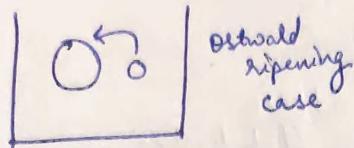
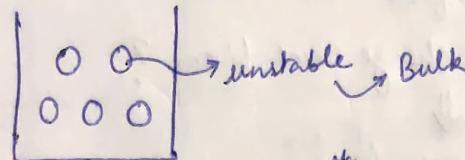


28]

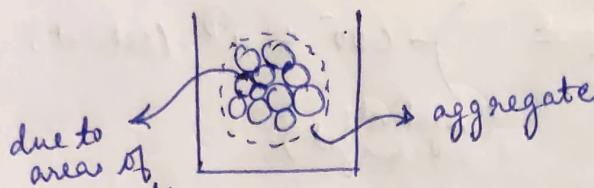
NOTE:



But even with similar size
they are unstable → since
nanoparticles
are inherently unstable



↓ Here, agglomeration
takes place to
make it stable



Surface area decreases as compared to Bulk case
↓ thus more stable

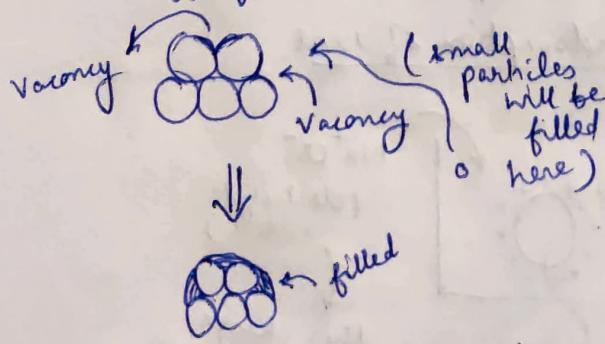
* However,
this is NOT desirable
for us

↓ Since we want to have the properties of nanomaterials

Hence to avoid Ostwald ripening and (more commonly)
↓ agglomeration

* we need to find a way to make nanomaterials stable.

NOTE: Once aggregate is formed



* and once this occurs, redispersion is also not possible

29]

Methods for stabilization

Electrostatic
stabilization

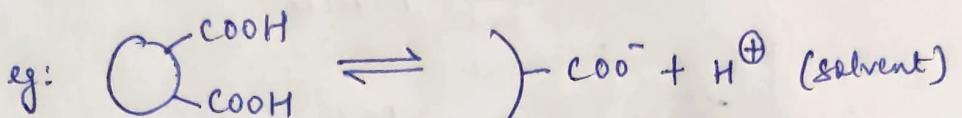
Steric
stabilization

for this there needs
to be charge on
surface

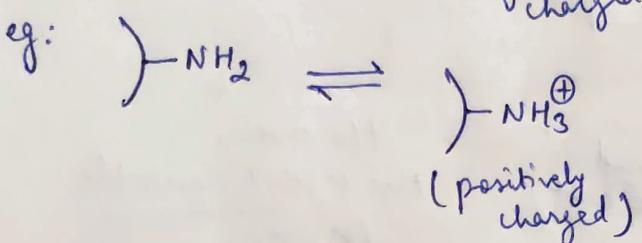
where does this charge come from?



- (1) * Charge comes from
Dissociation of functional group

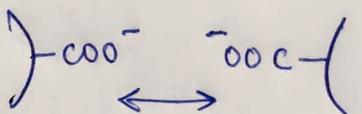


(negatively charged)



Due to charge
generation

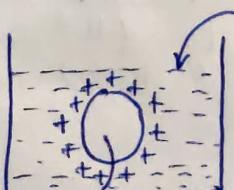
+
particles will not
be able to come
close (thus * preventing
agglomeration)



- (2) Another way by which charge
can develop is

Preferential adsorption of ion

eg:



Some
polymer

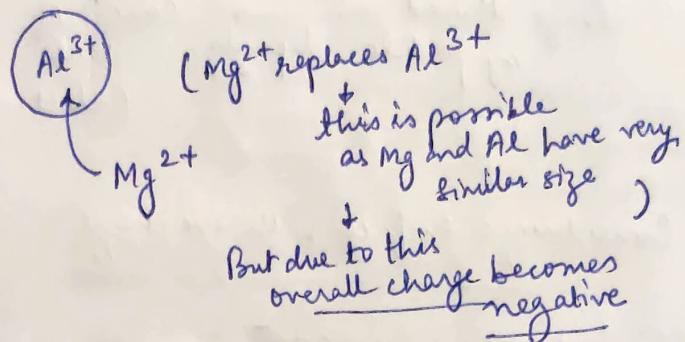
$\text{Na}^+ \text{Cl}^-$
(electrolyte
added)

this charge
will start getting
adsorbed over the
originally neutral surface

(3) Isomorphic Substitution

this refers to
substitution of
an ion ↓
by another ion
of similar size

e.g.:

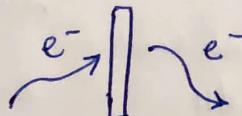


{ NOTE: This method
does not disturb
the overall crystal structure }

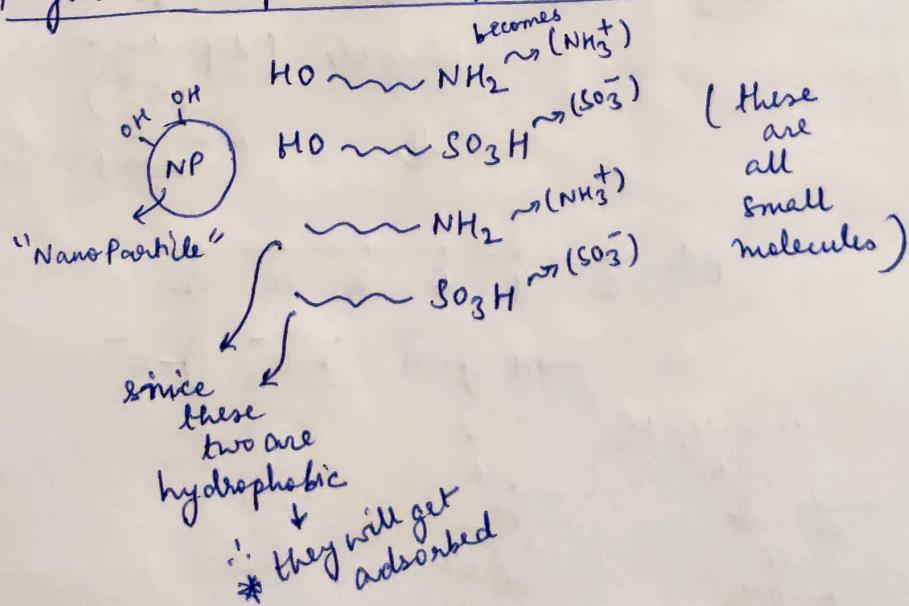
e.g.: $Al_2O_2(OH)_2$ (neutral)

↓
 $AlMgO_2(OH)_2$ (-ve charge)

(4) Accumulation / Depletion of electrons



(5) Physical adsorption of charged molecules



30] We can write Nernst Equation as:

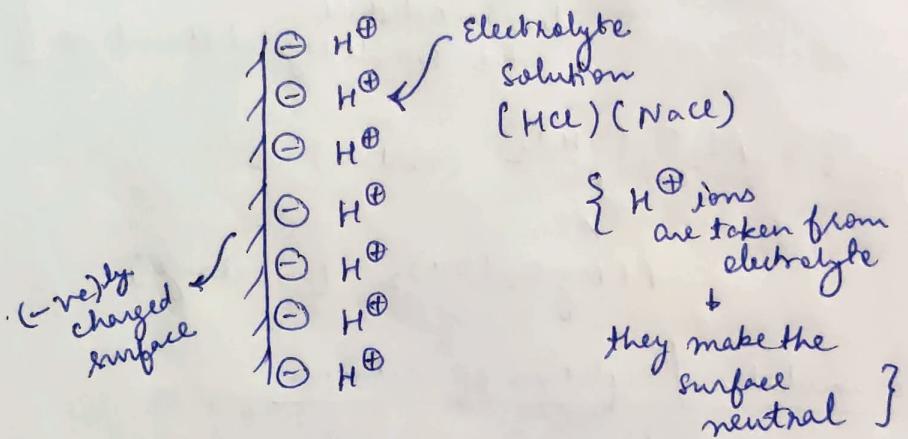
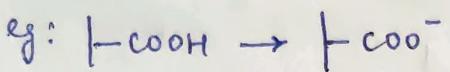
$$E = E_0 + \frac{RgT}{n_f} \ln a$$

$$\Rightarrow E = E_0 - \frac{0.0592}{n} \log a$$

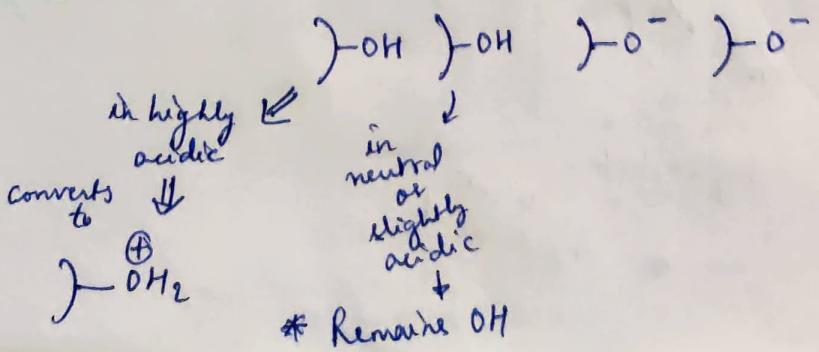
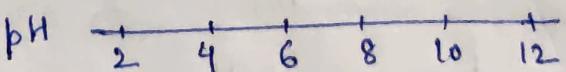
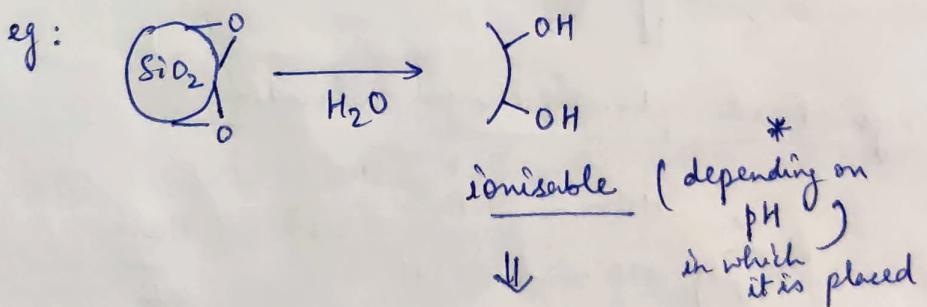
(58 mV for NaCl)

