CRYSTALLIZATION

By
Dr.S.VIDYADHARA
Principal, CHIPS

DEFINITION

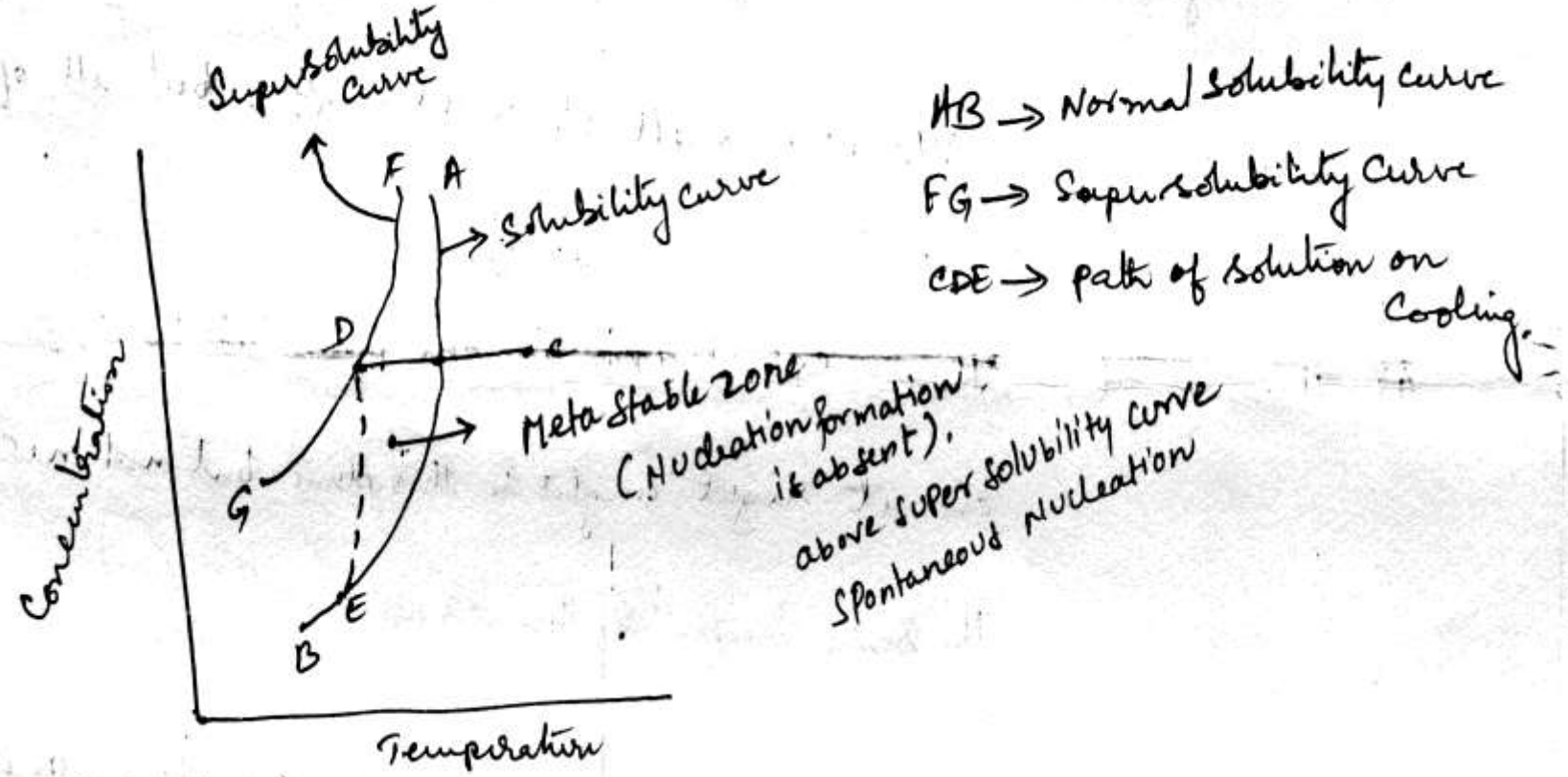
- Crystallization is the formation of solid particles within a homogeneous phase.

Various forms of Crystals

- Cubic
- Tetragonal
- Orthorhombic
- Hexagonal
- Monoclinic
- Triclinic

Theory of Crystallization

Miers Supersaturation theory:



HB → Normal solubility curve

FG → Supersolubility Curve

CDE → path of solution on Cooling.

