged species)

→ Onium word is used when an central atom makes bonds more than its valency.

⇒ Wrp 14 tk jo valene e^- honge utni hi valency hogi IUPAC suggest these names.

($2e^- \rightarrow 1$ bond)

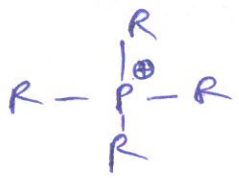
(ammonia)

(ammonium ion)

→ normal valency se ek bond extra bnaya h.

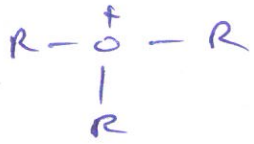
* Valance → outmost shell me e^-

Valency → Normal form me kitne bond bnayenge

*  → Phosphonium ion

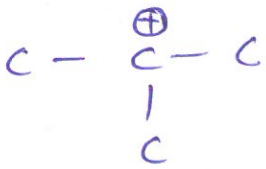
Valence e^- → 3
makes bond → 4
(valency)
So, onium word is used

* $R-\ddot{O}-R$ → Normal valency (valency = 2)

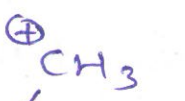
 - oxonium ion

*  sulphonium ion

S forms 2 bonds in normal valency

1) Carbonium Ion!- 

Here, carbon is not making bonds more than its valency (normal). So, onium word cann't used here.
So, the name is changed to Carbenium ion.



carbenium ion

ohla scientist gives this name.
Bonds less than their normal valency.

carbonium ion
↳ bonds more than their normal valency

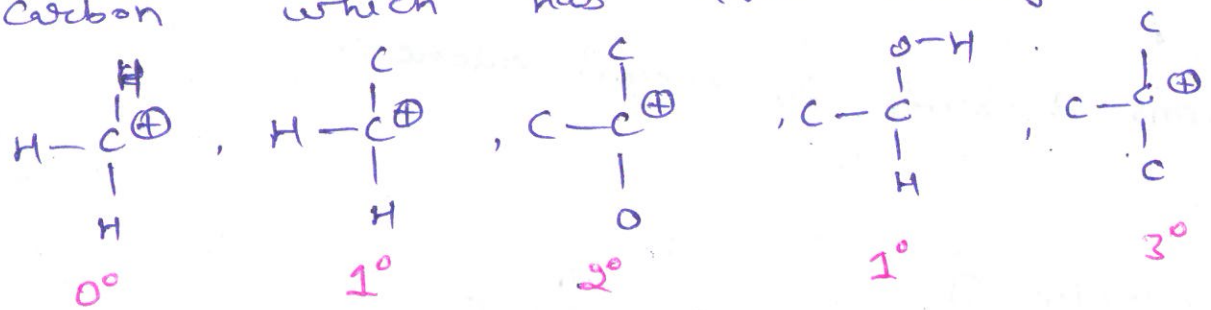
Then also, there is lot of confusion. then the generic name comes known as Carbocation.

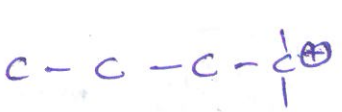
→ carbocation is a generic name which means the species in which carbon containing positive charge.

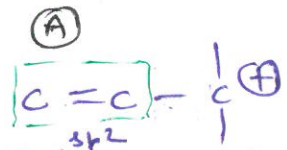
→ Carbocation contains both carbonium + carbenium ions both.

Degree of carbocation! –

The no. of carbon attached to the carbon which has +ve charge.



