

** Chapter 6. Multiphase systems:

* Chemical engineers often separate Components of mixtures by introducing a phase Change for at least one Component of the mixture ; examples:

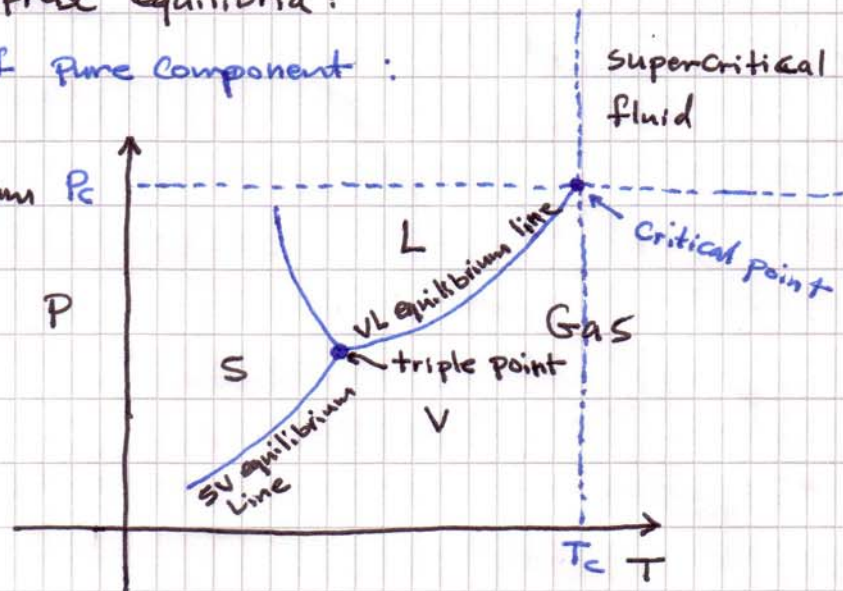
- Distillation : It is V-L operation . Its principle is based on boiling point difference: ΔT_b
- Extraction : It is L-L operation. Its principle is based on miscibility of liquids.
- Crystallization: It is S-L operation . Its principle is based on freezing point difference ΔT_f
- Adsorption : It is S-L operation. Its principle is based on the ability of liquid molecules to be attached on solid surfaces.
- Leaching : It is S-L operation . Its principle is based on miscibility of chemicals, present in solids, in the liquid solvents.
- Absorption: It is V-L operation. Its principle is based on solubility of vapors in liquid solvents.
- Drying, humidification, dehumidification, etc .

* To design separation processes, we need to know how species distribute themselves between phases at equilibrium.

** Single Component phase equilibria:

* phase diagrams of pure component:

(A) PT phase diagram



" PT phase diagram "

- at most T and P , a single pure substance exists as a solid, liquid or gas.

- Along VL equilibrium curve:

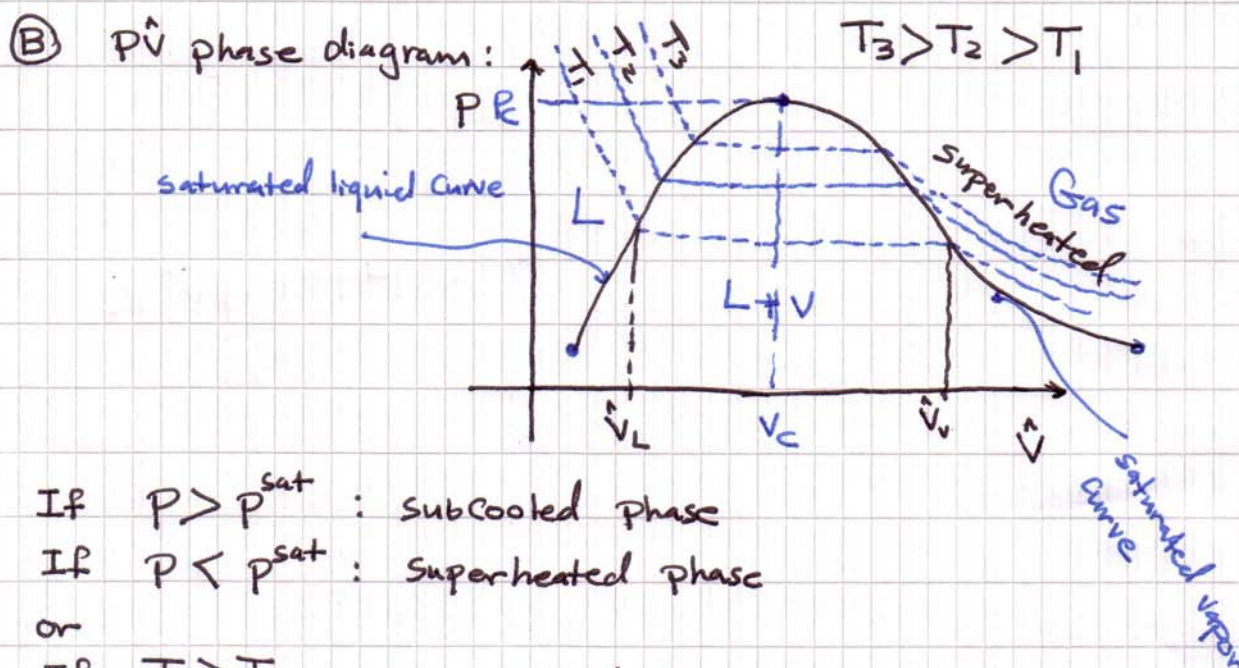
- P is called Vapor pressure, P^* or P^V , or saturation pressure; P^{sat} .

- T is known as boiling point of liquid, T_b , or dew point of vapor, T_d , or condensate point, T_{can} of vapor

- Along SL equilibrium Curve: T is known as melting or fusion point; T_m , T_{fus} . or freezing point, T_f .

— Along SV equilibrium curve: T is known as sublimation temperature, T_s

* The values of T and p at which substance exists as solid, liquid and solid is known as triple point.



If $P > P^{\text{sat}}$: subcooled phase

If $P < P^{\text{sat}}$: superheated phase

or

If $T > T_b$: superheated phase

$T < T_b$: subcooled phase

If $P = P^{\text{sat}}$ or $T = T_b$: Saturated phase:

If saturated phase then:

If: $\hat{V} = \hat{V}_L$: Saturated liquid

$\hat{V} = \hat{V}_v$: Saturated vapor

$\hat{V}_L < \hat{V} < \hat{V}_v$: Saturated liquid-vapor mixture.

* For saturated mixture, we define quality.

