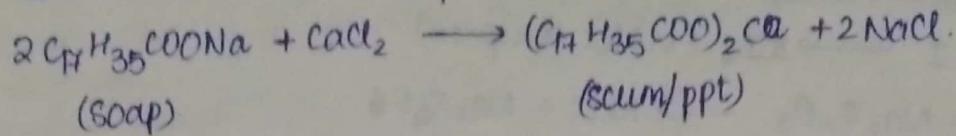


* Hardness of Water:

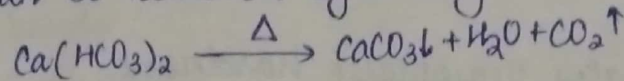
→ Hard water when treated with soap produces a scum or ppt.



→ Types of Hardness:

(i) Temporary - • due of carbonates, bicarbonates & hydroxides of Ca, Mg & other metals.

• can be removed by boiling.



(ii) Permanent - • due to chlorides and sulphates of Ca, Mg, Fe

→ Equivalence of $CaCO_3$ = $\frac{\text{mass of hardness producing subst.} \times 50}{\text{chemical eq. of hardness producing subs.}}$

Softening of Hard water:

(i) Lime-Soda Process (ppt of $CaCO_3$ & $Mg(OH)_2$)

• cold lime soda process - 50 to 60 ppm of residual hardness

• Hot " " " - 15 to 30 ppm

↳ Better b/cz -

• rxn is faster

• hot process inc softening capacity

• no coagulant req & ppt settles easily

• dissolved gases are removed.

• viscosity is lower thus filtration becomes easy.

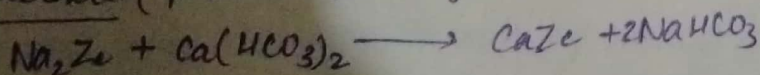
Advantages:

→ economical

→ pH of water inc thus corrosion is reduced.

→ quantity of minerals is reduced.

(ii) Zeolite method: (produces water of residual hardness 10 ppm)



10% conc brine solⁿ converts $CaZe$ back into zeolite

Limitation:

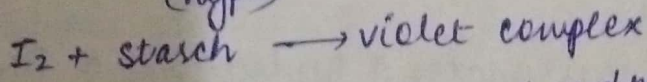
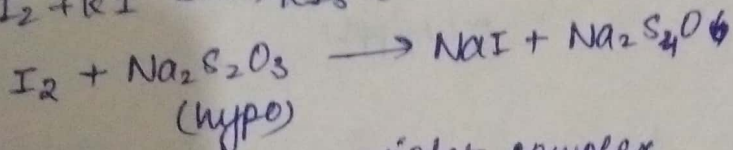
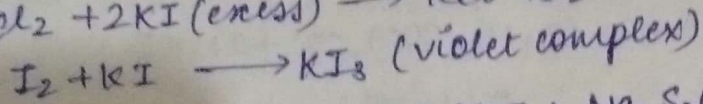
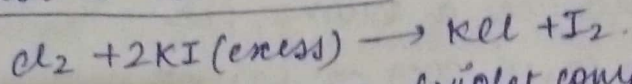
(i) turbidity should be removed before zeolite treatment.

(ii) coloured ions of Mn^{2+} & Fe^{2+} must be removed else zeolite cannot be regenerated.

(iii) mineral acids should be neutralized first.

chlorine safe limit - 250ppm

→ chlorine estimation:



→ Elements causing temporary hardness require only lime for softening while elements causing permanent hardness require both (soda + lime)

→ methyl orange indicates temporary hardness

→ For calculation of hardness by soda lime process Ca^{+2} is not considered in lime part and only in soda part.