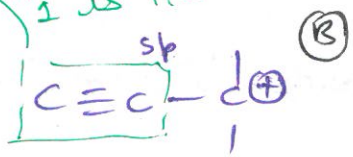
*  1°

*  Ⓐ

sp²

1°/allylic carbocation

1π is far & 1 is all

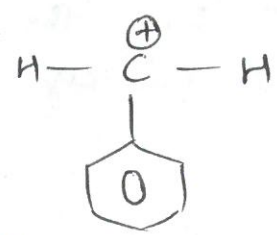
*  Ⓑ

sp

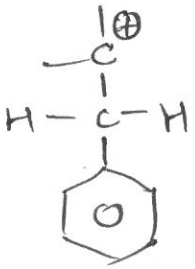
1°/Propargylic carbocation

So, conjugation takes place ($\pi \rightarrow p^E$)

More conjugation in Ⓐ bcoz less s- character due to sp^2.

* 

1°/Benzylic carbocation

* 

Homobenzylic carbocation.

Reagents in organic Synthesis :-

8/9/19

(A) oxidation

(B) Reduction

(C) Organometallic reagents

(D) Misscellenous Functions.

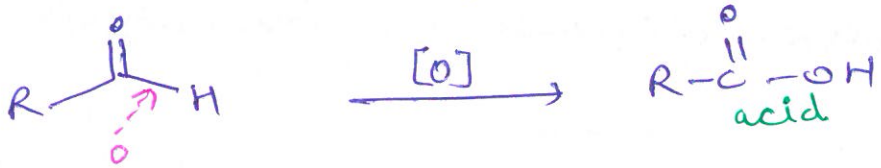
(A) Oxidation :-

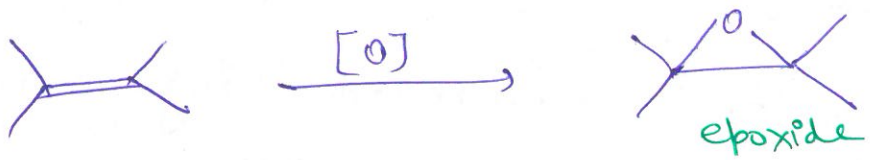
→ Removal of hydrogen.

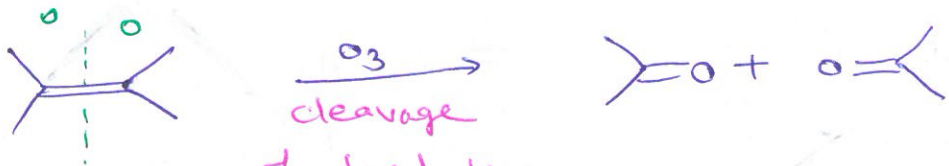
$R-CH_2-OH \xrightarrow{-H_2} R-\overset{H}{\underset{|}{C}}=O$

Primary alcohol → aldehyde

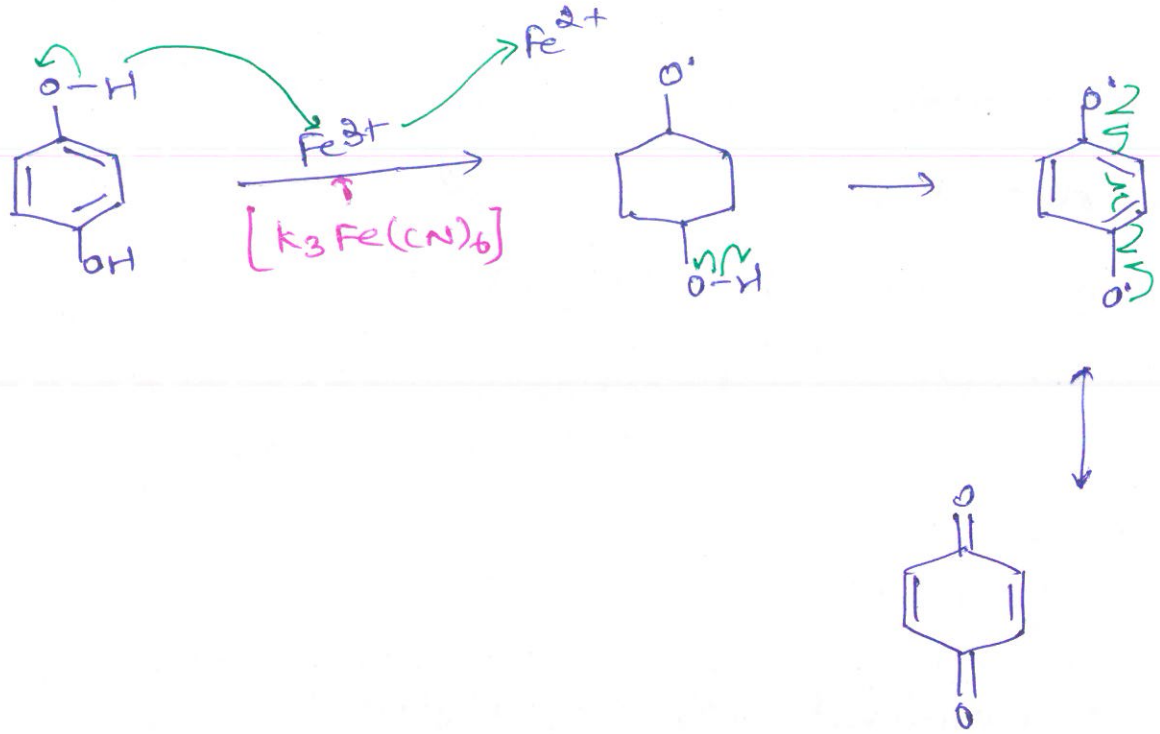
→ Addition of oxygen.