Limitations of Miers theory:

1) It is known that sufficiently great lengths of time nuclei can form even well below the supersolubility curve. The formation of such nuclei depends on such accidental collisions of molecules of solute into aggregates large enough to persist. It would seem that the larger the volume of the solution the more chance of such cases. (This phenomenon makes it doubtful that any exact line such as FG. can be drawn)

2) Miers theory hold good only for the pure saturated solution. But it has been found that any foreign body can act as the nucleus. It is unavoidable that in commercial practice, when solutions are exposed to air, millions of dust particles may fall into the solution. Any foreign body may fall into the solution may act as nucleus so in actual practice the curve FG is not possible.

Significance of Miers theory:

1) It points out that greater the degree of super saturation there is more chance of nuclei formation.

2) If the supersaturation passes a certain range of values, nucleus formation is apt to be extremely rapid.

Nucleation

- Nucleation is process of giving birth to a very small solid body in a super saturated homogenous medium.

Rate of Nucleation

- Is the formation of number of new solid particles per unit time per unit volume of mother liquor.

Types of Nucleation

- Homogenous
- Heterogenous
- Spurious

  a) Needle Breeding

  b) Vieled Growth

Stages of Crystal Growth

- Cluster $\longleftrightarrow$ Embryo $\longleftrightarrow$ Nucleus $\longrightarrow$ Crystal

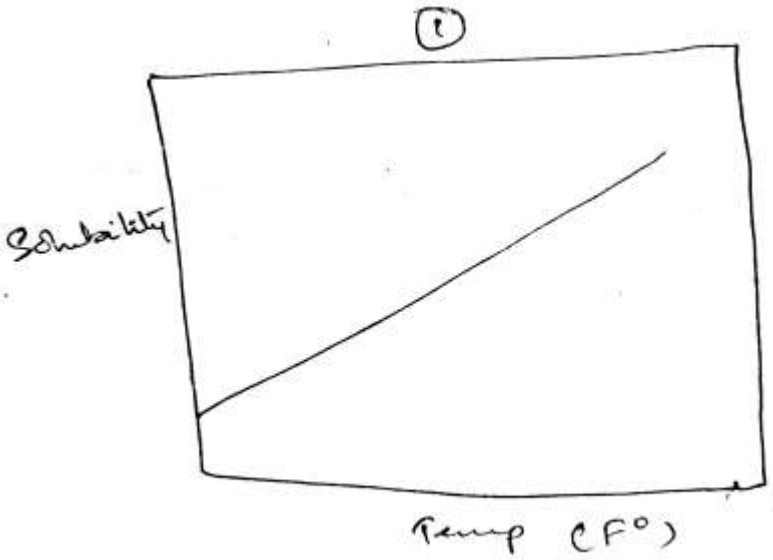
Rate of Crystal Growth

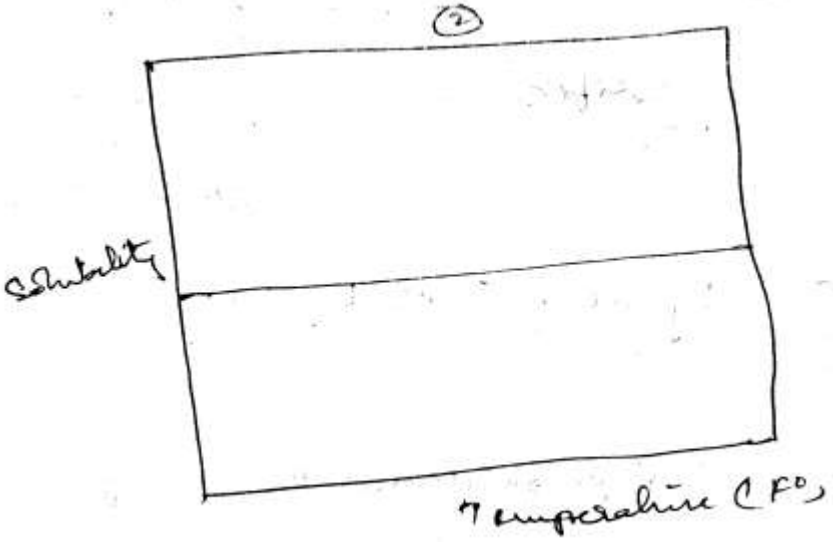
Factors :

