

# CRYSTALLISATION

In this chapter, our discussion is restricted to crystallisation from solution.

Crystallisation is an operation in which solid particles are formed from a liquid solution.

It is a solid-liquid operation used to separate a solute from its solution in the form of crystals. In this operation, mass is transferred from the liquid phase (solution) to a pure solid crystalline phase.

Crystallisation is an important operation in the chemical industry as the number of salable products have to be in the form of crystals. This operation gives almost pure product in the form of crystals of a desired size ranging from relatively impure solutions in a single processing step. From the energy point of view, crystallisation requires much less energy for separation as compared to other purification methods (e.g., distillation). It may be carried out at relatively low temperatures and on a scale ranging from a few grams to thousands of tons per day.

Crystallisation usually involves : (i) concentration of solution (by evaporating a part of the solvent) and (ii) cooling of solution until the concentration of solute becomes higher than its solubility at the prevailing temperature. The solute then comes out of the solution (i.e., precipitates) in the form of pure crystals.

The performance of crystallisation process is evaluated in terms of size, shape, structure, yield and purity of crystals. So in commercial crystallisation, the size and shape of crystals are as important as the yield and purity of crystals.

## Solubility :

The solubility of a solute in a given solvent is the *concentration of the solute in a saturated solution at a given temperature.*

The concentration of a solute in a saturated solution is called the solubility of the solute in the solvent.

The solubility of a solute in a given solvent depends on the nature of the solute, the nature of the solvent and the prevailing temperature (solubility mainly depends on temperature). Solubility data are generally given as parts by weight of anhydrous solute material per 100 parts by weight of the solvent, e.g., the solubility of  $\text{MgSO}_4$  in water at



293 K (20° C) is 35.5 kg  $\text{MgSO}_4$  per 100 kg water. Solubility data are plotted as solubility curves—curves wherein solubilities are plotted against temperature.

**The solubility of the solute in a given solvent is different at different temperatures and it forms the basis of crystallisation by cooling.**

### Saturation :

Consider a process of dissolving copper sulphate in water (solvent) at a given temperature. Initially, when some amount of copper sulphate is added, all of it goes in the solution (i.e., it dissolves in water). Additional amount can be dissolved further till a stage comes when no more copper sulphate can be dissolved in a given amount (i.e. a fixed amount) of the solvent. At this stage, the solution is called a saturated solution.

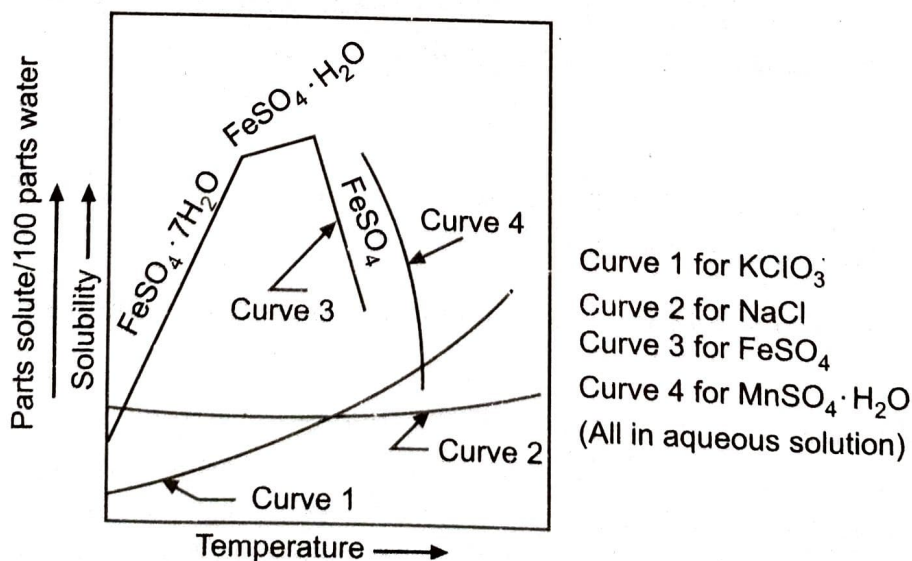
A saturated solution is defined as the *one which is in equilibrium with an excess of solid solute at a given temperature.*

If the temperature of the solution is increased, more solute [ $\text{CuSO}_4$ ] can be dissolved. Therefore, a saturated solution will contain different amounts of the solute dissolved in it at different temperatures. When a saturated solution at a higher temperature (say at  $T_1$ ) is cooled to a lower temperature say to  $T_2$ , then theoretically the amount of the solute corresponding to the difference in solubilities of the solute at these two temperatures will come out of the solution in the form of crystals.

### Solubility Curves :

A graphical relationship between the solubility of a solute and temperature is termed as the solubility curve.

The concentration necessary for crystal formation and chemical species that separate can be determined from solubility curves. Such curves are obtained by plotting the solubility of a solute as a function of temperature (solubilities against temperature). It shows the effect of temperature on the solubility of the solute. The solubility of solutes in a given solvent may increase, decrease, or remains more or less constant with temperature. Solubility curves have no general shape or slope.



**Fig. 11.1 : Solubility curves : Solubilities of salts in water**



Solubility curves of potassium chlorate, sodium chloride are continuous solubility curves as they show no sharp breaks anywhere. Sometime, the solubility curve exhibit sudden changes of direction and these curves are therefore referred to as discontinuous solubility curves, e.g., that of  $\text{FeSO}_4$ ,  $\text{Na}_2\text{SO}_4$ , etc.

For some substances, their solubility decreases with increase in temperature and in such cases their solubility curves are called as inverted solubility curves (e.g., that of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ ).

Usually, an increase in temperature of the solution increases the solubility of the solute when no true compounds are formed between the solute and solvent, e.g.,  $\text{KClO}_3$ ,  $\text{KNO}_3$  in  $\text{H}_2\text{O}$ . In case of a hydrated salt, the solubility increases with increase in temperature over a certain temperature range and then decreases. Fig. 11.1 shows solubility curves for a number of salts in water. In case of potassium chlorate, the solubility increases with temperature so it can be readily crystallised by cooling its saturated solution. The solubility of  $\text{NaCl}$  in water is almost independent of temperature (a slight increase in the solubility results by a large increase in temperature), so for crystallisation to occur, some of the solvent should be evaporated.

### Supersaturation :

Consider an equilibrium solution (solid solute + liquid solvent). If we disturb this equilibrium either by cooling the solution or evaporating a portion of the solvent, then the quantity of solute will exceed the equilibrium concentration and the system will try to attain a new state of equilibrium by expelling (precipitating) an excess solute present in it in the form of crystals. This process of forming crystals is called crystallisation from solution and the concentration difference driving force is called supersaturation.

**Supersaturation :** It is the quantity of solute present in a solution (in which crystals are growing) compared with the quantity of solute that is in equilibrium with the solution (i.e., the equilibrium solubility at the temperature under consideration). The supersaturation is expressed as a coefficient, given as

$$s = \frac{(\text{Parts solute} / 100 \text{ parts solvent}) \text{ at prevailing condition}}{(\text{Parts solute} / 100 \text{ parts solvent}) \text{ at equilibrium}} \geq 1.0$$

Crystallisation cannot take place/occur (i.e., crystals can neither form nor grow) unless a solution is supersaturated. The amount of crystals formed however depend upon the difference in saturation concentration since once the crystallisation begins the extra solute held in the solution due to supersaturation also comes out of the solution in the form of crystals.

### Mechanism of crystallisation / crystal formation :

A knowledge of the mechanism by which crystals form and grow is required in the design and operation of an equipment used for crystallisation. The formation of a crystal from a solution is a two-step process.

The first step is called nucleation (the birth of new small particles or nuclei) and the second one is called crystal growth (growth of crystals to macroscopic size).



