SURFACE CHEMISTRY

→ Occurs only at surface, Not in bulk

Adsorption → Accumulation of species at surface and not in bulk

Adsorbate → Substance which accumulates

Adsorbent → Material on which, accumulation occurs.

Desorption → Removal of adsorbate from adsorbent.

Adsorption In Action

1) $O_2, N_2, Cl_2, NH_3, SO_2$ $\xrightarrow{\text{powdered}}$ charcoal — Pressure reduces becoz adsorption of gases on charcoal takes place.

2) $\xrightarrow[\text{charcoal}]{\text{animal}}$ colourless — sol.^{n} of dye, (methylene blue) — molecules of dye adsorbed on surface of charcoal

3) aq. sol.^{n} of raw sugar $\xrightarrow[\text{charcol}]{\text{animal}}$ Colourless

→ air becomes dry in presence of Silica Gel. Water molecule gets absorbed on silica Gel.

Adsorption	Absorption
Substance concentrated only at surface, and don't penetrate in bulk	Substance is uniformly distributed throughout bulk of solid
→ Silica gel	→ anhydrous $CaCl_2$
Surface Phenomena	Bulk phenomena
Rate ↑↑ in start, and decreases till eq.^{m}	Rate remains Constant

Sorption → when adsorption and absorption take place simultaneously

Thermodynamics of adsorption

→ During adsorption → decrease in residual forces of surface, → ↓↓ surface energy ↓ heat

adsorption is exothermic process

$\boxed{\Delta H = -ve}$

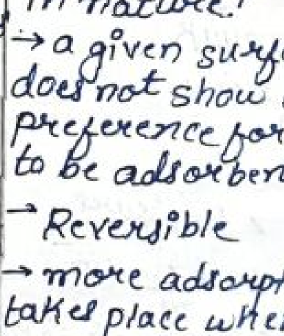
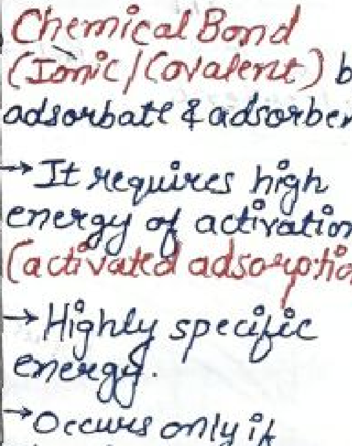
→ after adsorption randomness of system ↓↓ $\boxed{\Delta S = -ve}$

→ for adsorption, thermodynamic requirement is that at constant T and P. $\boxed{\Delta G = -ve}$

$$\boxed{\underbrace{\Delta G}_{-ve} = \underbrace{\Delta H}_{(\text{more}(-ve)\text{ value})} + \underbrace{T\Delta S}_{+ve \text{ value}}}$$

→ for spontaneous process.

Types of Adsorption

Physisorption	Chemisorption
(physical adsorption)	(chemical adsorption)
Vanderwall force b/w adsorbate and adsorbent	Chemical Bond (Ionic / Covalent) b/w adsorbate & adsorbent.
→ It is not specific in nature.	→ It requires high energy of activation (activated adsorption)
→ a given surface does not show any preference for gas to be adsorbent.	→ Highly specific energy.
→ Reversible	→ Occurs only if chemical bonds are formed.
→ more adsorption takes place when pressure is increased.	→ Irreversible.
Since, it is an exothermic process, Low temp. favourable. at high temp. physisorption decreases	→ Requires high energy of activation.
Lechatelier principle	
	
→ Low temp favourable	→ High temp. favourable. Tc → critical temp.
→ Depends on nature of gas	→ Depends on nature of gas

easily liquifiable gas are more adsorbed.

gases with high critical temp. is easily adsorbed

Enthaly of adsorption (20-40 KJ/mol)

$\boxed{\uparrow\uparrow \text{Surface area}, \uparrow\uparrow \text{adsorption.}}$

It is multilayered

eg-Gases which form chemical bond, shows chemisorption

Enthalpy - (8-240) KJ/mol.

↑↑ surface area, ↑↑ chemisorption

Unilayered

$\boxed{\uparrow\uparrow T_c \rightarrow \uparrow\uparrow \text{internal forces of attraction, easily gas liquified}}$

Adsorption Isotherm

↳ Shows amount of gas adsorbed with pressure (Temp. Constant)

Freudlich Isotherm → single layer.