→ lime requirement for softening:

$$= \frac{74}{100} \left[\text{Temp. } \text{Ca}^{+2} + 2 \times \text{Temp. } \text{Mg}^{+2} + \text{Perm. } (\text{Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{+3}) + \text{CO}_2 + \text{H}^+ (\text{HClO}_4, \text{H}_2\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2 \right]$$

→ soda requirement for softening:

$$= \frac{106}{100} \left[\text{Perm. } (\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Al}^{+3} + \text{Fe}^{+2}) + \text{H}^+ - \text{HCO}_3^- \right]$$

UV-Vis spectroscopy (mainly involves excitation of π or n e⁻)

• Ultraviolet region: 200-400 nm

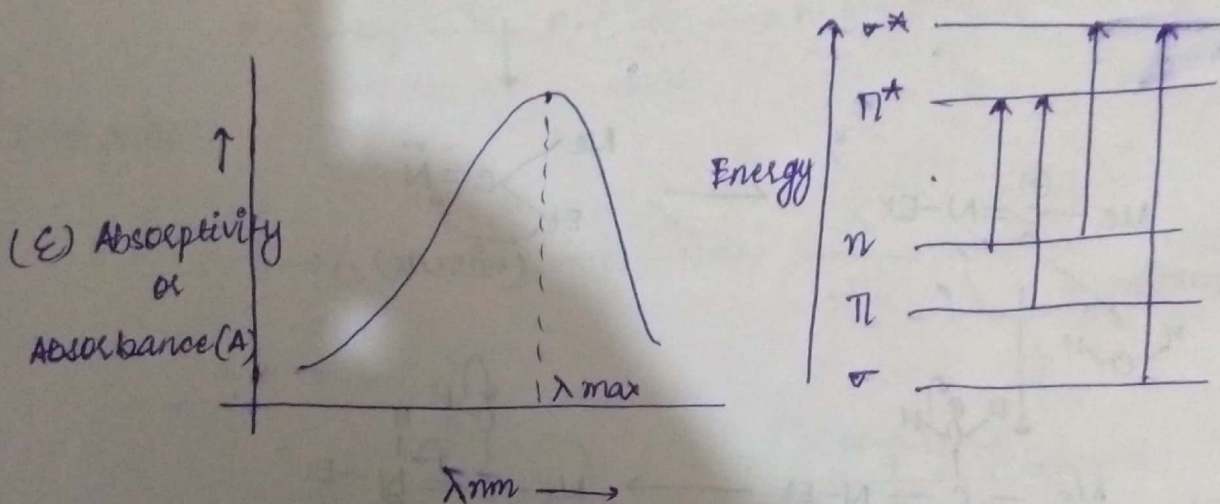
• chemical Info. $\xrightarrow{\text{source}}$ Transducer $\xrightarrow{\text{Signal Conditioner}}$ Display system

• four possible type of transitions: ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$)
in the order: $\sigma \rightarrow \sigma^*$ (alkanes) $>$ $n \rightarrow \sigma^*$ (containing lone pair) $>$ $\pi \rightarrow \pi^*$ (unsaturated) $>$ $n \rightarrow \pi^*$ (double bond with hetero atom)
(Energy req.)

light source \rightarrow monochromator \rightarrow slit \rightarrow Detector or photodiode \rightarrow Amp \rightarrow Recorder

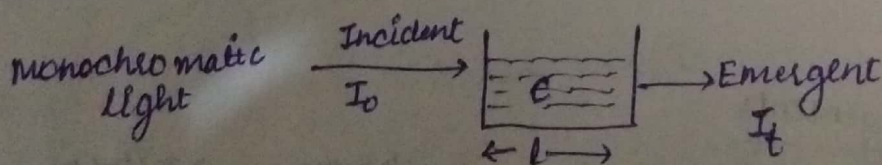
— Tungsten filament lamp (specifically emit 375 nm)

— Hydrogen-Deuterium lamps (emits < 375 nm)



λ_{max} corresponds to electronic transition rest λ corresponds to vibrational or rotational transitions.

Beer-Lambert Law



$$A = \log \frac{I_0}{I_t} = \epsilon c l$$

A = Absorbance

c = mol L⁻¹

l = cm

ϵ = Absorptivity

$$(T) \text{ Transmittance} = \frac{I_t}{I_0}$$

$$A = \log \left(\frac{1}{T} \right)$$

* alkenes & alkynes show $\pi \rightarrow \pi^*$ transition but at low λ . However conjugation inc. the absorption at higher λ . This change is known as bathochromic shift.

UV-Vis Spectroscopy & IR Spectroscopy:

→ IR Spectroscopy:

- gives info about molecular vibrations.
- When a molecule absorbs IR radiation in IR region, there is vibrational rotational spectrum.
- gives information about
 - Functional groups
 - Bonds.

- vibrational energy depends upon:

(i) Mass of atom present in molecule

(ii) strength of bonds.

(iii) arrangement of atoms

wavenumber.

• vibrational frequency for diatomic molecule
$$= \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} = \frac{1}{2\pi c} \sqrt{\frac{k}{\left(\frac{m_1 m_2}{m_1 + m_2}\right)}} = \bar{\nu}$$

$$k = \begin{cases} \text{single bond} = 5 \times 10^5 \\ \text{double bond} = 10 \times 10^5 \\ \text{triple bond} = 15 \times 10^5 \end{cases}$$

- Energy diff. b/w 2 successive vibrations

$$\Delta E = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

- stretching vib:

→ atoms remain in same bond axis.

→ oscillate without changing bond angle.

- Degree of vibration freedom:

(a) non-linear polyatomic molecule $= (3n-6)$

(b) for linear molecule $= (3n-5)$

- for IR active:

→ dipole moment of the molecule must change.

→ triatomic molecules having symmetry are inactive. eg CO_2 , CS_2

for ~~wavenumber~~ frequency
$$= \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1}$$

IR spectra

Functional group region

→ 4000-1500 cm^{-1}

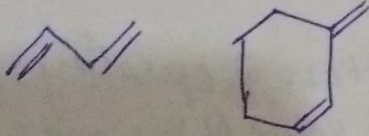
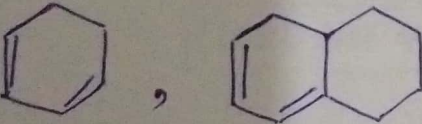
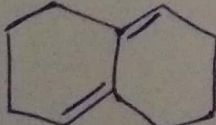
→ detecting presence of functional groups

Finger print region.

< 1500 cm^{-1}

- Fermi resonance takes place resulting in the shift of first level towards higher frequency.
 - Fundamental vibration + overtone/combination = Fermi resonance
- More conjugation in functional group \Rightarrow less absorption freq.

Woodward Fieser (Only for conjugated diene system)

1.  - acyclic dienes - 217nm
2.  - homocyclic dienes - 253nm.
3.  - heterocyclic dienes - ~~215nm~~ 214nm.
4. acyclic triene = 245nm.

Addition:

1. alkyl substitute & ring substrate - 5nm
2. Endo double bond - ~~30nm~~ 5nm.
3. = extending double bond - 30nm

Polar substituents:

- Cl, -Br, -I = +5nm.
- OR = +6nm.
- SR = +30nm.
- NR₂ = 60nm.
- OCOR = 0nm.

Woodward Fieser rule for α,β unsaturated carbonyl

Base value:

- Acyclic α,β -unsaturated ketones = 215 nm.
- 6-membered or higher α,β -unsaturated cyclic ketone = 215 nm.
- 5 membered α,β -unsaturated cyclic ketone = 202 nm.
- α,β -unsaturated aldehyde = 207 nm
- α,β -unsaturated carboxylic acid and ester = 193 nm.

Increment:

- = extending conjugation = 30 nm
- exocyclic double bond = 5 nm.
- Homoannular diene component = 39 nm.

For substituents:

Alkyl / ring residue	α	β	γ	δ
	10	12	18	18
-OH	35	30	50	50
-ONe	35	30	17	31
-Cl	15	12	12	12
-Br	25	30	25	25
-OAc	6	6	6	6

when dissolved in solvent:

- water $\rightarrow -8$
- methanol $\rightarrow 0$
- chloroform $\rightarrow +1$
- Dioxane $\rightarrow +5$
- Ether $\rightarrow +7$
- Hexane $\rightarrow +11$

$$\rightarrow \frac{3I}{4} \quad \frac{3I}{16} \quad \frac{3I}{64}$$

$$\frac{\frac{I}{64}}{I} \times 100 = \frac{3I}{4} \rightarrow$$