* quality: ratio of mass (moles) of vapor to mass (mole) of total liquid-vapor mixture: $X = \frac{n_v}{n_{total}}$

$$V_{total} = V_v + V_L$$

$$\text{But } \hat{V} = \frac{V}{n}$$



$$\Rightarrow \hat{V} n_{total} = n_v \hat{V}_v + n_L \hat{V}_L$$

Dividing by n_{total} :

$$\hat{V} = X \hat{V}_v + \frac{n_L}{n_{total}} \hat{V}_L$$

$$n_{total} = n_v + n_L \Rightarrow 1 = \frac{n_v}{n_{total}} + \frac{n_L}{n_{total}}$$

$$1 = X + \frac{n_L}{n_{total}} \Rightarrow \frac{n_L}{n_{total}} = 1 - X$$

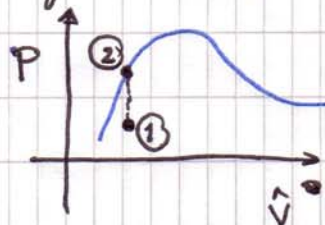
$$\text{Now: } \hat{V} = X \hat{V}_v + (1 - X) \hat{V}_L$$

$$\text{or } X = \frac{\hat{V} - \hat{V}_L}{\hat{V}_v - \hat{V}_L} = \frac{\hat{V} - \hat{V}_L}{\hat{V}_{Lv}}$$

Ex: suppose that you have a closed tank which contains VL mixture of pure component at equilibrium. Is it possible that the content will become liquid by heating process?

yes. see pv-diagram:

$$T_2 > T_1$$



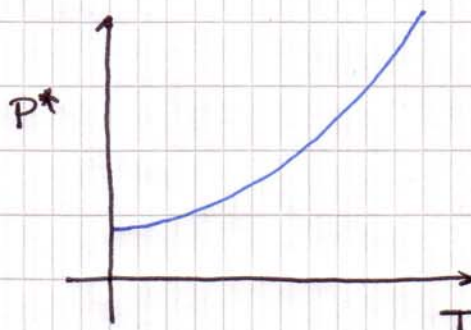
* Remember that you can:

- Condense vapor to liquid by $T \downarrow$ or $P \uparrow$
- Convert Gas to liquid by $T \downarrow$ only (see PT diagram)
- Evaporate Liquid to vapor by $T \uparrow$ or $P \downarrow$
- Freeze liquid by $T \downarrow$ or $P \uparrow$

** Estimation of vapor (saturation) pressure: P^v , P^{sat} , or P^*

- Vapor pressure is function of T : as $T \uparrow$ $P^* \uparrow$

$P^*(T)$



- Vapor pressure is absolute pressure
- Vapor pressure is physical property of the liquid.

* methods of estimation:

① Clausius-Clapeyron eq.: $\ln P^* = \frac{-\Delta \hat{H}_v}{RT} + B$

where;

$\Delta \hat{H}_v$: latent heat of vaporization to vaporize 1 g/mol of liquid
(see table B.1)

T : absolute temperature in Kelvin or Rankine.

B : Constant that varies from one substance to another.

② Antoine's equation : It is empirical (experimental) eq.

$$\log p^* = A - \frac{B}{T(^{\circ}\text{C}) + C}$$

where p^* is in mmHg and T is in $^{\circ}\text{C}$

Values of the constants, A , B , and C are given in table B.4 for different components.

③ Cox chart :

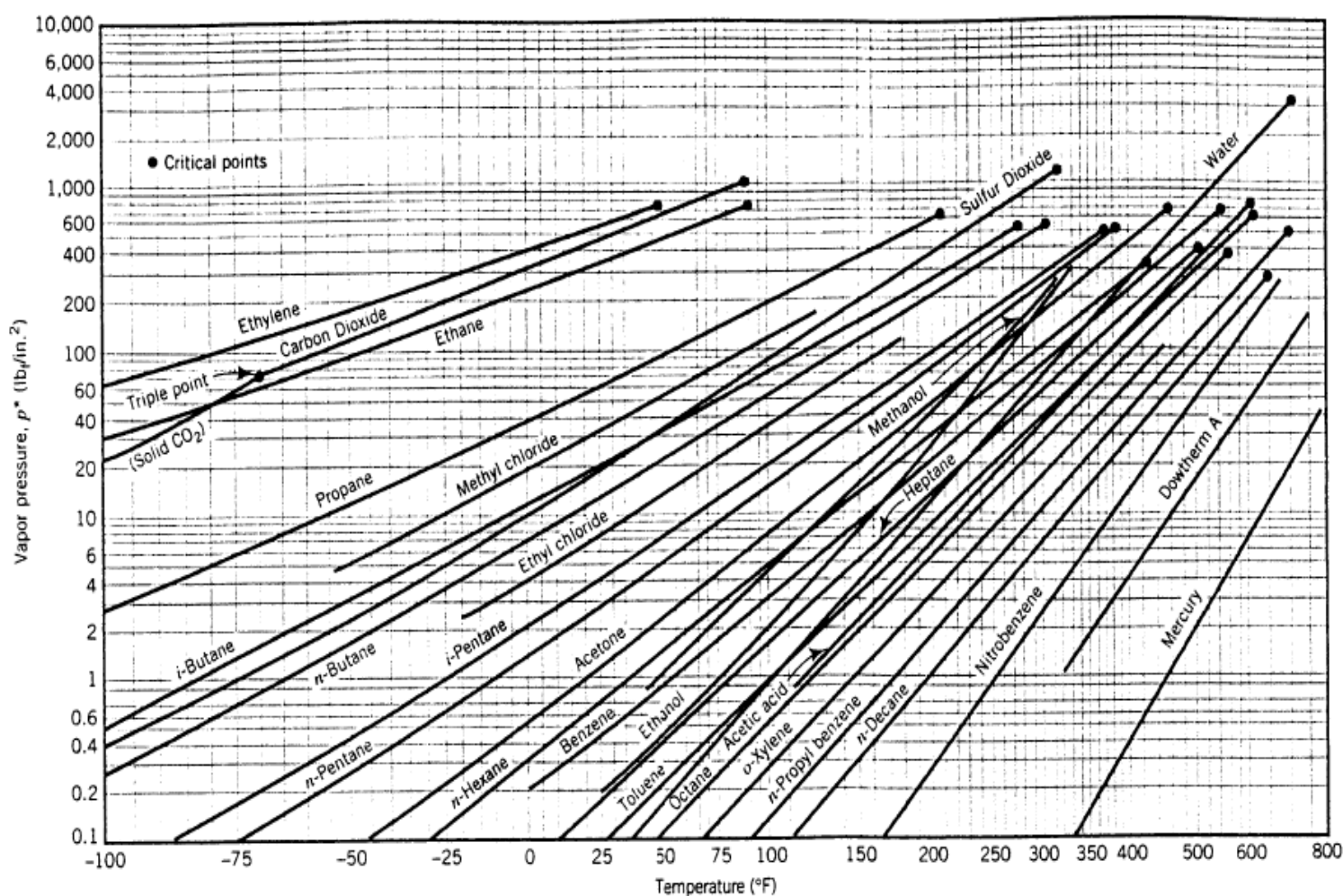


Figure 6.1-4 Cox chart vapor pressure plots. (From A. S. Foust et al., *Principles of Unit Operations*, Wiley, New York, 1960, p. 550.)

④ Steam tables as table B.3.

**** The Gibbs phase rule :**

thermodynamic Degree of freedom (F) for a system at equilibrium is :

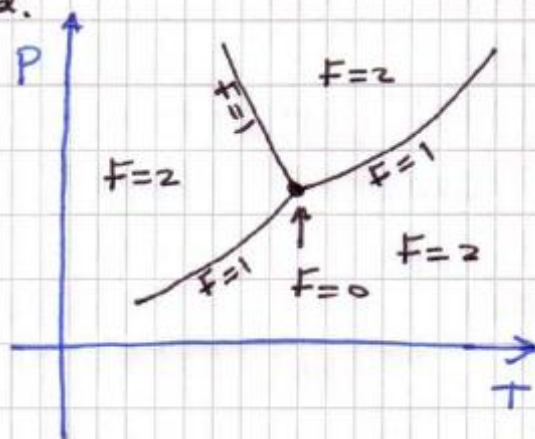
$$F = 2 + c - p - r \geq 0$$

c : # of chemical species

p : # of phases

r : # of indept. chem. reactions.