*The generation of a new solid phase (i.e., new small particles) either on an inert material in the solution or in the solution itself is called **nucleation**. The increase in size of these nuclei with a layer-by-layer addition of solute is called **crystal growth**.* Supersaturation is the common driving force for nucleation and crystal growth. Crystals can neither form nor grow unless a solution is supersaturated.

The number of nuclei formed and the rate of growth of crystals depend upon the temperature of operation. The number of nuclei and growth rate of crystals increase with increase in temperature upto a certain point and then decreases. The temperature corresponding to a maximum number of nuclei formation is different than the temperature at which a growth rate is maximum.

If initially a large number of nuclei is formed, then the yield of the process contains many small or tiny crystals and if a few nuclei are formed initially (at the start), then the yield of the process contains large size crystals. Slow cooling results in the formation of a less number of nuclei and hence large size crystals are formed (as the material deposits on a relatively few nuclei), whereas rapid cooling results in the/leads to the formation of a large number of nuclei, giving the yield containing a large number of tiny crystals.

### **Methods of Supersaturation :**

Unless a solution is supersaturated, neither nucleation nor crystal growth occurs (i.e., crystals can neither form nor grow). Thus, for crystallisation to occur, supersaturation can be generated by any one of the following methods :

- (a) By cooling a concentrated, hot solution through indirect heat exchange.
- (b) By evaporating a part of the solvent/By evaporating a solution.
- (c) By adiabatic evaporation and cooling (i.e., by vacuum cooling) : by flashing of a feed solution adiabatically to a lower temperature and inducing/causing crystallisation by simultaneous cooling and evaporation of the solvent.
- (d) By adding a new substance (i.e., a third substance) which reduces the solubility of the original solute, i.e., by salting.
- (e) By chemical reaction with a third substance.

When the solubility of the solute increases with increase in temperature, a saturated solution becomes supersaturated, i.e., supersaturation is generated by cooling and temperature reduction. This is the case with many inorganic salts and organic substances (e.g. potassium nitrate, potassium chlorate, oxalic acid, etc.). When the solubility of the solute is relatively independent of temperature (as is the case with common salt (NaCl) in  $H_2O$ ), supersaturation is generated by evaporating a part of the solvent. When the solubility of the solute is very high then neither cooling nor evaporation helps and supersaturation may be generated by adding a new substance (a third component). The added component may get mixed physically with the original solvent to form a mixed solvent in which the solubility of the solute is reduced. This technique is called salting. The third component added may react with the original solute and form an insoluble substance. This technique is called precipitation and it is used in wet quantitative analysis. The rapid creation of very large



supersaturations is possible by the addition of a third component but it is not common in industry.

### Miers' Supersaturation theory :

According to Miers' theory there is a definite relationship between the concentration and temperature at which crystals will spontaneously form in a pure solution. This relationship is represented by the supersolubility curve which is approximately parallel to the solubility curve. Both the curves are shown in Fig. 11.2. The curve AB is the solubility curve and the curve PQ is the supersolubility curve. The curve AB represents the maximum concentration of solutions which can be achieved by bringing solid solute into equilibrium with a liquid solvent. If a solution having the composition and temperature indicated by point C is cooled in the direction shown by an arrow, it first crosses the solubility curve AB and we would expect here crystallisation to start. Actually if we start with initially unseeded solutions, crystal formation will not begin until the solution is supercooled considerably past the curve AB. According to the Miers' theory, crystallisation will start in the neighbourhood of point D and the concentration of the solution then follows roughly along the curve DE. For an initially unseeded solution, the curve PQ represents the limit at which spontaneous nuclei formation begin and consequently, crystallisation can start. According to Miers' theory, under normal conditions, nuclei cannot form and crystallisation cannot then occur in area between the solubility curve and the supersolubility curve i.e. at any position short of point D along the line CD.

Miers' theory is useful for discussing the qualitative aspects of nucleation from seeded and unseeded solutions.

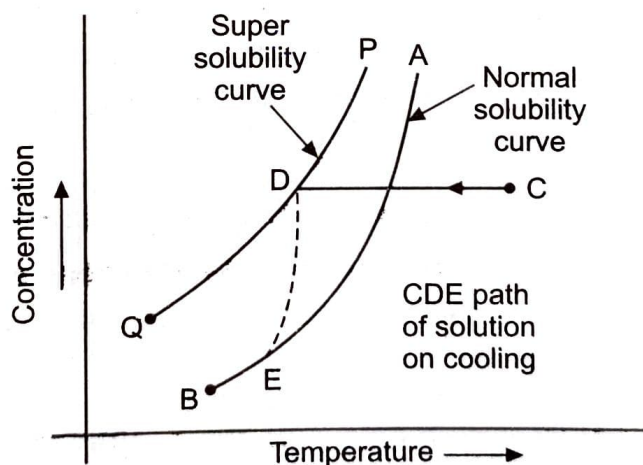


Fig. 11.2 : The Miers' Supersaturation Theory

### Yield of crystallisation process :

Usually, crystallisation processes are carried out slowly and the mother liquor is in contact with sufficiently large crystals so that at the end of the process, the mother liquor is saturated at the final temperature. In such cases, the yield of crystallization process is calculated from the initial solution composition and the solubility of the solute material at the final temperature. If appreciable evaporation of the solvent occurs during the crystallisation process, the solvent evaporated must be taken into account in determining the yield. Whenever crystals are anhydrous, the yield is obtained by taking the difference between the initial composition of the solution and the solubility of the solute corresponding the final



temperature of the process. In cases where material precipitates as a hydrated salt, we have to take into account the water of crystallisation (in crystals), as this water is not available for retaining solute in the solution. Under these circumstances, the key to the calculations of yields is to express all the compositions in terms of hydrated salt and excess water (free water), as the excess water remains constant during crystallisation operation and the compositions or amounts thus expressed on the basis of excess water can be deducted in order to obtain the correct results.

The percentage yield of a crystallisation process is the amount of the solute crystallised/expressed as a percentage of the amount of the solute present in the feed solution.

### **Crystal form :**

The constituent particles of a crystal are arranged in an orderly and repetitive manner. The constituent particles may be atoms, molecules or ions. They are arranged in orderly three dimensional arrays called space lattices. Crystals are classified according to the angle between the faces and this is the area of the science of crystallography. Different forms of crystals based upon the angle between faces and lengths of axes are : cubic, tetragonal, orthorhombic, hexagonal, monoclinic, triclinic and trigonal.

### **Caking of Crystals :**

Caking of crystalline materials is caused by a small amount of dissolution occurring at the surface of crystals and subsequent re-evaporation of the solvent. Due to caking, the crystals can get very tightly bonded together.

Since the vapour pressure of a saturated solution of a crystalline solid is less than that of pure water at a given temperature, condensation can take place on the surface of the crystals even though the atmospheric relative humidity is less than 100 percent. The solution thus formed enters into/penetrates into the pack of crystals as a result of capillary action of the small gaps between the crystals and caking can result due to subsequent evaporation of moisture when the atmospheric humidity falls. Crystalline materials can also cake at a constant relative humidity, as the vapour pressure of a solution is less in a small capillary as compared to it in a large capillary as a result of temperature effect. As condensation occurs, the small particles get first dissolved and therefore average size of capillaries increases and the vapour pressure of the solution may increase sufficiently for evaporation to take place. When the particle size is non-uniform, a crystalline material will cake more rapidly as the porosity of a bed of particles of mixed sizes is less and fine particles are more readily soluble. Thus, the tendency of crystalline materials to cake can be reduced by forming crystals of relatively large and uniform sizes or by adding a water repellent agent, such as stearic acid.

