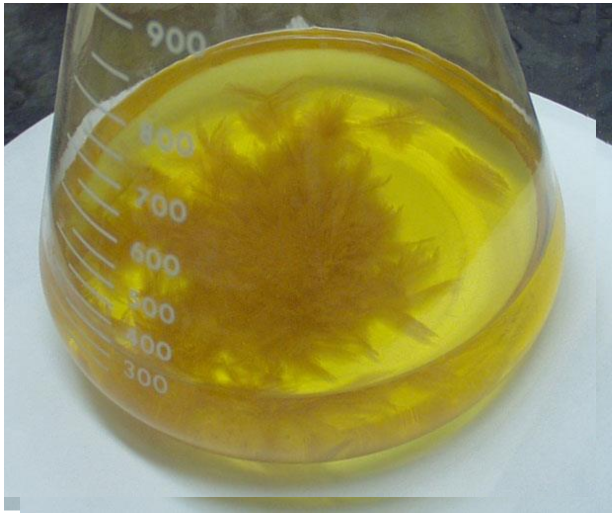
CRYSTALLIZATION

- **important industrially because:**

  i) a crystal formed from an impure solution and itself pure

  ii) Practical method of obtaining pure chemical substances in a satisfactory condition for packaging and storing

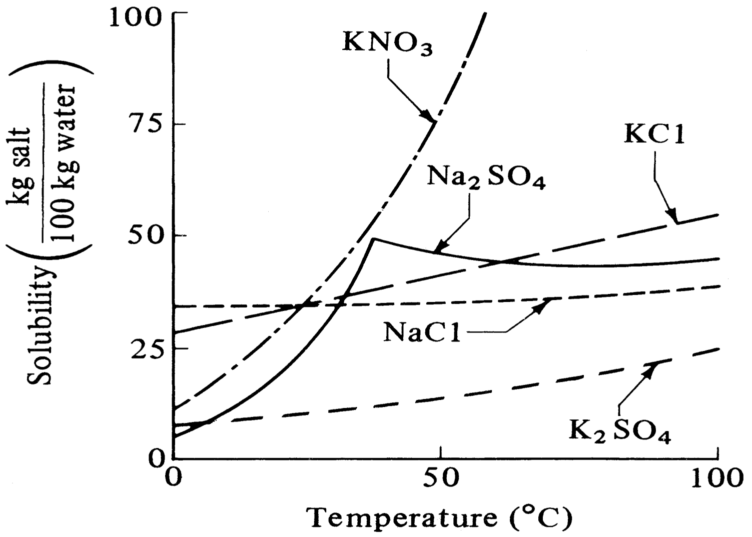


- **solid-liquid separation process**
- **yield , purity, sizes & shapes of crystals important**
- **crystals - uniform in size**

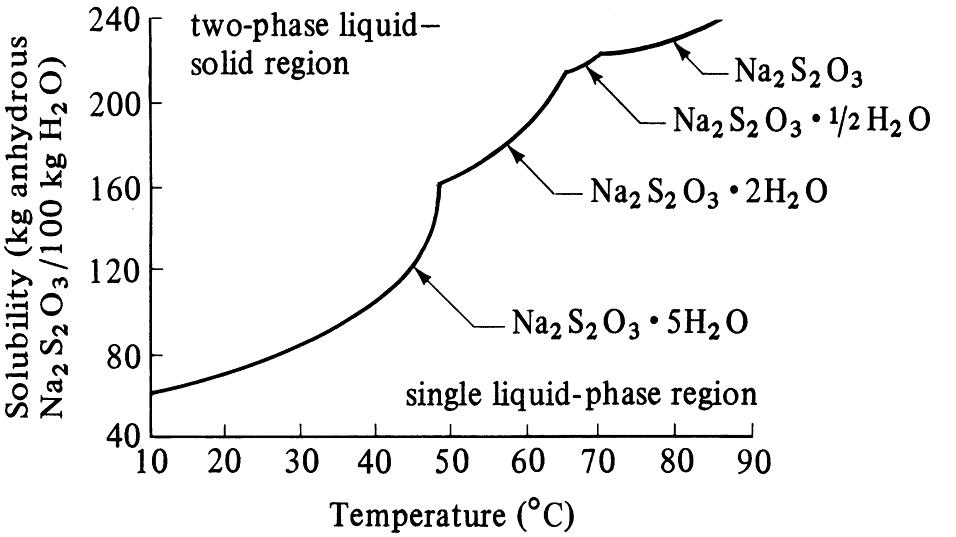
- **formation of 1,4-naphthoquinone crystals from a liquid solution**