Surface charge attached by particle depends on conc. of ions (electrolyte)

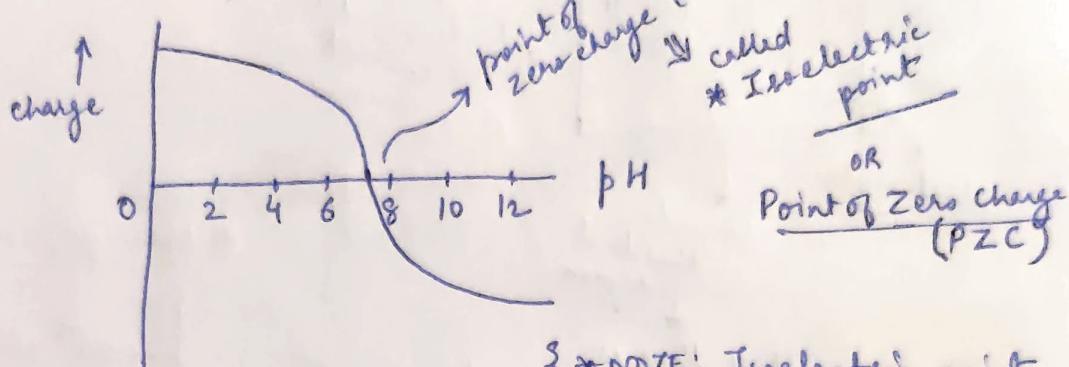
31] Considering a surface with -ve charge:



32]



\therefore We observe the following curve:



{ *NOTE! Isoelectric point is v. important for nanomaterials }

We can modify earlier eqⁿ: as :

$$E = \frac{2.303 R_g T (PZC - pH)}{F}$$

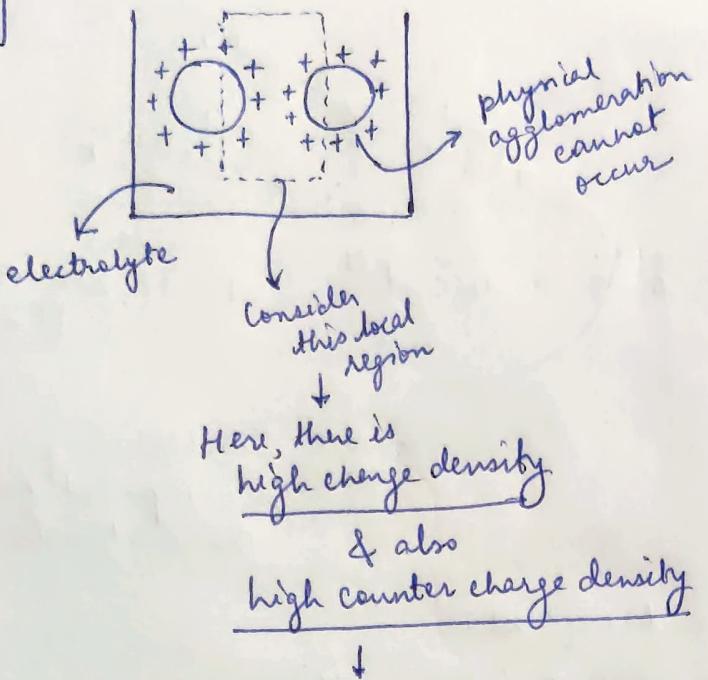
$$\therefore E = 0.06 (PZC - pH)$$

<u>NOTE:</u>	<u>Material</u>	<u>PZC</u>
	W ₀ ₃	0.5
	V ₂ O ₅	1-2
	δ -MnO ₂	1.5
	β -MnO ₂	7.3
	SiO ₂	2.5
	Quartz	3.7
	TiO ₂	6
	TiO ₂ (calcined)	3.2
	ZrO ₂	6.7
	Fe ₂ O ₃	8.6
	ZnO	8
	Al ₂ O ₃	9
	MgO	12

→ This means
that upto a pH of 12
MgO will remain with +ve
charge

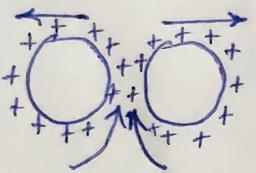
only after 12
will it become
-ve

33]



* Thus, solution will flow into this region to compensate for this charge density

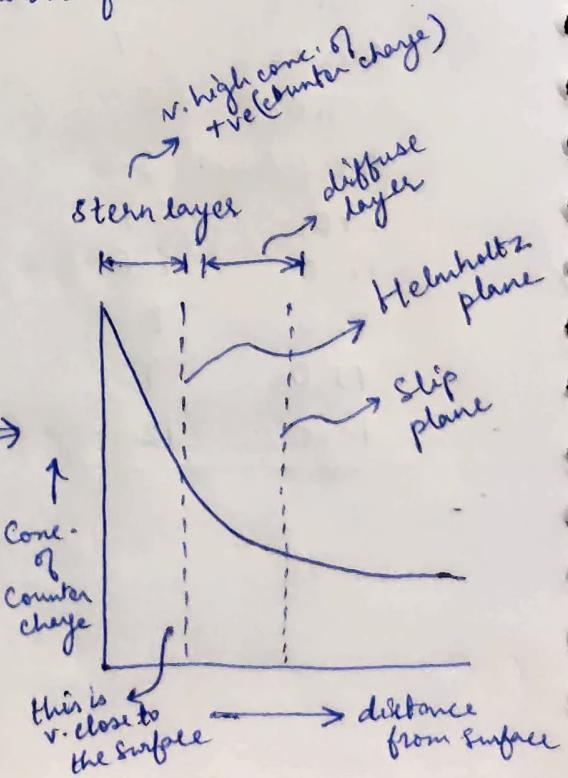
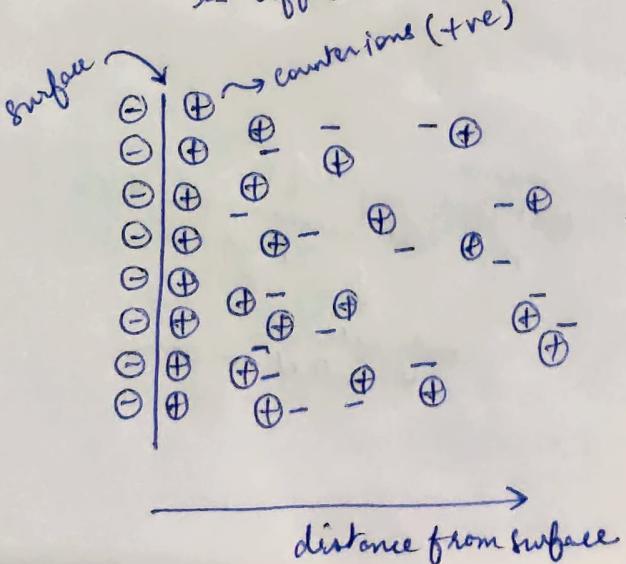
\therefore this will not allow the charged particles to come close



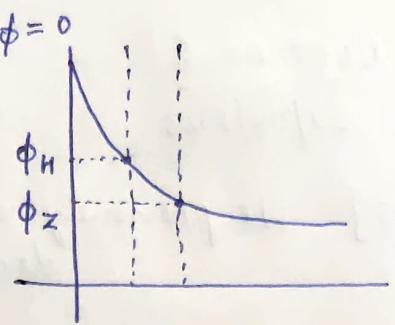
Factors that play a role here are:

- Coulombic force / electrostatic force
- Entropic force / dispersion force
- Brownian motion

34] Also, the distribution of charges is affected



The two layers
(steric & diffuse)
are tightly
bonded to each other
and called
Electrical Double Layer
(EDL)

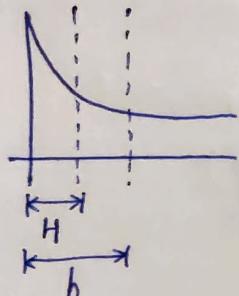


ϕ_H : Helmholtz potential
 ϕ_z : Zeta potential

* If zeta potential is +ve
if -ve then surface also has -ve charge
if zero then surface is at pzc (isoelectric point)