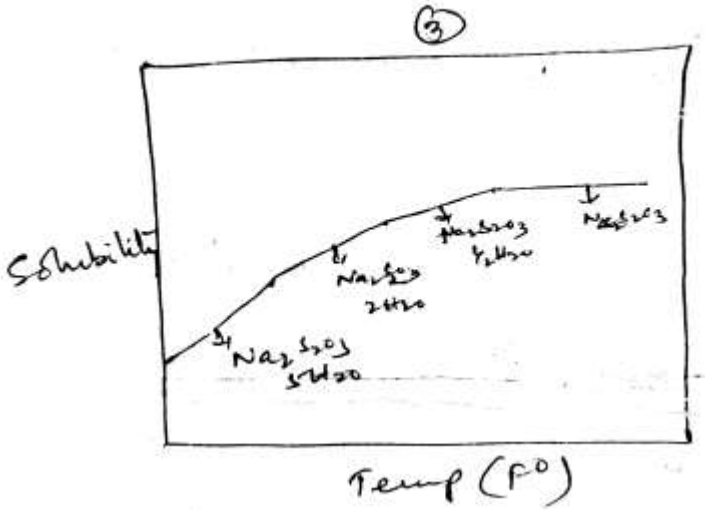
a) Rate of Diffusion

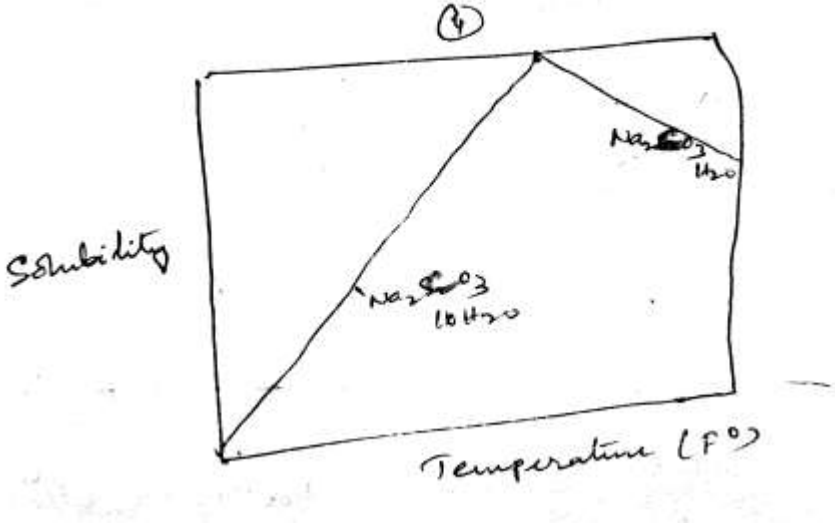
b) Effect of Viscosity

Solubility Curves









Classification of Crystallizers

1) Supersaturation by Cooling
   - A) Batch process
     - I) Tank crystallization
     - II) Agitated batch crystallizer
   - B) Continuous process
     - I) Swenson walker crystallizer
     - II) others
2) Supersaturation by adiabatic cooling
   - A) Vacuum crystallizers
     - I) without external classifying seed bed
     - II) with external classifying seed bed
3) Supersaturation by Evaporation
   - A) Salting Evaporators
   - B) Krystal Evaporators.

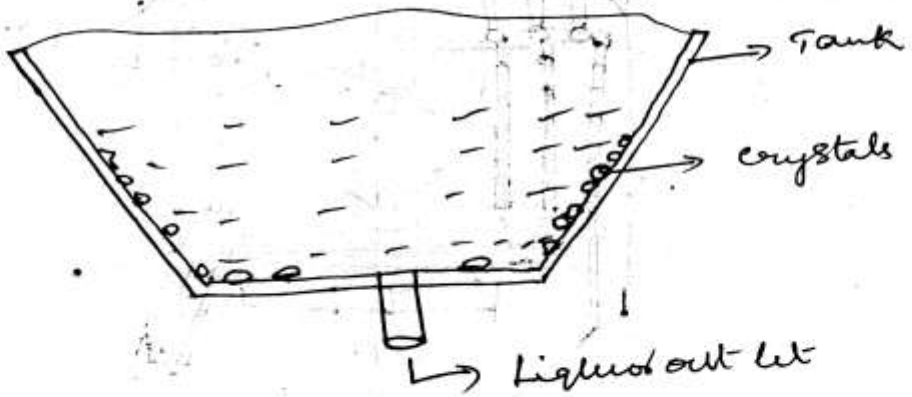
Disadvantages:

1) crystal formation is slow

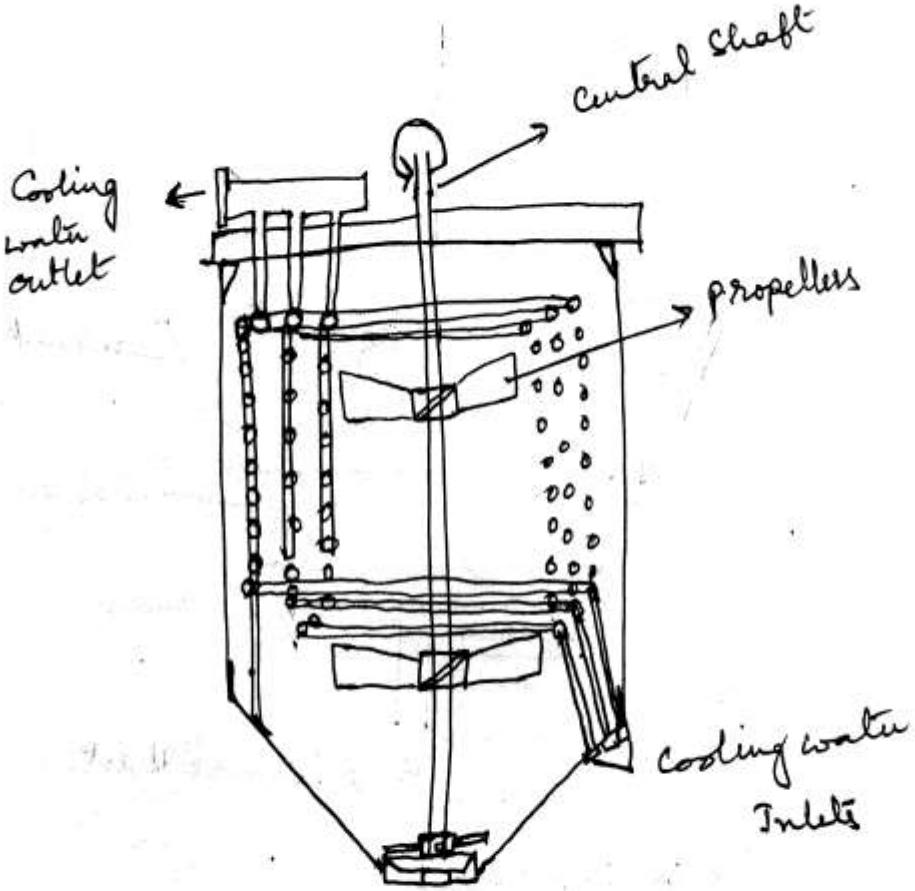
2) crystals formed are large and interlocked which results in occulsion of mother liquor, thus introducing impurities.

3) Requires much labour

4) Requires more floor space.