SOLUBILITY CURVE

- equilibrium is attained when the solution or mother liquor is saturated (represented by solubility curve)
- solubility dependent mainly on temperature
- solubilities of most salts increase slightly or markedly with temperature



Solubility curve for some typical salts in water



Solubility curve for sodium thiosulfate

SOLID-LIQUID PHASE DIAGRAM

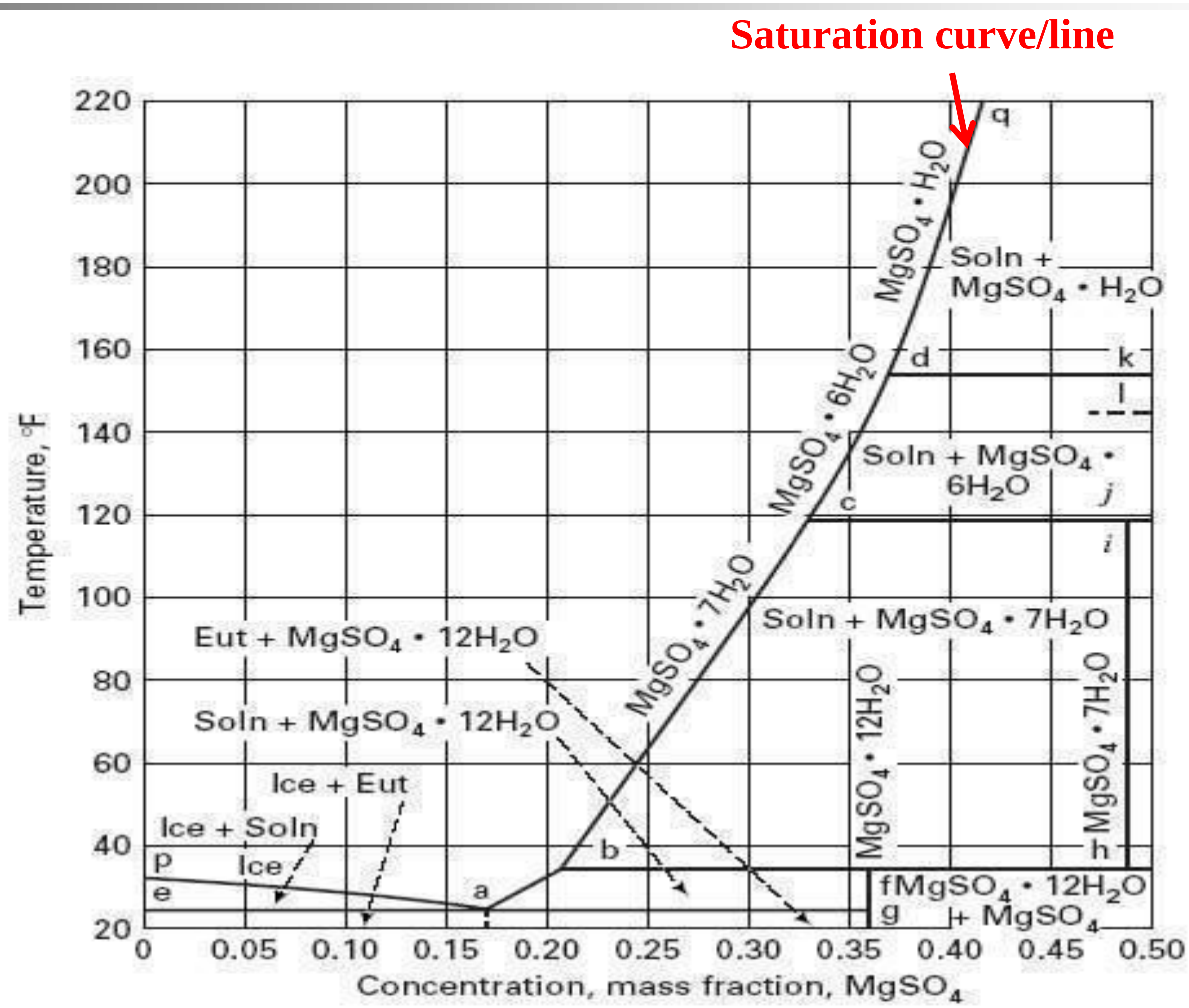


Figure 27.3-Solubility curve for the $MgSO_4$-nH_2O system at 1 atm

YIELD & MATERIAL & HEAT BALANCES