$F \equiv$ # of intensive variables that have to be specified independently and then the other intensive thermodynamic variables can be calculated.

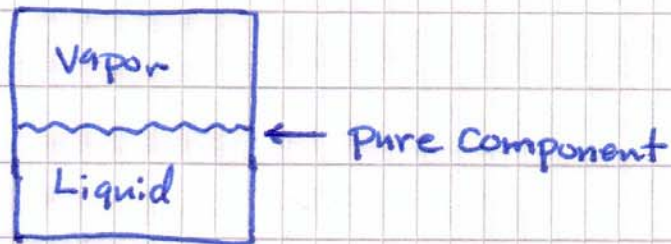


Ex: Suppose that you find in the laboratory a vessel which has VL mixture. Someone told you that it is a mixture of non-reactive components. is it possible to have this situation?

$$F = 2 + c - p - r = 2 + c - 2 - 0 \geq 0$$

$c \geq 0$. **no it is not possible.** There must be at least two reactions, $r=2$, to have a mixture of two components or more

** Vapor-Liquid system of pure Component :



at equilibrium: $P = P^*(T)$

In other words: boiling occurs when the operating pressure equals the vapor pressure of the liquid at the operating temperature.

$$F = 2 + C - p - r = 2 + 1 - 2 - 0 = 1$$

This means that at this situation, you can specify just one intensive property (variable) and you can then calculate the others.

Ex: If you would like to have a mixture of V and L of water at $T = 60^\circ\text{C}$. what is the pressure and specific molar volumes of V and L.

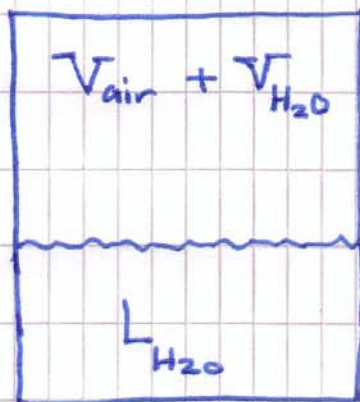
$F = 1$ $T = 60$ is specified then you can calculate the others:

$$P = P^*(60^\circ\text{C}) = \dots$$

and use EOS to find two roots: $\hat{V}_L, \hat{V}_V$ at $T = 60^\circ\text{C}$ and the calculated P .

** Gas - liquid system : with one Condensable Component

Ex: air-water
system (wet air)



at equilibrium :

- The gas-phase is saturated with the vapor.
- The vapor in the gas-phase is referred to as saturated vapor.
- Equilibrium $\equiv$ Saturation
- Equilibrium Condition: partial pressure of the vapor in the gas-phase must equal the vapor pressure of the liquid at the system temperature:

$$P_i = y_i P = P_i^*(T)$$

$i \equiv$ water in the above example.

y_i : mole fraction of Condensable Component in the gas-phase

P_i : Partial pressure = = = = =

$$F = 2 + C - p - r = 2 + 2 - 2 - 0 = 2$$

$\Rightarrow$ you can specify just two intensive properties

Ex: Specify y_i and P and calculate T_d

→ If $P_i = y_i P < P_i^*(T)$: vapor in the gas phase is less than its saturation amount

∴ Superheated vapor.

→ Saturation refers to any gas-vapor combinations while (humidity) refers specifically to an (air-water) system

* Relative Saturation (Relative humidity):

$$S_r \text{ or } h_r = \frac{y_i P}{P_i^*(T)} * 100 \%$$

relative humidity of 40% means that the partial pressure of water vapor equals 0.4 of the vapor pressure of water at system T.

* Molal Saturation (Molal humidity):

$$\begin{aligned} S_m \text{ or } h_m &= \frac{P_i}{P - P_i} = \frac{y_i}{1 - y_i} \\ &= \frac{\text{moles of vapor}}{\text{moles of dry gas}} \end{aligned}$$

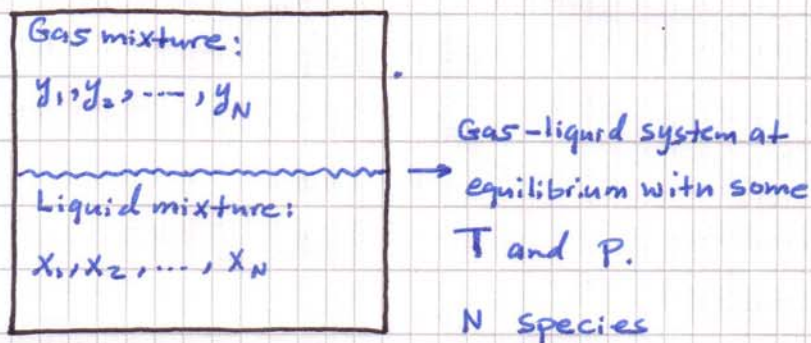
* Absolute Saturation (Absolute humidity)

$$S_a \text{ or } h_a = \frac{\text{mass of vapor}}{\text{mass of dry gas}} = \frac{P_i M_{wti}}{(P - P_i) M_{wt \text{ dry gas}}}$$

** Multi-Component Gas-Liquid systems :

⇒ Mixtures in gas and liquid phases:

⇒ General Case :



at equilibrium: $\phi_i y_i P = \gamma_i x_i P_i^*(T) \quad i=1, 2, \dots, N$

where :

- ϕ_i : fugacity coefficient of species i
- y_i : mole fraction of species i in gas phase
- P : total pressure
- γ_i : activity coefficient of species i
- x_i : mole fraction of species i in liquid phase
- P_i^* : vapor (saturation) pressure of species i at T

- The above gas-liquid equilibrium relation show how Species i is distributed between two phases at equilibrium.
- There are different thermodynamic models to estimate fugacity and activity coefficients.
- If gas phase is ideal $\Rightarrow \phi_i = 1.0 \quad i=1, 2, \dots, N$
- If liquid phase is ideal $\Rightarrow \gamma_i = 1.0 \quad i=1, 2, \dots, N$

- when ideal gas? see the rules of chapter 5
- when ideal liquid solutions?

- Molecules are similar in molecular weights.
- Molecules have similar intermolecular interactions.
- $X_i \rightarrow 1.0$ "dilute solution."

Ex: Benze-Toluene solution

If ideal gas and liquid phases: $\gamma_i = 1$, $\phi_i = 1$ $i=1,2,\dots,N$
and

$$y_i P = X_i P_i^*(T) \quad \text{"Raoult's law"} \quad i=1,2,\dots,N$$

- In this course we consider ideal gas and liquid phases.

$$F = 2 + C - P - R \quad (R=0 : \text{no reactions})$$

Ex: If you have vapor-liquid mixture:

$$F = 2 + C - 2 - 0 = C = N$$

Thus, you can specify N intensive properties and then you can calculate all other quantities at equilibrium.