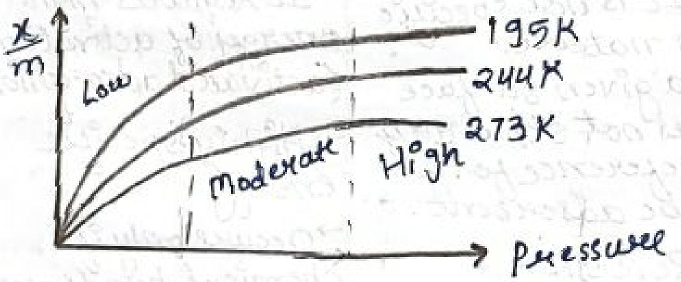
$$\frac{x}{m} = K P^{1/n}$$

x → mass of gas adsorbed

m → mass of adsorbent

P → pressure.

K, n = Constant (depends on nature of adsorbate and adsorbent)



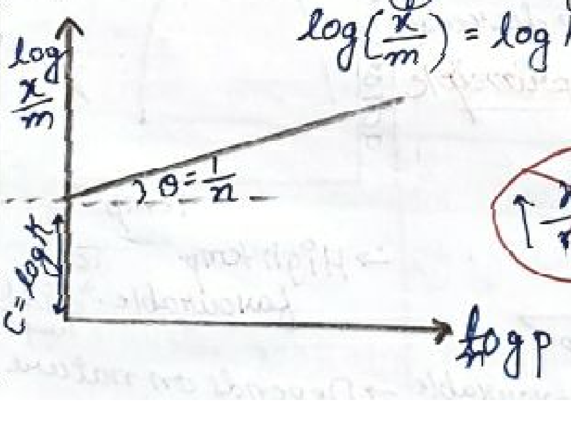
Low pressure region → $\frac{1}{n} = 1 \rightarrow \frac{x}{m} = KP$

Moderate pressure region → $0 < \frac{1}{n} < 1 \rightarrow \frac{x}{m} = KP^{1/n}$

High pressure region → $\frac{1}{n} = 0 \rightarrow \frac{x}{m} = \text{Const.}$

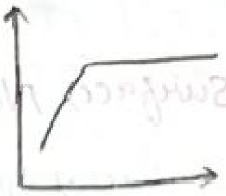
$\frac{x}{m} = KP^{1/n}$ → Take log both sides

$$\underset{(y)}{\log\left(\frac{x}{m}\right)} = \underset{(c)}{\log K} + \underset{(m)(x)}{\frac{1}{n}\log P}$$



$\cancel{\uparrow \frac{x}{m} \propto P \uparrow}$

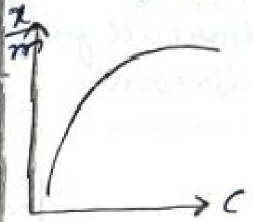
Experimental Graph →

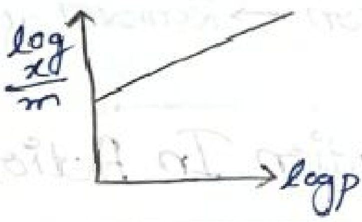


Adsorption from Solution phase

$$\frac{x}{m} = K[C]^{1/n}$$

$$\rightarrow \log\frac{x}{m} = \log K + \frac{1}{n}\log[C]$$





Catalysis

accelerate the rate of a reaction and themselves remains unchanged called Catalysis.

Promortors → Substance which enhance activity of a catalyst

Haber's Process → $N_2 + 3H_2 \xrightarrow[Mo]{Fe} 2NH_3$

Poison → Opposite of promoter

Homogenous Catalyst →

Reactant and Catalyst, both in same phase

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO(g)} 2SO_{3(g)}$$

$$CH_3COOCH_{3(l)} + H_2O_{(l)} \xrightarrow{HCl(l)} CH_3COOH + CH_3OH$$

$$C_{12}H_{22}O_{11(aq)} + H_2O_{(l)} \xrightarrow{H^+(aq)} C_6H_{12}O_{6(aq)} + C_6H_{12}O_{6(aq)}$$