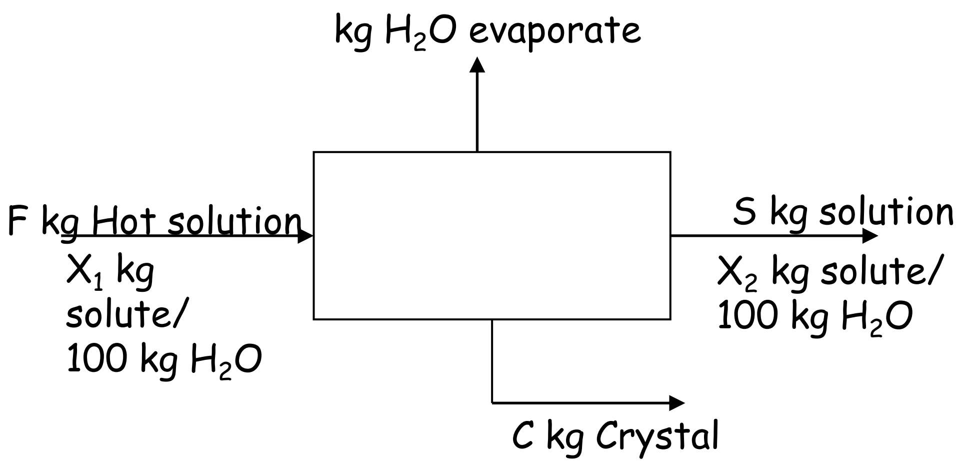
- **yield of crystals can be calculated by knowing:**

  initial concentration of solute

  final temperature

  solubility at this temperature

- **material balances**



Mass balance :

Water balance : Input = Output

Solute balance : Input = Output

solute crystals are anhydrous - simple water & solute material balances

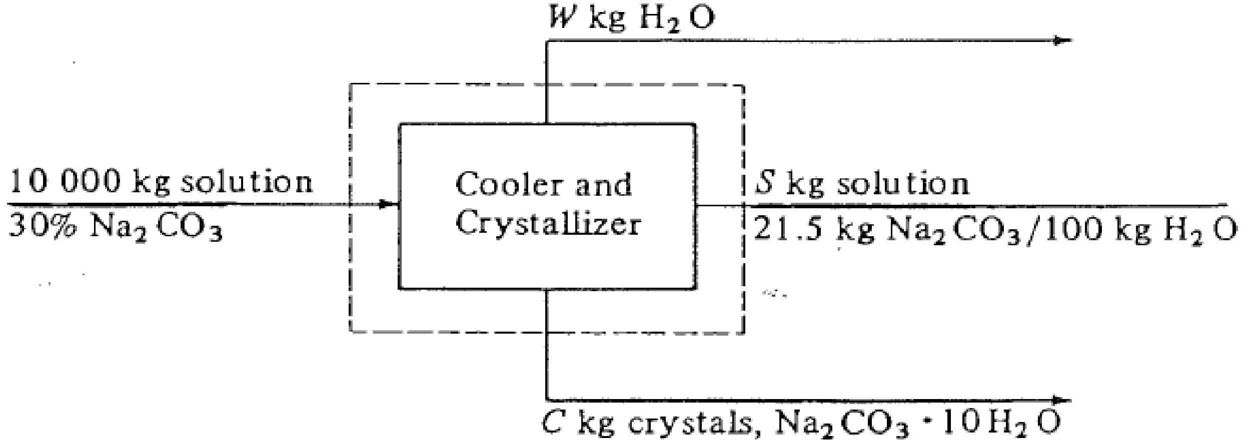
crystals are hydrated - some water in the solution is removed with crystals