Here we can write:

$$E \propto e^{-K(h-H)}$$



"kappa"
, K = double layer thickness

$\frac{1}{K}$ = Debye-Hückel Screening strength
= Debye length

The value of K can be calculated using:

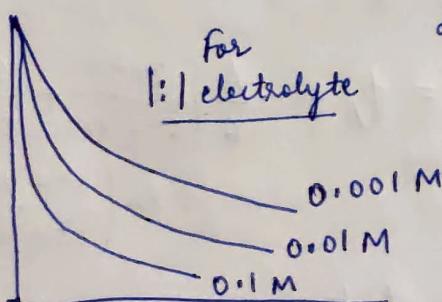
$$K = \sqrt{\frac{F^2 \sum_i c_i z_i^2}{\epsilon_r \epsilon_0 R g T}}$$

* it gives the extent of interaction b/w counter ions

($K = \sim 10 \text{ nm}$
or more)

depends on type/conc. of ion

NOTE:



for 1:1 electrolyte

0.001 M

0.01 M

0.1 M

NOTE:

For 0.001 M

1:1

3:3 2:2

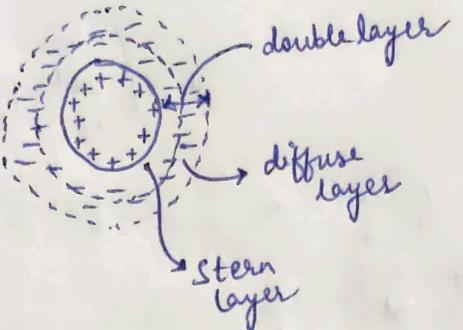
i.e. with increase in valency \rightarrow Debye length decreases

LECTURE 6

29/08/2023

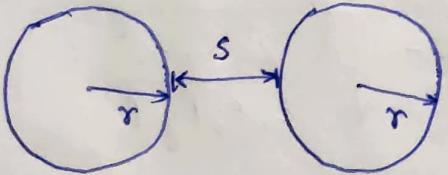
35] We previously discussed double layer thickness

$$\text{given by: } K = \sqrt{\frac{F^2 \sum_i c_i z_i^2}{\epsilon_r \epsilon_0 R g T}}$$



36] If we have another particle whose double layer overlaps with this particle's double layer
↓
then repulsion will occur

{ However if they are further away (& thus not overlapping)
↓
then repulsion is v. small }



Repulsion force due to double layer , $\phi_R = 2\pi \epsilon_r \epsilon_0 r E^2 e^{-Ks}$

$$\text{Van der Waal's attraction force} = \phi_A = -\frac{A}{6} \left\{ \frac{2r^2}{s^2 + 4rs} + \frac{2r^2}{s^2 + 4rs + 4r^2} \right. \\ \left. + \ln \left(\frac{s^2 + 4rs}{s^2 + 4rs + 4r^2} \right) \right\}$$

* here, A is the Hamaker constant (magnitude: $10^{-19} - 10^{-20} \text{ J}$)

Hamaker const.

depends on the
polarization properties of the
molecules

in the two particles
& in the medium which separates them

Value of Hamaker const. (A)

For most metals	$16.2 - 45.5 \times 10^{-20}$
Gold	45.3
SiO_2	6.5
Water	4.55
Polymers	$6.15 - 6.6$
PVC	10.82
PEO	7.51
Acetone	4.2

37] For separation distance (s) \ll radius (r)

$$\text{i.e. } \frac{s}{r} \ll 1$$

We will get:

$$\phi_A = \frac{-Ar}{12s}$$

for
(spheres with
some radii)

for spheres with different radii:

$$\phi_A = \frac{-Ar_1 r_2}{6s(r_1 + r_2)}$$

Also, we find the relation of ϕ_A with s being (for two molecules):

$$\phi \propto -s^{-6}$$

(i.e. it will be
attractive \rightarrow that's
why there is
-ve sign)

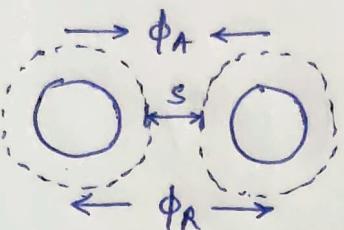
38]

We know:

ϕ_R : Electrostatic repulsion } Potentials
 ϕ_A : Van der Waal's attraction }



for stability : there needs to be balance between ϕ_R & ϕ_A



DLVO Theory

{ D : Derjaguin (pronounced: <Derja-guin>)
 L : Landau
 V : Verwey (<Ferry>)
 O : Overbeek }

As per their theory, we get :

$$\phi_A = -\frac{AR}{12s} \quad \phi_R = 2\pi\epsilon_r\epsilon_0 r E^2 e^{-ks}$$

Here:
the assumptions taken are

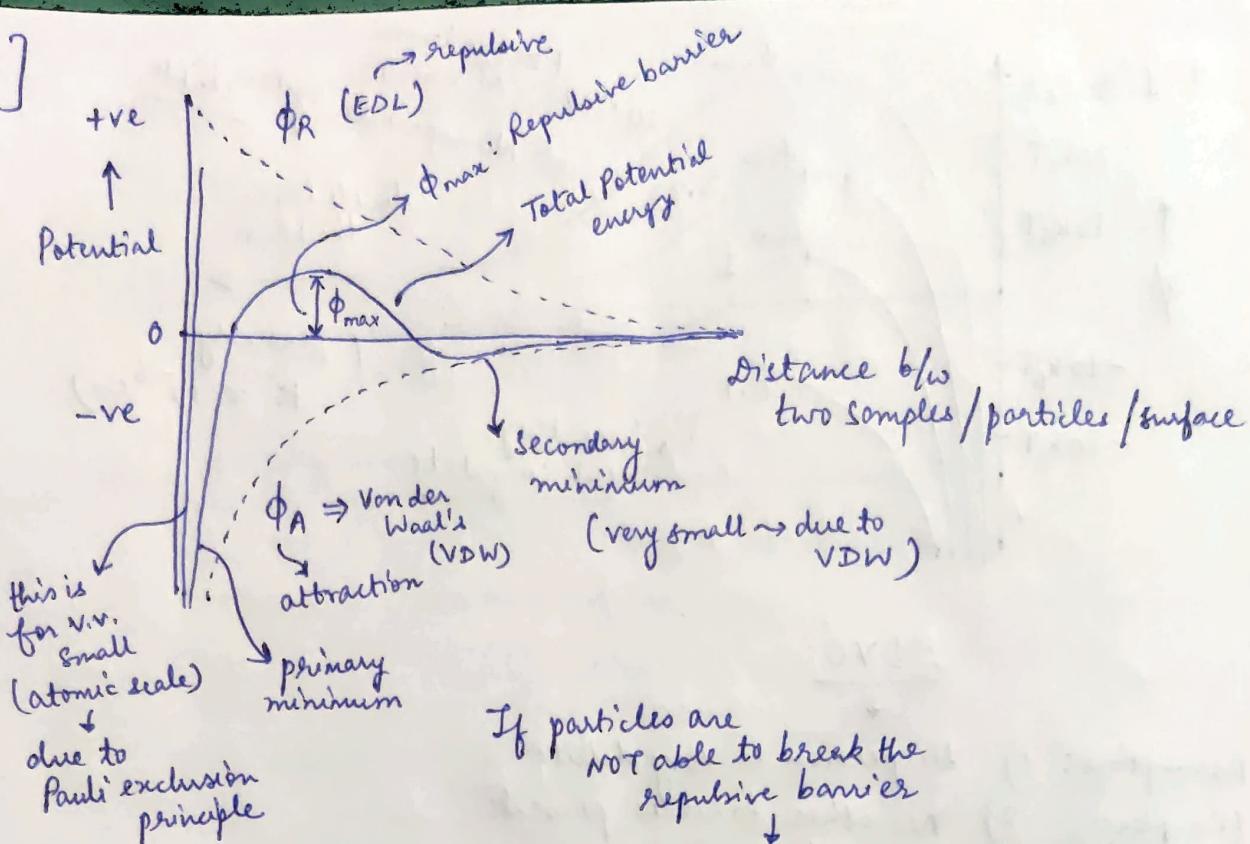
- 1) Infinite flat solid surface
- 2) Uniform surface charge density
- 3) No redistribution of surface charges
- 4) No change in conc. profile of counterions & surface charge determining ions



so it turns out electrical potential is roughly constant away from surface

- 5) Solvent exerts influence via dielectric constant only
(i.e. no chemical interaction)

39]



If particles are
NOT able to break the
repulsive barrier
↓

they will not collide/agglomerate
(& will just separate
from each other)