Tank crystallizer



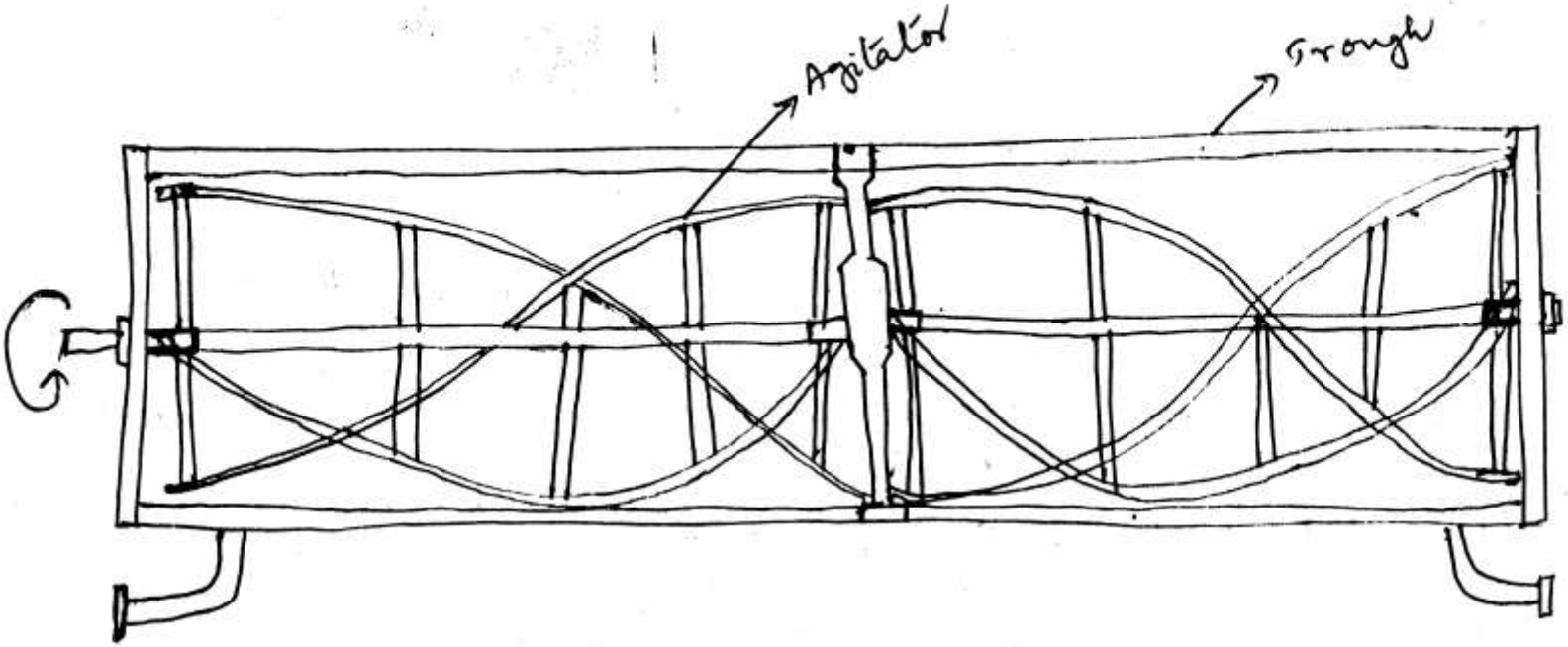
Agitated Batch Crystallizer

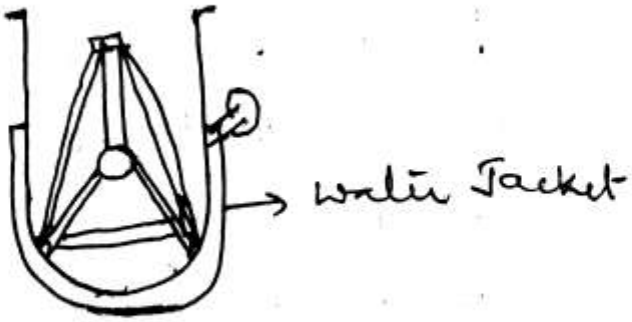
Advantages:

1) The product obtained is more uniform and finer than the tank crystallizer.

Disadvantages: 1) It is a batch or discontinuous process.

2) Solubility is least at the surface of the cooling coils. Crystal growth is most rapid at this period and coils rapidly build up with a mass of crystals that lows the rate of heat transfer.