EXAMPLE 2

A salt solution weighing 10000 kg with 30 wt. % Na_2CO_3 is cooled from 333K to 293K. The salt crystallizes as the decahydrate. What will be the yield of $Na_2CO_3.10H_2O$ crystals if the solubility is 21.5 kg anhydrous Na_2CO_3/100kg water?

a) Assume that no water is evaporated.

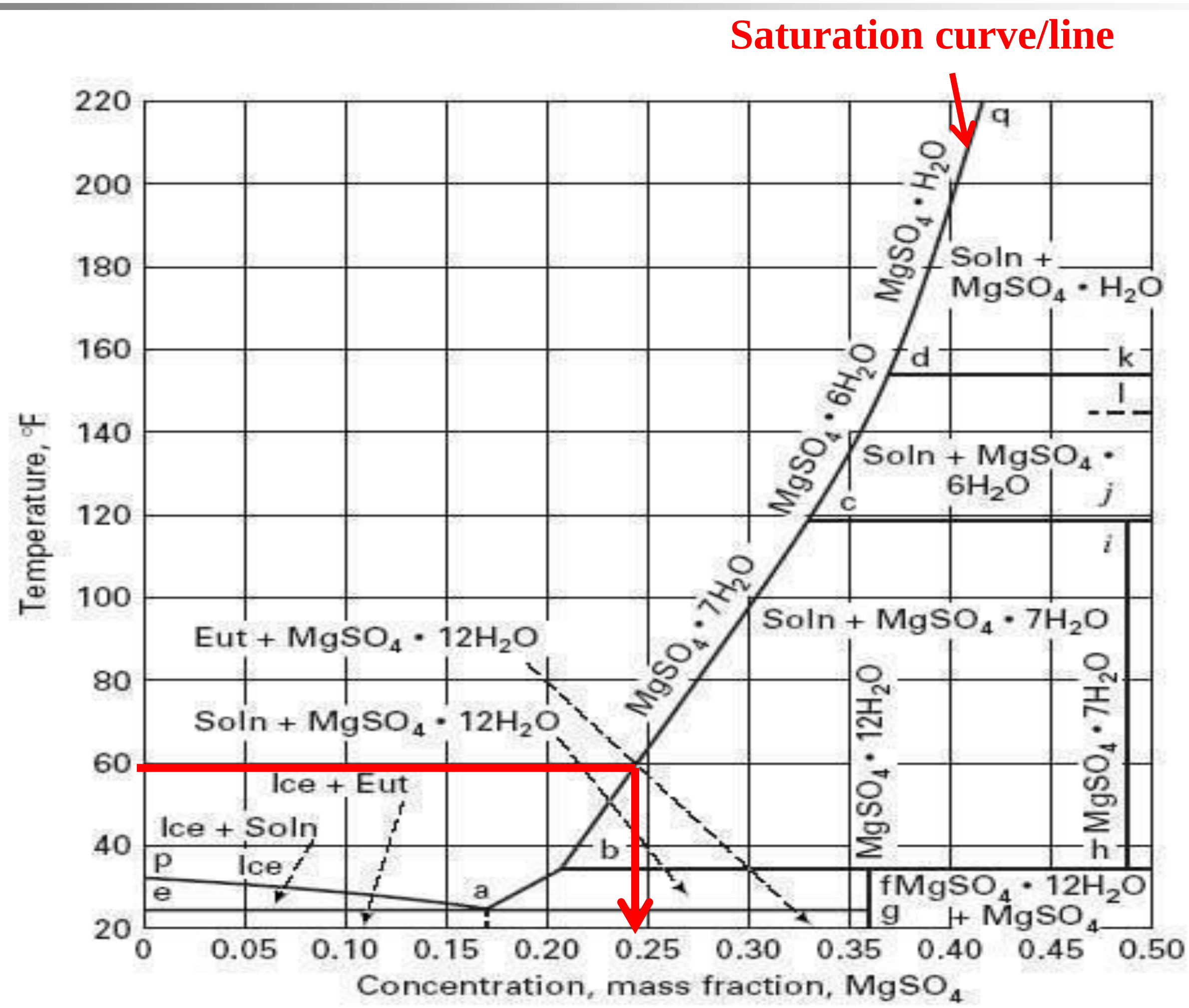
b) Assume that 3% of the total weight of the solution is lost by evaporation of water in cooling.



