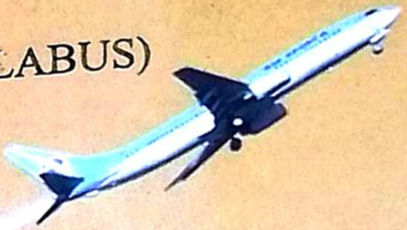
No 1

BASED ON C.B.C.S. SYLLABUS

Vidya Guess™

VINOBA BHAVE UNIVERSITY
SEMESTER – III
2021–24
(AS PER NEW REVISED SYLLABUS)



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GEN./ELE. (NEW)

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SEMESTER - III

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Objective questions
(choose the correct option)

Q1. First Law of thermodynamics is the law of

a) entropy b) Free energy c) Conservation of energy d) None of these.

2. "Total enthalpy change of a process is always constant whether the change is brought in one step or in more than one step." This statement is known as

a) Joule's law b) Boyle's Law c) Hess's Law d) None of these

3. Effect of temperature on the heat of a reaction is called

a) Joule's law b) Hess's law c) Kirchoff's law d) None of these

4. Mathematical form of 1st law of thermodynamics is

a) $dq = dE + dw$ b) $dq = dE - dw$ c) $dE = dq + dw$ d) all of these

5. A reversible process

a) can be achieved b) can not be achieved

c) can be achieved under conditions d) Concept is useless.

6. Standard state means

a) 1 atm pressure & 25°C temp. b) 1 atm pressure & 100°C Temp.

c) 1 atm pressure & 0°C temp. d) none of these

7. Adiabatic Process has

a) $\Delta q = 0$ b) $\Delta T = 0$ c) $\Delta V = 0$ d) none of these.

8. Standard heat of formation of an element is

a) infinite b) Zero c) 200 KJ d) 100 KJ

9. Which of the following is not a state function

a) E b) H c) S d) W

10. In which of the following cases, does the reaction go farthest for completion?

a) $K = 10$ b) $K = 1$ c) $K = 10^5$ d) $K = 10^{-3}$

2

11. Ostwald's dilution law is applicable for

a) Strong electrolyte b) weak electrolyte c) both d) none of these

12. Degree of ionization for weak electrolyte w.r.t. dilution

a) increases b) decreases c) remains same d) increases for some substance & decreases for another substance

13. On addition of small amount of an acid or a base, the pH of a Buffer solution

a) increases b) decreases c) remains constant d) depends upon substance

14. with increase in temperature, the solubility of a substance

a) increases b) decreases c) remains same d) depends upon substance either increases or decreases

15. Which relation is true for Kp and Kc

a) $K_p = K_c (RT)^{\Delta n}$ b) $K_p = K_c (RT)^{-\Delta n}$ c) $K_p = K_c (RT)^{\Delta n^2}$ d) none of these

16. In Reimer—Tiemann reaction, the attacking reagent is

a) Electrophile b) Nucleophile c) Free radical d) none of these

17. Nitration of phenol can be done by

a) dil HNO_3 b) concn HNO_3 c) concn HNO_3 + concen H_2SO_4 d) None of these

18. Picric acid is

a) Inorganic acid b) -COOH containing substance c) Strong acid d) weak acid.

19. Which of the following compounds is least acidic?

a) HCl b) Phenol c) Acetylene d) Picric acid

20. Bakelite has the following characteristics

a) A Polymer made from Phenol and formaldehyde

b) A thermosetting Plastic

c) Can be used as adhesive

d) All of the above

21. Phenol is acidic because of

a) Resonance b) Electromeric effect c) Inductive effect d) Peroxide effect

22. Pheno is used

a) in alcoholic beverages b) as anesthetic c) in antiseptics d) as moth repellant.

23. SN^1 reaction gives

a) Retention b) Inversion c) both retention and inversion d) None of these

24. S_N^2 reaction gives

a) Retention b) Inversion c) both d) none of these

25. S_N^1 reaction is

a) one step reaction b) two step reaction c) three step rkn d) four-step rkn

26. S_N^2 reaction is

a) one step rkn b) two step rkn c) three step rkn d) four-step rkn

27. In Wurtz reaction, the metal used is

a) Sodium b) Zinc c) Magnesium d) none of these

28. Hydroboration – oxidation of propane gives

a) Isopropyl alcohol b) n-propyl alcohol

c) Isobutyl alcohol d) t-Butyl alcohol

29. Pinacolone contains

a) $-OH$ gr b) $-\overset{O}{C}-$ gr c) both d) none of these

30. In Sandmayer's reaction, the final product is

a) chloro arene b) Bromo arene c) cyano arene d) all the three

ANSWERS :-

1. c 2. c 3. c 4. d 5. b 6. a 7. a 8. b 9. d 10. c 11. b 12. a 13. c 14. d 15. a
16. a 17. a 18. c 19. c 20. d 21. a 22. c 23. c 24. b 25. b 26. a 27. a 28. b
29. b 30. d

Group - A (INORGANIC)

Q write note on DE BROGLIE HYPOTHESIS

OR

Discuss the theory which describes dual nature of matter and radiation.

Answer → Light has particle nature (as suggested by Newton), as well as wave nature. On the basis of this concept Louis de Broglie (1924) proposed an idea that like photons, all material particles like electron, proton, atom, molecule, a piece of stone, a ball (ie all particles big or small) possessed dual character ie particle character and wave character.

The wave associated with a particle is called a matter wave or de Broglie wave.

Derivation of de Broglie Relation →

According to Planck's quantum Theory, $E = h\nu$ — ①

where, E = energy
h = Planck's constant
ν = Frequence of wave

According to Einstein mass-energy relationship,

$$E = mc^2 \quad — ②$$

where m = mass of Photon
c = velocity of light

Equating equations ① & ②,

$$h\nu = mc^2$$

$$h\frac{\nu}{c} = mc$$

$$h \times \frac{\cancel{\nu}}{\cancel{\nu}\lambda} = p \quad \left[\because \begin{array}{l} mc = p = \text{momentum} \\ c = \nu\lambda \end{array}\right.$$

or, $\boxed{\lambda = \frac{h}{p}}$ —③ Here λ is called de-Broglie wavelength

Significance of de-Broglie equation → Although the de Broglie equation is applicable to all material objects but it has significance only in case of microscopic particles.

Experimental verification of wave character → a) By Davison and Germer's Expt.
b) Thomson's experiment

Experimental verification of particle character → a) Black body radiation & Photoelectric effect
b) Millikan oil drop experiment

Q Write note on Heisenberg's uncertainty Principle.

Answer → In 1927, Heisenberg, gave a principle about the uncertainties (error) in simultaneous measurement of position and momentum of small (microscopic) Particle which is named after his name, as Heisenberg's uncertainty Principle.

"It is imposible to measure simultaneously the position and momentum of a microscopic (small) particle with absolute accuracy." If one of the two quantities are measured with accuracy then the other quantity becomes less accurate. The product of the uncertainty in position (Δx) and the uncertainty in momentum (Δp) is always constant and is equal to $\frac{h}{4\pi}$ where h = Planck's constant."

ie,

$$\Delta x \cdot \Delta p \cong \frac{h}{4\pi}$$

$$\because \quad \Delta p = m \times \Delta v$$

where m = mass of Particle

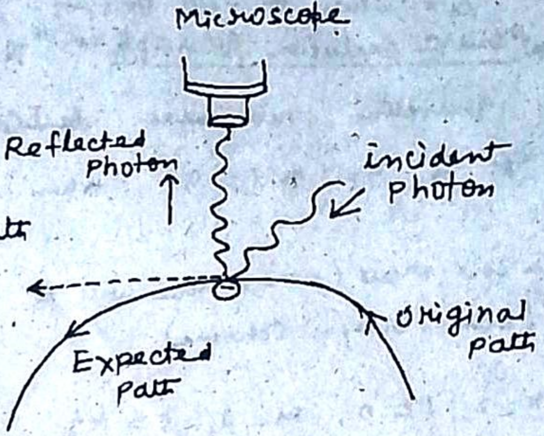
& Δv = uncertainty in velocity.

$$\therefore \quad \Delta x \cdot (m \cdot \Delta v) = \frac{h}{4\pi}$$

$$\text{or} \quad \Delta x \cdot \Delta v = \frac{h}{4\pi m}$$

ie, position and velocity of a Particle can not be measured simultaneously with certainty.

Explanation of Heisenberg's uncertainty Principle →



Change of momentum and position of electron due to impact with a photon.

Let we try to measure both the position and momentum of an electron. To locate the position of the electron, we have to use light, so that the photon of light strikes the electron and the reflected photon is observed in the microscope. Due to hitting by the photon, the position as well as the velocity of the electron are changed.

Significance of Heisenberg's uncertainty principle →

Although this principle can be applied for all objects (big or small) but it is significant only for microscopic particles. This can be better understood with the help of following example.

For a particle of mass 1 g,

$$\Delta x \cdot \Delta v = \frac{h}{4\pi m} = \frac{6.62 \times 10^{-34}\ kg\ m^2 s^{-1}}{4 \times 3.141 \times (10^{-3}\ kg)} \cong 10^{-25}\ m^2 s^{-1}$$

This is extreamly low value and hence negligible.

But, For an electron,

$$\Delta x \cdot \Delta v = \frac{h}{4\pi m} = \frac{6.62 \times 10^{-34}\ kg\ m^2 s^{-1}}{4 \times 3.141 \times (9.1 \times 10^{-31}\ kg)} \cong 10^{-4}\ m^2 s^{-1}$$

This value is not very small and hence significant.