**Magma :** It is a two-phase mixture of mother liquor and crystals that occupies the crystalliser and withdrawn as a product.

In order to reduce the load on a crystalliser, evaporation may be carried out to remove the excess solvent from a solution. Crystallisation is generally followed by filtration for the separation of crystals from the mother liquor.



**Effect of impurities on crystal formation :**

- (i) Soluble impurities may get adsorbed on the surface of the nuclei or crystals nucleation sites and hinder the rate of nucleation and crystal growth.
- (ii) The shape of crystal may get modified as the adsorption of impurities may occur preferentially on a particular face.

The impurities may decrease the rate of crystal growth. In some cases it is desirable, e.g., addition of a small quantity of glue or tannin to boiler feed water prevents nucleation and growth of calcium carbonate crystals and thus reduces scaling.

**Classification of Crystallisers :**

Crystallisers may be classified on the basis of mode of operation. These may be operated batch wise or continuously.

1. Batch crystalliser : stir-tank crystalliser
2. Continuous crystalliser : Swenson-Walker crystalliser.

Crystallisers may also be classified according to the method by which supersaturation is achieved. Thus, agitated tank crystalliser, Swenson Walker crystalliser are examples of crystallisers wherein supersaturation is achieved by cooling (or temperature distribution) which is a usual practice for materials of which the solubility decreases with decrease in temperature. Krystal crystalliser is an example of evaporative crystalliser wherein supersaturation is achieved by evaporating a part of the solvent and is a usual practice for materials whose solubility remains almost constant with variation in temperature. Vacuum crystalliser is an example of crystalliser wherein supersaturation is achieved by adiabatic evaporation and cooling which is most suitable for heat sensitive materials. This is used for large scale production in which supersaturation is achieved by introducing the hot solution into a vacuum in which pressure is less than the vapour pressure of the solvent at the temperature at which it is fed, the solvent thus flashes or evaporates and the solution is cooled adiabatically. Salting out with the help of a third substance is not in use and at present, deliberate introduction of a foreign substance to decrease the solubility is rarely found.

**Classification based on the method of achieving supersaturation :**

1. Supersaturation by cooling alone :
  - (a) Batch – Agitated tank crystallisers
  - (b) Continuous – Swenson-Walker crystalliser
2. Supersaturation by adiabatic evaporation and cooling :
  - (a) Vacuum crystallisers with and without external classifying seed bed
3. Supersaturation by evaporation :
  - (1) Krystal crystallisers
  - (2) Draft-tube crystallisers.

Crystallisers are also classified according to the method of suspending the growing crystals : (a) where the suspension is agitated in a tank, (b) where the suspension is circulated through a heat exchanger, e.g., vacuum crystalliser and Oslo crystalliser, (c) where the suspension is circulated through a scraped surface exchanger.

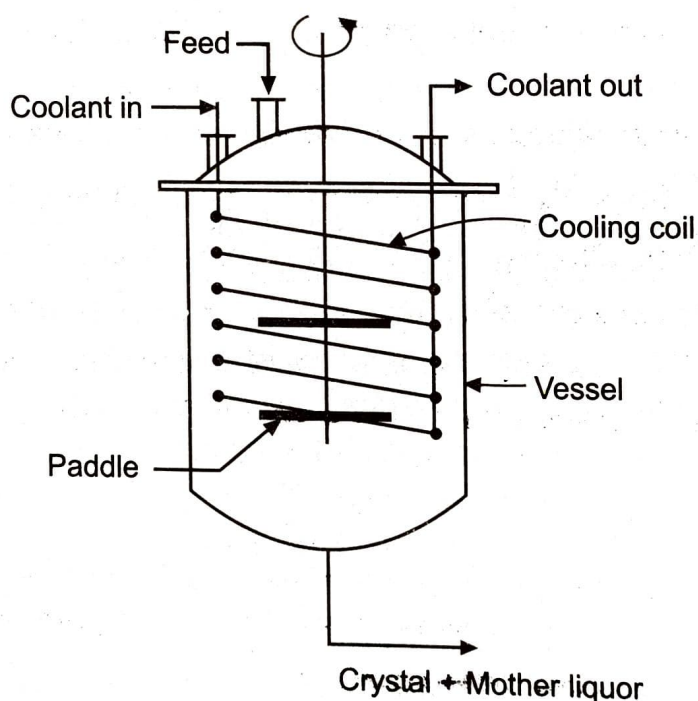


### Agitated Tank Crystalliser :

It is also known as a stir-tank crystalliser or agitated batch crystalliser. This is the simplest and perhaps the most economical unit. In this crystalliser, supersaturation is generated by cooling so it is a cooling crystalliser.

This type of crystalliser is commonly used in small scale production or batch processing due to several advantages, such as low initial cost, simple in construction and flexibility. These are having capacities more than tank crystallisers.

**Construction :** Agitated tank crystalliser consists of a cylindrical tank provided with a low speed agitator and a cooling coil. The tank is having a conical bottom through which the product is withdrawn. The agitator improves the heat transfer rate, keeps the temperature of the solution uniform and keeps the fine crystals in suspension which is essential for uniform growth of the crystals.



**Fig. 11.3 : Agitated tank crystalliser**

**Working :** A known quantity of hot solution is charged to the crystalliser, cooling is applied by circulating a coolant through the coil and agitator is started. The mass in the crystalliser cools due to heat transfer to the circulated coolant and as the temperature decreases, crystals are formed due to decrease in the solubility of the solute. The mass is cooled to a predecided temperature and finally a product stream containing crystals plus mother liquor is withdrawn from the bottom of the crystalliser.

The disadvantages of this crystalliser include : the solids deposited on the surface of the coil add resistance to heat transfer so that it ceases to function efficiently, difficulty in controlling nucleation and size of crystals, frequent washing and scrapping of the cooling surface and high labour costs.



This type of crystalliser is used to produce fine chemicals, pharmaceutical products and dye intermediates.

### Scrapped surface crystalliser :

- (i) Swenson-Walker crystalliser and (ii) Double pipe crystalliser.

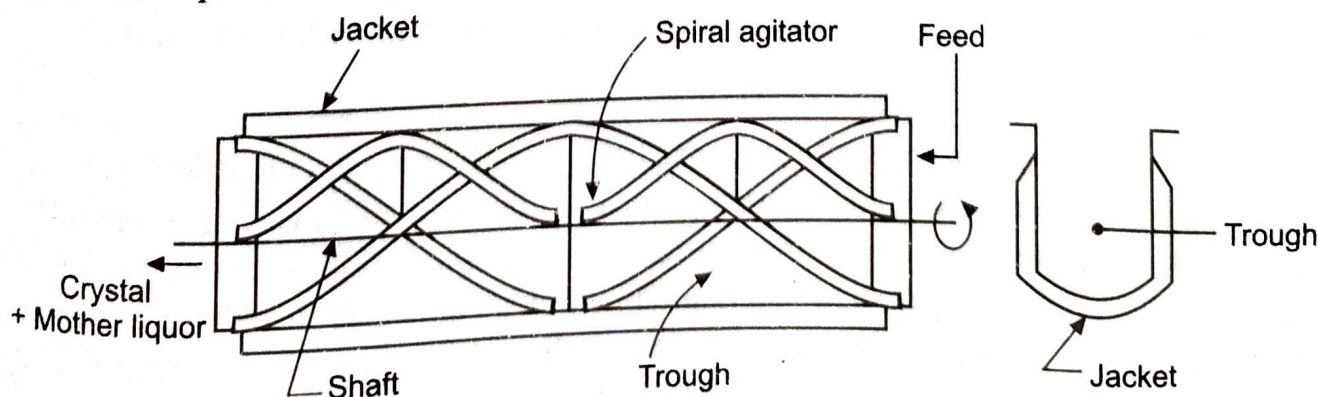
### Swenson-Walker Crystalliser :

The Swenson-Walker crystalliser is a cooling type, continuous, jacketed trough crystalliser. It is an example of the scrapped surface crystalliser and is probably the most widely used crystalliser.