EXAMPLE 3

A solution consisting of 30 wt% $MgSO_4$ and 70% water is cooled to 60°F. During cooling 5% of the total water in the system evaporates. How many kilograms of crystals are obtained per 1000 kg of the original mixture?

SOLID-LIQUID PHASE DIAGRAM



Solubility curve for the $MgSO_4$-nH_2O system at 1 atm

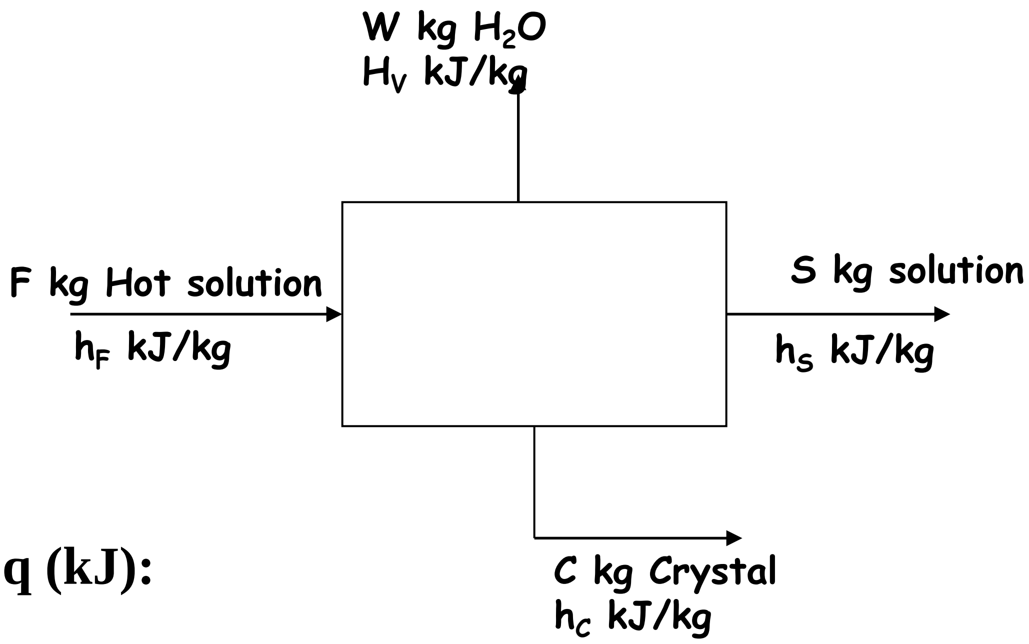
EXAMPLE 4

A feed of solution of 2268 kg at 327.6 K (54.4^{o}C) containing 48.2 kg $MgSO_4$/100 kg total water is cooled to 293.2 K (20^{o}C), where $MgSO_4.7H_2O$ crystals are removed. The solubility of the salt is 35.5 kg $MgSO_4$/100 kg total water. The average heat capacity of the feed solution can be assumed as 2.93 kJ/kg.K. The heat of solution at 291.2 K (18^{o}C) is 13.31 x 10^3 kJ/kg mol $MgSO_4.7H_2O$.

Calculate the yield of crystals.