Heterogeneous Catalyst

not in same phase →

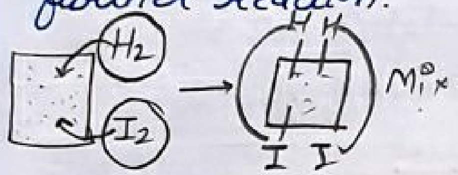
$$2SO_{2(g)} + O_{2(g)} \xrightarrow{Pt(s)} 2SO_{3(g)}$$

$$NH_3 + O_2 \xrightarrow{Pt(s)} NO + H_2O$$

$$\underset{(l)}{\text{Vegetable fat}} + H_{2(g)} \xrightarrow{Ni(s)} \text{Vegetable ghee}$$

Adsorption Theory Of Homogeneous Catalyst

① Diffusion of reactant to the surface of catalyst.
② Adsorption of reactant on Catalyst.
③ Reactant molecules Combine.
④ Desorption of products occur.
⑤ Catalyst is again available for further reaction.



Catalyst shows selectivity

$CO + H_2 \xrightarrow{Ni} CH_4 + H_2O$

$CO + H_2 \xrightarrow{Cu} HCO$

$CO + H_2 \xrightarrow[Cr_2O_3]{Cu\text{-}ZnO} CH_3OH$

Enzyme Catalyst

Complex Nitrogeneous Organic Compound (protiens)

Biochemical Catalyst.

Inversion Of Cane Sugar.

$C_{12}H_{22}O_{11}(aq) + H_2O \xrightarrow{Invertase} C_6H_{12}O_6 + C_6H_{12}O_6$
(glucose, fructose)

Glucose → Ethyl Alcohol

$C_6H_{12}O_6 \xrightarrow{zymase} C_2H_5OH + 2CO_2$

Starch → Maltose

$2(C_6H_{10}O_5)_n \xrightarrow{Diastate} C_{12}H_{22}O_{11}$
(starch, maltose)

Maltose → Glucose

$C_{12}H_{22}O_{11} \xrightarrow{maltase} C_6H_{12}O_6$

Milk $\xrightarrow{lactobacilli}$ Curd

Protein $\xrightarrow{pepsin}$ Peptide

protein $\xrightarrow{trypsin}$ amino acid.

Mechanism Of Enzyme →

Step ① →

Enzyme + Substrate ⇌ Enzyme Substate

Step ② →

Enzyme Substrate → Enzyme product → Enzyme + Product

Catalyst

Haber's process → Fe, Mo (promorter)
Ostwald process → Pt
Contact process → V_2O_5
Decan process → $CuCl_2$
Bosch process → $Fe_2O_3 + Cr_2O_3$

Colloidal Solution

property	True Solution or Crystalloid	Colloid	Suspension
particle Size	10^{-9} m	10^{-9} – 10^{-6} m	10^{-6} – 10^{-4} m
Visibility	Not visible	Visible with ultramicroscope.	Visible with naked eye
Separation ① filter paper	Not possible	Not possible	possible
② ultra-membrane	Not possible	possible	possible
Diffusion	Diffuses rapidly	Diffuses very slowly.	Does not diffuse.
settling	Does not settle	Settle under centrifuge.	Settle due to gravity
Nature	Homogenous	Heterogenous	Heterogenous
Tyndall effect and Brownian moment	does not show	shows	may or may not show

Types of Colloidal Solution →

Colloidal Solution (Heterogenous)

- Dispersed phase (DP) (lessamt)
- Dispersion medium (DM) (moreamt)

A. On basis of physical state of DP and DM → 8 types

B. Interaction b/w DP and DM → Lyophilic sol.^{n}, Lyophobic sol.^{n}

C. Types of DP particles → Multimacro molecular colloids, Macro-molecular colloids, Associated colloids

Dispersed phase	Dispersion medium	Type of Colloidal Sol.^{n}	Example →
Solid	Solid	Solid sol	Ruby glass (gold dispersed in glass), Gem stones, minerals
Solid	liquid	sol	Ink, Colloidal gold, paint, Cell fluids, Slit, proteinsol, starchsol
Solid	air	aerosal.	Dust, soot in air, smoke.
liquid	Solid	Gel	Cheese, curd, jellies, boot polish, opal, Butter.
liquid	liquid	Emulsion	Milk, Hair Cream, Butter, Cold cream.
liquid	gas	Aerosol	Fog, mist, Clouds, insectisides sprays.
gas	Solid	Solid foam	Cork, Pumice Stone, Foam Rubber, Break, Cake
gas	liquid	foam	Whiped cream, Shaving cream, Soda Water, Soap lather.

property	Lyophilic Solution	Lyophobic Solution
Ease of preparation	By directly mixing with liq. dispersion medium	prepared by special method only
Stability	Quite stable, not easily precipitated	Easily presipitated by addition of small amout of suitable electrolyte.
Nature	Reversible in nature	Irreversible in nature
Hydration	Highly hydrated	Not much hydrated
Nature of substances	Organic substances like starch, gum etc.	Usually Inorganic substance

Viscosity	Much higher than medium	almost same as that of medium.
Surface Tension	Usually lower than medium	Nearly same to medium

③ Classification →

① Multi Molecular Colloids →

On dissolution, large no. of atom/ smaller molecules of substance aggregate together to form species having size in colloidal range.
eg- Gold Sol, Sulphur Sol.

② Macromolecules Colloids →

Macromolecules in suitable solvents forms solutions in which size of macromolecules may be in colloidal range
→ Stable, resemble true Solutions.
eg- Starch, polymerase, cellulose, proteins, enzymes, nylon - - -

③ Associated Colloids (Micelles) →

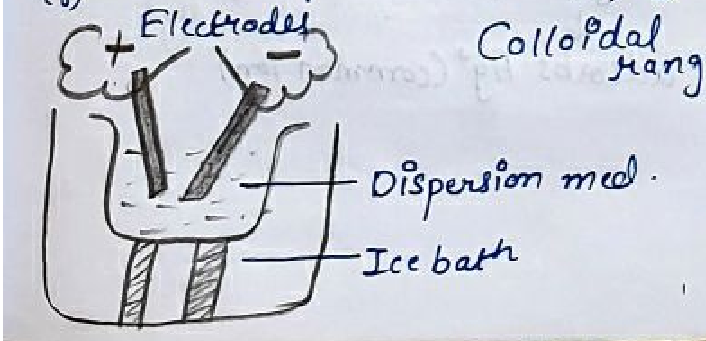
at low Conc.^{n} → normal electrolyte.
at high conc.^{n} → Colloidal behavior (micells)
↓
formation of aggregates

★★ → Formation of micelles takes place only above particular temp. called Kraft Temperature (T_K) and above particular con. called Critical Micelle Concentration (CMC)

↳ Electrical disintegration or Bredig's arc Method →

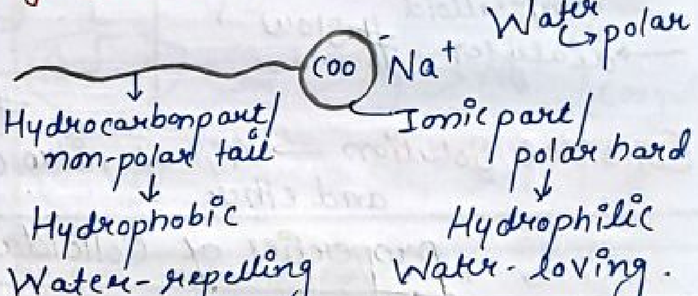
↳ dispersion, Condensation.
→ gold, silver, platinum etc...

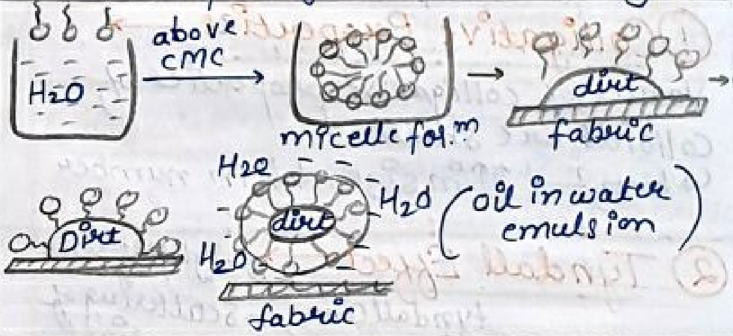
$Metal_{(s)} \xrightarrow{\Delta} Metal\ Vapours \xrightarrow{cool} Metal_{(s)}$ ↓ Colloidal range.



Mechanism of Micelle formation →

Soap → Sodium/potassium salt of long chain monocarboxylic acid (fatty acid).
eg - Sodium Stearate → $C_{17}H_{35}COO^-Na^+$





Preparation Of Colloids →

↳ Chemical Methods →

molecules aggregate to form Sols.

① $As_2O_3 + 3H_2S \xrightarrow[displacement]{double} As_2S_3_{(sol)} + 3H_2O$

② $SO_2 + 2H_2S \xrightarrow{oxid.^n} 3S(sol) + 2H_2O$

③ ★ $2AuCl_3 + 3HCHO + 3H_2O \xrightarrow{red.^n} 2Au_{(sol)} + 3HCOOH + 6HCl.$

★★ ④ $FeCl_3 + 3H_2O \xrightarrow{hydrolysis} Fe(OH)_3{}_{(sol)} + 3HCl.$

↳ peptization →

$precipitate \xrightarrow[electrolyte]{small\ amt.\ of} colloid\ sol.$
↳ peptizing agent

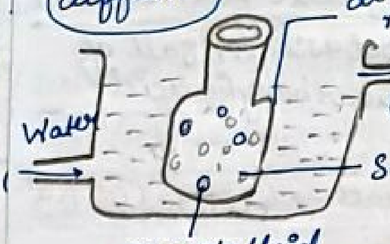
Shake

precipitate adsorb ions of electrolyte.
(+ve) (-ve) → Colloid

purification of Colloidal Solution →

① Dialysis →

(diffusion)



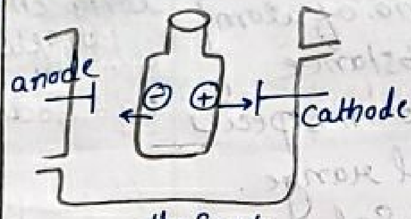
→ dialyser #slow

② Electro-dialysis →

Electric field.

Cathode(−) ← Cation(+)

Anode(+) ← anion(−)



#fast

③ Ultrafilteration

→ Soaking filter paper in colloidal sol^n

↓

Hardning by formaldehyde (HCHO)

↓

drying.

Impurity → passes

Colloid → Stays

#slow

→ fast → Suction.

Colloidal Solution → 4% of nitro cellulose in mixture of alcohal and ether

---

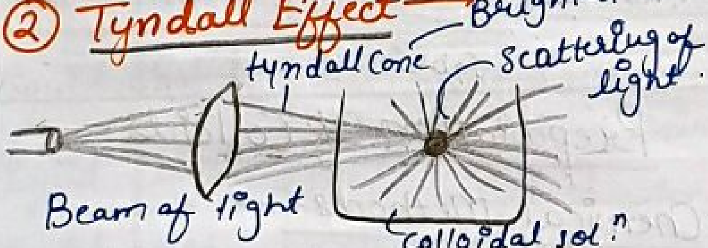
properties of Colloidal Solutions →

① Colligative Properties →

Values of colligative properties of colloids are small

↳ bcoz → ↑↑ in size, ↓↓ in number

② Tyndall Effect →



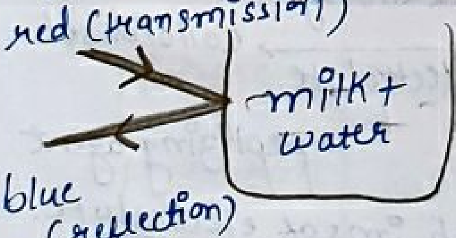
→ Light get scattered ~~to~~ due to colloidal particles

→ Tyndall effect observed only when →

① Diameter of dispersed particle is not much smaller than wavelenght of light.

② Refractive Index of dispersed phase and medium differ verymuch in magtitude.

③ Colour → Depends on wavelength of light scattered ~~by~~ due to particle.



④ Brownian Motion →

Zig-Zag motion of Colloidal particle

Ultra-microscope

Motion is independent of nature of colloids but depends of size and Viscosity

$$\boxed{\text{Motion} \propto \frac{1}{\text{Size, Viscosity}}}$$

⑤ Charge on Colloidal particles →

Charge → due to e^- captured by sol particles during electro-dispersion of metals

↙ ↘

(−) (+)

→ adsorption of ions

→ formulation of electrical double layer.

eg 1 → $AgNO_3 + KI$ (excess) → $AgI + KNO_3$ (aq)

↳ adsorbs I^- (from KI)

$(AgI)\, I^-\, I^-\, I^-$

eg. 2 → $AgNO_3$ (excess) $+ KI$ → $AgI + KNO_3$

↓

adsorbs Ag^+ (common ion)

$(AgI)\, Ag^+\, Ag^+\, Ag^+$

eg-3 → $Fe_2O_3.xH_2O$ Fe^{3+} Fe^{3+} [$FeCl_3$ + ΔH_2O excess]

Fe^{3+} positively charged ion adsorbed

$Fe_2O_3.xH_2O$ OH^- OH^- [$FeCl_3$ + NaOH]

OH^- negatively charged.

↳ Combina.ⁿ of 2 layer of oppo charges around Colloidal particle is called Helmholtz electrical double layer

Types Of Sols →

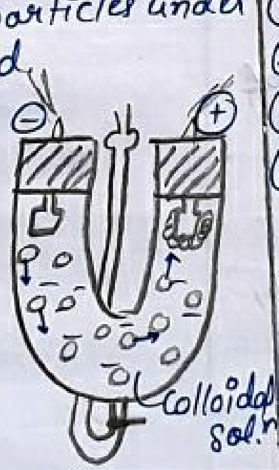
+vely charged Sols.	-vely charged sols.
Hydrated metal oxides.	copper, silver, gold sols.
$Al_2O_3.xH_2O$,	Metallic sulphides
$CrO_3.xH_2O$,	↳ As_2S_3, Sb_2S_3, CdS sol
$Fe_2O_3.xH_2O$---	Acidic dye stuff. (oesin, congored sols)
Basic dyes stuff. (mythylene blue sol)	Sols of starch, gum, gelatin, clay, charcoal --
Hamoglobin (blood)	
Oxides - eg - TiO_2 sol.	

6 Electrophoresis →

movement of colloidal particles under an applied Electric field.

⊕ particle → Cathode ⊖

⊖ particle → anode ⊕



7 Coagulation / precipitation →

Coagulat.ⁿ of Colloids due to neutralisation of charge, due to which particles comes near and form aggregate and settle down under gravity

Coagulati.ⁿ of sol → Settling of Colloidal particles.

Coagulation of lyophobic sols → unstable

1. Electrophoresis
2. Mixing 2 oppo. charged Sols.
3. Boiling.
4. persistant dialysis
5. add.ⁿ of electrolytes

Hardy Schulze Rule →

↑↑ Valency of ion ∝ ↑↑ coagulating power.

for -ve → $Al^{3+} > Ag^{2+} > Na^+$ } Coagul. power

for +ve → $PO_4^{3-} > SO_4^{2-} > Cl^-$ }

↓↓ Quantity needed $\propto \frac{1}{\text{Coagulating power of ion} \uparrow\uparrow}$

Coagulating Value →

Min. conc. of an electrolyte is millimoles per litre required to cause precipitation of a sol in 2 hrs.

Colloids Around Us →

1. Blue Colour of Sky.
2. Fog, Mist Rain
3. Milk, Butter, Ice Cream, Halwa.
4. Blood → (albuminoid substance) of colloid)

alum + $FeCl_3$ → Coagulation of bloot (clot buster)

5. Soils → absorb moisture and nourishes material.
6. Formation of Delta →

Clay + Sea Water + Electrolytes.

River + Sea | Ocean →

Application of Colloids →

① Electrical precipitation of smoke →

Chimney → chamber → ⊕ ⊖ ← particles
↓
precipitated.

Cottrell precipitator.

② Medicines → Kala Azar → Colloidal antimony

Colloidal Gold → Intramuscular injection

Milk of Magnesium, Emulsion - Stomach

③ Cleansing action of Soaps and detergents

④ photographic plates and films →
↳ light sensitive Silver Bromide in gelatin over glass plates or celluloid films

⑤ Tanning → Animal hides
Hide → ⊕ particles → soaked in tannin
↓
⊖ colloids

$\underbrace{\hspace{6em}}$
Mutual Coagulation
↓
Hardening of leather → Tanning.

Alternative → Chromium Salts.

⑥ Rubber Industry → Coagulation of Latex
↓
Rubber.

⑦ Industrial products
↓
paints, inks, synthetic plastic, rubber,

⑧ purification of drinking water
↓
water + Alum → coagulate suspended impurities
↓
make it fit for Drinking