### Construction :

It consists of a long open rectangular trough with a semi-cylindrical bottom, i.e., U-shaped trough, of width 0.6 m and length 3 to 6 m. The trough is jacketed externally for circulating the coolant during operation. A spiral agitator rotating at about 7 rpm is incorporated in the trough in such a way that it is as close to the bottom of the trough as possible. The capacity of this crystalliser can be increased by arranging a number of units in series (four troughs of 3 metre length each may be arranged). At one end of the crystalliser, an inlet for the hot solution is provided and at the other end of the crystalliser, an overflow gate for the crystals and mother liquor discharge is provided. The functions of the spiral agitator are : (i) to scrap the crystals from the cooling surface (i.e., to prevent accumulation of the crystals on the heat transfer surface), (ii) to lift and shower the crystals through the solution so that the crystals will be held in suspension and thereby the crystals of uniform size can be obtained (as deposition occurs mainly by build up on previously formed crystals) and (iii) to convey the crystals from one end of equipment to the other end.

The trough is formed out of metal sheets welded to an angle-iron frame at the top. A jacket is usually made of mild steel. The spiral agitator is supported at either ends outside the trough. A stuffing box assembly is attached to the cover on either ends that prevents leakage of the liquor from the opening provided for a shaft. The shaft is driven by belt, etc.



**Fig. 11.4 : Swenson - Walker Crystalliser**



**Working :**

A hot concentrated solution is fed at one end of the open trough and flows slowly towards the other end of the trough. Water is fed to the jacket in such a way that it flows in a counter current fashion with respect to the solution. The solution while flowing through the trough cools by heat transfer to water. Once the solution becomes supersaturated, crystals start forming and building. A spiral agitator keeps the crystals in suspension so that previously formed crystals grow instead of formation of new crystals and ultimately the two phase mixture of crystals and liquor leaves the crystalliser through an overflow gate.

Advantages of this crystalliser include : saving in floor space, in material in process and saving in labour.

This crystalliser is suitable only when supersaturation can be achieved by cooling alone.

**Double pipe scrapped surface crystalliser :**

Less common type of continuous scrapped surface crystalliser that is somewhat similar to the jacketed trough crystalliser, i.e., Swenson-Walker crystalliser is a double pipe crystalliser. It consists of a concentric double pipe, the outer pipe acting as a jacket. Cooling water flows through the annular space between the two pipes and a long pitch spiral agitator rotates in the inner pipe at 5 to 30 rpm. These are also arranged in series (3 pipes each of 3 m long). The other constructional features and the method of operation is the same as of the Swenson-Walker crystalliser.

It is used in crystallising ice cream and plasticizing margarine.

**Vacuum Crystalliser :**

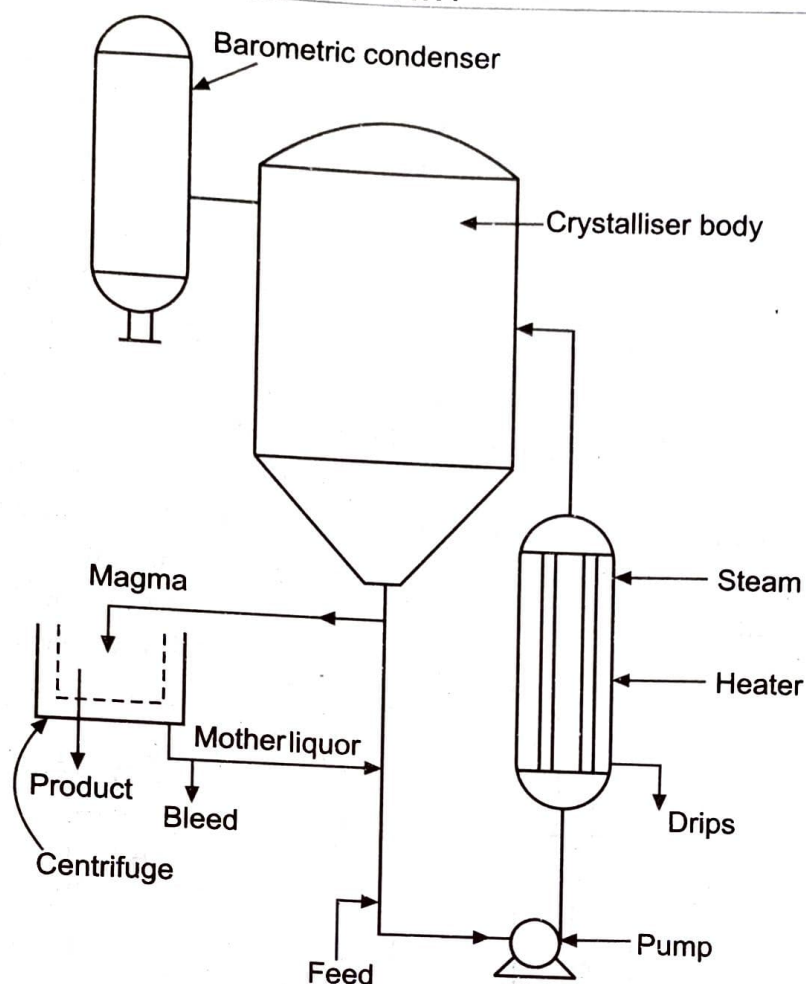
In this crystallizer, supersaturation is achieved by adiabatic evaporative cooling. A hot solution (feed) is introduced into a vessel wherein a vacuum is maintained that corresponds to the boiling point of the solution lower than the temperature of the feed solution. Evaporation will result due to flashing. The energy needed for vaporisation is taken from the feed (sensible heat), so that the temperature of a liquor-vapour mixture after flashing becomes much lower than the temperature of the liquor before flashing.

Vacuum crystallisers often operated continuously but they can also be operated batch-wise. These crystallisers are very simple and contain no moving parts and therefore, they can be constructed out of corrosion resistant materials or lead or rubber lined mild steel.

**Construction :**

A continuous vacuum crystalliser consists of a tall vertical cylindrical vessel with a conical bottom, a circulating pump (screw pump) of low head and a vertical tubular heater on the shell side of which, steam is condensing. A low pressure (i.e., vacuum) in the vertical cylindrical vessel (crystallising body) is maintained by a condenser, usually with the help of a steam jet ejector. A tangential inlet is provided on the cylindrical vessel for introducing a hot solution into it and a vapour outlet is provided on the top. A discharge connection for mother liquor and crystal is provided on a down-pipe just above the feed connection.





**Fig. 11.5 : Continuous Vacuum Crystalliser / Circulating magma vacuum crystalliser**

#### Working :

The magma from the bottom of a cylindrical vessel goes to a pump via a down-pipe and is pumped through a vertical tubular heater where it is heated by means of condensing steam and finally a hot stream enters the cylindrical vessel tangentially just below the level of the magma surface. Flash evaporation of the solution takes place and produces rapid cooling, resulting into supersaturation, which is the driving force for nucleation and growth. Fresh solution enters the down pipe just before the suction of the circulating pump and a suspension of crystals is continuously taken out from a discharge pipe located above the feed inlet in the down pipe. The suspension of crystals is fed to a centrifuge machine, the crystals are taken out as a product, and the mother liquor is recycled to the down-pipe with a small part of it continuously bled.

It is used for the production of large crystals.

#### Krystal or Oslo Crystalliser :

It is used whenever large quantities of crystals of controlled size are to be produced.