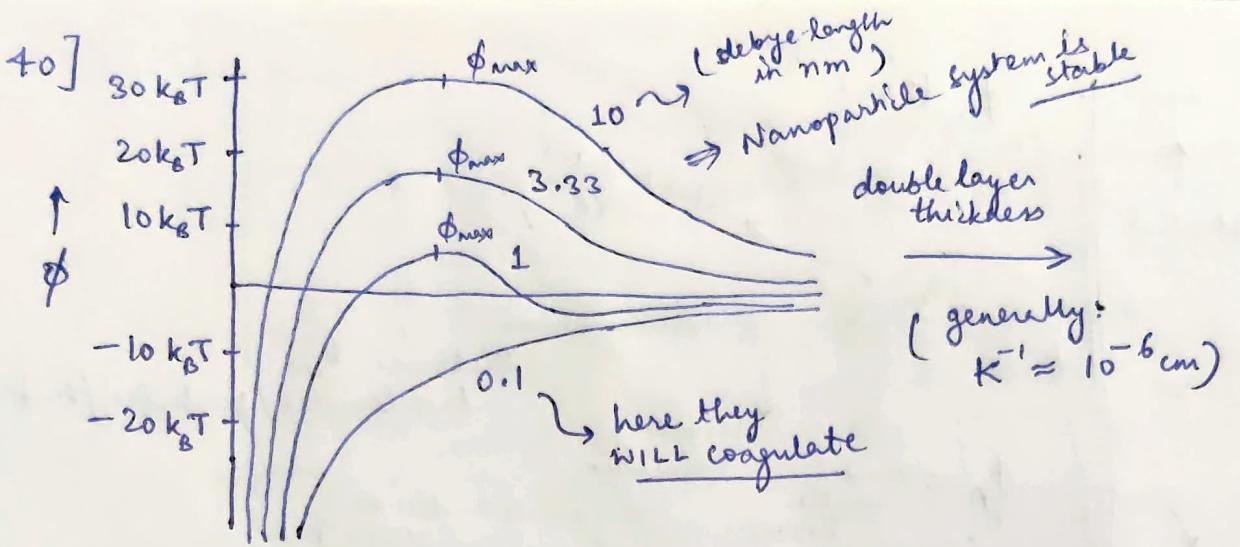
- * At Primary minimum : Coagulation occurs
- * At Secondary minimum : Flocculation happens } you can read about what these terms mean

NOTE: Generally the barrier ϕ_{\max}
↓
if it is $> 10 k_B T$
+
then there will
be No coagulation

NOTE! The electrical potential (ϕ_R)
depends on conc., charge, and valency state

But ϕ_R only depends on conc.
(VDW)

{ eg: If we vary charge
 ϕ_R changes but ϕ_A remains same }



DLVO

- Assumptions:
- 1) Dispersion is very dilute
(i.e. places where it is applicable)
 - 2) No other force is present except VDW & EDL
 - 3) Geometry of the particles is simple
 - 4) Double layer \rightarrow purely diffuse
(low conc.)

* [NOTE]: This theory is applicable to all kinds of particles

+ ranging from metals to polymers

However it is NOT very applicable to

heterogeneous particles]

{ e.g. if we take Au & polystyrene
they'll have diff. charges, diff. Hamakers constants, diff. polarizabilities, etc. } \rightarrow violates the assumption of uniform charge density (& homogeneous charge distribution)

41] Steric Stabilization

due to: Hindrance b/w nanoparticles

(b/cz of 3rd object/material)

{ using this: v. high conc. of nanoparticles can be stabilized }

(1) Polymer stabilization:

they get redispersed

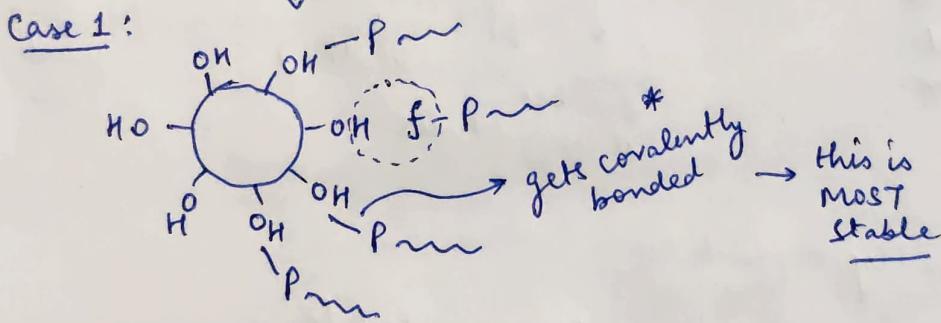


- i) This method is electrolyte sensitive
- ii) multiphase

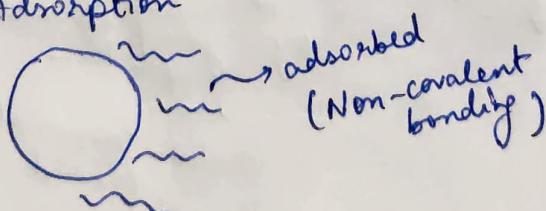
{ NOTE: The solvent used
↓
must be a
good solvent }

NOTE: Also, the polymers which get adsorbed over the particles + form a diffusion barrier (that causes steric stabilization) + this prevents Ostwald ripening as well

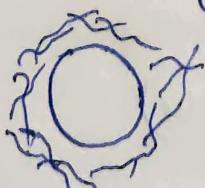
NOTE: For particle with functional group



Case 2: Adsorption



Case 3: Surrounds the particle (No interaction)



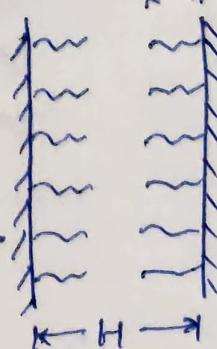
(χ : "chi")

Here: ↑

$$L = \alpha \chi^{1/6} N^{2/3}$$

* NOTE:

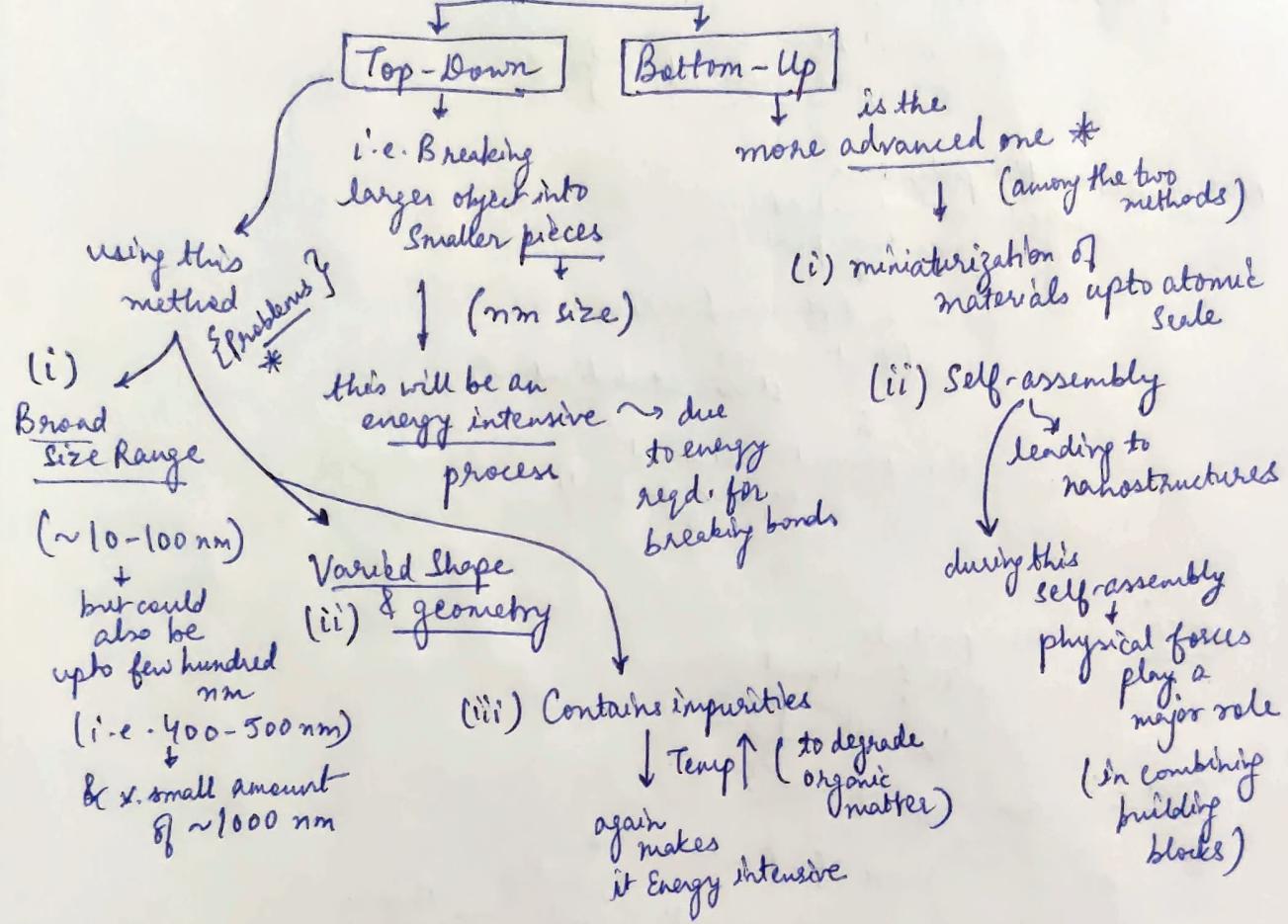
particle surface ↴



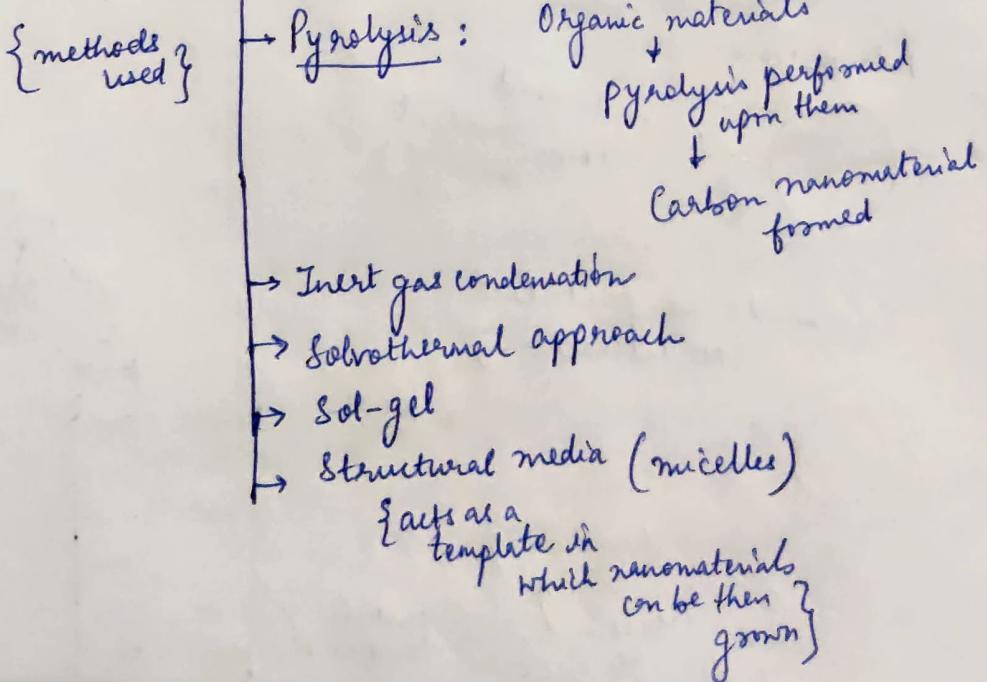
LECTURE 7

01/09/2023

4.2] Nanomaterial Synthesis Procedures



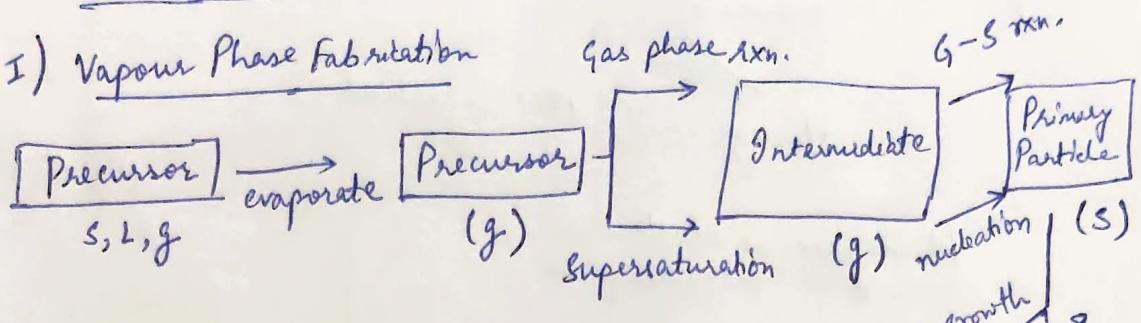
4.3] Bottom-up approach



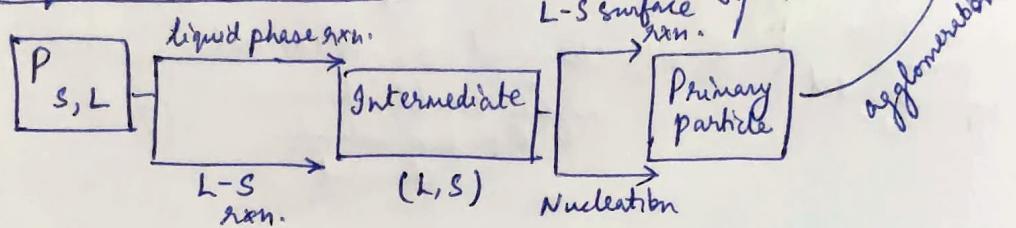
44]

Bottom-Up approach

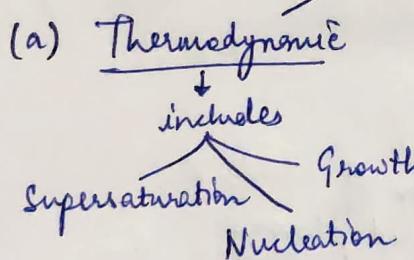
I) Vapour Phase Fabrication



II) Liquid Phase Fabrication



45] These steps can be grouped into 2 categories

(b) Kinetic

includes
limiting the amount of precursor

Confining the process into a limited space (micelle)

{ essentially the same steps are present in kinetic case

just that they are controlled by being in confined space & controlled concn.]

46] Particles synthesized should have following properties

Nanoparticles
Identical morphology
size/shape

identical chemical potential
(?)

47] The nucleation can occur through

Homogeneous Heterogeneous

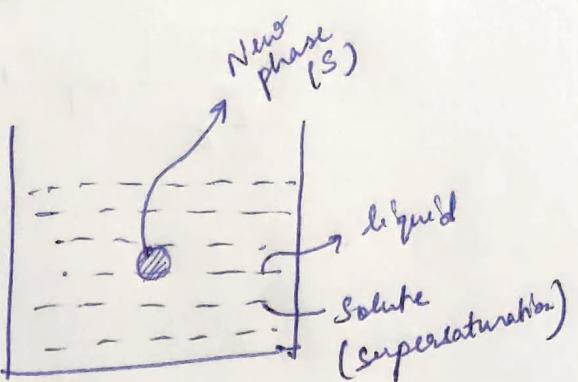
Homogeneous Nucleation

involves
supercooling
↓

i.e. reduction in
temp. of a saturated
equilibrium mixture/solution

OR

In situ chemical rxn, to convert
highly soluble chemical
to less soluble
chemical



methods
by
which we can
form a
supersaturated
solⁿ

{ Note: Due to supersaturation

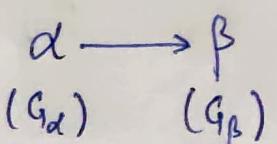
+
cone of solution becomes
more than its equilibrium
cone. (at that
same temp.) }

After this

+
Phase Transformation

+ occurs
leading to formation of
a new solid phase

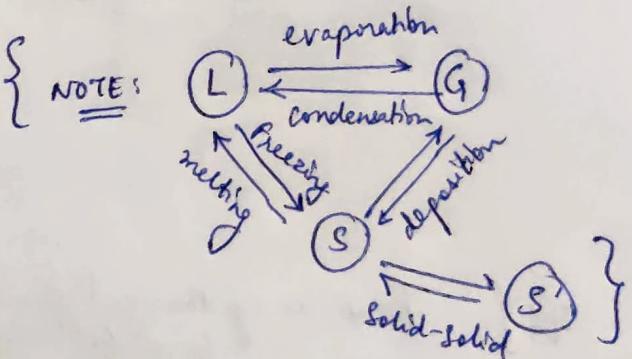
{ for such a
process
the driving
force can be
determined by:



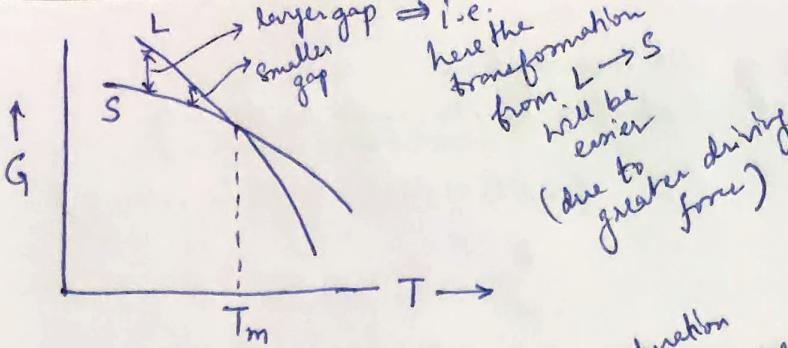
if G_β < G_α

$$\Delta G = G_{\beta} - G_{\alpha} < 0$$

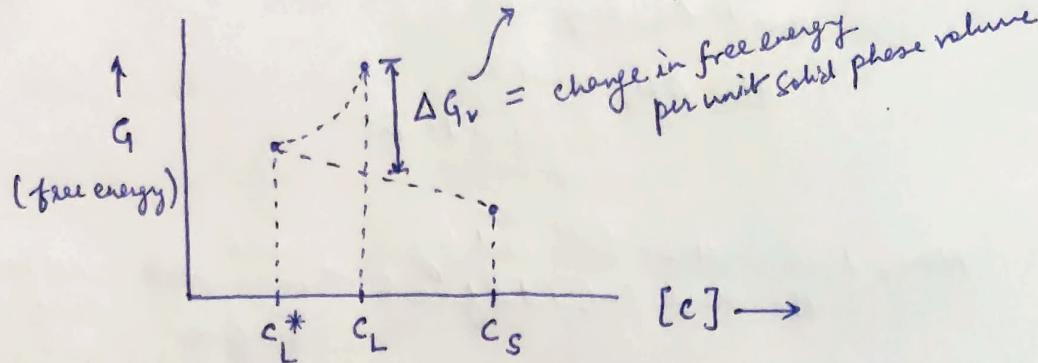
this is the
driving force



NOTE:



48] We see the following : due to supersaturation we create a greater driving force



c_L^* = conc. of sol^{liq} in equilibrium

c_L = conc. of supersaturated sol^{liq}

c_S = conc. of solid phase

We get that:

$$\Delta G_v = -\frac{k_B T}{\Omega} \ln\left(\frac{c}{c_0}\right) \quad (\text{where } \Omega = \text{atomic volume})$$

$$= -\frac{k_B T}{\Omega} \ln(1 + \sigma) \quad , \text{ where } \sigma = \text{supersaturation}$$

$$= \frac{c - c_0}{c_0}$$

Now, for $\sigma = 0$

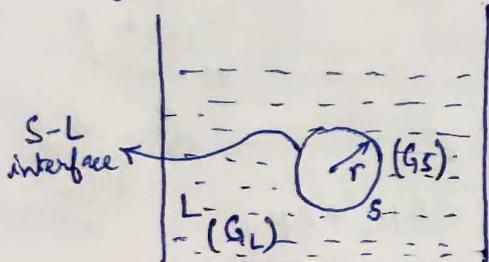
we thus see that

there will be No Nucleation *

for $c > c_0 \Rightarrow \Delta G_v = -ve$

(i.e. spontaneous nucleation)

49]



(L → S transformation)

$$\text{Here: } A = 4\pi r^2$$

$$V = \frac{4}{3}\pi r^3$$

← Here, G_S = free energy per unit vol^m of solid

G_L = free energy per unit vol^m of liquid

By taking the assumption
that there is NO change in density

(and thus, no change in volume)

Thus:

$$\Delta \mu_v = \frac{4}{3} \pi r^3 \Delta G_v \quad (\text{where, } \Delta G_v = \underbrace{G_s - G_L}_{\text{this is -ve}})$$

due to ΔG_v being -ve

this $\Delta \mu_v$ must be
also a
negative term

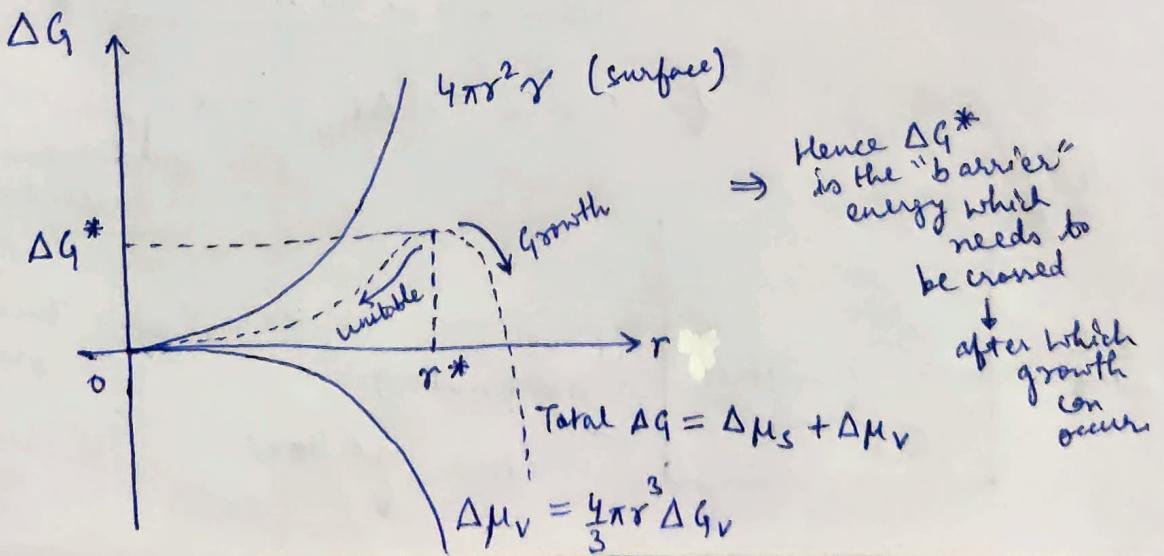
Now, this will be balanced by
the new S-L interface ^{counter-}
which is a new surface \Rightarrow will have
surface energy *

The increase
in surface energy
is given by:

$$\Delta \mu_s = 4\pi r^2 \gamma \quad (\gamma = \text{S.E. / area})$$

Hence, overall ΔG will be:

$$\begin{aligned} \Delta G &= \Delta \mu_v + \Delta \mu_s \\ &= \underbrace{\frac{4}{3} \pi r^3 \Delta G_v}_{\text{Driving force}} + \underbrace{4\pi r^2 \gamma}_{\text{"obstruction"}} \end{aligned}$$



From here we can see that:

$$\left. \frac{\partial \Delta G}{\partial r} \right|_{r=r^*} = 0$$

For $r < r^*$ $\Rightarrow \Delta G$ is increasing $\xrightarrow{i.e.}$ No growth

For $r > r^*$ $\Rightarrow \Delta G$ is decreasing $\xrightarrow{i.e.}$ growth of particle will occur
at $r^* \Rightarrow \Delta G$ is max^m.

50] Now, we can see:

$$\begin{aligned} \frac{\partial \Delta G}{\partial r} &= \frac{4}{3}\pi(3r^2)\Delta G_v + 4\pi(2r)\gamma \\ &= 4\pi r^2 \Delta G_v + 8\pi r \gamma \end{aligned}$$

$$At r^* \Rightarrow \left. \frac{\partial \Delta G}{\partial r} \right|_{r^*} = 4\pi r^* \Delta G_v + 8\pi r^* \gamma = 0$$

$$\Rightarrow r^* = -\frac{2\gamma}{\Delta G_v}$$

and using this:

$$\Delta G^* = \frac{16\pi r^3}{3\Delta G_v^2}$$

where,
 $(G_s - G_L = \Delta G_v)$

from here we
can thus see
the relation!

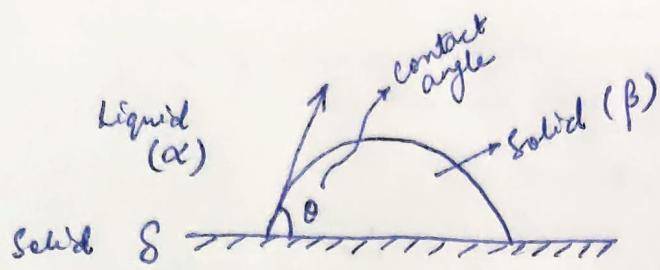
$$r^* \propto \frac{1}{\Delta G_v}$$

LECTURE 8

05/09/2023

51] Heterogeneous Nucleation

Here the surface
helps by aiding
nucleation



Here we have 3 interfaces:

$\gamma_{\alpha\beta}$, $\gamma_{\beta S}$ and $\gamma_{\alpha S}$ \Rightarrow these are the interface energies

We get the following relation:

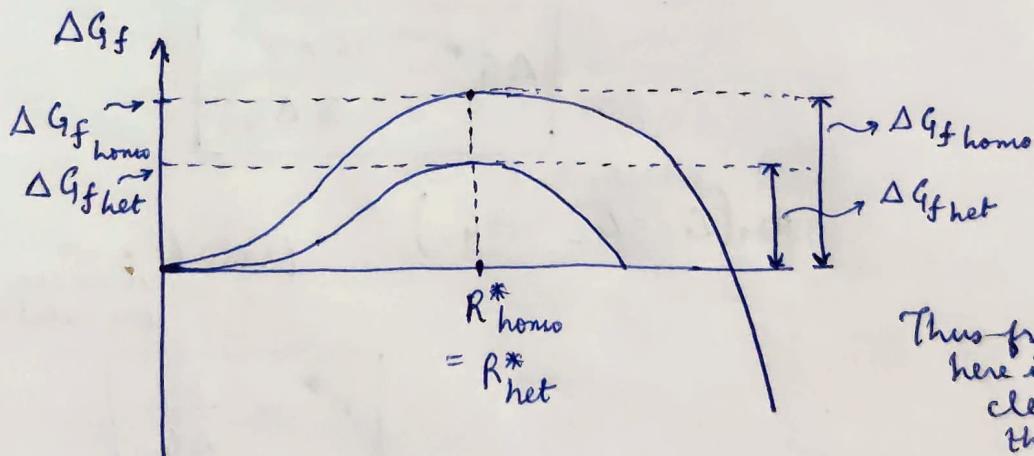
$$\cos \theta = \frac{\gamma_{\alpha S} - \gamma_{\beta S}}{\gamma_{\alpha\beta}}$$

$$\Rightarrow \boxed{\gamma_{\alpha S} = \gamma_{\beta S} + \gamma_{\alpha\beta} \cos \theta}$$

further, we also know that:

this is called YOUNG'S EQUATION

$$R_{\text{het.}}^* = \frac{2\gamma_{\alpha\beta}}{\Delta G_f} = R_{\text{homo}}^*$$



Thus from here it is clear that:

Energy Barrier for hetero < homo

We can say:

$$\boxed{\Delta G_{f\text{het}}^* = \Delta G_{f\text{homo}}^* \cdot S(\theta)}$$

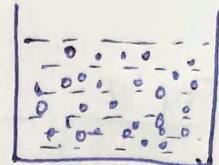
52] Sol-Gel process

e.g.: {
Plasma Arcing }
{ CVD & PVD }

this is a
process
involving

Stable suspension of
colloidal particles
in a liquid

these
colloidal
particles
could be
metallic
polymer ceramic (etc.)