- Let us discuss some types of calculations:

- A- Bubble p calculations
- B- Dew p calculations
- C- Bubble T calculations
- D- Dew T calculations.

A- Bubble P Calculations:

Given: $x_1, x_2, \dots, x_N, T$ Calculate: $y_1, y_2, \dots, y_N, P$ # of unknowns = $N+1$ # of equations = $N+1$: $\Rightarrow$

It can be solved

$$\sum y_i = 1 \quad \text{eq. 1}$$

$$y_1 P = x_1 P_i^*(T) \quad \text{eq. 2}$$

$$y_2 P = x_2 P_2^*(T) \quad \text{eq. 3}$$

$$\vdots$$

$$y_N P = x_N P_N^*(T) \quad \text{eq. N}$$

How?

$$y_i P = x_i P_i^*(T)$$

$$\text{Take sum: } \sum y_i P = \sum x_i P_i^*(T)$$

$$P \sum y_i = \sum x_i P_i^*(T)$$

$$\sum y_i = 1$$

$$\Rightarrow \boxed{P = \sum x_i P_i^*(T)}$$

Then find:

$$\boxed{y_i = \frac{x_i P_i^*(T)}{P} \quad i=1, 2, \dots, N}$$

B. Dew P Calculation:

Given: $y_1, y_2, \dots, y_N, T$ Calculate: $x_1, x_2, \dots, x_N, P$ How to solve: $y_i P = x_i P_i^*(T) \quad i=1, 2, \dots, N$ Divide by $P_i^*(T)$ then take the sum

$$\frac{y_i P}{P_i^*(T)} = x_i \quad i=1, 2, \dots, N$$

$$\sum \frac{y_i P}{P_i^*(T)} = \sum x_i = 1$$

$$\text{oo} \quad P = \frac{1}{\sum \frac{y_i}{P_i^*(T)}}$$

Then find $x_i = \frac{y_i P}{P_i^*(T)} \quad i=1, 2, \dots, N$

C. Bubble T calculations:

Given: $x_1, x_2, \dots, x_N, P$

Calculate: $y_1, y_2, \dots, y_N, T$

$$y_i P = x_i P_i^*(T)$$

$$\sum y_i P = \sum x_i P_i^*(T) \Rightarrow P = \sum x_i P_i^*(T) \quad i=1, 2, \dots, N$$

solve this nonlinear equation to obtain T then find:

$$y_i = \frac{x_i P_i^*(T)}{P} \quad i=1, 2, \dots, N$$

D. Dew T calculation: Give: $y_1, y_2, \dots, y_N, P$

Calculate: $x_1, x_2, \dots, x_N, T$

$$\sum \frac{y_i P}{P_i^*(T)} = \sum x_i = 1 \Rightarrow \frac{1}{P} = \sum \frac{y_i}{P_i^*(T)} \quad \text{Solve to obtain } T$$

Then find $x_i = \frac{y_i P}{P_i^*(T)} \quad i=1, 2, \dots, N$

** Other methods to relate x_i with y_i at equilibrium:

Δ Vapor-Liquid Equilibrium (VLE) ratio method or it is called distribution coefficient method or K-value method:

$$y_i = K_i x_i \quad i=1, 2, \dots, N$$

K_i is the VLE ratio or a distribution coeff. or K-value of species i that can be found at handbooks at some T and P .

Note that
$$K_i = \frac{P_i^*(T)}{P}$$

Thus K_i is the ratio of the vapor pressure of species i to the total pressure.

Δ Henry's law: $y_i P = x_i H_i(T) \quad i=1, 2, \dots, N$

where H_i is the Henry's constant for species i at T in specific solvent.

– Henry's law is generally valid for dilute solutions of species i : i.e. $x_i \rightarrow 0$

Ex: air dissolved in water

– see Perry's Chemical Engineer's Handbook.

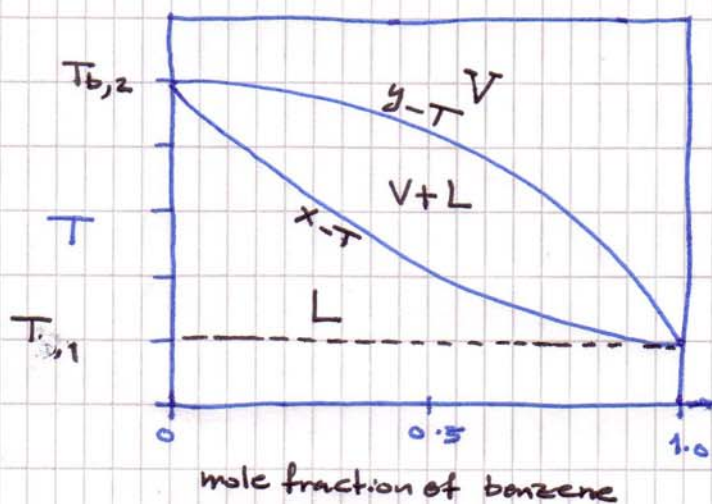
** Graphical representation of Vapor-liquid equilibrium for binary system:

Ex: Benzene - Toluene system:

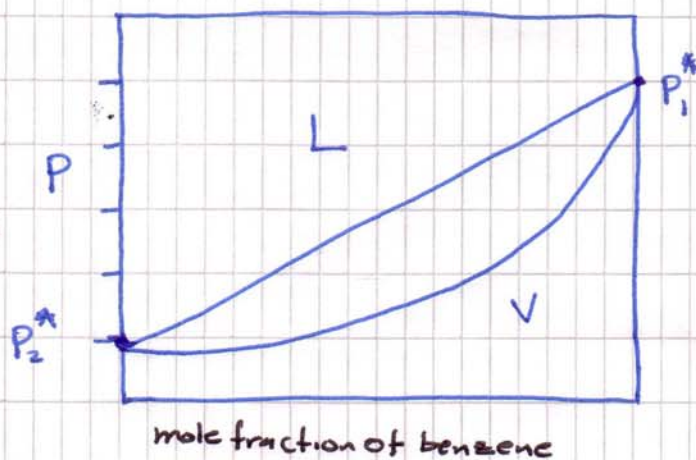
let Benzene be Component 1

Toluene be Component 2

* T-xy phase diagram: $p = 1 \text{ atm}$

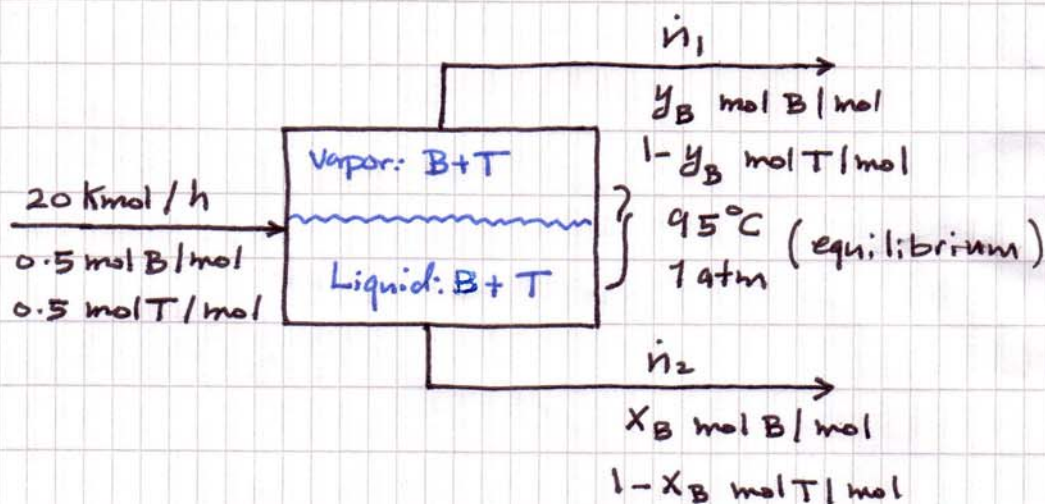


$$\begin{aligned}
 y_i p &= x_i P_i^*(T) \\
 \sum y_i p &= \sum x_i P_i^*(T) \\
 p &= \sum x_i P_i^*(T) \\
 &= x_1 P_1^*(T) + x_2 P_2^*(T) \\
 &= (P_1^* - P_2^*) x_1 + P_2^*
 \end{aligned}$$