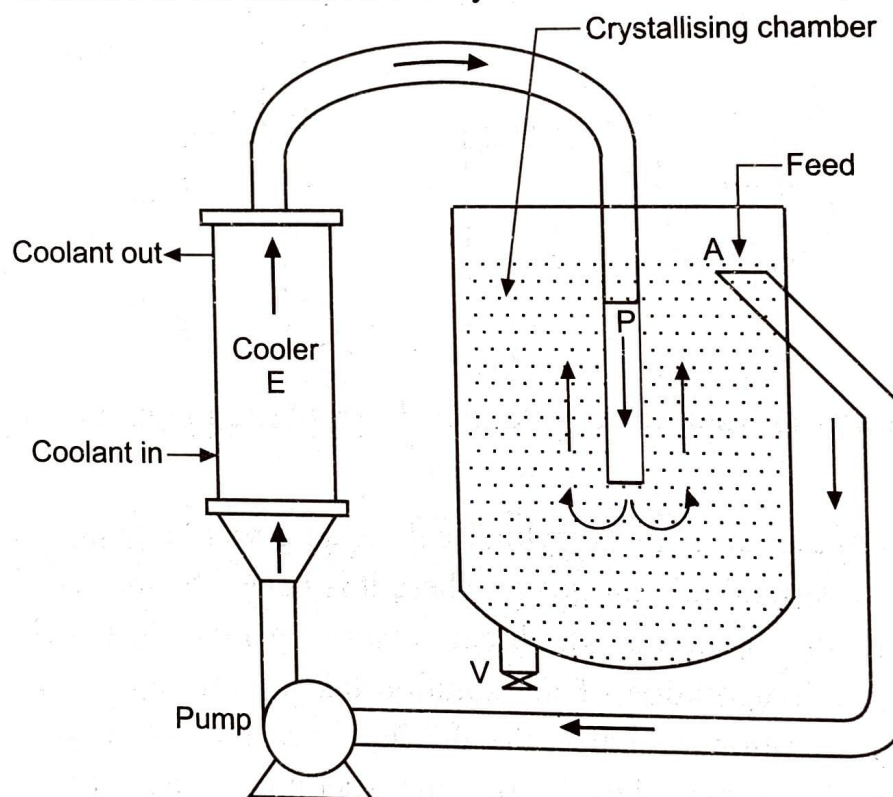
In this crystalliser, a supersaturated solution is passed upward through a bed of crystals which are maintained in a fluidised state whereby uniform temperature is maintained and the crystals segregate in the bed with large ones at the bottom and small ones at the top.



### Oslo Cooler Crystalliser :

In this crystalliser, supersaturation is generated by indirect cooling. It consists of a crystallising chamber, a circulating pump, and an external cooler for cooling the solution. It is a circulating liquid cooling crystalliser.

The solution to be crystallised is fed from the top. Mother liquor from a crystallising chamber is withdrawn near a feed point 'A' with the help of a circulating pump and it is then admitted to a cooler (E) wherein supersaturation is achieved by cooling. The supersaturated solution from the cooler is finally fed back to the bottom of the crystallising chamber through a central pipe (P). Usually, nucleation takes place in the bed of crystals in the crystallising chamber. The nuclei formed circulate with mother liquor and once they grow sufficiently large, they will be retained in the fluidised bed. Once the crystals grow to a required size, they are removed as product from the bottom of the crystallising chamber through a valve 'V' as these cannot be retained in the fluidised bed by the circulation velocity.



**Fig. 11.6 : Oslo / Krystal Cooling Crystalliser**

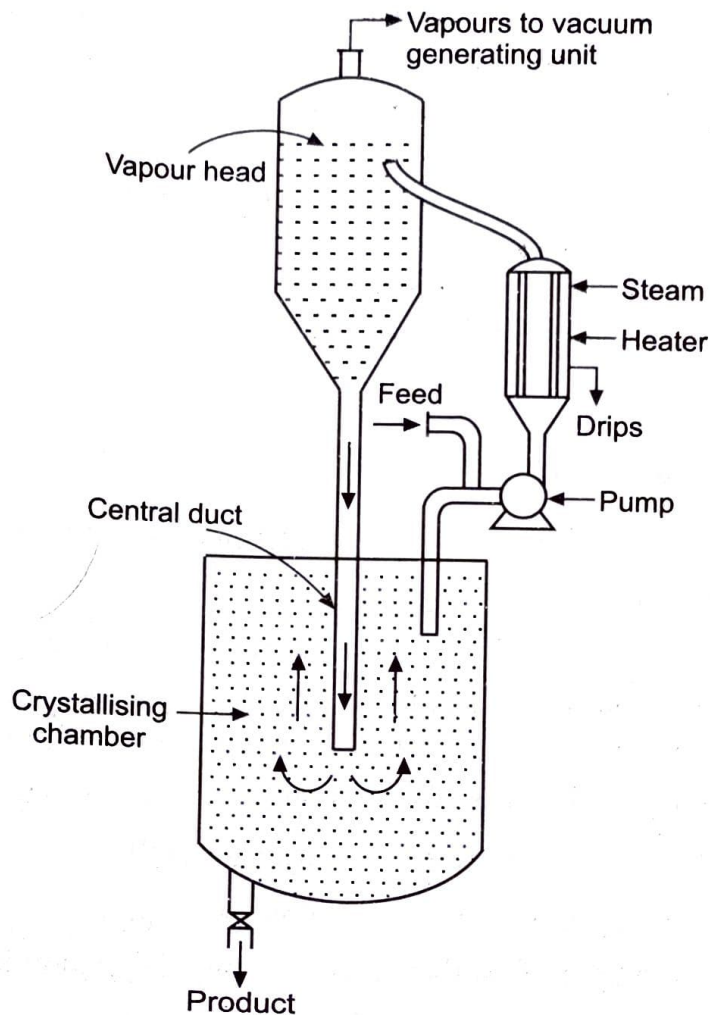
### Oslo Evaporative Crystalliser :

In this crystalliser, supersaturation is generated/achieved by evaporation. It is a circulating liquid evaporative crystalliser.

It consists of a crystallising chamber containing a bed of forming and growing crystals, a circulating pump, an external heater for heating the solution with the help of condensing steam and a vapour - head wherein reduced pressure is maintained by a vacuum generating equipment. The heater is maintained under sufficient hydrostatic head to avoid the boiling on the heating surface.

It is used for the production of small and uniform crystals.





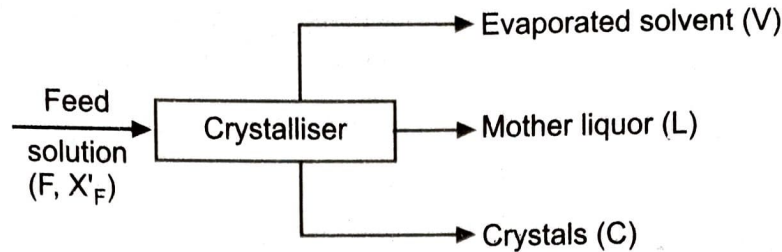
**Fig. 11.7 : Oslo/Krystal Evaporative Crystalliser**

The solution from the crystallising chamber is pumped by a circulating pump on the suction side of which the feed solution forming a small part of the total circulating liquid is introduced into a heater, where it is heated by means of condensing steam (on the shell side of the heater) and then fed to a vapour head wherein some of the solution flashes into vapour resulting into some degree of supersaturation. The supersaturated solution is then returned to the bottom of the crystallising chamber through a central duct prolonged from the vapour head into the crystallising chamber. Nucleation takes place in the crystal bed which is maintained in a fluidised state by means of an upward flowing stream of liquid through the duct. The nuclei formed circulate with the mother liquor and once they grow sufficiently large they will be retained in the fluidised bed. When the crystals grow to a required size, they will be withdrawn as a product from the bottom of the crystallising chamber as they will not be maintained in the fluidised bed by the circulation velocity.