Q→ Write ~~o~~ notes on:—

Pauli's exclusion Principle→ "No two electrons in an atom can have all the four quantum numbers identical."

eg If $n=2$, then, $l = 0, 1$ when $l=0$ then $m=0$ & $s = +\frac{1}{2}$ & $-\frac{1}{2}$

" $l=1$, then $m = -1, 0, +1$

in 2nd orbit ($n=2$) there will be maximum 8 electron according to formula $2n^2$

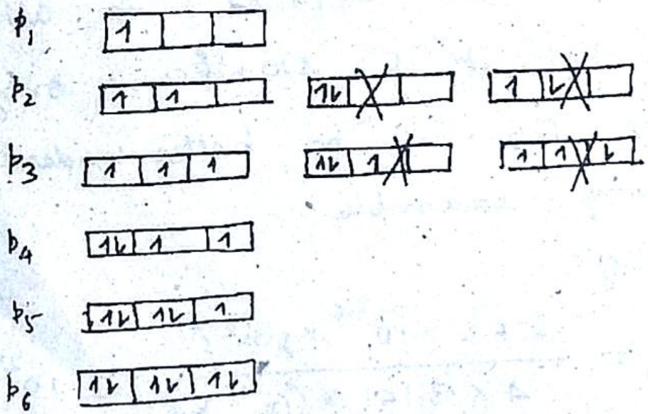
(Bohr-Bury-Schema)

$n=2$, $l=0$, $m=0$, $s=+\frac{1}{2}$
$n=2$, $l=0$, $m=0$, $s=-1/2$
$n=2$, $l=1$, $m=-1$, $s=+1/2$
$n=2$, $l=1$, $m=-1$, $s=-1/2$
$n=2$, $l=1$, $m=0$, $s=+1/2$
$n=2$, $l=1$, $m=0$, $s=-1/2$
$n=2$, $l=1$, $m=+1$, $s=+1/2$
$n=2$, $l=1$, $m=+1$, $s=-1/2$

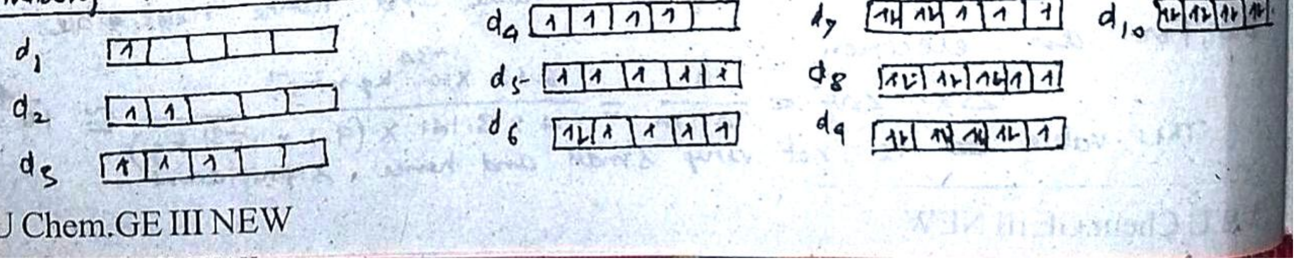
similarly for $n=3$, ie 3rd orbit 18 configuration can be written

ie Total 8 configurations.
(No set is same with any other)

② Hund's rule → "In the orbitals of equivalent energy electrons are filled one by one with parallel spin and then they are paired with opposite spin so as to give minimum energy and maximum stability." eg for p-orbital

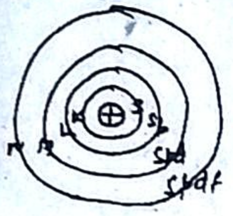


Similarly for d-orbitals



3. Aufbau's Principle → Aufbau means building up.

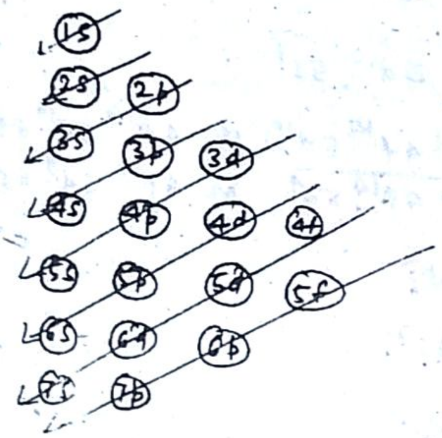
" Electrons are filled in different orbits and Orbitals according to their increasing order of energy i.e. orbit and orbitals with lower energy are filled 1st and orbits & orbitals with higher energy are filled



$$K \xrightarrow{\text{energy increases}} K < L < M < N < \ldots \quad \& \quad s \xrightarrow{E} s < p < d < f$$

$$\underbrace{1s}_{K-} < \underbrace{2s < 2p}_{L-} < \underbrace{3s < 3p < 3d}_{M-} < \underbrace{4s < 4p < 4d < 4f}_{N-} \ldots\ldots$$

However the above order of increasing energy when verified by spectroscopic method some irregularities were found hence correct order can be given by following diagram.



$$1s < 2s < 2p < 3s < 3p < \underline{4s} < 3d < 4p < \underline{5s} < \ldots\ldots$$

$(n+l)$ rule explanation →

① Orbitals are filled 1st for which $(n+l)$ value is lower. eg For 4s $(n=4, l=0)$ $n+l = 4+0 = 4$
& for 3d $(n=3, l=2)$, $n+l = 3+2 = 5$
Hence 4s orbital will fill 1st than 3d.

② If $(n+l)$ value is same for two orbitals then orbital with lower value of n is filled 1st.
eg. 3s and 2p
For 3s, $n+l = 3+0 = 3$
2p $n+l = 2+1 = 3$
Hence 2p orbital will fill 1st because it has lower value of n.

Limitation:- ① It does not tell, which electron are removed when an ion is formed from an atom

② In case of Pd $(Z=46)$, the predicted configu is $5s^2 4d^8$ but observed configu is $5s^0 4d^{10}$.

③ observed Configu of Cu, Ag & Au is different than Predicted by Aufbau's principle.

Q → Write down the electronic configurations of following elements (atoms or ions).

$_{19}K$ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

$_{21}Sc$ $1s^2 2s^2 2p^6 3s^2 3p^6 \underline{4s^2 3d^1}$ or $3d^1 4s^2$

$_{24}Cr$ $1s^2 2s^2 2p^6 3s^2 3p^6 \underline{4s^1 3d^5}$ or, $3d^5 4s^1$

$_{25}Mn$ $1s^2 2s^2 2p^6 3s^2 3p^6 \underline{4s^2 3d^5}$ or $3d^5 4s^2$

$_{29}Cu$ $1s^2 2s^2 2p^6 3s^2 3p^6 \underline{4s^1 3d^{10}}$ or $3d^{10} 4s^1$

$_{30}Zn$ $1s^2 2s^2 2p^6 3s^2 3p^6 \underline{4s^2 3d^{10}}$ or $3d^{10} 4s^2$

$_{47}Ag$ $1s^2, 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 \underline{5s^1 4d^{10}}$ or $4d^{10} 5s^1$

$_{79}Au$ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 \underline{6s^1 4f^{14} 5d^{10}}$ or $4f^{14} 5d^{10} 6s^1$

$_{78}Pt$ - .. $6s^1 4f^{14} 5d^9$ or $4f^{14} 5d^9 6s^1$

$_{26}Fe$ $1s^2 2s^2 2p^6 3s^2 3p^6 \underline{4s^2 3d^6}$ or $3d^6 4s^2$

$_{27}Co$ $1s^2 2s^2 2p^6 3s^2 3p^6 \underline{4s^2 3d^7}$ or $3d^7 4s^2$

$_{28}Ni$ $1s^2 2s^2 2p^6 3s^2 3p^6 \underline{4s^2 3d^8}$ or $3d^8 4s^2$

Cu^+ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

Cu^{++} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

Fe^{++} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

Fe^{+++} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

Co^{++} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$

Ni^{++} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$

Q → Define and explain quantum numbers.

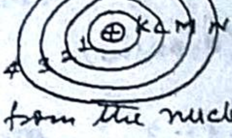
Ans → Quantum Numbers →

For explaining the complete behavior of an electron in an atom some constants are required. These constants are called as Quantum numbers. There are four types of Quantum Numbers.

A. Principal Quantum Number.
B. Azimuthal " "
C. Magnetic " "
D. Spin " "

A. Principal Quantum Number → It is denoted by n. It gives an idea about the size of an atom. It also gives an idea about the energy of an electron its distance from the nucleus. It may have values from 1 to ∞ but the permissible values are from 1 to 7. When n=1 ie 1st orbit or K-shell

n=2, ie 2nd " or L-shell and so on



The energy of orbit increases as we move farther from the nucleus.

B. Azimuthal Quantum Number → It is denoted by l. It is also called as Orbital quantum no. or angular momentum no. or subsidiary quantum no. It gives an idea of angular momentum of electron in the atom.

Its value depend upon the values of n. ie Principal Quantum no. For a given value of n, l can have values from 0 to (n−1) ie Total n no. of values. eg.

If $n=1$, $l = 0$ to $(n-1)$
$= 0$ to $(1-1)$
$= 0$ to 0
$= 0$.

If $n=2$, $l = 0$ to $(n-1)$
$= 0$ to 1
$= 0, 1$

If $n=3$, $l = 0$ to $(3-1)$
$= 0$ to 2
$= 0, 1, 2$

If $n=4$, $l = 0, 1, 2, 3$.

When $l=0$ it is called s-orbital
$l=1$, " " " p- "
$l=2$, " " " d- "
$l=3$, " " " f- "

Thus we see that Principal quantum no (n) is further sub-divided into orbitals. There are four types of orbitals s, p, d & f.

c. Magnetic Quantum no → It is denoted by m. It gives an idea about the no. of orientation of orbitals in space. ie how orbitals are sub-divided into sub-orbitals.
Its value depend upon the values of l ie azimuthal quantum no.
For a given value of l, there are values of m ranging from $-l$ to $+l$ ~~$(-l)$~~ to ~~$(+l)$~~. ie Total $(2l+1)$ values.

If $l = 0$, then $m = -l$ to $+l$
(s-orbital) $= -0$ to $+0$ ie There is only one type of s-orbital.
$= 0$
Box diagram ☐

If $l = 1$, then $m = -1$ to $+1$
(p-orbital) $= -1, 0, +1$ ie There are three types of p-orbital
p_x, p_y & p_z
Box diagram ☐☐☐

If $l = 2$, then $m = -2$ to $+2$
(d-orbital) $= -2, -1, 0, +1, +2$ ie There are five types of d-orbital
d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, d_{z^2}
Box diagram ☐☐☐☐☐

If $l = 3$ then $m = -3$ to $+3$
(f-orbital) $= -3, -2, -1, 0, +1, +2, +3$. ie There are seven types of f-orbital

Box diagram ☐☐☐☐☐☐☐

D. Spin Quantum Number → It is denoted by s.

Electron while revolving around the nucleus also revolves around its own orbit. This is called spining. Due to this spining an angular momentum is produced which is called spin angular momentum and is given by $\sqrt{s(s+1)}\cdot\frac{h}{2\pi}$ where s = spin quantum no

s has only two values ie $+\frac{1}{2}$ for clockwise revolution

& $-\frac{1}{2}$ " anti-clockwise revolution.