→ Removal of electrons

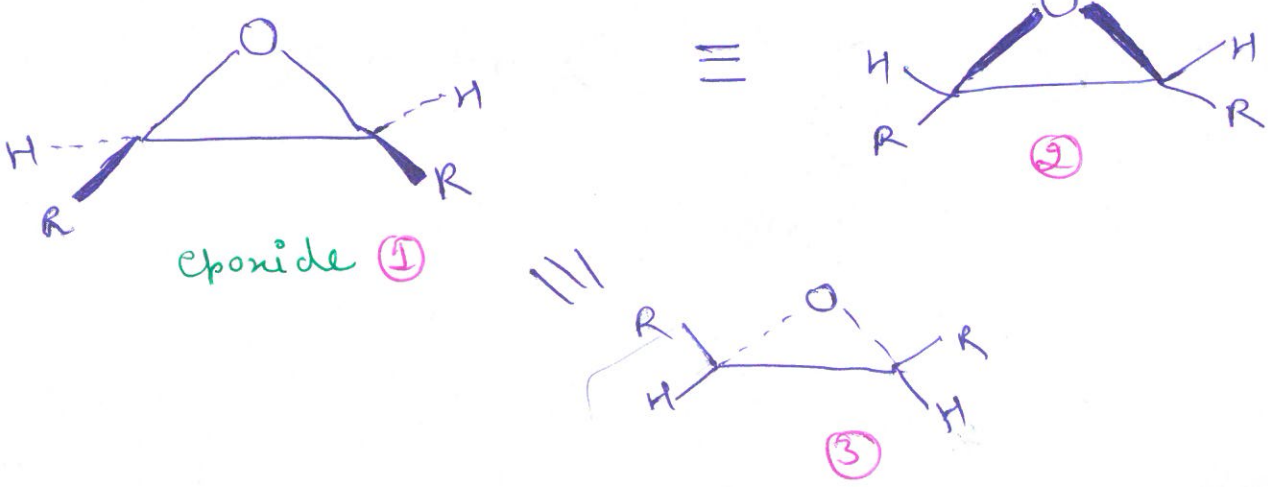


1) Oxidation of alkene :-

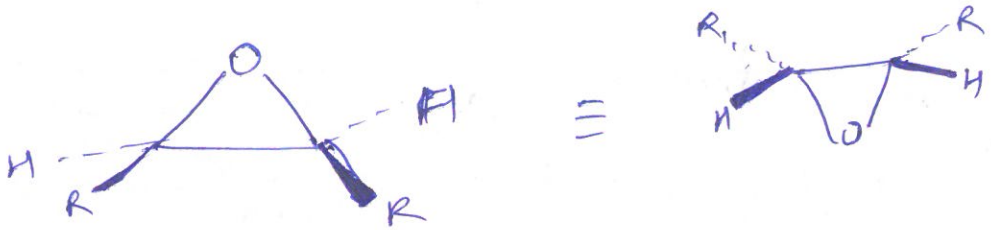
* Epoxidation
* Dihydroxylation
* Oxidative cleavage → ozonolysis