### **Material balances of crystalliser**

Material balances are used to calculate the yield of crystallisation operation which is the mass of crystals obtained from a given mass of solution.



**Fig. 11.8**

Consider the crystallisation process carried out under steady state conditions and shown in Fig. 11.8.

Let

$F$  be the mass flow rate of feed solution in kg/h

$X_F'$  be the weight fraction of anhydrous solute in the feed solution

$C$  be the kg/h of crystals obtained

$V$  be the mass flow rate of evaporated solvent in kg/h

$X'$  be the solubility of the solute at the final temperature of operation expressed as a weight ratio of anhydrous salt to solvent

$M_1$  be the molecular weight of anhydrous solute salt

$M_2$  be the molecular weight of hydrated salt

$L'$  be the kg/h of solvent in the mother liquor

$L$  be the kg/h of mother liquor leaving the crystalliser

**Overall material balance :**

$$F = C + L + V \quad \dots (11.1)$$

**Material balance of solvent :**

Solvent in feed = Solvent evaporated + Solvent in mother liquor  
+ Solvent in hydrated crystals

$$\therefore F(1 - X_F') = V + L' + \left( \frac{M_2 - M_1}{M_2} \right) C \quad \dots (11.2)$$

Rearranging the above equation, we get

$$L' = F(1 - X_F') - V - \left( \frac{M_2 - M_1}{M_2} \right) C \quad \dots (11.3)$$

**Material balance of solute :**

Solute in feed = Solute as product crystals + Solute in mother liquor

$$F \cdot X_F' = C \cdot \frac{M_1}{M_2} + \left[ F(1 - X_F') - V - \left( \frac{M_2 - M_1}{M_2} \right) C \right] X' \quad \dots (11.4)$$

If the crystals obtained are anhydrous then above equation takes the following form :

$$F X_F' = C + [F(1 - X_F') - V] X' \quad \dots (11.5)$$



If no evaporation takes place and anhydrous salts are crystallised, then

$$V = 0 \text{ and Equation (10.5) becomes}$$

$$F \cdot X_F' = C + [F (1 - X_F')] X' \quad \dots (11.6)$$

$C$  – kg/h of crystal obtained (anhydrous/hydrated) and is the yield of the process.

$$\% \text{ yield crystals} = \frac{\text{Amount of solute crystallised}}{\text{Amount of solute in feed solution}} \times 100$$

### Energy balances :

Energy balance calculations in a crystallisation process are essential to determine the cooling requirements or to determine the final conditions. In these calculations, heat of crystallisation is important and it is the latent heat evolved when crystals are formed from a solution. Generally, the crystallisation process is exothermic and heat of crystallisation varies with temperature and concentration. Heats of crystallisation are not available, but heat of solution data are available. The process of crystallisation is the reverse of dissolution. Therefore, the heat of solution (i.e., the heat of dissolution) with a reverse sign is taken as heat of crystallisation (heat of crystallisation = – heat of solution). In case of a cooling crystalliser with no evaporation, the heat balance is

$$\text{Heat to be removed} = Q = F C_{p_F} \Delta T + C \lambda_c$$

When specific heat data are available for the initial feed solution over a range of temperature, then the heat to be removed is equal to the heat to be removed to cool the feed from the initial temperature ( $T_1$ ) to the final temperature ( $T_2$ , such that  $T_1 > T_2$ ) without any crystal precipitating plus the heat liberated/evolved due to formation of crystals from the supersaturated solution at the final temperature.

$$\begin{aligned} \text{Heat with solution at } T_1 + \text{Heat liberated due to crystallisation} &= \\ &= \text{Heat with solution at } T_2 + \text{Heat to be removed} \end{aligned}$$

$$F C_p T_1 + C \lambda_c = F C_p T_2 + Q$$

$$\therefore Q = F C_p T_1 - F C_p T_2 + C \lambda_c = F C_p \Delta T + C \lambda_c$$

(valid for crystallisation by cooling and with no evaporation)

where

$$\Delta T = \text{cooling range } (T_1 - T_2), \text{ where } T_1 > T_2$$

$$C_{p_F} = \text{specified heat of feed solution, kJ/(kg} \cdot \text{K)}$$

$$F = \text{feed or feed rate, kg or kg/h}$$

$$C = \text{crystal formed, kg or kg/h}$$

$$\lambda_c = \text{heat of crystallisation, kJ/kg}$$

$$Q = U A \Delta T_{lm} = \dot{m}_c \cdot C_{p_c} (t_2 - t_1)$$

where  $\dot{m}_c$  is the mass flow rate of the coolant and  $C_{p_c}$  is the specific heat of the coolant,  $t_1$  and  $t_2$  are the inlet and outlet temperatures of the coolant.

$$\Delta T_{lm} = \frac{(T_1 - t_2) - (T_2 - t_1)}{\ln [(T_1 - t_2) / (T_2 - t_1)]}$$



**SOLVED EXAMPLES**

**Example 11.1 :** A solution of sodium nitrate in water contains 48 %  $\text{NaNO}_3$  by weight at 313 K (40° C) temperature. Calculate the percentage yield of  $\text{NaNO}_3$  crystals that may be obtained when the temperature is reduced to 283 K (10° C). Also, calculate the quantity of  $\text{NaNO}_3$  crystals obtained from 100 kg of the solution.

**Data :** Solubility of  $\text{NaNO}_3$  in water at 283 K (10° C) is 80.18 kg  $\text{NaNO}_3$  per 100 kg water.

**Solution : Basis :** 100 kg feed solution.

$$F = 100 \text{ kg}$$

$$X'_F = \frac{48}{100} = 0.48 \text{ weight fraction of } \text{NaNO}_3 \text{ in the feed}$$

$$C = \text{yield of crystals (kg of } \text{NaNO}_3 \text{ crystals obtained)}$$

$$X' = \text{solubility of } \text{NaNO}_3 \text{ at 283 K}$$

$$= 80.18 \text{ kg/100 kg water}$$

$$L' = \text{kg of solvent in mother liquor}$$

**Water (solvent) balance :**

$$\text{Solvent in feed} = \text{Solvent in mother liquor}$$

$$F(1 - X'_F) = L'$$

$$100(1 - 0.48) = L'$$

$$\therefore L' = 52 \text{ kg}$$

**$\text{NaNO}_3$  balance – (Anhydrous salt as crystal) :**

$$\text{NaNO}_3 \text{ in feed} = \text{NaNO}_3 \text{ obtained as crystals} + \text{NaNO}_3 \text{ in mother liquor}$$

$$X'_F \cdot F = C + L' \cdot X'$$

$$X'_F F = C + [F(1 - X'_F)] X'$$

$$0.48 \times 100 = C + [100(1 - 0.48)] \left( \frac{80.18}{100} \right)$$

$$C = \text{yield of crystals}$$

$$= 6.3 \text{ kg}$$

... Ans.

$$\% \text{ yield of crystals} = \frac{\text{kg of } \text{NaNO}_3 \text{ crystallised}}{\text{kg of } \text{NaNO}_3 \text{ in feed solution}} \times 100$$

$$= \frac{6.3}{48} \times 100$$

$$= 13.12 \%$$

... Ans.