These two values are selected in such a way so that they satisfy three condition.

1. They must be equal in magnitude
2. " " " opposite " direction
3. They must differ by unity.

Q write a note on Lattice energy. or Derive Born-Lande equation for Lattice energy.

Answer → Lattice energy →

Lattice energy of a crystal is the energy evolved when one gram-molecule of a crystal is formed from its constituent gaseous ions. It is denoted by U.

eg. $Na^{\oplus}_{(g)} + Cl^{\ominus}_{(g)} \longrightarrow NaCl_{(crystal)}$, $U = -782$ KJ/mol

Here, in the formation of NaCl crystal by gaseous $Na^{\oplus}$ and $Cl^{\ominus}$ 782 KJ/mol energy is released.

It may also be defined as the energy required to remove ions of one gram molecule of a solid ionic crystal from their equilibrium position in the crystal to infinity.

eg. $NaCl_{(crystal)} + 782\ KJ \longrightarrow Na^{\oplus}_{(g)} + Cl^{\ominus}_{(g)}$

Lattice energy can not be measured directly, but experimental values are obtained from thermodynamic data using Born—Haber cycle

Lattice energy may also be calculated Theoretically:-

Theoretical Calculation of Lattice energy:—

Lattice energy of an ionic crystal is determined by coulombic interaction between all its ions eg attractive forces acting between the ions of opposite charges and repulsive forces resulting from the interpenetration of their outermost electron clouds.

The ions are treated as point charges and the electrostatic force of attraction (P.E$_{attraction}$) can be given as $E_{attraction} = \frac{(Z^+e)(-Z^-e)}{r}$

$$= \frac{-Z^+Z^-e^2}{r} \quad \text{— ①}$$

where Z^+ and Z^- are charges on +ve and -ve ions

e = charge on an electron

r = inter ionic distance

For more than two ions, E$_{attraction}$ depends on the number of ions and also on their arrangements in the space. Hence a new term 'A' is introduced in equation ①, called as Madelung constant. The value of 'A' depends upon the geometry of the crystal and can be calculated by summing the contribution of all the ions in a lattice crystal. The value of 'A' remains independent of the values of Z^+ and Z^- and also 'r'.

Now, the equation ① becomes

$$E = -\frac{N_0 A Z^+ Z^- e^2}{r} \text{ for 1 mole}$$

where N_0 = Avogadro's number
$= 6.022 \times 10^{23}$.

Here, E is inversely proportional to 'r'.

∴ When 'r' (inter ionic distance) = 0, infinite amount of energy will be evolved.

But in actual practice, this does not happen.. Actually, when the inter ionic distance becomes enough small, they begin to repel each other due to the mutual repulsion of electron clouds.

The repulsive force ($P.E_{repulsive}$) increases rapidly as r decreases.

The repulsive forces, according to Born can be given as $P.E_{repul.} = \frac{B'}{r^n}$

Where B' and n are constant as yet undermined characteristic of the ion pair concerned.

Therefore, repulsive forces for a particular ion in a crystal can be written as

$$E_{repul} = \frac{N_0 B}{r^n} \quad \text{— ②} \quad \text{for 1 mole}$$

Where B = repulsive constant and depends upon structure

n = a constant called as Born exponent

Born exponent may be determined from compressibility measurement.

Generally, Born-exponent is taken as 9. But it may vary from 5 to 12 and it is better to use the value for a particular ion in the crystal.

The lattice energy can be given as the sum of these two energies in equn ① and ②.

$$\therefore \; U = \underbrace{-\frac{N_0 A Z^+ Z^- e^2}{4}}_{\text{attractive force}} + \underbrace{\frac{N_0 B}{r^n}}_{\text{Repulsiv effec}} \quad \text{— ③}$$

Differentiating w.r.t. r

$$\frac{dU}{dr} = -\frac{N_0 A Z^+ Z^- e^2}{(-r^2)} + N_0 B \left(-\frac{n}{r^{n+1}}\right)$$

$$\frac{dU}{dr} = +\frac{N_0 A Z^+ Z^- e^2}{r^2} - \frac{n N_0 B}{r^{n+1}} \quad \text{— ④}$$

At equilibrium, $\frac{dU}{dr} = 0$, & $r = r_0$

hence; equation ④ becomes

$$0 = \frac{N_0 A Z^+ Z^- e^2}{r_0^2} - \frac{n N_0 B}{r_0^{n+1}}$$

or, $$\frac{n N_0 B}{r_0^{n+1}} = \frac{N_0 A Z^+ Z^- e^2}{r_0^2}$$

or, $$B = \frac{\cancel{N_0} A Z^+ Z^- e^2}{r_0^2} \times \frac{r_0^{n+1}}{n \cancel{N_0}}$$

$$B = \frac{A Z^+ Z^- e^2}{n} r_0^{n-1} \quad — ⑤$$

Putting the value of 'B' in equn. ③

$$U = -\frac{N_0 A Z^{\oplus} Z^{\ominus} e^2}{r_0} + \frac{N_0}{\cancel{r_0^n}} \times \frac{A Z^+ Z^- e^2 \cancel{r_0^{n-1}}}{n} \atop r_0$$

Here $r = r_0$

$$\therefore U = -\frac{N_0 A Z^+ Z^- e^2}{\text{[redacted]}\ r_0}\left(1 - \frac{1}{n}\right) \quad — ⑥$$

This is called Born–Lande equn

using SI units equn ⑥ becomes

$$U = -\frac{N_0 A Z^+ Z^- e^2}{4\pi \epsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

Group - B (ORGANIC)

Q→ Write a note on Hyperconjugation.

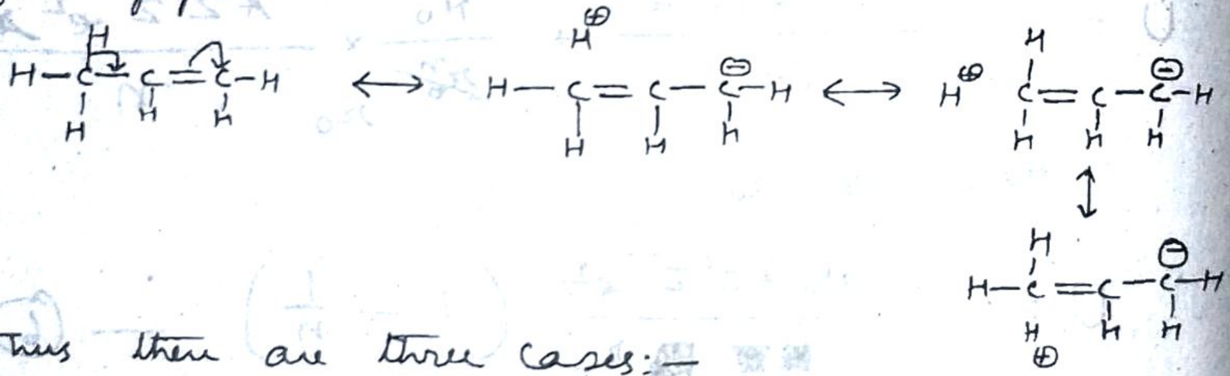
Answer→ This is also called as Baker-Nathan effect (1935) or No bond resonance.

The overlap of π-orbital with π-orbital or π-orbital with p (vacant or filled) orbital gives rise to conjugation. But overlap of σ-orbital with π-orbital or σ-orbital with p (vacant or incomplete) orbital gives rise to hyperconjugation. σ-orbital generally involves C—H or C—X (X = F or Cl) bond.

Necessary conditions of Hyperconjugation:-

1. Compound should have at least one sp^2-hybrid carbon
2. α-carbon w.r.t sp^2-hybrid carbon should have at least one hydrogen atom

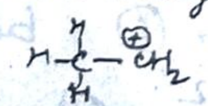
Following examples explains the Phenomenon of hyperconjugation.



Thus there are three cases:-

Case I → σ(C—H), π conjugation

case II → σ(C—H), +ve charge (vacant p-orbital) conjugation

eg 

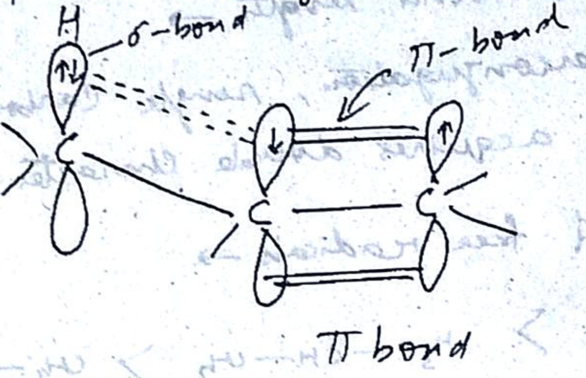
$H-\overset{H}{\underset{H}{C}}-\overset{\oplus}{C}H_2$

Case III → σ(C—H), odd electron (incomplete p-orbital) conjugation

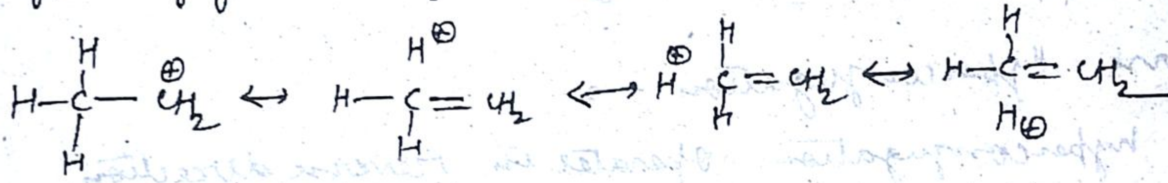
eg $CH_3-\dot{C}H_2$

It has been observed that
Number of resonating structures = No. of α-hydrogen +1

The orbital picture of hyperconjugation can be given by



Isovalent Hyperconjugation → Hyperconjugation in which resonating structures possess, same number of Co-valent bond, it is known as Isovalent hyperconjugation. eg



$$H-\underset{H}{\overset{H}{C}}-\overset{\oplus}{C}H_2 \leftrightarrow H-\underset{H}{\overset{H^{\oplus}}{C}}=CH_2 \longleftrightarrow \overset{\oplus}{H}\ \underset{H}{\overset{H}{C}}=CH_2 \leftrightarrow H-\underset{H^{\ominus}}{\overset{H}{C}}=CH_2$$