Ex: An equimolar liquid mixture of benzene (B) and Toluene (T) is to be distilled in a Continuous distillation unit operating at steady state. The mixture is fed to the distillation unit at rate of 20 kmol/h . The vapor phase is in equilibrium with liquid phase at temperature 95°C and pressure 1 atm (absolute).

Find the flow rates and composition of the overhead and the bottom product streams.



Basis: 20 kmol/h of the feed

$$\text{DOF} = 4 - 2 - 2 = 0 \quad \checkmark \text{ Go ahead}$$

n_1, n_2, x_B, y_B
B and T
mole balance

other equation: VLE relations:

$$y_B P = x_B P_B^*(T) \quad \dots \textcircled{1}$$

$$y_T P = x_T P_T^*(T) \Rightarrow$$

$$(1 - y_B) P = (1 - x_B) P_T^*(T) \quad \dots \textcircled{2}$$

→ Data for Vapor pressure Calculations:

From table B.4, pick up the constants A, B, and C for using Antoine eq.:

For Toluence: $A = 6.95805$ $B = 1346.773$
 $C = 219.693$

$$\Rightarrow \log P_T^*(T) = A - \frac{B}{T(^{\circ}\text{C}) + C} = 6.95805 - \frac{1346.773}{95 + 219.693}$$

$$\Rightarrow P_T^*(95^{\circ}\text{C}) = 476.88 \text{ mmHg}$$

For benzene: $T = 95^{\circ}\text{C}$ is not within the range to use Antoine eq. The range for B: (14.5-80.9).

Thus look for another method.

let us use Cox chart: Fig. 6.1-4:

$$T = 95^{\circ}\text{C} = (1.8)(95) + 32 = 203^{\circ}\text{F}$$

$$\text{at } T = 203^{\circ}\text{F}: P_B^* = 23 \text{ Psi} = 23 \frac{\text{lb}_f}{\text{in}^2}$$

$$= 23 \frac{\text{lb}_f}{\text{in}^2} \left| \frac{760 \text{ mmHg}}{14.69 \frac{\text{lb}_f}{\text{in}^2}} \right|$$

$$= 1189.9 \text{ mmHg}$$

→ Apply Raoult's law for B and T:

$$\underline{B}: y_B P = x_B P_B^* \Rightarrow (y_B)(760) = (x_B)(1189.9) \dots$$

$$\Rightarrow y_B = 1.5656 x_B \dots \textcircled{1}$$

$$\text{I: } y_T P = X_T P_T^*$$

$$y_T (760) = X_T (476.83)$$

$$\text{or } (1 - y_B) = (0.62747)(1 - X_B) \dots \textcircled{2}$$

Solve eqns ① and ② To obtain: $X_B = 0.397$

$$y_B = 0.622$$

→ Now apply molecular species balances:

$$\text{B mole balance: } (0.5)(20) = (0.622) \dot{n}_1 + (0.397) \dot{n}_2 \text{ --- } \textcircled{1}$$

$$\text{Total mole balance: } 20 = \dot{n}_1 + \dot{n}_2 \text{ --- } \textcircled{2}$$

Solve eqns ① and ② to obtain: $\dot{n}_1 = 9.16 \text{ kmol/h}$

$$\dot{n}_2 = 10.84 \text{ kmol/h}$$

Some discussion: not the the given Temperature = 95 is below the boiling point of pure Toluence (110.62°C at 1atm) and above the boiling point of pure Benz (80.1°C at 1atm).

what will happen if the operating T is less than the boiling point of benzene or above the boiling point of Toluence?

** Boiling point elevation and freezing point depression :

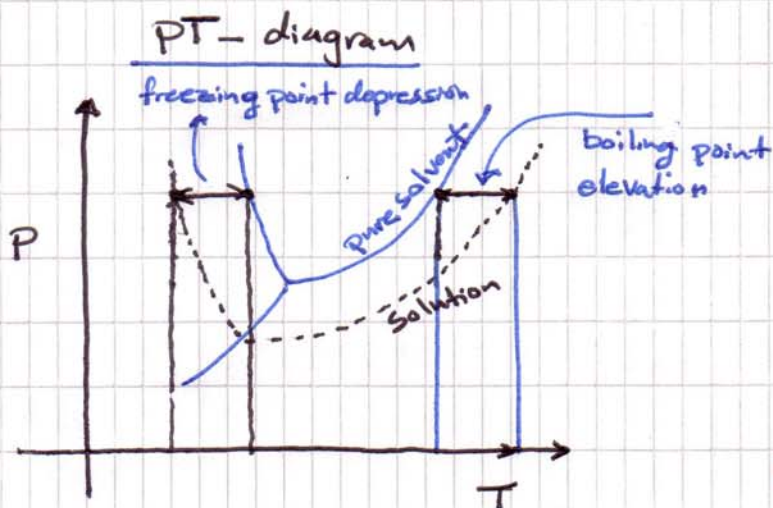
* Boiling point elevation: solvent in solution at a given pressure boils at higher temperature than does pure solvent at the same pressure.

Ex: The boiling point of saline water is greater than that of pure water at the same operating pressure.

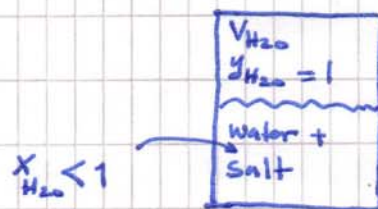
* Freezing point depression: solvent in solution at a given pressure freezes at lower temperature than does pure solvent at the same pressure.