**Example 11.2 :** Find the yield of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  crystals when 100 kg of 48%  $\text{Na}_2\text{S}_2\text{O}_3$  solution is cooled to 293 K (20° C). Also calculate the percentage yield of the hydrated crystals. (At. Wt. : Na = 23, S = 32, O = 16, H = 1)

**Data :** Solubility of  $\text{Na}_2\text{S}_2\text{O}_3$  is 70 parts per 100 parts water at 293 K (20° C).

**Solution : Basis :** 100 kg of feed solution.

It contains 48 kg of  $\text{Na}_2\text{S}_2\text{O}_3$  and 52 kg of water. Let 'C' be the yield of crystals.

$$M_1 = \text{Molecular weight of } \text{Na}_2\text{S}_2\text{O}_3 = 158$$

$$M_2 = \text{Molecular weight of } \text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{ H}_2\text{O} = 248$$

$$X_F = \text{weight fraction of solute in the feed solution}$$

$$= \frac{\text{weight \%}}{100} = \frac{48}{100} = 0.48$$

**Material balance of water :**

$$\text{Water in feed} = \text{Water of crystallisation in crystals} + \text{Water in mother liquor}$$

$$52 = C \cdot \frac{M_2 - M_1}{M_2} + L'$$

$$L' = 52 - \frac{C [248 - 158]}{248}$$

**Material balance of solute :**

$$\text{Solute in feed} = \text{Solute in crystals produced} + \text{Solute in mother liquor}$$

$$0.48 \times 100 = C \left( \frac{158}{248} \right) + \left[ 52 - \left( \frac{248 - 158}{248} \right) C \right] X'$$

$X'$  – Solubility expressed as weight ratio of solute to solvent at 293 K.

$$48 = 0.637 C + [52 - 0.363 C] \times \left( \frac{70}{100} \right)$$

$$= 0.637 C + 36.4 - 0.254 C$$

$$\therefore C = 30.3 \text{ kg}$$

Yield of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{ H}_2\text{O}$  crystal = **30.3 kg**

... Ans.

$$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{ H}_2\text{O} \text{ in the feed solution} = 48 \times \frac{248}{158} = 73.34 \text{ kg}$$

$$\% \text{ yield of hydrated crystals} = \frac{\text{hydrated crystals obtained}}{\text{hydrated crystals in feed solution}} \times 100$$

$$= \frac{30.3}{73.34} \times 100 = \mathbf{41.31}$$

... Ans.



**Example 11.3 :** Calculate the yield of  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$  crystals when 1000 kg saturated solution of  $\text{MgSO}_4$  at 353 K (80° C) is cooled to 303 K (30° C) assuming 10 % of the water is lost by evaporation during cooling.

**Data :** Solubility of  $\text{MgSO}_4$  at 353 K (80° C) = 64.2 kg/100 kg water

Solubility of  $\text{MgSO}_4$  at 303 K (30° C) = 40.8 kg/100 kg water

At. Wt. : Mg = 24, S = 32, H = 1 and O = 16

**Solution : Basis :** 1000 kg of solution at 353 K (80° C)

$$\therefore F = 1000 \text{ kg}$$

$$X'_F = \text{weight fraction of } \text{MgSO}_4 \text{ in the feed}$$

$$= \frac{64.2}{164.2} = 0.391$$

$$\text{Water in the feed solution} = F (1 - X'_F)$$

$$= 1000 (1 - 0.391) = 609 \text{ kg}$$

$$V = \text{kg of water evaporated during cooling}$$

$$= 609 \times 0.1 = 60.9 \text{ kg}$$

$$X' = \text{solubility of } \text{MgSO}_4 \text{ at 303 K} = 40.8 \text{ kg/100 kg water}$$

$$M_1 = \text{Molecular weight of } \text{MgSO}_4 = 120$$

$$M_2 = \text{Molecular weight of } \text{MgSO}_4 \cdot 7 \text{H}_2\text{O} = 246$$

$$C = \text{Yield of } \text{MgSO}_4 \cdot 7 \text{H}_2\text{O} \text{ crystals from feed solution}$$

$$M_2 - M_1 = \text{water of crystallisation}$$

$$= 246 - 120 = 126 \text{ kg}$$

**Material balance of  $\text{MgSO}_4$  :**

$$X'_F F = C \cdot \frac{M_1}{M_2} + \left[ F (1 - X'_F) - V - C \left( \frac{M_2 - M_1}{M_2} \right) \right] X'$$

$$\text{MgSO}_4 \text{ in feed} = \text{MgSO}_4 \text{ in hydrated crystal}$$

$$+ \text{MgSO}_4 \text{ in mother liquor at 303 K}$$

$$\therefore 0.391 (1000) = C \left( \frac{120}{246} \right) + \left[ 1000 (1 - 0.391) - 60.9 - \frac{C (126)}{246} \right] \frac{40.8}{100}$$

$$391 = 0.488 C + [609 - 60.9 - 0.512 C] (0.408)$$

$$\text{MgSO}_4 \cdot 7 \text{H}_2\text{O} \text{ yield} = C = \mathbf{599.7 \text{ kg}}$$

... Ans.



**Example 11.4 :** A hot solution containing 25 % by weight  $\text{Na}_2\text{CO}_3$  is cooled to 293 K (20 °C) and crystals of  $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$  are precipitated. At 293 K (20 °C), the solubility is 21.5 kg anhydrous  $\text{Na}_2\text{CO}_3$  per 100 kg of total water. Calculate the yield of hydrated  $\text{Na}_2\text{CO}_3$  crystals obtained if 5 % of the original water in the system evaporates on cooling and the quantity of mother liquor based on 5000 kg of the hot solution.

At. Wt. : Na = 23, C = 12, O = 16, H = 1.

**Solution : Basis :** 5000 kg of hot solution of  $\text{Na}_2\text{CO}_3$ .

It contains :

$$\text{Na}_2\text{CO}_3 = 0.25 \times 5000 = 1250 \text{ kg}$$

$$\text{Water} = 0.75 \times 5000 = 3750 \text{ kg}$$

$$M_1 = \text{Mol. Wt. of } \text{Na}_2\text{CO}_3 = 106$$

$$M_2 = \text{Mol. Wt. of } \text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O} = 286$$

$$M_2 - M_1 = \text{water of crystallisation} = 10 \text{H}_2\text{O} = 180$$

$$\therefore F = 5000 \text{ kg}$$

$$X'_F = \text{weight fraction of } \text{Na}_2\text{CO}_3 \text{ in the feed solution}$$

$$= \frac{25}{100} = 0.25$$

Given : 5% of water is evaporated. Therefore,

$$V = \text{kg of water evaporated during cooling}$$

$$= 0.05 \times 3750 = 187.5 \text{ kg}$$

**Material balance of water :**

$$\begin{aligned} \text{Water in feed} &= \text{Water of crystallisation} \\ &+ \text{Water in mother liquor} + \text{Water evaporated} \end{aligned}$$

$$0.75 (5000) = C \left( \frac{M_2 - M_1}{M_2} \right) + L' + 187.5$$

$$3750 = C \left( \frac{286 - 106}{286} \right) + L' + 187.5$$

$$3562.5 = C \left( \frac{180}{286} \right) + L'$$

$$L' = 3562.5 - C \left( \frac{180}{286} \right)$$

**Material balance of solute :**

$$\text{Solute in feed} = \text{Solute in crystals produced} + \text{Solute in mother liquor}$$

$$X'_F F = C \frac{M_1}{M_2} + L' X'$$



where,

$C$  = yield of hydrated crystals

$L'$  = kg of solvent water in mother liquor

$X'$  = solubility of anhydrous solute as kg solute/kg solvent.

$$X'_F F = C \frac{M_1}{M_2} + \left[ 3562.5 - C \left( \frac{180}{286} \right) \right] \times X'$$

$$0.25 \times 5000 = C \frac{106}{286} + \left[ 3562.5 - C \left( \frac{180}{286} \right) \right] \frac{21.5}{100}$$

$$1250 = 0.37 C + [3562.5 - 0.629 C] 0.215$$

$$1250 = 0.37 C + 765.94 - 0.135 C$$

$$0.235 C = 484.06$$

$$C = 2059.83 \text{ kg}$$

$$\therefore \text{yield of } \text{Na}_2\text{CO}_3 \cdot 10 \text{ H}_2\text{O} \text{ crystals} = 2059.83 \text{ kg}$$

... Ans.

$$\text{Quantity of mother liquor obtained} = \text{kg of feed} - \text{kg of crystals} - \text{kg water evaporated}$$

$$= 5000 - [2059.83 + 187.5]$$

$$= 2752.67 \text{ kg}$$

... Ans.