Gel:

This refers to
porous 3D continuous
solid network

surrounding & supporting
a continuous liquid phase $\xrightarrow{\text{then}}$ Wet Gel
or $\xrightarrow{\text{or}}$ Dry Gel (e.g.: aerogel/xerogel)

Sol-Gel

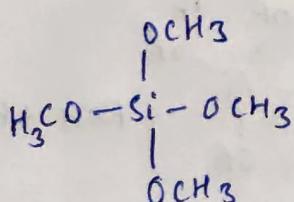
refers to transition
into
Ionic bonding
Covalent bonding
H-bonding



NOTE: A very common
example of particle used is

Silica particles

This occurs
in liquid phase
reaction



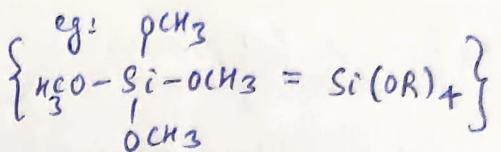
Precursor
(silane)

Hydrolysis
Sol-phase

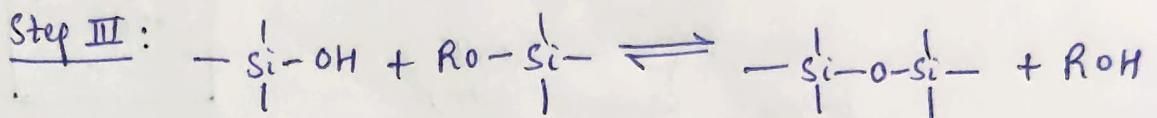
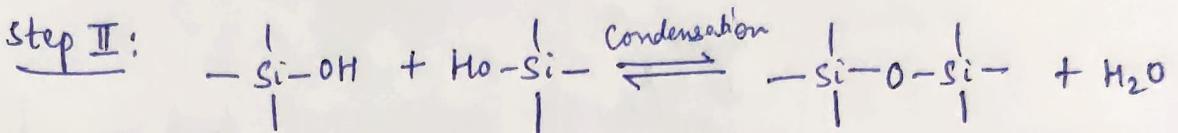
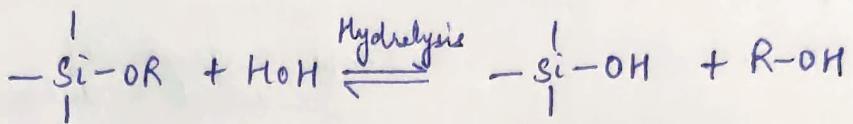
\rightarrow Crosslinking \rightarrow Gel \rightarrow Aerogel
(retain its shape)

Xerogel

53] The steps involved in Sol-Gel process are:



Step I :

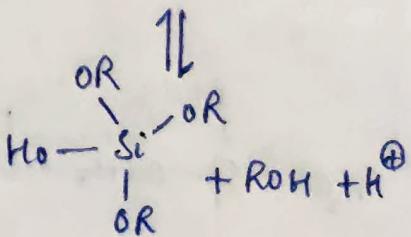
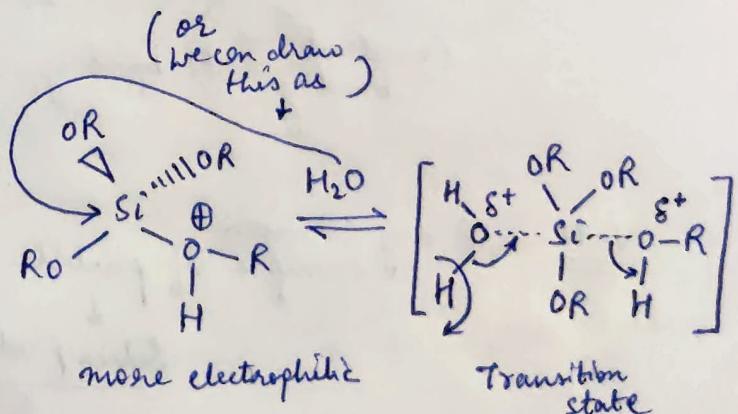
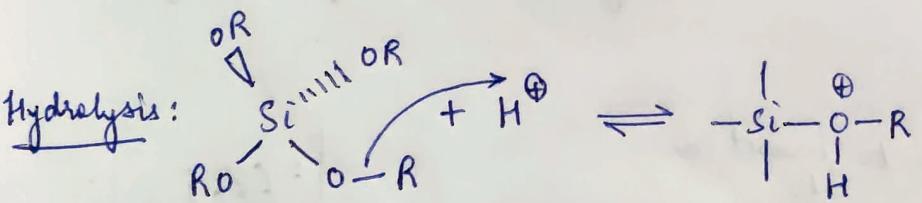
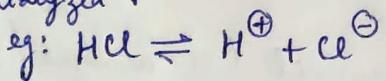


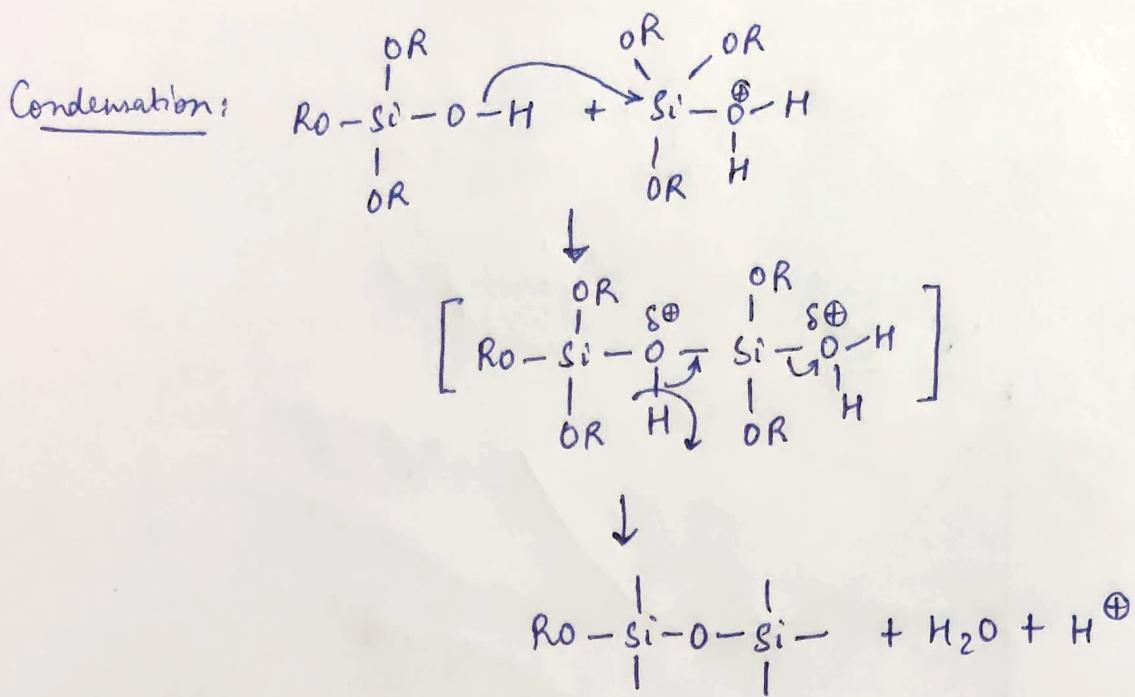
{ NOTE: With Si we get Silanes

Similarly we can also use Ti, Zr, etc. }

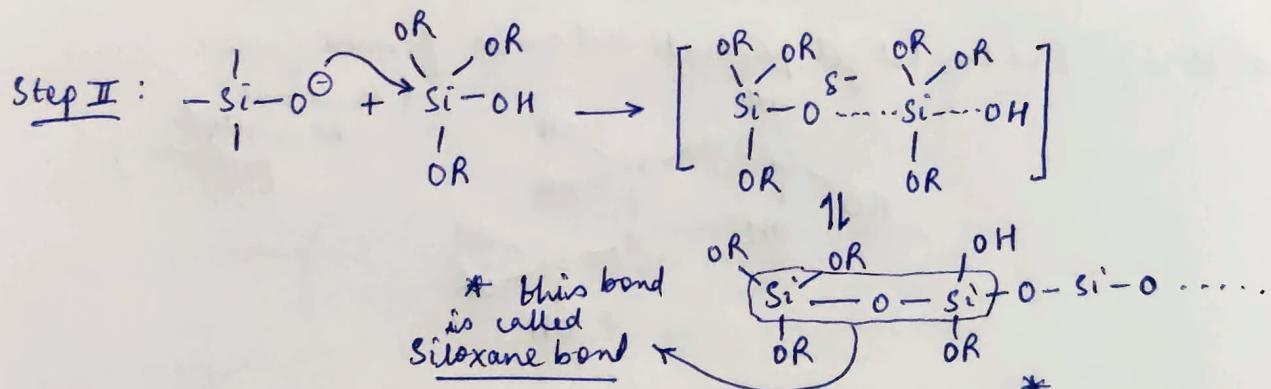
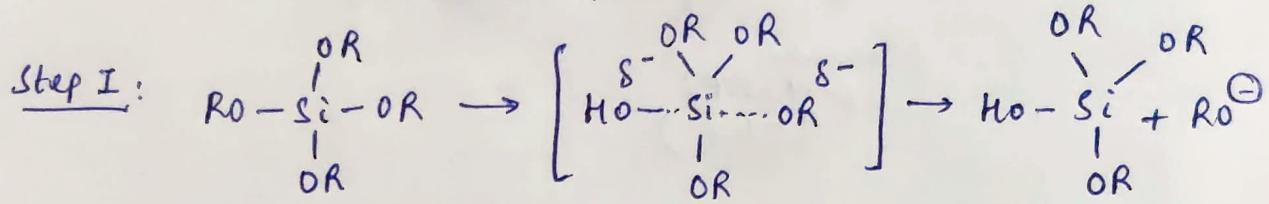
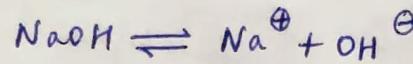
54] Acid catalyzed / Base catalyzed

and catalyzed \downarrow





55] Base catalyzed

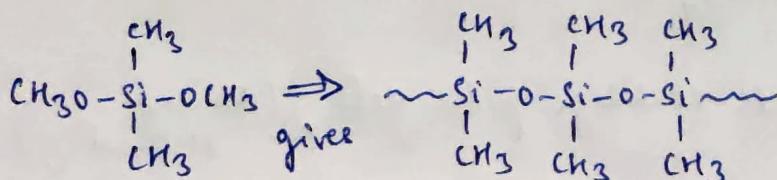


* NOTE: Acid catalyzed hydrolysis is faster than condensation \rightarrow * produces less branched chain