The Properties which can be explained by hyperconjugation are as follows:—

a) stability of alkene
b) Carbon- Carbon bond length
c) stability of free radicals
d) Electron donating Power of alkyl gr in alkyl-benzene

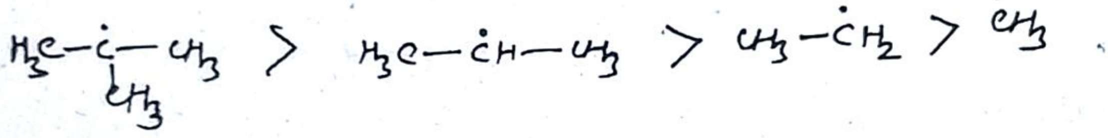
a) stability of alkenes → It has been found that

Tetrasubstituted > Trisubstituted > Disubstituted > mono substituted > $CH_2=CH_2$

b) Carbon–Carbon bond length →

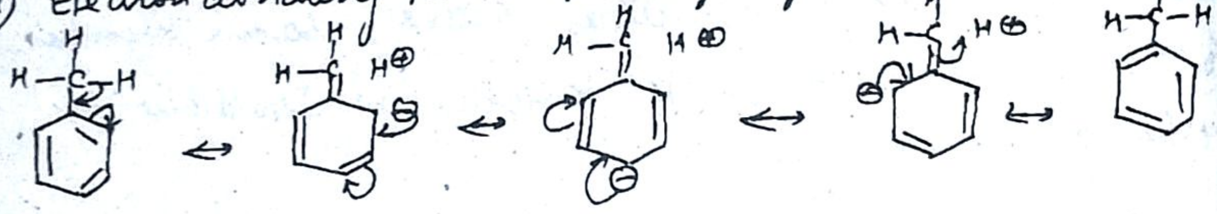
Due to hyperconjugation, single carbon–carbon bond in alkane acquires double character and vice-versa

c) Stability of free radicals →



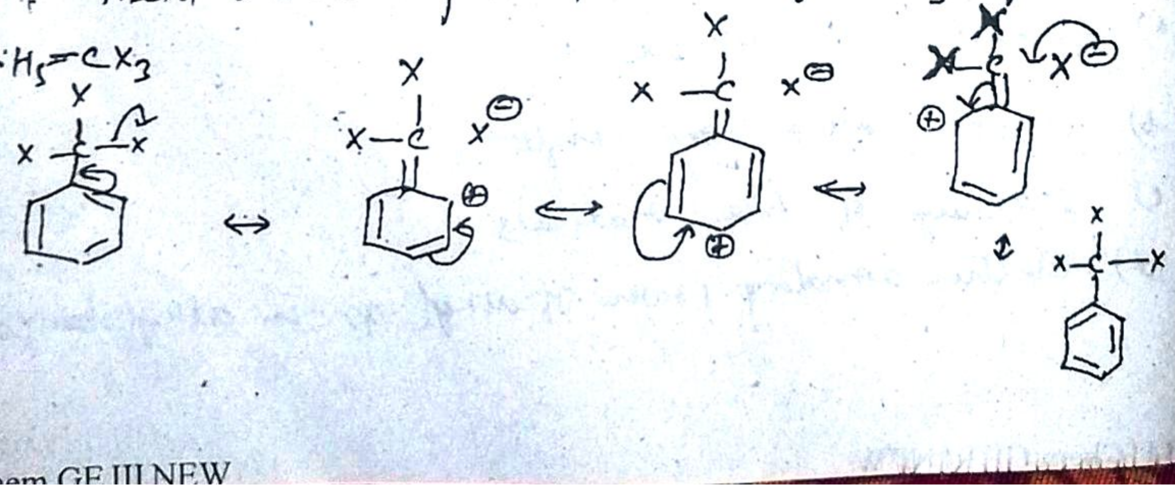
$H_3C-\dot{C}(CH_3)-CH_3 > H_3C-\dot{C}H-CH_3 > CH_3-\dot{C}H_2 > \dot{C}H_3$

d) Electron donating power of alkyl group in alkylbenzene



Reverse Hyperconjugation →

If hyperconjugation operates in reverse direction, it is called as reverse hyperconjugation. eg. meta directing influence of CX_3 group in $C_6H_5-CX_3$



Q. Discuss Preparation, geometry, hybridisation, stability and imp reactions of Free radical.

Answer → Definition → Any species containing one or more, odd (unpaired) electron may be called as Free radical. It may be charged or neutral.

eg $_{11}Na$ 2, 8, 1 It has one odd electron hence, it may be termed as free radical.

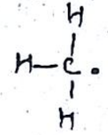
$H_3C\cdot$ → Methyl free radical

$\underset{..}{\dot{N}} = \underset{..}{\ddot{O}}$ contains odd no. of electrons hence, free radical.

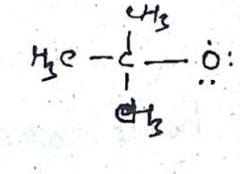
classification →

1. On the basis of presence of odd electron on a particular atom:—

eg



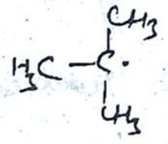
$H{-}\overset{H}{\underset{H}{C}}\cdot$ → Carbon free radical



$H_3C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}\ddot{\underset{..}{O}}:$ → oxygen free radical

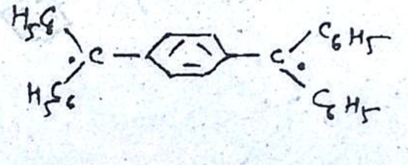
2. On the basis of no. of unpaired electrons:—

eg mono radical



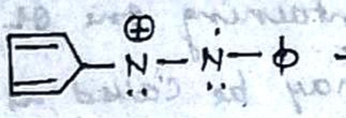
$H_3C{-}\overset{CH_3}{\underset{CH_3}{C}}\cdot$ (t-Butyl free radical)

diradical

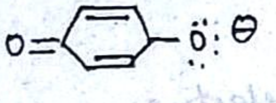


3. On the basis of nature of charge:-

eg $H_3C\cdot$ → neutral free radical



→ Cationic free radical



→ Anionic free radical

4. Spectroscopic classification →

Mono radicals → $H_3C\cdot$ Spin will be $+\frac{1}{2}$ or $-\frac{1}{2}$

Hence, two peaks are obtained, and called as doublets

Diradicals → Two unpaired electrons are there

↑ ↑ $+\frac{1}{2}$ $+\frac{1}{2}$ $= +1$

↑ ↓ $+\frac{1}{2}$ $-\frac{1}{2}$ $= 0$

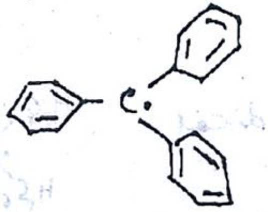
↓ ↓ $-\frac{1}{2}$ $-\frac{1}{2}$ $= -1$

Here three peaks are obtained, hence called as triplets.

5. Based on stability.—

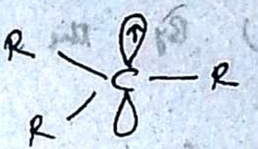
Short lived free radical eg $\cdot CH_3$

Stable free radical eg

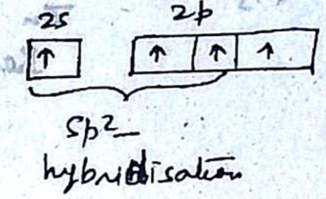


Geometry and hybridisation :—

Free radical is sp^2 hybridised and is planar, Bond angle = 120°



The odd electron is in p-orbital which is not hybridised



Stability →

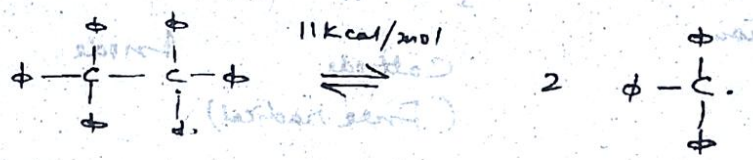
Greater the delocalisation of odd electron, greater will be the stability

$$3^\circ > 2^\circ > 1^\circ > \cdot CH_3$$

Preparation :—

A) Preparation of short lived free radical →

i) due to homolytic fission which is caused by collision



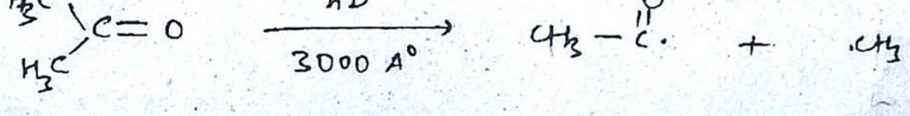
$$\phi_3C-C\phi_3 \underset{}{\overset{11\,kcal/mol}{\rightleftharpoons}} 2\ \phi_3C\cdot$$

Hexa phenyl ethane Triphenyl methyl radical

ii) By thermal decomposition →

$$Pb(CH_3)_4 \xrightarrow[600-800^\circ C]{Ni} Pb + 4\ \cdot CH_3$$

iii) By Photo chemical fission of a bond →



$$(H_3C)_2C=O \xrightarrow[3000\,A^\circ]{h\nu} CH_3-\overset{O}{\overset{\|}{C}}\cdot + \cdot CH_3$$

B) Preparation of long lived free radical →

a) By the action of metal on halide.