HEAT BALANCES IN CRYSTALLIZATION

normally, crystallization is exothermic



Total heat absorbed, q (kJ):

When $T_{datum} = 32^oF = 0^oC$,

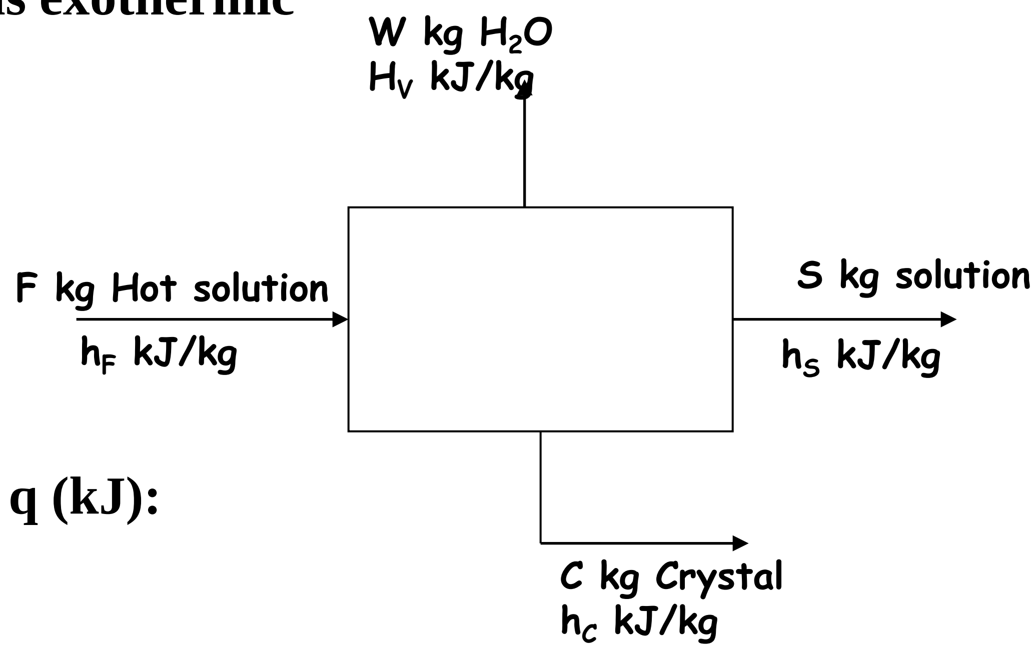
$$Fh_F + q = (S + C)h_M + WH_V$$

or

$$Fh_F + q = Sh_S + Ch_C + WH_V$$

HEAT BALANCES IN CRYSTALLIZATION

normally, crystallization is exothermic



Total heat absorbed, q (kJ):

When $T_{datum} = T_{equil./sat.}$, $$Fh_F + q = W\lambda + Ch_C = W\lambda + C\Delta H^{\infty}_{crys}$$

heat of crystallization, ΔH_{crys} = - heat of solution at infinite dilution, ΔH^{∞}_{soln}