1) Epoxidation :-

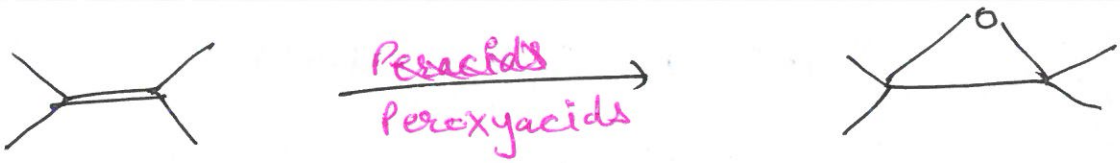
Epoxide : Three membered ring containing hetro atom as oxygen.



① , ② & ③ are identical st.

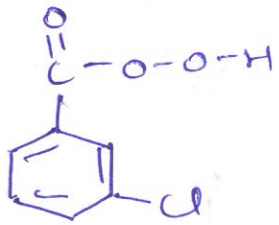


⇒



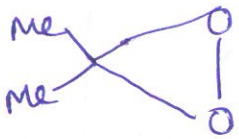
Peroxyacids are used for epoxidation of alkenes.

Peroxyacids →
- CH_3CO_3H
- $PhCO_3H$
- m-CPBA
- H_2O_2-AcOH
- CF_3CO_3H



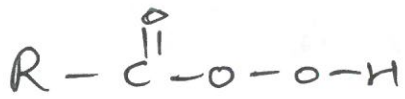
m-chloroperbenzoic acid

AcOH → acetic acid

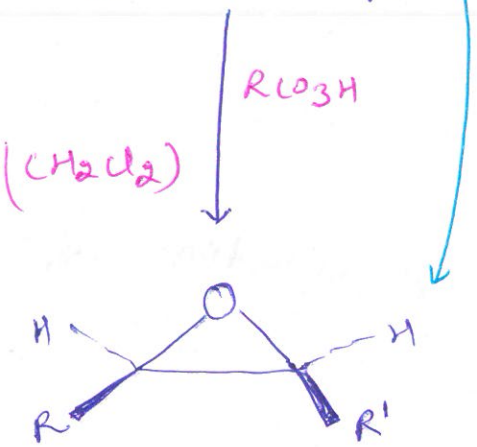
-  DMDO (Dimethyle dioxirane)
- Transition metal catalyst / t_{BuOOH}

(Name Rxn) → Sharpless Asymmetric epoxidation

Ti, V, Mo, Re



Representation of alkene :