**Example 11.5 :** 2000 kg of a hot solution at 330 K (57 °C) containing 30 wt. %  $\text{MgSO}_4$  is cooled to 293 K (30 °C) and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  crystals are removed from it. The solubility at 293 K (30 °C) is 35.5 kg  $\text{MgSO}_4$  per 100 kg water. Calculate the yield of crystals. Assume that no water is evaporated.

At. Wt. : Mg = 24, S = 32, O = 16, H = 1.

**Solution : Basis :** 2000 kg hot solution

$$\therefore F = 2000 \text{ kg}$$

The solution contains 30%  $\text{MgSO}_4$ . Therefore,

$$X'_F = \frac{30}{100} = 0.30 \dots \text{weight fraction of } \text{MgSO}_4 \text{ in the solution}$$

$$M_1 = \text{Mol. Wt. of } \text{MgSO}_4 = 120$$

$$M_2 = \text{Mol. Wt. of } \text{MgSO}_4 \cdot 7 \text{ H}_2\text{O} = 246$$

**Material balance of water :**

Water in feed = Water of crystallisation + Water in mother liquor

$$(1 - X'_F) F = C \left( \frac{M_2 - M_1}{M_2} \right) + L'$$

$$(1 - 0.30) 2000 = C \left( \frac{246 - 120}{246} \right) + L'$$

$$L' = 1400 - \frac{126}{246} C = 1400 - 0.5122 C$$

where  $C$  is the yield of hydrated crystals.



**Material balance of solute :**

$$\text{MgSO}_4 \text{ in feed} = \text{MgSO}_4 \text{ in crystals produced} + \text{MgSO}_4 \text{ in mother liquor}$$

$$X'_F F = C \frac{M_1}{M_2} + L' X' \quad \dots (1)$$

where

$$\begin{aligned} X' &= \text{solubility of MgSO}_4 \text{ as kg MgSO}_4/\text{kg solvent} \\ &= \frac{35.5}{100} = 0.355 \end{aligned}$$

$$M_1 = 120$$

$$M_2 = 246$$

$$X'_F = 0.3 \quad F = 2000 \text{ kg}$$

Substituting the values of various terms, Equation (1) becomes

$$0.3 (2000) = C \left( \frac{120}{246} \right) + [1400 - 0.5122 C] 0.355$$

$$600 = 0.488 C + 497 - 0.182 C$$

$$C = 336.6 \text{ kg}$$

$$\text{Yield of MgSO}_4 \cdot 7 \text{ H}_2\text{O crystal} = 336.6 \text{ kg}$$

... **Ans.**

**Example 11.6 :** Find the per cent yield of Glauber salt ( $\text{Na}_2\text{SO}_4 \cdot 10 \text{ H}_2\text{O}$ ) if a pure 32 % solution is cooled to 293 K (20° C) without any loss due to evaporation ?

**Data :** Solubility of  $\text{Na}_2\text{SO}_4$  in water at 293 K (20° C) is 19.4 g per 100 g water.

At. Wt. : Na = 23, S = 32, O = 16, H = 1.

**Solution : Basis :** 100 kg of original solution

It contains 32 kg of  $\text{Na}_2\text{SO}_4$  and 68 kg of water

$$F = 100 \text{ kg}$$

$$\begin{aligned} X'_F &= \text{weight fraction of Na}_2\text{SO}_4 \text{ in the feed} \\ &= 32/100 = 0.32 \end{aligned}$$

$$M_1 = \text{Mol. Wt. of Na}_2\text{SO}_4 = 142$$

$$M_2 = \text{Mol. Wt. of Na}_2\text{SO}_4 \cdot 10 \text{ H}_2\text{O} = 322$$

**Material balance of water :**

$$\text{Water in feed} = \text{Water of crystallisation} + \text{Water in mother liquor}$$

$$0.68 \times 100 = C \frac{(M_2 - M_1)}{M_2} + L'$$

$$68 = C \left( \frac{322 - 142}{322} \right) + L'$$

$$68 = 0.559 C + L'$$

$$L' = 68 - 0.559 C$$



**Material balance of solute :**

Solute in feed = Solute in crystals produced + Solute in mother liquor

$$X'_F F = C \frac{M_1}{M_2} + L' X' \quad \dots (1)$$

C = yield of hydrated solute

L' = kg of solvent in mother liquor

X' = solubility of anhydrous solute as kg solute/kg solvent

$$= \frac{19.4}{100} = 0.194$$

Substituting the values, Equation (1) becomes

$$0.32 \times 100 = C \left( \frac{142}{322} \right) + L' \times 0.194$$

$$32 = 0.441 C + 0.194 L'$$

We have,

$$L' = 68 - 0.559 C$$

$$32 = 0.441 C + 0.194 (68 - 0.559 C)$$

$$32 = 0.441 C + 13.192 - 0.1084 C$$

$$0.3326 C = 18.808$$

$$C = 56.55$$

$$\text{Na}_2\text{SO}_4 \cdot 10 \text{ H}_2\text{O in the feed solution} = 32 \times \frac{322}{142} = 72.56$$

$$\% \text{ yield of Glauber salt} = \frac{56.55}{72.56} \times 100 = 77.93$$

... Ans.

**Alternate method :**

**Basis :** 100 kg free water

100 kg of the original solution contain 32 kg  $\text{Na}_2\text{SO}_4$  and 68 kg water.

$$\begin{aligned} \text{Water associated with } 32 \text{ kg Na}_2\text{SO}_4 \text{ in 100 kg solution} &= \frac{\text{Mol. Wt. of } 10 \text{ H}_2\text{O}}{\text{Mol. Wt. of Na}_2\text{SO}_4} \times 32 \\ &= \frac{(10 \times 18)}{142} \times 32 = 40.56 \text{ kg} \end{aligned}$$

$$\text{Free water in 100 kg original solution} = 68 - 40.56 = 27.44 \text{ kg}$$

$$\begin{aligned} \text{Glauber salt (Na}_2\text{SO}_4 \cdot 10 \text{ H}_2\text{O)} \\ \text{present in 100 kg of free water} &= (32 + 40.56) \times \frac{100}{27.44} \end{aligned}$$

At 293 K, the final liquor contains 19.4 kg  $\text{Na}_2\text{SO}_4$  in 100 kg water.

$$\begin{aligned} \text{Water associated with Na}_2\text{SO}_4 \\ \text{in the final solution} &= \frac{180}{142} \times 19.4 = 24.6 \text{ kg} \end{aligned}$$



$$\text{Free water in the final solution} = 100 - 24.6 = 75.4 \text{ kg}$$

$$\text{Glauber salt present in 100 kg water} = \frac{(19.4 + 24.6)}{75.4} \times 100$$

$$\begin{aligned} \text{Yield of Glauber salt per 100 kg} \\ \text{free water} &= 264.43 - 58.35 \\ &= 206.08 \text{ kg Na}_2\text{SO}_4 \cdot 10 \text{ H}_2\text{O} \end{aligned}$$

$$\% \text{ yield of Glauber salt} = \frac{206.08}{264.43} \times 100 = 77.93$$

... Ans.