$$2\,(C_6H_5)_3CCl \xrightarrow[\text{Zn in Benzene}]{\text{Ag, Hg,}} \underset{\text{Colourless}}{(C_6H_5)_3C:C(C_6H_5)_3}$$

$$\upharpoonleft\downharpoonright$$

$$\underset{\text{(Yellow)}}{(C_6H_5)_3C\cdot}$$

b) By reduction of triphenyl carbonium ion salt with Titanous chloride →

$$(C_6H_5)_3C^{\oplus} \xrightarrow[\text{or } V^{++}]{Ti^{++}} (C_6H_5)_3C\cdot + Ti^{+++}\ (\text{or } V^{+++})$$

c) By Kolbe's electrolysis →

$$\underset{\text{aq. solution}}{CH_3-\overset{O}{\overset{\|}{C}}-O\,Na} \xrightleftharpoons{\text{electrolysis}} \underset{\substack{\text{Cathode}\\\text{(Free radical)}}}{CH_3-\overset{O}{\overset{\|}{C}}-\ddot{\underset{..}{O}}\cdot} + \underset{\text{Anode}}{Na^{\oplus}}$$

Reactions of Free radical :—

1. Chain reaction
2. Disproportionation rxn
3. Addition "
4. Rearrangement "
5. Decomposition "
6. Oxidation "
7. Reduction "

1. Chain reaction :—

Initiation → $Cl_2 \xrightarrow{h\nu} 2Cl\cdot$

Propogation → $R-H + \cdot Cl \rightarrow R\cdot + HCl$

$R\cdot + Cl_2 \rightarrow R-Cl + Cl\cdot$

Termination → $\cdot Cl + \cdot Cl \rightarrow Cl_2$

$R\cdot + \cdot Cl \rightarrow R-Cl$

$R\cdot + \cdot R \rightarrow R-R$

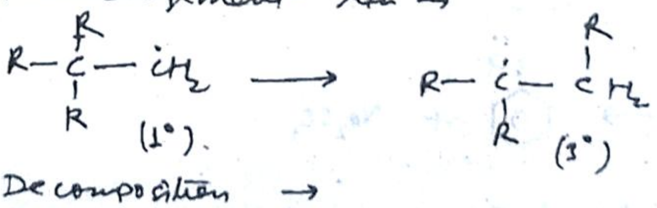
2. Disproportionation rxn. →

$2\ CH_3-\dot{C}H_2 \longrightarrow CH_2=CH_2 + CH_3-CH_3$

3. Addition rxn →

$R\cdot + >C=C< \longrightarrow R-\overset{|}{\underset{|}{C}}-\overset{\cdot}{\underset{|}{C}}-$

4. Rearrangement rxn →



$R-\overset{R}{\underset{R}{C}}-\dot{C}H_2 \longrightarrow R-\underset{R}{\dot{C}}-\overset{R}{C}H_2$

(1°) (3°)

5. Decomposition →

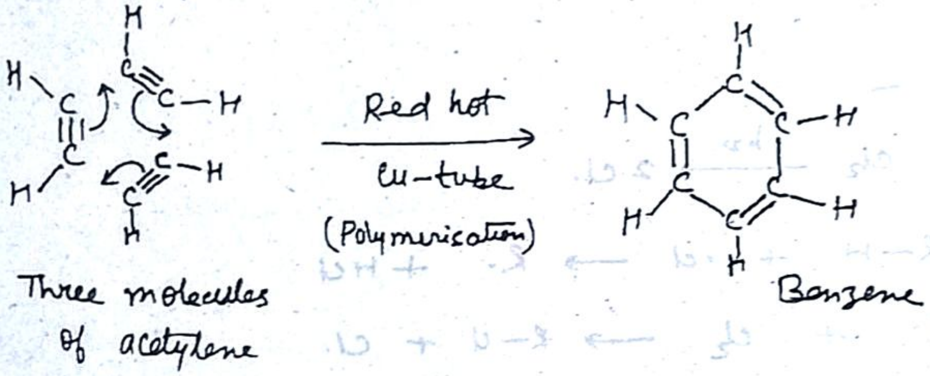
Banzyol free radical

Q Discuss the preparation of benzene

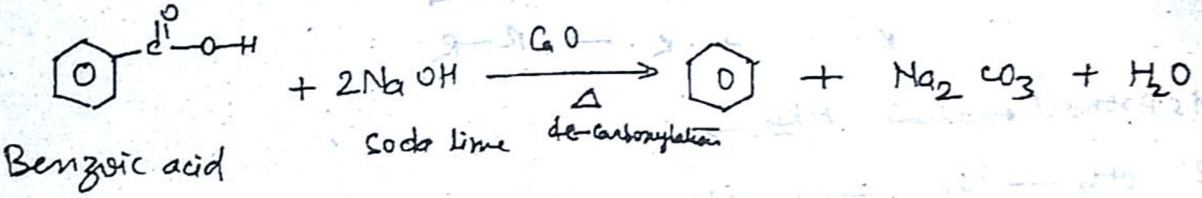
Ans → Benzene can be prepared by following methods

1. From phenol →

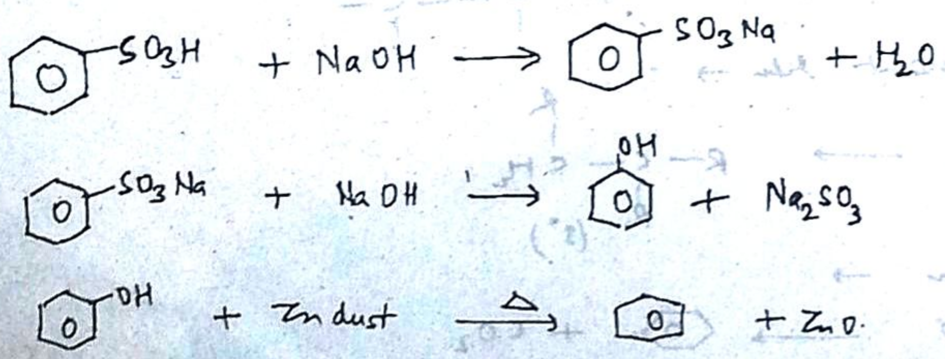
2. From acetylene →



3. From Benzoic acid →



4. From Benzene sulphonic acid →



Q What are electrophiles ?

Ans → Electrophile word has two parts electron + phillus Phillus mean attracting or loving. ie species which can attract -ve charge (there is -ve charge on electron). are called electrophiles.

Electrophiles are of two types

A) +vely charge species → eg $H^{\oplus}$, $H_3O^{\oplus}$, $\overset{\oplus}{N}O_2$, $\overset{\oplus}{S}O_3H$ etc

B) Neutral species with incomplete octet → eg $AlCl_3$, BF_3, CH_2

Substitution

Reactions taking place with the help of electrophiles are called electrophilic substitution reaction.

Q. What are nucleophiles ?

Ans → Nucleophile word has two parts nucleus + Phillus. Thus nucleophiles are species which attract +ve charge. Nucleophiles are of t types

A) -vely charge species → eg $^{\ominus}OH$, $\overset{\ominus}{O}R$, $\overset{\ominus}{C}N$, $X^{\ominus}$ etc

B) Neutral species having lone pair of electrons → eg $H_2\underset{\cdot\cdot}{\ddot{O}}$, $R-\underset{\cdot\cdot}{\ddot{O}}-H$, $R-\underset{\cdot\cdot}{\ddot{O}}-R$, $R-\ddot{N}H_2$ etc.

C) Ambident nucleophiles → Nucleophiles which can attack through two or more atoms eg

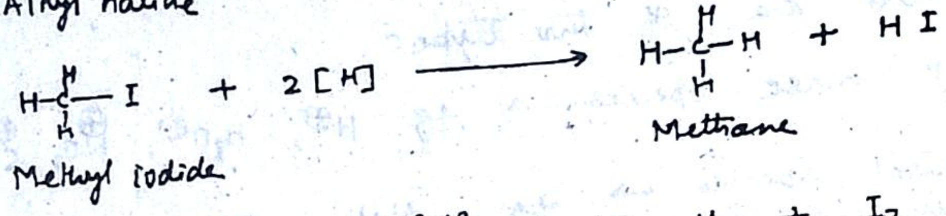
R–CN cyanide
R–NC iso cyanide

Substitution reactions which takes place with the help of nucleophiles are called nucleophilic substitution reaction.

General methods of preparation of alkanes

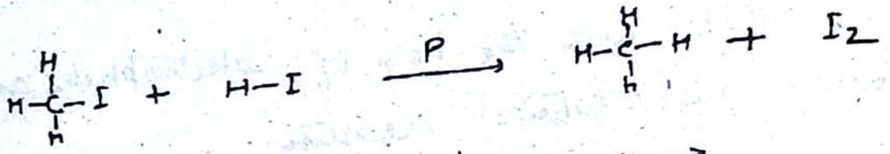
1. By reduction of alkyl halides →

$$\underset{\text{Alkyl halide}}{R-X} + 2[H] \xrightarrow[\text{Zn/Acetic acid}]{\text{Zn-Cu/alcohol}} \underset{\text{Alkane}}{R-H} + H-X$$



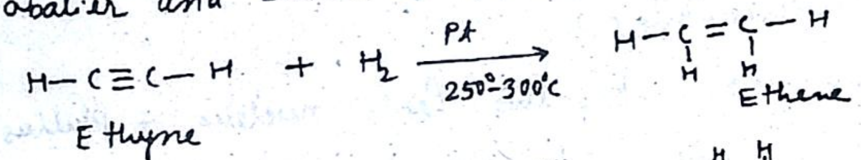
$$\underset{\text{Methyl iodide}}{CH_3-I} + 2[H] \longrightarrow \underset{\text{Methane}}{CH_4} + HI$$

$$R-I + H-I \xrightarrow[\text{423 K}]{\text{Red P}} R-H + I_2 .$$

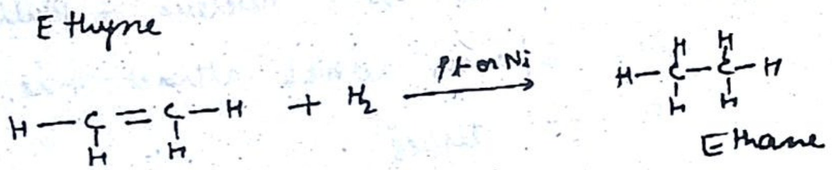


$$CH_3-I + H-I \xrightarrow{P} CH_4 + I_2$$

2. Sabatier and Senderen's process →



$$\underset{\text{Ethyne}}{H-C\equiv C-H} + H_2 \xrightarrow[250^\circ-300^\circ C]{Pt} \underset{\text{Ethene}}{H_2C=CH_2}$$

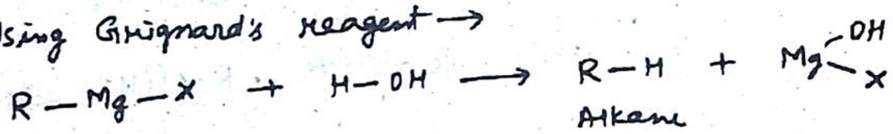


$$H_2C=CH_2 + H_2 \xrightarrow{\text{Pt or Ni}} \underset{\text{Ethane}}{CH_3-CH_3}$$

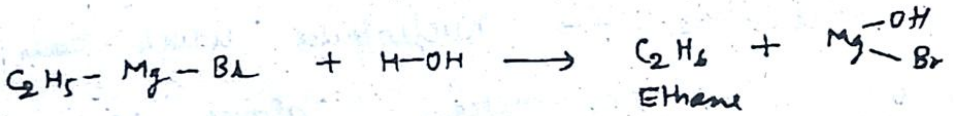
3. Wurtz reaction →

$$R-X + 2\,Na + X-R \xrightarrow[\text{Ether}]{\text{Dry}} \underset{\text{Alkane}}{R-R} + 2\,NaX$$

4. Using Grignard's reagent →

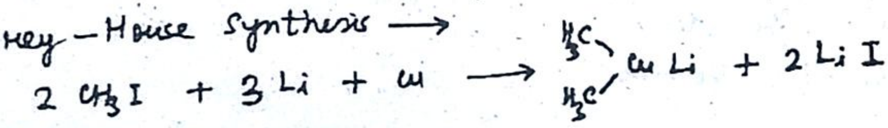


$$R-Mg-X + H-OH \longrightarrow \underset{\text{Alkane}}{R-H} + Mg(OH)X$$

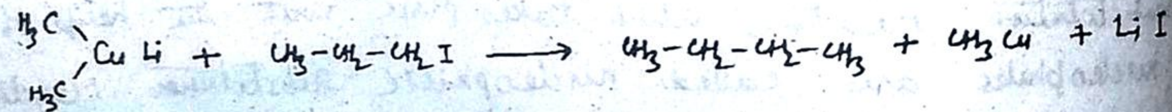


$$C_2H_5-Mg-Br + H-OH \longrightarrow \underset{\text{Ethane}}{C_2H_6} + Mg(OH)Br$$

5. Corey-House synthesis →



$$2\,CH_3I + 3\,Li + Cu \longrightarrow (H_3C)_2CuLi + 2\,LiI$$



$$(H_3C)_2CuLi + CH_3-CH_2-CH_2I \longrightarrow CH_3-CH_2-CH_2-CH_3 + CH_3Cu + LiI$$

Group - C (PHYSICAL)

Q → Write down the Postulates of Kinetic Theory of Gases. Derive the Kinetic Gas equation $PV = \frac{1}{3} m N \overline{c^2}$

Ans → Postulates are as follows:—

1. Gases are composed of very small Particles called as molecules. The volume of one molecule of the gas is considered as negligible in comparison to the total volume of the gas.

2. The gas molecules are in constant random motion colliding with each other and also with the walls of the container. These gas molecules possess different molecular velocities.

3. The number of collisions per sec per cc of the gas is called collision frequency.

4. The distance covered by a molecule between two successive collisions is called Free Path and average of such Paths is called Mean Free Path.

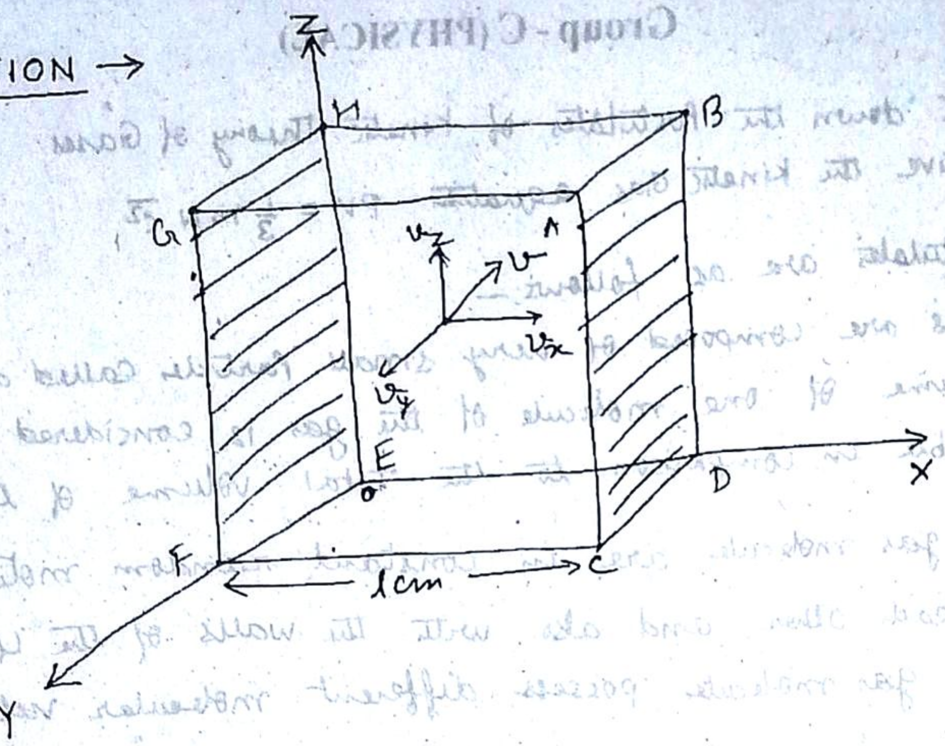
5. The gas molecules do not attract or repel each other. ie intermolecular forces are absent.

6. The collisions of gas molecules are perfectly elastic in nature ie there is no loss of energy after collisions.

7. The Pressure of gas inside the container is due to bombardment of gas molecules on the walls of the container

8. Average kinetic energy of the gas molecules is a measure of absolute temperature of the gas.

DERIVATION →



Let us consider 'N' molecules of a gas are enclosed in a cubical vessel having length "l cm" of each side.

Let, mass of each molecule is "m" and are moving with different velocities in random directions.

Let us consider a molecule whose velocity is v cm/sec in the direction as shown in fig.

This velocity v can be resolved in three ⊥ar components v_x, v_y & v_z parallel to three coordinate axes x-, y- & z respectively such that

$$v^2 = v_x^2 + v_y^2 + v_z^2 \quad ①$$

Consider the X- component of the velocity which is v_x.

With velocity v_x the molecules collides with wall ABCD.

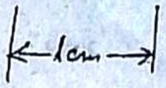
Hence momentum before collision = mv_x

after collision it returns in opposite direction with same velocity.

Hence momentum after collision = $-mv_x$

∴ change in momentum $= mv_x - (-mv_x) = 2mv_x$

A molecule covers "l cm" distance before a collision. and also covers a distance "l cm" after collision.



i.e for one collision it covers "$2l$" cm distance.

∴ For $2l$ cm distance covered no. of collision $= 1$

∴ " 1 cm " " " " " $= \frac{1}{2l}$

∴ " v_x cm " " " " " $= \frac{v_x}{2l}$

(∵ v_x cm is the distance covered in 1 sec)

∴ No of collisions in 1 sec $= \frac{v_x}{2l}$.

∴ Total momentum change in 1 sec by one molecule on wall ABCD $= \cancel{2}mv_x \times \frac{v_x}{\cancel{2}l}$

$= \frac{mv_x^2}{l}$

∴ Total " " " 1 sec " one molecule on two opposite walls along X-axis $= \frac{2mv_x^2}{l}$

Similarly, we can write,

Total momentum change in 1 sec by one molecule on two opposite walls along Y-axis & Z-axis are $\frac{2mv_y^2}{l}$ & $\frac{2mv_z^2}{l}$ respectively.

∴ Total momentum change by 1 molecule in 1 sec due to collision on all the six faces $= \frac{2mv_x^2}{l} + \frac{2mv_y^2}{l} + \frac{2mv_z^2}{l}$

$= \frac{2m}{l}(v_x^2 + v_y^2 + v_z^2)$

$= \frac{2mv^2}{l}$ (using equ ①)

Different molecules are moving with different velocities

Let 1st molecule has velocity c_1

2nd " " " c_2 and so on.

Total momentum change in 1 sec by all the molecules

$$= \frac{2mc_1^2}{l} + \frac{2mc_2^2}{l} + \cdots\cdots + \frac{2mc_n^2}{l}$$

$$= \frac{2m}{l}(c_1^2 + c_2^2 + \cdots\cdots + c_n^2)$$

$$= \frac{2m}{l} \times N\frac{(c_1^2 + c_2^2 + \cdots\cdots + c_n^2)}{N}$$

$$= \frac{2m}{l} \times N \times \overline{c^2}$$ where $\overline{c^2}$ is called Mean square velocity

Now from Newton's 2nd Law of motion we know that "Rate of change of momentum is equal to the force acting on the body."