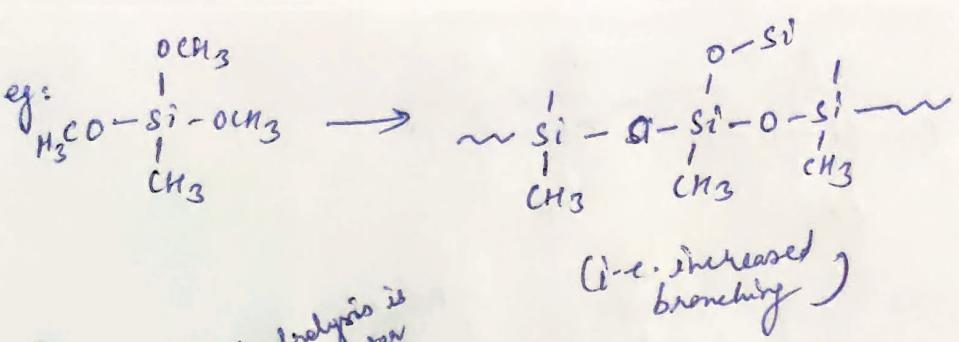
Base catalyzed hydrolysis is slower, and condensation is faster \rightarrow * produces more branched chain

NOTE:

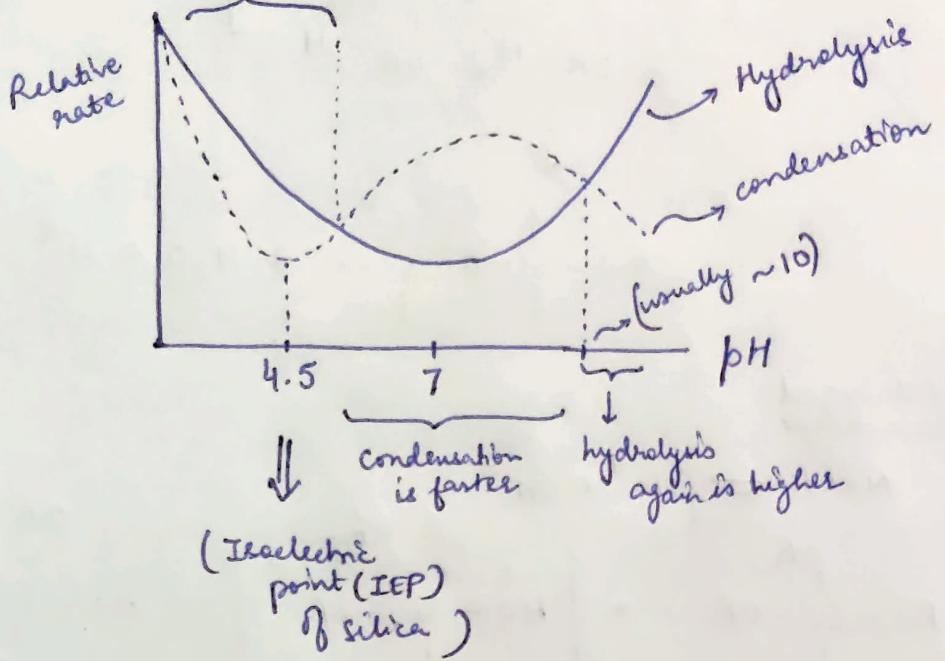
e.g.:



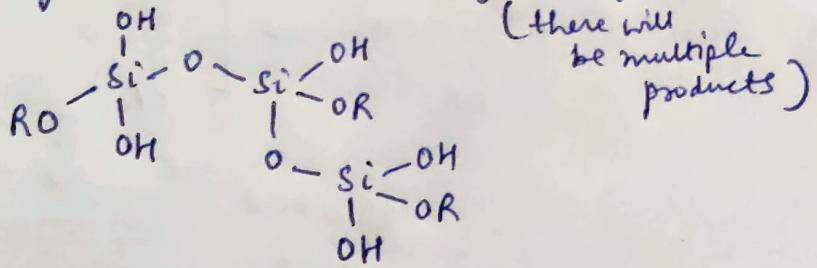
(called poly-dimethylsiloxane)



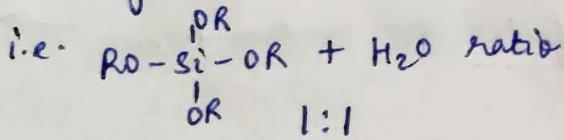
56]



* [H.W.]: Find the sol-gel products that can be formed from:



Also alkoxy to water ratio is



NOTE: Some useful information

* Trend: $\text{Si(OMe)}_4 > \text{Si(OEt)}_4 > \text{Si(OPr)}_4 > \text{Si(OBu)}_4$

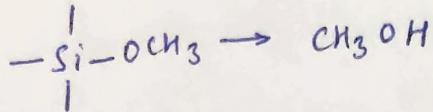
* Polar solvents stabilize polar gels (through H-bonding)
AND

Non-polar solvents stabilize non-polar gels (also called organically-modified gels)

↖ trend for rate of hydrolysis
{ * this happens due to steric hindrance }

57] In Sol-gel process

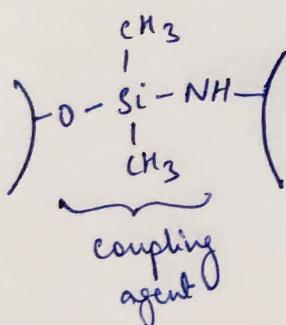
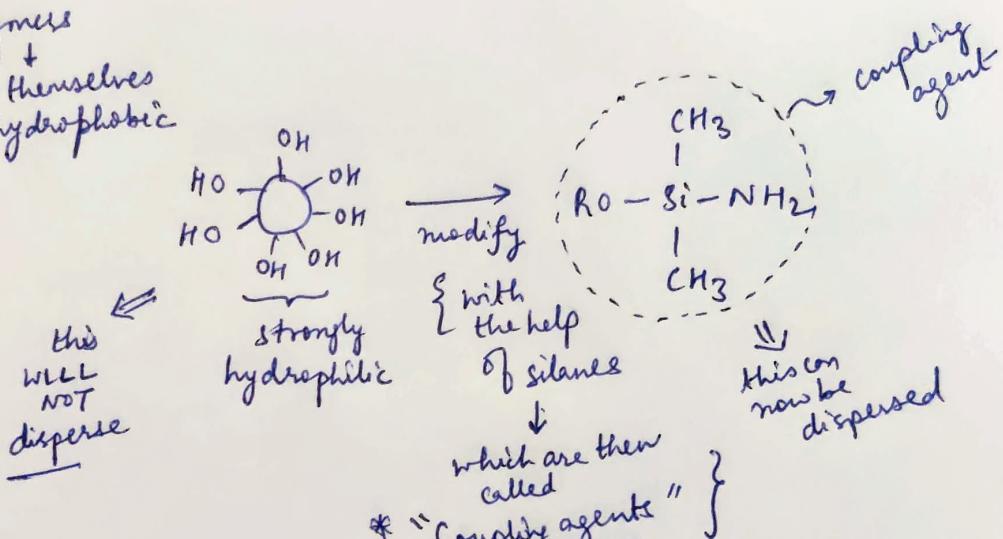
alcohol is added
 + Al_2O_3
 this is done in
 order to suppress
alcohol exchange rxn.
 to homogenize
 the sol



(NOTE: To avoid
 alcohol
 exchange rxn.)

we generally add some
 alcohol that
 will be produced
 by the rxn.)

NOTE: Polymers
 +
 are themselves
 hydrophobic



this process is
 called
 * surface modification

(i.e. structures)

58] Possible systems we can
 have in the rxn. :

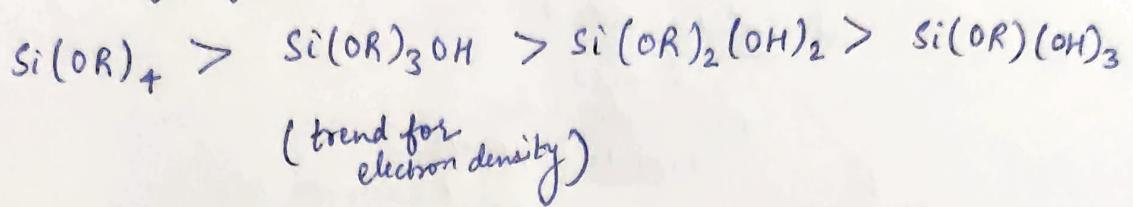


(R group
 has
 + I effect)

* (Trend for electron
 density on Si atom)

using this
 you can determine
 what will
 happen in acid/base
 catalysis *

Similarly for different hydrolyzed products:



* NOTE: Stober

↓
method used
for synthesis of
nanoparticles
(you can read
about it)