Ex: The freezing point of saline water is lower than that of pure water at the same operating pressure. Thus salt is used to melt snow rapidly.

why? phase diagram and VLE relation explain this behavior:



VLE relation



at equilibrium (boiling):

$$y_{H_2O} P = x_{H_2O} P_{H_2O}^*(T)$$

$$\Rightarrow P = x_{H_2O} P_{H_2O}^*(T)$$

$$P_{H_2O}^* = \frac{P}{x_{H_2O}} \quad \text{more } P^* \Rightarrow \text{Higher } T$$

→ For dilute solutions ($X \rightarrow 0$; where X is solute mole fraction:

The boiling point elevation ; ΔT_b , can be calculated using :

$$\Delta T_b = T_{bs} - T_{bo} = \frac{R T_{bo}^2 X}{\Delta \hat{H}_v}$$

and the freezing point depression ; $\Delta T_f = T_{fo} - T_{fs}$, can be calculated using :

$$\Delta T_f = T_{fo} - T_{fs} = \frac{R T_{fo}^2 X}{\Delta \hat{H}_m}$$

where : T_{bo} : boiling point of pure solvent

T_{fo} : freezing (melting) point of pure solvent

$\Delta \hat{H}_v$: latent heat of vaporization of pure solvent

$\Delta \hat{H}_m$: latent heat of fusion of pure solvent

R : universal gas constant

X : mole fraction of solute

** Solid-Liquid equilibrium systems :

Ex: Crystallizer, Dryer, Filter, Adsorption, etc.

* **Solubility** : maximum amount of solid substance that can be dissolved in a specified amount of liquid at equilibrium.

- at equilibrium, the solution must be saturated with solid solute.

Ex: Solubility of AgNO_3 in water :

at 20°C : $\frac{222 \text{ g AgNO}_3}{100 \text{ g water}}$

at 100°C : $\frac{952 \text{ g AgNO}_3}{100 \text{ g water}}$

- Thus solubility increases by increasing temperature.
- The figure 6.5-1 on the next page shows How solubility of some inorganic solutes in water is affected by temperature.
- **superheated solution** : the Concentration of solute in solution is higher than the equilibrium value (solubility)
- see Perry's chemical engineer's handbook to pick up solubility values.

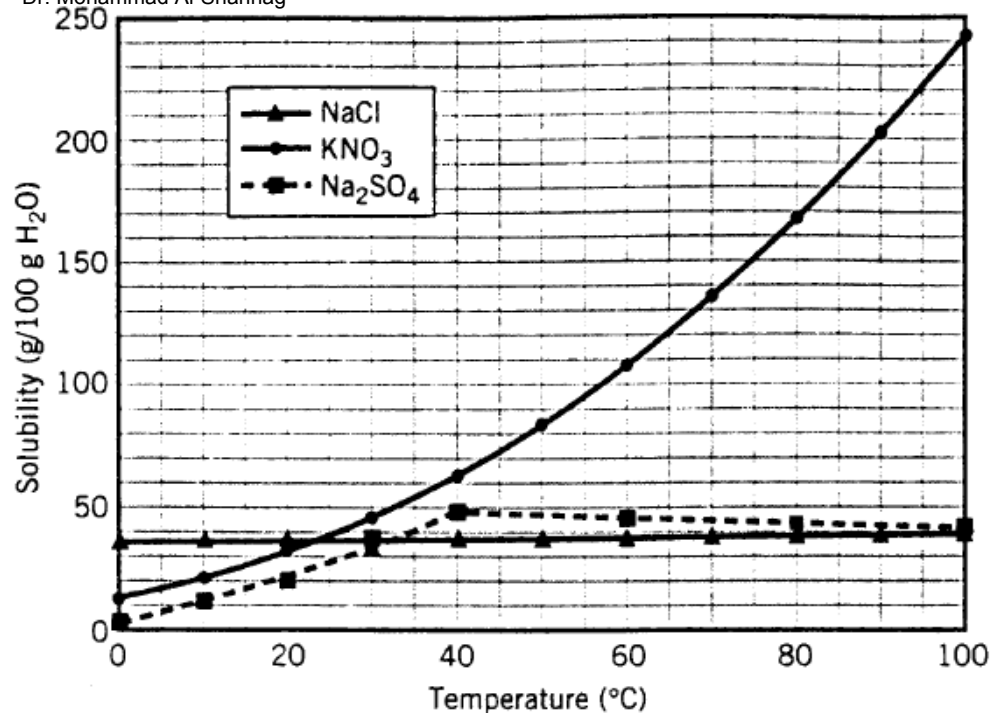
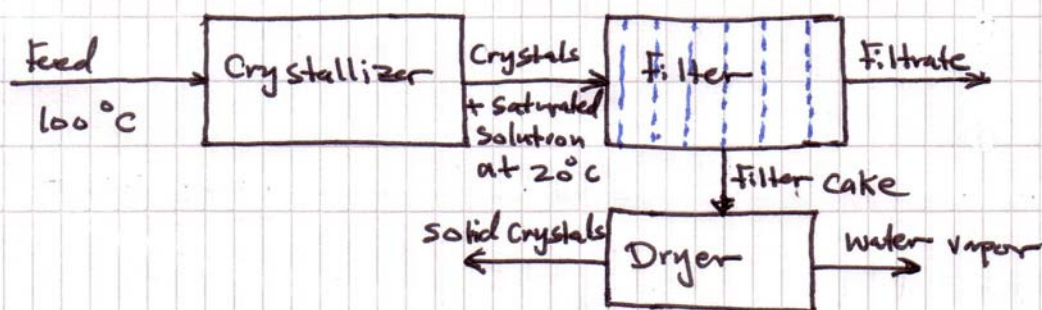


Figure 6.5-1 Solubilities of inorganic solutes.

EX: one hundred fifty kilograms of a saturated solution of AgNO_3 at 100°C is cooled to 20°C , thereby forming AgNO_3 crystals, which are filtered from the remaining solution. The wet filter cake, which contains 80% solid crystals and 20% saturated solution by mass, passes to a dryer in which the remaining water is vaporized. Calculate:

- (1) The amount of recovered dry crystals and the percent recovery relative to AgNO_3 in the feed.
- (2) The amount of water that must be removed in the drying state.



Let us use solubility data since the feed solution is saturated at 100°C and also the filter cake, filtrate, and the outlet from crystallizer have all saturated solution at 20°C :

* Solubility at feed temperature; $T = 100^{\circ}\text{C}$

$$\frac{952 \text{ Kg AgNO}_3}{100 \text{ Kg H}_2\text{O}} \Rightarrow$$

$$X_{\text{AgNO}_3} \text{ in the feed} = \frac{952}{100 + 952} = \frac{952}{1052} = 0.905 \frac{\text{Kg AgNO}_3}{\text{Kg Solution}}$$