Hence Force $(F) = \frac{2mN}{l}\overline{c^2}$

Also, Pressure $(p) = \frac{\text{Force}}{\text{Area}}$

$$p = \frac{\frac{2mN}{l}\overline{c^2}}{6l^2}$$ where $6l^2$ = Surface Area of cube

$$p = \frac{2mN}{l} \times \frac{1}{6l^2}\overline{c^2}$$

$$p = \frac{1}{3}\frac{mN}{l^3}\overline{c^2}$$

$$p = \frac{1}{3}\frac{mN}{V}\overline{c^2}$$ [∵ $V = l \times l \times l$

or $\boxed{pV = \frac{1}{3}mN\overline{c^2}}$ Required equation

Q Derive relations between K_p, K_c and K_x

Answer → Let us consider a reversible reaction

$$aA + bB \rightleftharpoons lL + mM \quad \text{— ①}$$

A and B are reactants
L and M are Products

a = no of moles of A
b = " " " " B
l = " " " " L
m = " " " " M.

using Law of mass action

$$K_p = \frac{p_L^l \cdot p_M^m}{p_A^a \; p_B^b} \quad \text{— ②}$$

$$K_c = \frac{[L]^l \; [M]^m}{[A]^a \; [B]^b} \quad \text{— ③}$$

$$K_x = \frac{x_L^l \; x_M^m}{x_A^a \; x_B^b} \quad \text{— ④}$$

For an ideal gas $PV = nRT$

or, $P = \frac{n}{V} RT$

or, $P = CRT$ where C = Concentration

$\therefore$ $C = \frac{P}{RT}$

or $C_i = \frac{P_i}{RT}$ — ⑤

using equation ⑤,

$$C_L = [L] = \frac{P_L}{RT}$$

$$C_M = [M] = \frac{P_M}{RT}.$$

$$C_A = [A] = \frac{P_A}{RT}$$

$$C_B = [B] = \frac{P_B}{RT}$$

Putting these values in equation ③

$$K_c = \frac{\left(\frac{P_L}{RT}\right)^l \left(\frac{P_M}{RT}\right)^m}{\left(\frac{P_A}{RT}\right)^a \left(\frac{P_B}{RT}\right)^b}$$

$$\text{or, } K_c = \frac{P_L^l \; P_M^m}{P_A^a \; P_B^b} \times \frac{\left(\frac{1}{RT}\right)^l \left(\frac{1}{RT}\right)^m}{\left(\frac{1}{RT}\right)^a \left(\frac{1}{RT}\right)^b}$$

$$\text{or, } K_c = K_p \times \frac{\left(\frac{1}{RT}\right)^{l+m}}{\left(\frac{1}{RT}\right)^{a+b}}$$

$$\text{or } K_c = K_p \times \left(\frac{1}{RT}\right)^{(l+m)-(a+b)}$$

$$\text{or, } K_c = K_p \times \left(\frac{1}{RT}\right)^{\Delta n} \qquad \Delta n = (l+m)-(a+b)$$

$$\text{or, } K_c = K_p \times \frac{1}{(RT)^{\Delta n}}$$

$$\therefore K_p = K_c (RT)^{\Delta n} \text{ —— } ⑥$$

Relation between K_p and K_x →

We know that $p_i = x_i \times P$

p_i = Partial pressure of ith component

x_i = mole fraction ,, ,,

P = Total pressure

$p_A = x_A \times P$

$p_B = x_B \times P$

$p_L = x_L \times P$

$p_M = x_M \times P$

Putting these values in equn ②

$$K_p = \frac{(x_L \times P)^l \, (x_M \times P)^m}{(x_A \times P)^a \, (x_B \times P)^b}$$

$$K_p = \frac{x_L^l \, x_M^m}{x_A^a \, x_B^b} \times \frac{P^l \cdot P^m}{P^a \cdot P^b}$$

or $K_p = K_x \times P^{(l+m)-(a+b)}$

or, $\boxed{K_p = K_x \times P^{\Delta n}}$ — ⑦

Relation between K_c and K_x →

Putting the value of K_p from equation ⑥ in equn ⑦

$$K_c \, (RT)^{\Delta n} = K_x \cdot P^{\Delta n}$$

or, $K_c = K_x \dfrac{P^{\Delta n}}{(RT)^{\Delta n}}$

or, $K_c = K_x \left(\dfrac{P}{RT}\right)^{\Delta n}$

or, $K_c = K_x \left(\dfrac{\cancel{P}}{\cancel{P}V}\right)^{\Delta n}$

or $K_c = \dfrac{K_x}{V^{\Delta n}}$

∴ $\boxed{K_x = K_c \, V^{\Delta n}}$ — ⑧

Q What are Electrolytes?

OR

Define electrolyte.

Ans → The substances which are decomposed by passing electricity and conduct electricity in their molten state or in their aqueous solution state, are called electrolytes.

eg – Most of the acids, bases and salts, like sulphuric acid (H_2SO_4), acetic acid (CH_3COOH), Sodium hydroxide ($NaOH$), Magnesium hydroxide [$Mg(OH)_2$], sodium chloride ($NaCl$) etc.

The substances which do not exhibit this type of property are called non-Electrolyte. eg Benzene (C_6H_6), Carbon tetrachloride (CCl_4) etc.

Q Define electrolysis.

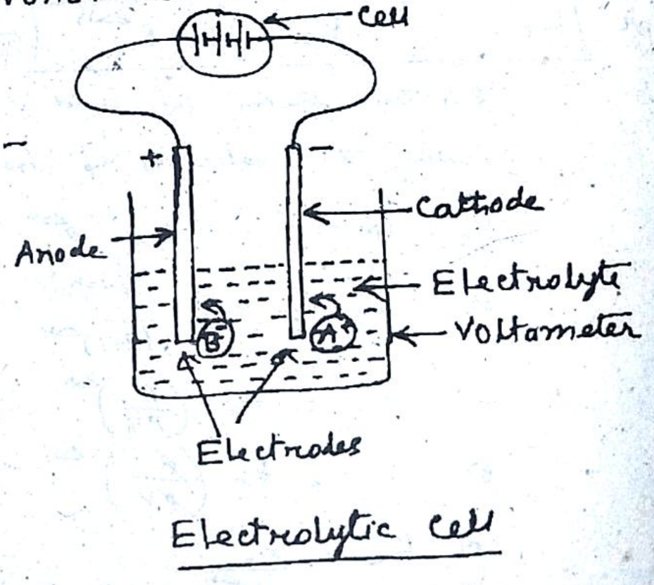
Ans → The phenomenon, in which, substances are decomposed by passing electricity and conduct electricity in their molten state or in their aqueous solution state, is called electrolysis.

Here, two metallic or non-metallic electrodes are used. The container is called Voltometer and entire arrangement is called electrolytic cell.

Cell reaction is as follows:–

Let, the electrolyte is AB

Then $AB \xrightleftharpoons{\text{Electricity}} \underset{\text{Cation}}{A^{\oplus}} + \underset{\text{Anion}}{B^{\ominus}}$



Electrolytic cell

At anode →

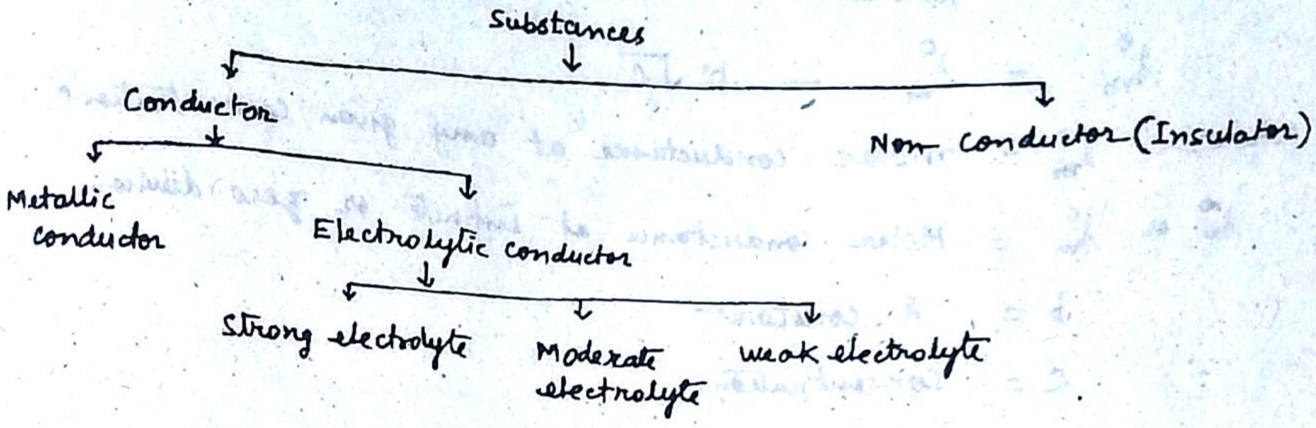
$B^{\ominus} \longrightarrow B + e$

At cathode →

$A^{\oplus} + e \longrightarrow A$

Q Discuss the types of electrolytes?
or
what do you understand by strong, moderate and weak electrolytes?

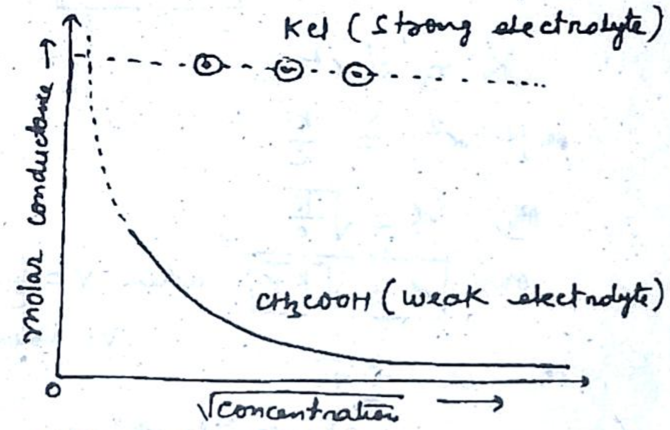
Ans →



Strong electrolyte → Strong electrolytes are those electrolytes which are supposed to be completely dissociated at almost all concentrations. ie. with increase in dilution there is no appreciable change in the conductance of electrolyte. eg KOH, NaOH, KCl etc.

Weak electrolyte → Weak electrolytes are those electrolytes whose conductances increase with increase in dilution. ie with increase in dilution, the dissociation of weak electrolyte increases. eg CH_3COOH, NH_4OH etc.

The variation of conductance of strong electrolyte and weak electrolyte can be shown with the help of given graph.



Moderate electrolyte →
Electrolytes which exhibit behaviour between strong and weak electrolyte are called moderate electrolytes.

The behaviour of strong electrolyte can be explained by 'Debye-Huckel-Onsagar equation' which is true for low concentration. Equⁿ is as follows:—

$$\lambda_m^c = \lambda_m^0 - b\sqrt{c}$$

where, λ_m^c = molar conductance at any given concentration 'c'.

λ_m^∞ or λ_m^0 = Molar conductance at infinite or zero dilution.

b = A constant

c = Concentration.

The behavior of weak electrolytes can be explained by 'ostwald dilution law'. Equation is as follows:-

$$\boxed{K = \frac{c\alpha^2}{1-\alpha}}$$

where,

K = Equilibrium constant

α = Degree of ionisation or dissociation

c = Concentration

for weak electrolytes,

$\alpha << 1$ ie $\boxed{1-\alpha \cong 1}$

$\therefore$ $K = c\alpha^2$

or, $\alpha^2 = \frac{K}{c}$

or, $\alpha = \sqrt{\frac{K}{c}}$

or $\boxed{\alpha = \sqrt{KV}}$ where $V = \frac{1}{c}$

V = volume

ie $\alpha \propto \sqrt{V}$

↖ Proportionality sign.

Q Derive Van der Waal's equation of state

OR

Derive equation of state for real gases.

Ans → The equation of state $PV = RT$ for a perfect gas (Ideal gas) can not describe the behaviour of a real gas. Real gases obey the perfect gas equation only under certain limiting condition ie at high temperature and low pressure.

Ideal gas equation is derived according to kinetic theory of gases which makes two very important assumptions.

(i) Gases are composed of very small particles / called as molecules. The volume of each molecule is considered as negligible in comparison to the total volume of the gas.

(ii) Gas molecules do not attract or repel each other ie intermolecular forces are absent.

However these — assumptions are not true for real gases Idea of mean free path and its verification confirm that gases molecules have definite volume similarly results of Joule-Thomson effect indicate that intermolecular forces are present.

Vander Waal considered these two facts and modified ideal gas equation such that it suited to the real gases.

Hence modified equation is called Van der Waal's equation.

Let us consider certain mass of a real gas at Temp. T.

Let P = Pressure and V = Volume of the real gas.

Now, for a perfect (ideal) gas for same mass.

At same temp, the Pressure and Volume will have different values than that for ...... Ideal gases

Let P_0 = Pressure of the ideal gas

V_0 = Volume " "

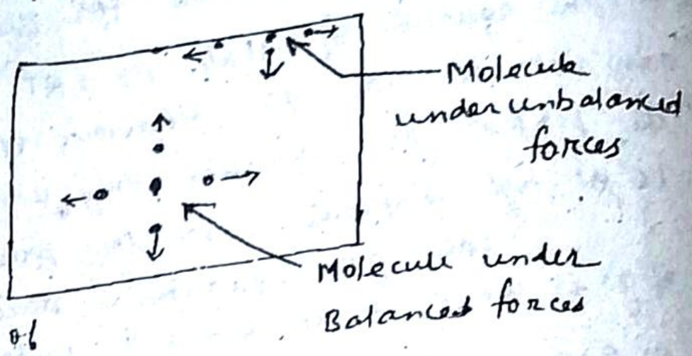
Then, $P_0 V_0 = nRT$ —— ① for n moles

Correction for volume →

Since the volume of molecules in real gases have definite value hence Volume in case of ideal gase will have lesser value and we can write $V_0 = V - b$.

For n moles, $V_0 = V - nb$ —② when b = correction for volume.

Correction for pressure →



Let us consider a gas is enclosed in a container.

Let us consider a molecule which is well inside the bulk of on the volume. This molecule is under balanced forces.

But the molecules which are just near the walls of the container, are under unbalanced forces and strike the walls of container with lesser force (or lesser pressure) in case of real gases.

Hence we can write

$$P_0 = P + f \quad —③$$ where f = correction factor

factor f, depends upon

(a) Force of attraction on a molecule by surrounding molecules

(b) The no of molecules that strike the unit area of the wall per second

Both these factors depend upon the no of molecules present per unit volume of the gas ie density of gas.

Let V volume contains n moles

1 " " $\frac{n}{V}$ moles

$\therefore f \propto \frac{n}{V}$

& $f \propto \frac{n}{V}$

$\therefore f \propto \frac{n^2}{V^2}$

$f = \frac{an^2}{V^2}$ where a = Vander Waal's constant

Eqn ③ is $P_0 = P + \frac{an^2}{V^2}$

Eqn ① is $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$ for n mole

Q. What are Ideal and real gases?
Discuss the deviations of real gases from ideal behaviour.
What are its causes?

Ans → Ideal gas → The gases which obey ideal gas equn ($PV = nRT$) at the condition of all temp. & pressure are called ideal gases.

In case of ideal gases intermolecular forces are absent.

In actual practice there is no ideal gas.

Real gas → The gases which do not obey ideal gas equn are called Real gases.

In case of real gases intermolecular forces are present.

All the available gases to us are real gases.

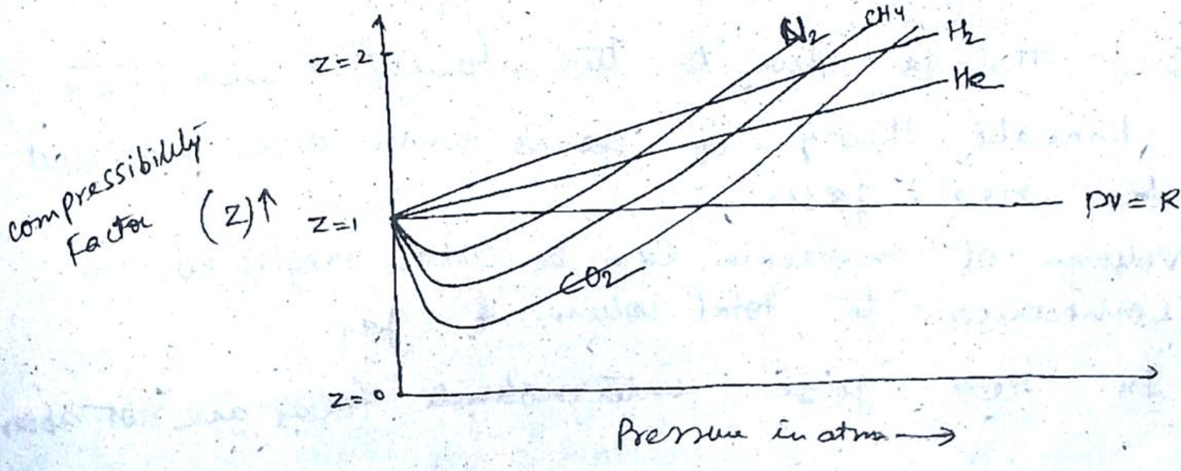
For real gases another equn is used which is called Van der Waal's equn of state.

The Vander Waal's equn is $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

or $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ for 1 mole

However, real gases obey ideal gas equn under certain limiting conditions of high temp & low pressure.

Deviation of real gases from ideal behaviour →



For showing the deviations of real gases from Ideal behaviour we plot a graph between Pressure (in atm) on X-axis and compressibility factor (Z) on Y-axis.

$$Z = \frac{PV}{RT}$$

when $Z = 1$, then, $PV = RT$ ie ideal gas eqn.

From graph it is clear that real gases show two types of deviations.

ⓐ Positive deviation → when value of Z is greater than one

ⓑ Negative deviation → when value of z is less than 1.

Also, we see that H_2 & He also show +ve deviation as the the Pressure is increased but gases like CO_2, CH_4 and N_2 ~~also~~ 1st show negative deviation at lower Pressure but finally they also show +ve deviation at high Pressures.

However all real gases, at very low Pressure show ideal gas behaviour (as $Z=1$)

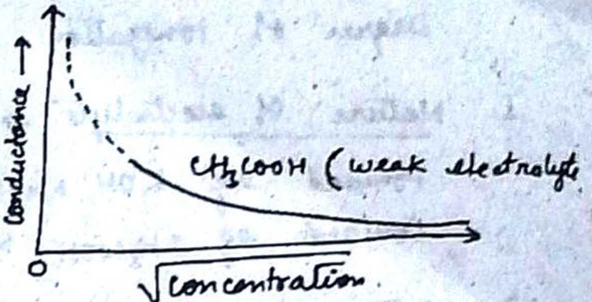
__Causes__:- This is due to two faulty assumptions in kinetic theory of gases which does not suit for real gases

① Volume of molecule can be taken negligible in comparison to total volume of gas

② In real gases intermolecular forces are not absent.

Q What do you understand by term 'degree of ionization'? Explain.

Ans. From graph, it is clear that as the dilution increases, the conductivity increases.
Also, the curve goes parallel to the Conductivity axis ie maximum Value of conductance is not exactly Known.



Hence, a term 'Degree of ionisation' is used. It is denoted by α.

$$\text{and} \quad \alpha = \frac{\text{No of molecules dissociated into ions}}{\text{Total no of molecules taken}}$$

Hence, degree of ionisation may be defined as the fraction of total number of molecules dissociated into ions.

Also, conductivity of a solution is due to presence of ions in solution hence, greater the number of ion, greater will be the conductivity.
hence Equivalent conductivity at a given dilution will be proportional to the no ions in the solution at that given dilution.

ie Equivalent conductance (λ_v) $\propto$ no of molecules dissociated at given dilution —①

ie λ_v $\propto$ no of ions produced at given dilution

and hence λ_∞ $\propto$ no of ions at infinite dilution

[* Infinite dilution is the dilution at which further dissociation of substance stops.]

or λ_∞ $\propto$ Total no of molecules taken —②

$$\text{But} \quad \alpha = \frac{\text{No of molecules dissociated into ions}}{\text{Total no of molecules taken}}$$

$$\alpha = \frac{\lambda_v}{\lambda_\infty} \quad \text{using equations ① \& (II)}$$

Thus, degree of ionisation may also be defined as the ratio of equivalent conductance at given dilution to the equivalent conductance at infinite or zero dilution.
λ_v can be determined by direct measurement of conductance
& λ_∞ can be determined by Kohlrausch's law ie $\lambda_\infty = \lambda_\infty^+ + \lambda_\infty^-$

Factors affecting degree of Ionization

Degree of ionization depends upon following factors:-

1. Nature of electrolyte → Some substances are considerably ionised eg KOH, NaOH etc. however some are partly (poorly) ionised eg CH_3COOH, NH_4OH
2. Nature of solvent → Solvents having high value of dielectric constant are fairly ionizing while solvents having low value of dielectric constant are poorly ionizing.
3. Presence of other solute → Due to presence of another solute the ionization of given solute may be increased or decreased
4. Dilution → Ionization increases with dilution and becomes maximum (unity) at infinite dilution
5. Temperature → Ionization increases with rise in temp.

END.

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