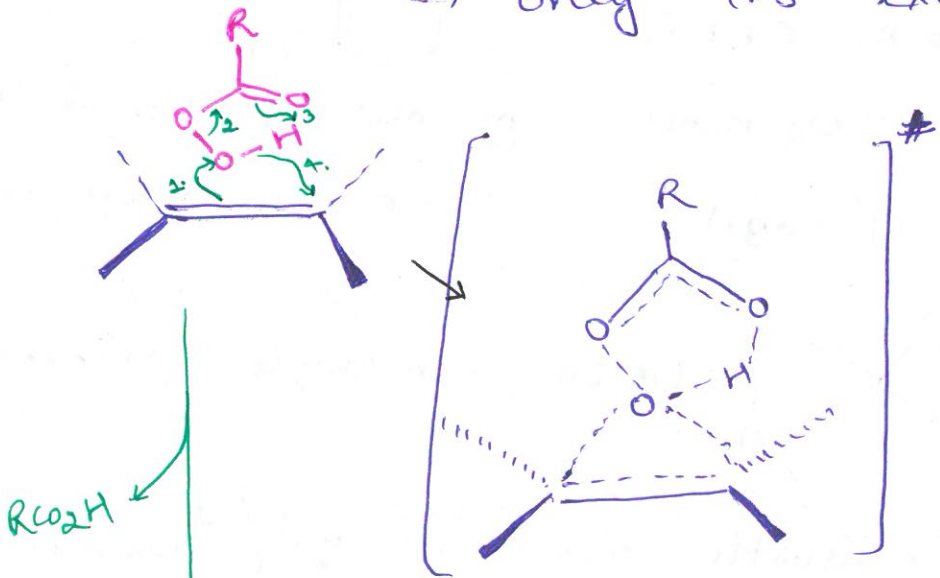


Mechanism:

→ concerted process

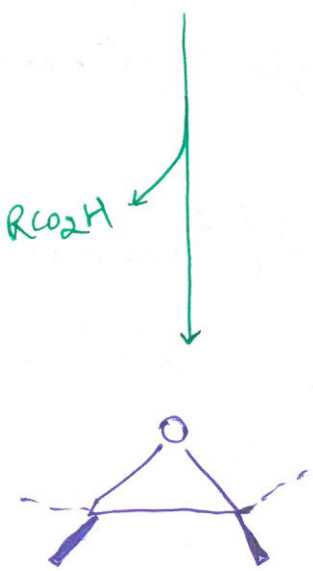
→ only T.S exist

1. Initiation



T.S (spiro comp.)

(Highly strained)



2. O—O (Peroxide) bond
↓
weak due to lp-lp repulsion
So, bond breakes

New bond bn the h or old bond break ho the h → Sbhi ko partial bond se represent krna h. — T.S

Thermodynamics

V. Imp

1) Basic Mathematics
- Unit conversion
- Differentiation
- Partial differentiation
- Total differentiation
- cyclic rule
- Definitions

2) Ist law of thermodynamics
- ΔU, ΔH
- Heat capacity
- Thermodynamic coefficient
- Isothermal Process
- Adiabatic Process ← Tricky Ques.
- Equipatition Theorem.

3) 2nd law of T.D
- carnot cycle
- Introduc
- ★ calcul of ΔS
- Refrigerato
- criteria of Spontanit

4) Miscellenous Topics:
- Kirchoff eqn
- ★ clausius clapeyron eqn
- Gibbs-Helmholtz eqn

5) Partial Molar Quantities
- chemical quantities Potential
- Gibb's Duhem eqn
- ★ ΔG_{mix} & ΔS_{mix}
- ★ Fugacity

$\log x = y$

$x = 10^y$

$\ln x = y$

$x = e^y$

Δz → large value change of z

dz → small value change of z

∂z → very small value change of z

UNIT CONVERSION :

1) Volume : $\boxed{1\,L = 1\,dm^3 = 10^{-3}\,m^3 = 10^{3}\,cm^3}$

$1\,mm = 10^{-1}\,cm$

$(1\,mm)^3 = (10^{-1}\,cm)^3 \Rightarrow 1\,mm^3 = 10^{-3}\,cm^3$

$1\,m^3 = 10^{6}\,mL$

$1000\,mL = 10^{-3}\,m^3$

10^{6}

2) Pressure :

S.I unit = Pascal (Pa)

$\boxed{\begin{aligned} 1\,atm &= 1.01325 \times 10^{5}\,Pa \\ 1\,bar &= 10^{5}\,Pa \end{aligned}}$

$1\,atm = 760\,mm\,Hg$

$1\,torr = 1\,mm\,Hg$

$1\,atm = 101325\,Pa$

$1\,atm = 101325\,N\,m^{-2}$

$1\,atm = 1.01325 \times 10^{5}\,N\,m^{-2}$

$= 1.01325 \times 10^{5}\,Pa$ (N m^{-2} = Pa)

$= 1.01325 \times \frac{10^{5}\,J}{Pa}\,Pa$

$= 1.01325\,bar$

3) Energy / Work :

S.I Unit = Joule

$\boxed{1\,cal = 4.18\,Joule}$

$w = -P_{ext}\,\Delta V$

$\boxed{\begin{aligned} 1\,Pa\,m^3 &= 1\,J \\ 1\,atm\,L &= 101.3\,J \\ 1\,bar\,L &= 100\,J \end{aligned}}$ → Most common.

$1\,atm\,L = 24.23\,cal$

Assignment - 1

1) $W = 3\ atm\ L$

$W = 101.3 \times 3\ J = 303.9\ J$

$W = \frac{101.3 \times 3}{4.18} \times 10^{-3} = 7.27 \times 10^{-2}\ kcal$

8) $1\ L\ Pa = \_\_\_\_\ atm\ m^3$

$1\ L\ Pa = \_\_\_\_\ 10^{-3} \times 101.3\ J$ (× $10^{+3}\ atm\ L$)

$\Rightarrow 1\ L\ Pa = \_\_\_\_\ atm\ m^3$

$V \times P \quad P \times V$

$\Rightarrow 1\ (1\ L)\ (1\ Pa)$

$\Rightarrow (10^{-3}\ m^3)\left(\frac{1}{1.01325 \times 10^5}\ atm\right)$

$\Rightarrow \frac{1}{1.01325} \times 10^{-8}\ m^3\ atm$

~~$1\ cm = 10\ dm$~~

~~$1\ cm^3 = 10^3\ dm^3$~~

11) $32\ Pa\ dm^3 = \_\_\_\_\ atm\ cm^3$

$1\ dm = 10\ cm$

$32 \times \frac{1}{1.01322 \times 10^5}\ atm\left(\frac{10^3}{10^2}\ cm^3\right)$

$\Rightarrow \frac{32}{1.01322} \times 10^{-2}\ atm\ cm^3$

$\simeq 31.9 \times 10^{-2}\ atm\ cm^3$

10) $1\ atm\ ml = \_\_\_\_\ Joule$

4) 14 7 torr L = _____ J = _____ Pam³

$7\left(\frac{1}{760}\ atm\right)(1\ L)$

$\Rightarrow 7 \times \frac{1}{760} \times 101.3\ J \Rightarrow \frac{7 \times 101.3}{760}\ J$

$= \frac{7 \times 101.3}{760}\ Pam^3$

$= 0.93\ Pam^3$

2) 1 mol CO_2 – 38 kJ

$44g\ CO_2 \rightarrow 38\ kJ$

$4g\ CO_2 \rightarrow \frac{38}{44} \times 4\ kJ = \frac{38}{11}\ kJ$

$= 3.4\ kJ$

32
12
44

3)

$0.1\ L = \_\ m^3$

$= 0.1 \times 10^{-3}\ m^3$

$0.1L = 10^{-4}\ m^3$

$0.1\ L = 10^{-4} \times 10^{3}\ dm^3$

$0.1\ L = 10^{-1}\ dm^3$

$0.1\ L = \frac{10^{-3}}{10^{3}}\ cm^3$

$0.1L = \div\ m^3$

$0.1 \times 10^{3}\ m^3 \Rightarrow 10^{2}\ m^3 = 0.1\ L$

6) $20K = \_\ ^\circ C$

$20 - 273\ K = +1^\circ C$

$0^\circ C = 273K$

$1K + 1^\circ C = 273.15$

$1^\circ C = \frac{5}{9}(F - 32)$

18) $n = 2$ moles

$T = 300K$

$P = 5$ atm

$PV = nRT \Rightarrow \frac{2 \times 300 \times 0.082}{5} \Rightarrow$