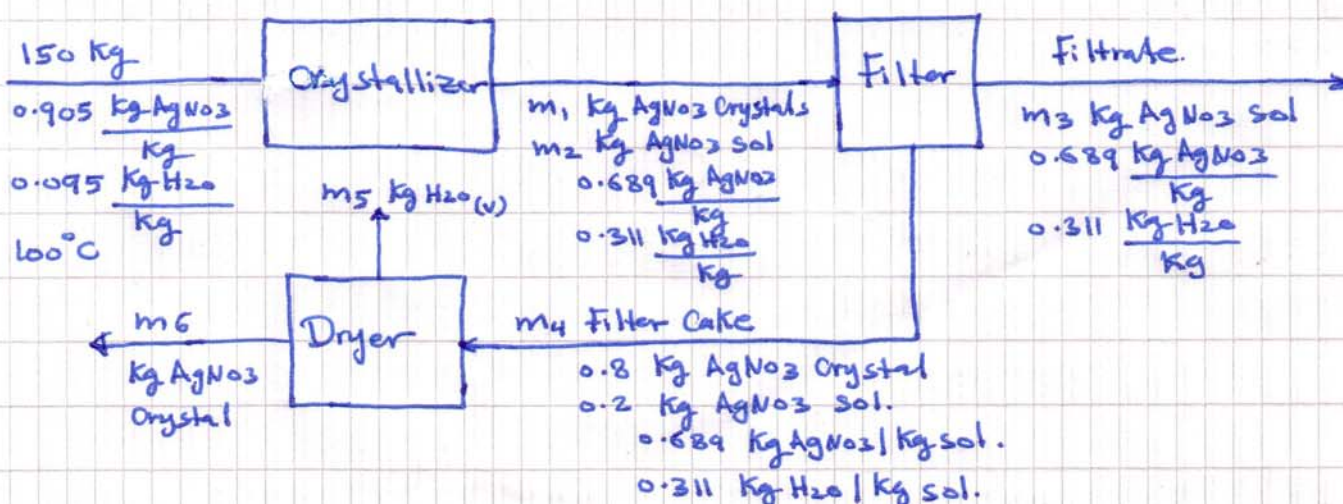
$$\text{and } X_{\text{H}_2\text{O}} \text{ in the feed} = 1 - 0.905 = 0.095 \text{ Kg H}_2\text{O} / \text{Kg solution}$$

$$\text{Solubility at } T = 20^{\circ}\text{C}: \frac{222 \text{ Kg AgNO}_3}{100 \text{ Kg H}_2\text{O}} \Rightarrow$$

$$X_{\text{AgNO}_3} \text{ in solution of filter cake, filtrate and the outlet from Crystallizer} = \frac{222}{222 + 100} = \frac{222}{322} = 0.689 \frac{\text{Kg AgNO}_3}{\text{Kg solution}}$$

$$\text{and } X_{\text{H}_2\text{O}} = 1 - 0.689 = 0.311 \text{ Kg H}_2\text{O} / \text{Kg solution}$$

Now let us draw a completely labeled flow chart:



Global analysis of DoF for the whole process:

- * The process has 3 units and 2 Components are involved in each unit which means that we can write 2 eqns. on each unit $\Rightarrow$

The total # of eqns. that can be written = $2 \times 3 = 6$

- * # of unknowns on the process = 6

The problem can be solved:

- you can write mass balances on Crystallizer since there are 2 unknowns (m_1 and m_2) and 2 species mass balances can be written ($\text{DoF} = 0$) but the amounts m_1 and m_2 are not required in the problem. The required amounts are m_5 and m_6 that are related to dryer. But on the streams of dryer there are 3 unknowns: (m_4, m_5 , and m_6) and 2 eqns. can be written thus for Dryer $\text{DoF now} = 3 - 2 = 1$.

- If you take a combination of crystallizer and filter, the unknowns are m_3 and m_4 (we do not mind about m_1 and m_2 since they are inside this combination); and the # of eqns. are 2. $\text{DoF for crystallizer + filter} = 0 \Rightarrow$ Start with this choice:

- * H_2O mass balance about crystallizer and filter:

$$(0.095)(150) = (0.311)m_3 + (0.2)(0.311)m_4$$

- * total mass balance about crystallizer and filter:

$$150 = m_3 + m_4$$

solve these two eqns. to find :

$$m_3 = 20 \text{ Kg solution}$$

$$m_4 = 130 \text{ Kg solution} + \text{Crystals}$$

- Now to find m_5 and m_6 you can apply balances on the whole process ($\text{DoF} = 2 - 2 = 0$) or on the dryer ($\text{DoF} = 2 - 2 = 0$)

- Let us apply balances on the whole process :

AgNO₃ mass balance : $(150)(0.905) = m_6 + (m_3)(0.689)$

$$\Rightarrow (150)(0.905) = m_6 + (20)(0.689) \Rightarrow m_6 = 122 \text{ Kg Crystals}$$

$$\Rightarrow \text{The recovered amount of AgNO}_3 \text{ Crystals} = 122 \text{ Kg}$$

and the percent recovery is $\frac{122}{(0.905)(150)} = 0.899$

$$= 89.9\%$$

total mass balance : $150 = 20 + m_6 + m_5$

$$150 = 20 + 122 + m_5$$

$$\Rightarrow m_5 = 8 \text{ Kg H}_2\text{O removed as vapor in the dryer}$$

Ex: An aqueous potassium nitrate (KNO_3) solution containing 60 wt% KNO_3 at 80°C is fed to a cooling crystallizer in which the temperature is reduced to 40°C .

- (a) Determine the temperature at which the solution reaches saturation
 (b) The percentage of the potassium nitrate in the feed that forms crystals.

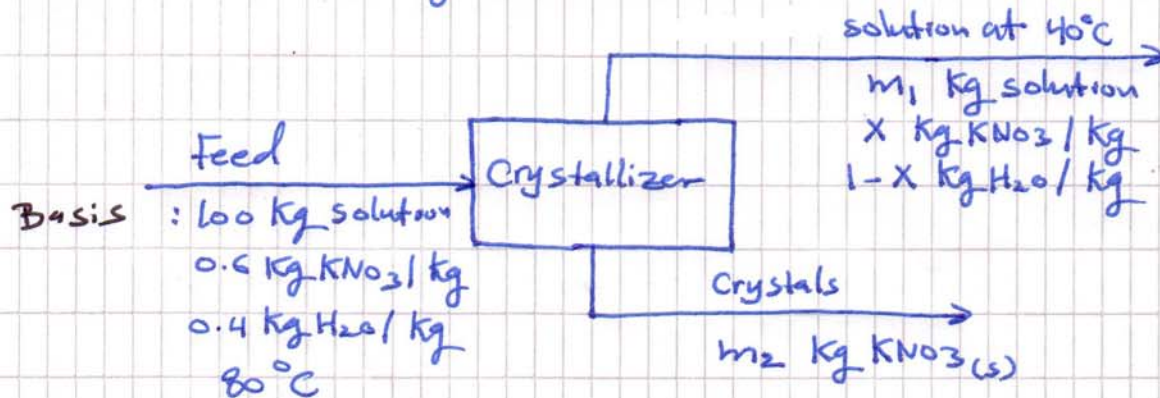
(a) The feed concentration can be converted to a solute/solvent ratio as solubility value:

100 g of feed solution contains: 60 g KNO_3
 40 g H_2O

$$\Rightarrow \frac{60 \text{ g } \text{KNO}_3}{40 \text{ g } \text{H}_2\text{O}} = 1.5 \frac{\text{g } \text{KNO}_3}{\text{g } \text{H}_2\text{O}} = \frac{150 \text{ g } \text{KNO}_3}{100 \text{ g } \text{H}_2\text{O}}$$

Now using Fig. 6.5-1, the saturation temperature of this solution is 74°C .