Swenson - walker crystallizer

Swenson Walker Crystallizer

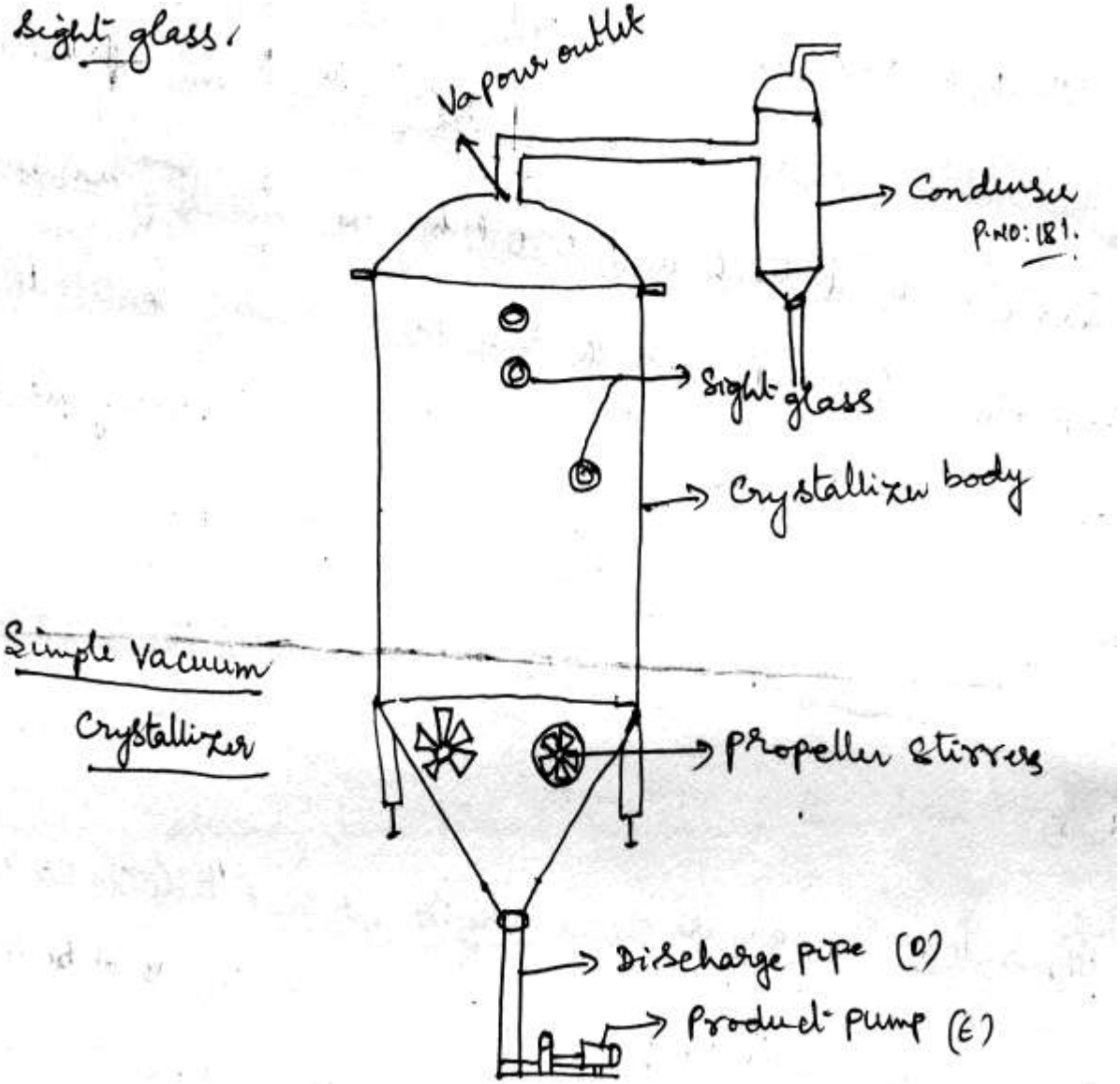
Advantages

- It can be operated continuously
- It produces uniform size and shaped crystals.
- Spiral agitator helps in proper crystal growth and prevents the crystals to accumulate on the surface of the crystallizer.

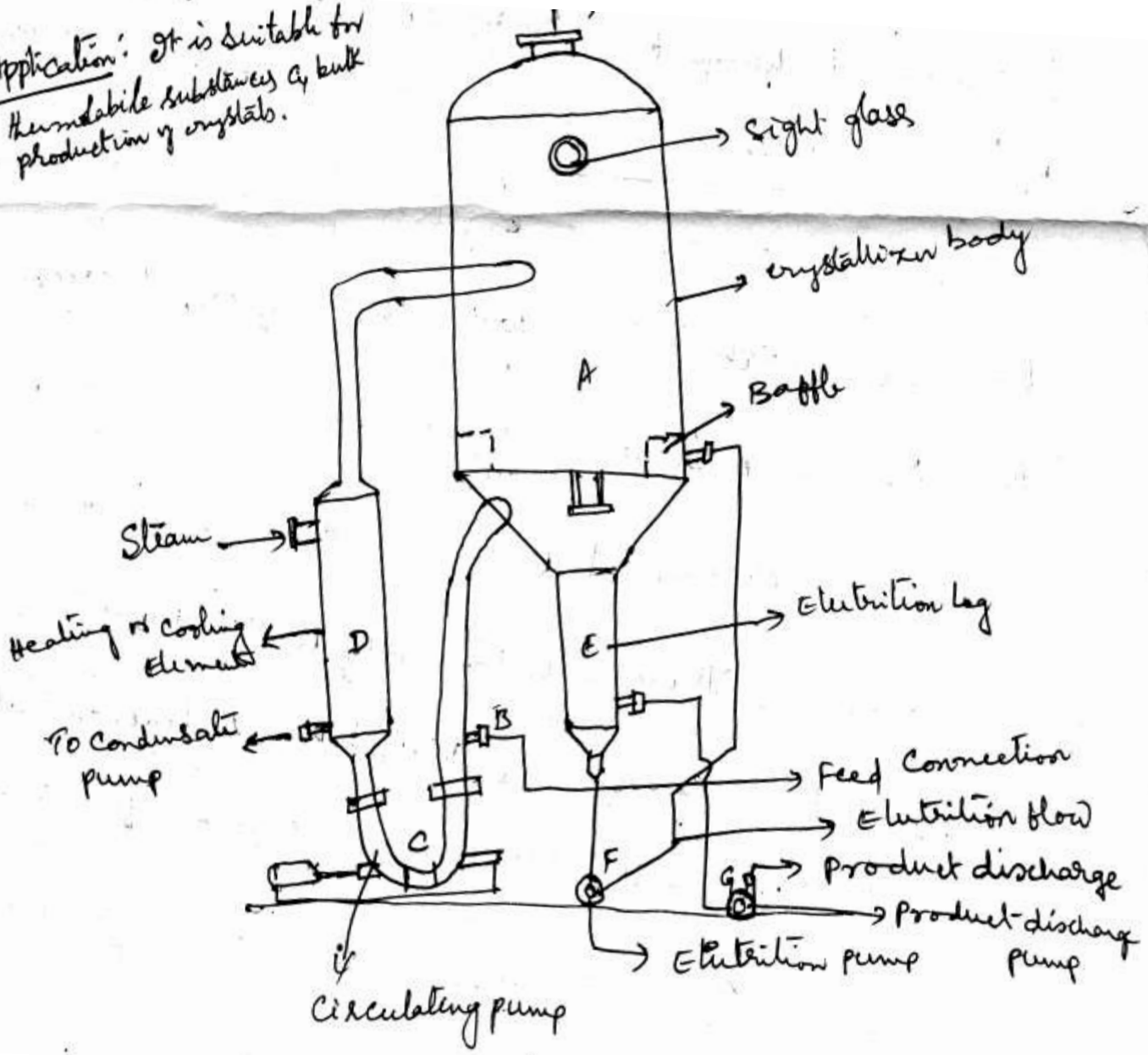
Disadvantages

- The apparatus is costly and its maintenance is difficult.

Sight glass:


Vapour outlet
Condenser
P.NO: 181.
Sight glass
Crystallizer body
Simple Vacuum Crystallizer
Propeller stirrer
Discharge pipe (D)
Product pump (E)

Application: It is suitable for thermolabile substances & bulk production of crystals.

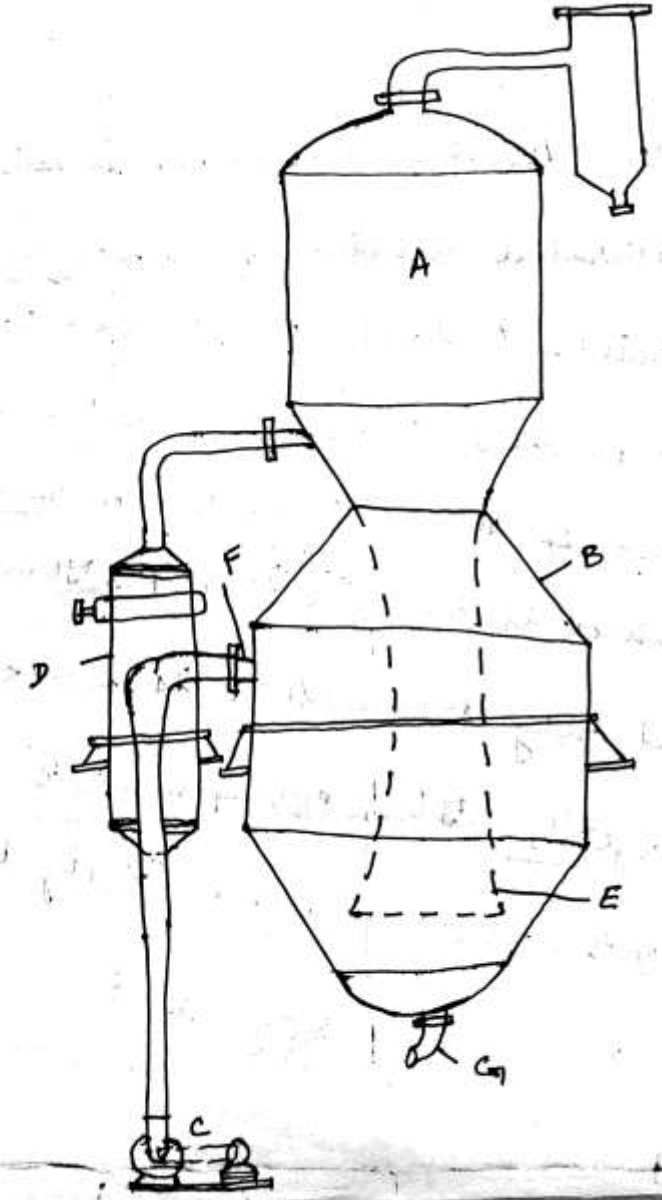


Advantages

- It is very simple without any moving parts.
- Corrosive materials can be used as inner surface can be made acid resistant.
- It can be constructed as large as desired.
- It can be operated continuously or batch wise.

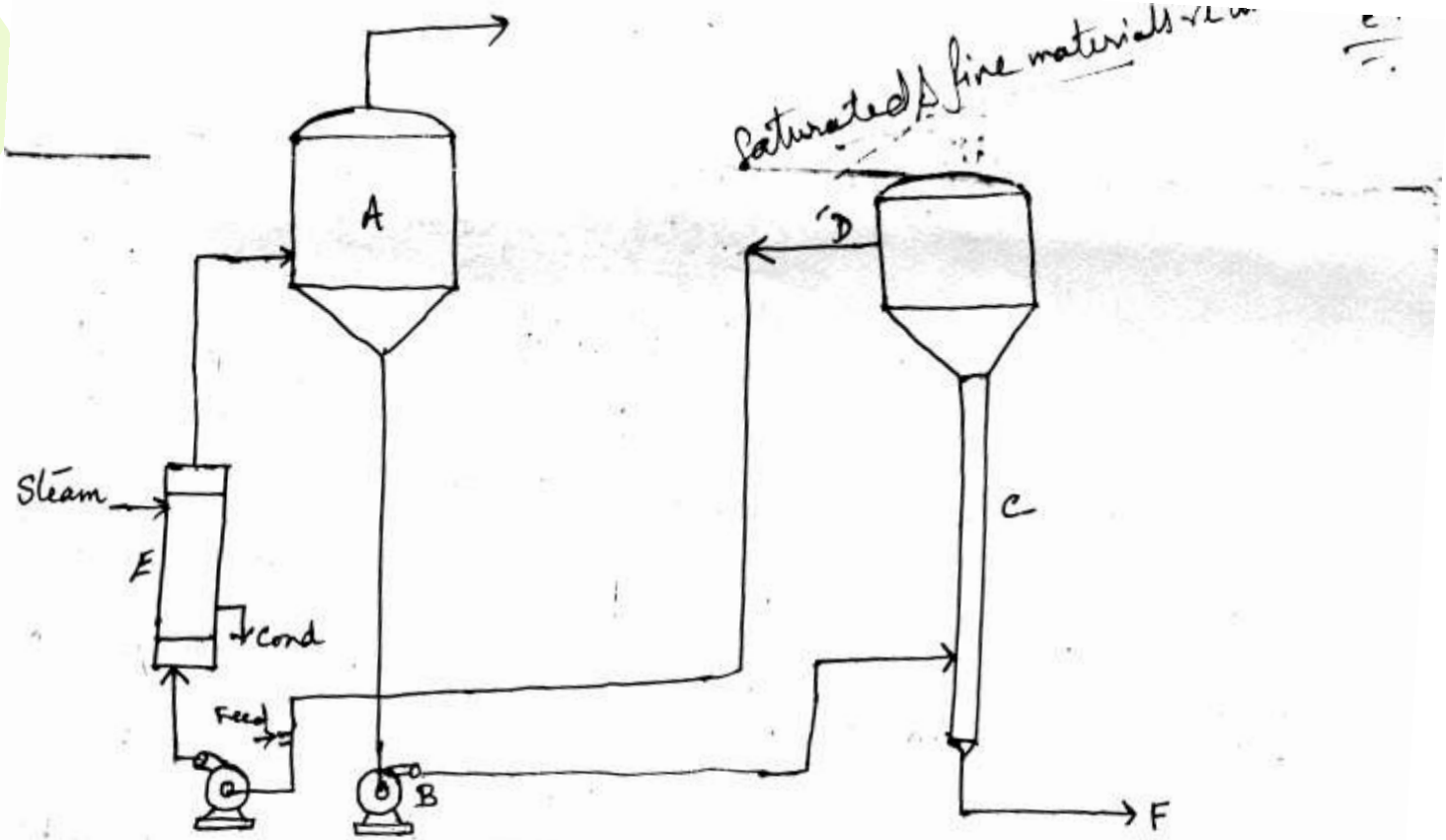
Disadvantages

- Requires many number of pumps.
- Complex piece of equipment.



A = Vapour Head
B = Crystal Growth Chamber
C = Circulating pump
D = Heater or Cooler
E = Discharge tube to bottom of crystal bed
F = overflowing to circulating pump
G = product discharge

Krystal Crystallizer



Growth-type crystallizer

A = Vapour head

B = Transfer pump

C = Growth column

D = overflow from growth column

E = Heater

Uses

- It is used for crystallization of Sodium Chloride & Magnesium Sulphate.

Advantages

- It is preferred when large quantity of crystals of controlled sizes are required.
- It is Available in very large sizes with a body upto 4.5 mts diameter and 6.0 mts height.

Caking of Crystals

- *Caking* can be defined as the process of formation of clumps or cakes when crystals are improperly stored.
- *Crystal Humidity* is the humidity above which crystals absorb moisture and below which they donot absorb moisture.

Factors effecting Caking

- Size of the crystals
- Shape of the crystals
- Humidity
- Time of exposure
- Impurities in crystals
- Melting point
- Temperature Fluctuations

Prevention of Caking

- Crystals must be more spherical in shape with least points of contact.
- Crystals must be larger in size with more void spaces & must have narrow size distribution.
- Crystals must have highest possible critical humidity.
- Crystals must be coated with powdery inert material to prevent absorption of moisture. Ex: Table salt is coated with Magnesia or TCP.

  Flake Calcium Chloride is coated with anhydrous Calcium Chloride.

Thank you