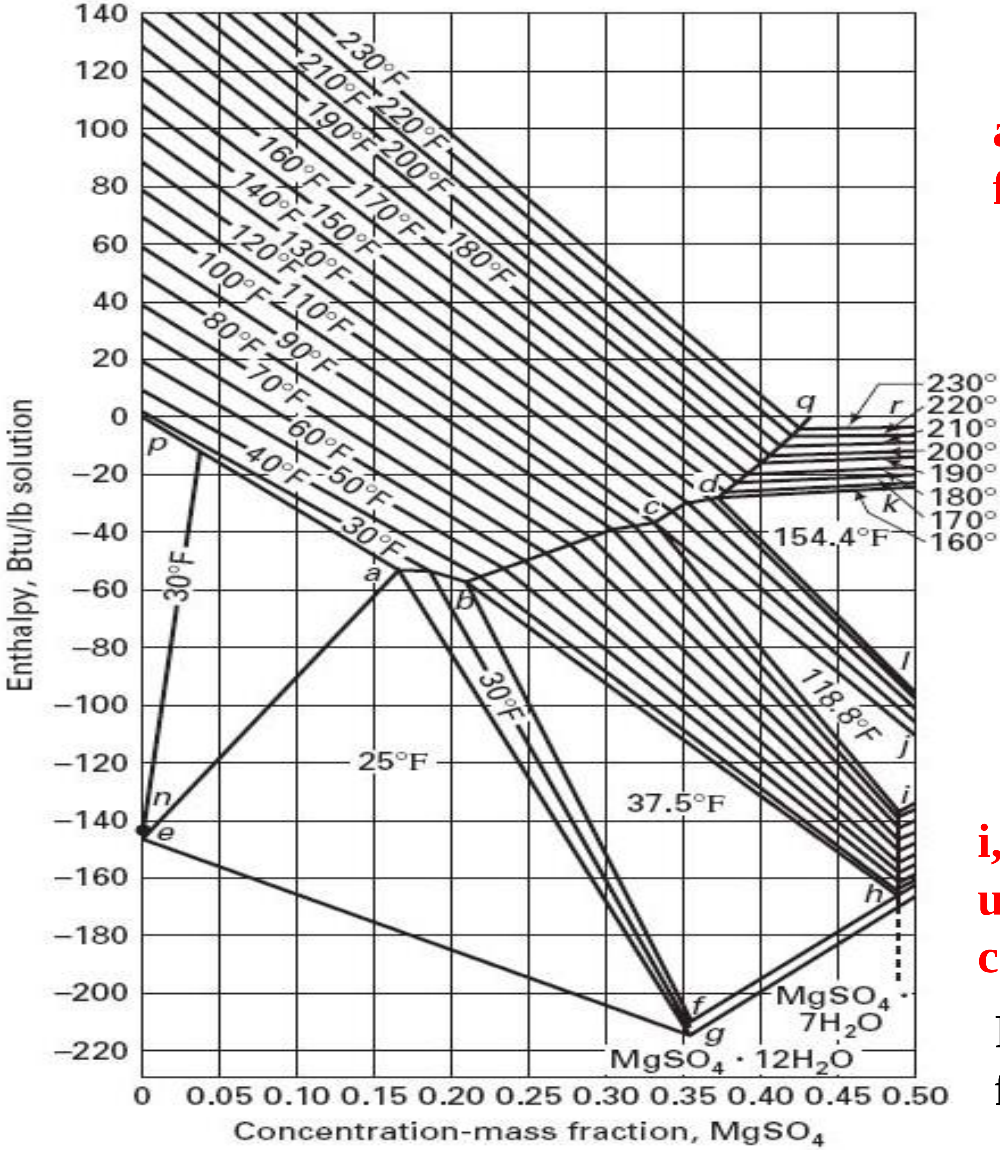
Heat absorbed, q = +'ve ,Heat given off , q = -'ve

EXAMPLE 4

A feed of solution of 2268 kg at 327.6 K (54.4^{o}C) containing 48.2 kg $MgSO_4$/100 kg total water is cooled to 293.2 K (20^{o}C), where $MgSO_4.7H_2O$ crystals are removed. The solubility of the salt is 35.5 kg $MgSO_4$/100 kg total water. The average heat capacity of the feed solution can be assumed as 2.93 kJ/kg.K. The heat of solution at 291.2 K (18^{o}C) is 13.31 x 10^3 kJ/kg mol $MgSO_4.7H_2O$.

Calculate the yield of crystals and make a heat balance to determine the total heat absorbed/released, q, assuming that no water is vaporized.

ENTHALPY-CONCENTRATION DIAGRAM



a, b, c, d – saturation line, use to find enthalphy of solution

i, h – complete crystallization, use to find enthalphy of crystallization

Fig 27.4-Enthalpy-concentration diagram for the $MgSO_4$-nH_2O system at 1 atm

EXAMPLE 5

A 32.5% solution of $MgSO_4$ at 120ºF (48.9ºC) is cooled, without appreciable evaporation to 70ºF (21.1ºC) in a batch-cooled crystallizer. How much heat must be removed from the solution per 100 Ib of the feed solution?

The average heat capacity of the feed solution is 0.72 Btu/Ib ºF and the heat of solution at 18ºC is 23.2 Btu/Ib of $MgSO_4.7H_20$.