(b) The completely labeled flowchart is :



$$\text{DOF} = 3 - 2 = 1 \quad \vee \text{ we need more information}^{\text{th}}$$

Make safe assumption: the solution leaves the crystallizer is saturated at 40°C :

Solubility of KNO_3 in water at 40°C can be picked up from figure 6.5-1:

$$\text{at } 40^\circ\text{C}: \frac{63 \text{ kg KNO}_3}{100 \text{ kg H}_2\text{O}} \Rightarrow$$

$$x_{\text{KNO}_3} = \frac{63}{100 + 63} = \frac{63}{163} = 0.386 \frac{\text{kg KNO}_3}{\text{kg solution}}$$

$$\text{Now } \text{DOF} = 2 - 2 = 0$$

H_2O mass balance:

$$(0.4)(100) = (1 - x)m_1 \Rightarrow 40 = (1 - 0.386)m_1$$
$$\Rightarrow m_1 = 65.1 \text{ kg}$$

Total mass balance:

$$100 = 65.1 + m_2 \Rightarrow m_2 = 34.9 \text{ kg KNO}_3 \text{ crystals}$$

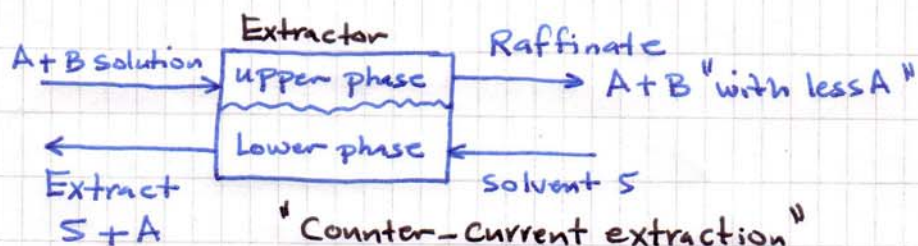
Thus the percent of KNO_3 in the feed that crystallizes is:

$$\frac{34.9}{(100)(0.6)} = 0.582 = 58.2\%$$

** Liquid-Liquid equilibrium systems:

Ex: Extraction process

- It is based on miscibility between liquids.
- If you have a solution of, let us say, A and B species and you like to extract some of A from this solution. you must find some solvent S such that A is miscible in it while B is not.



For Liquid-liquid systems as extraction, distribution coefficient or partition ratio is used to describe the phase equilibria:

Distribution Coefficient; $K_i = \frac{y_i}{x_i}$

where i is the species distributed between two liquid phases

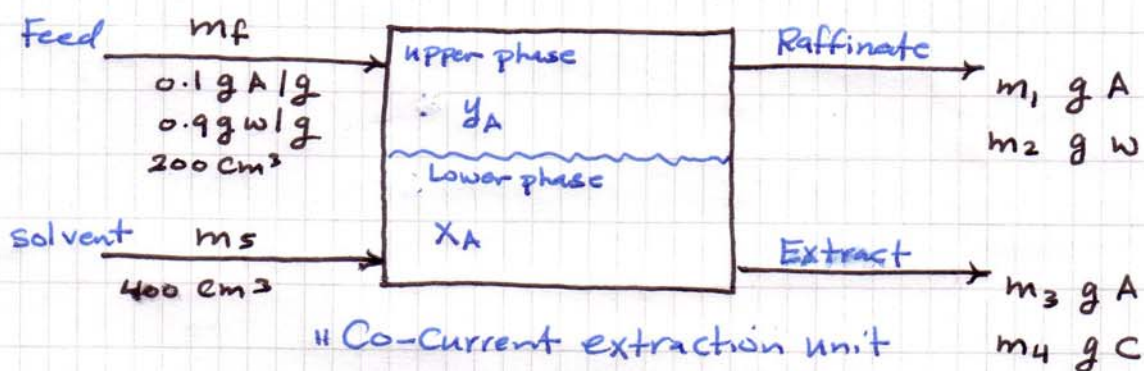
y_i : mass fraction of species i in the upper liquid phase

x_i : mass fraction of species i in the lower liquid phase

Ex: 200 cm³ of acetone - water mixture that contains 10 wt% acetone is mixed with 400 cm³ of Chloroform at 25°C. Since acetone is miscible in Chloroform while water is not two liquid phases are formed and they allowed to settle. What percentage of acetone is extracted from water to Chloroform? the distribution Coeff. of acetone = 0.581

This is extraction process;

let us denote Acetone: A; water: W; Chloroform: C



Basis of Calculation: No any stream has an amount to take it as basis. let us see if the given information permits us to calculate an amount of a stream

Since the feed stream has volume and also the solvent stream we can pick up densities to calculate an amount from table B.1, the densities of pure substances are as follows:

$$\begin{aligned} S_A &= 0.792 \text{ g/cm}^3 & S_W &= 1.000 \text{ g/cm}^3 \\ S_C &= 1.489 \text{ g/cm}^3 \end{aligned}$$

The feed has $V_f = 200 \text{ cm}^3$

$$m_f = S_f V_f$$

S_f is the density of feed mixture which can be calculated from (see Chap 3):

$$\begin{aligned} \frac{1}{S_f} &= \sum x_i / S_i = \frac{x_A}{S_A} + \frac{x_W}{S_W} \\ &= \frac{0.100}{0.792} + \frac{0.9}{1.000} = 1.026 \frac{\text{cm}^3}{\text{g}} \end{aligned}$$

$$\Rightarrow S_f = \frac{1}{1.026} = 0.974 \text{ g/cm}^3$$

$$\text{so } m_f = S_f V_f = (0.974)(200) = 195 \text{ g}$$

also the solvent volume is $V_s = 400 \text{ cm}^3$, the solvent is chloroform, thus:

$$m_s = S_c V_s = (1.489)(400) = 596 \text{ g}$$

so Basis: 195 g of feed solution

we have distribution coefficient of acetone:

$$K_A = 0.581 = \frac{y_A}{x_A} = \frac{m_1 / (m_1 + m_2)}{m_3 / (m_3 + m_4)} = 0.581$$

DoF = 4 - 3 - 1 = 0

$\downarrow$ $\downarrow$ $\downarrow$
 m_1, m_2 A, C, S m_3, m_4

The problem can be solved

C MB : $m_s = m_4 \Rightarrow m_4 = m_s = 596 \text{ g}$

W MB : $(0.9)(m_f) = m_2 \Rightarrow m_2 = (0.9)(195) = 175.5 \text{ g}$

Total MB: $m_f + m_s = m_1 + m_2 + m_3 + m_4$

$$\Rightarrow m_1 + m_3 = m_f + m_s - m_2 - m_4$$

$$= 195 + 596 - 175.5 - 596$$

$$m_1 + m_3 = 19.5 \quad \dots \quad (1)$$

other eq. Distribution Coefficient of acetone eq.

$$K = 0.581 = \frac{m_1 / (m_1 + m_2)}{m_3 / (m_3 + m_4)}$$

$$0.581 = \frac{m_1 / (m_1 + 175.5)}{m_3 / (m_3 + 596)} \quad \dots \quad (2)$$

Solve Eqs. (1) and (2) to obtain

$m_1 = 2.7 \text{ g A in Raffinate stream}$

$m_3 = 16.8 \text{ g A in Extract stream}$

The percentage of acetone extracted is $= \frac{16.8}{(6.1)(195)} * 100\%$

$$= 86.1 \%$$

Ex: An industrial company has a solution of A and B Components. The company is interested to produce from this solution an amount of A of high purity. It is found that the boiling points of pure A and pure B are very closed to each other. at the same time the company has some solvent whose boiling point is much greater than either pure A or B. In addition component B is immiscible in S while A is miscible in it. propose a separation strategy to achieve this target which is illustrated in a flowchart.

For such situation it is proposed to use first extraction followed by distillation of the extract stream:

