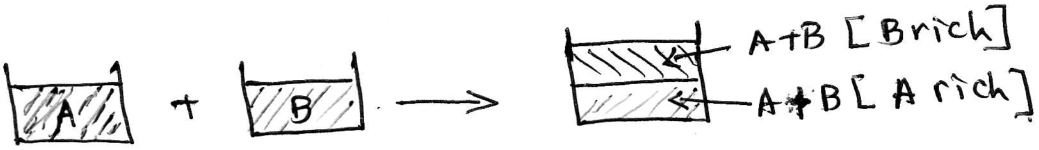
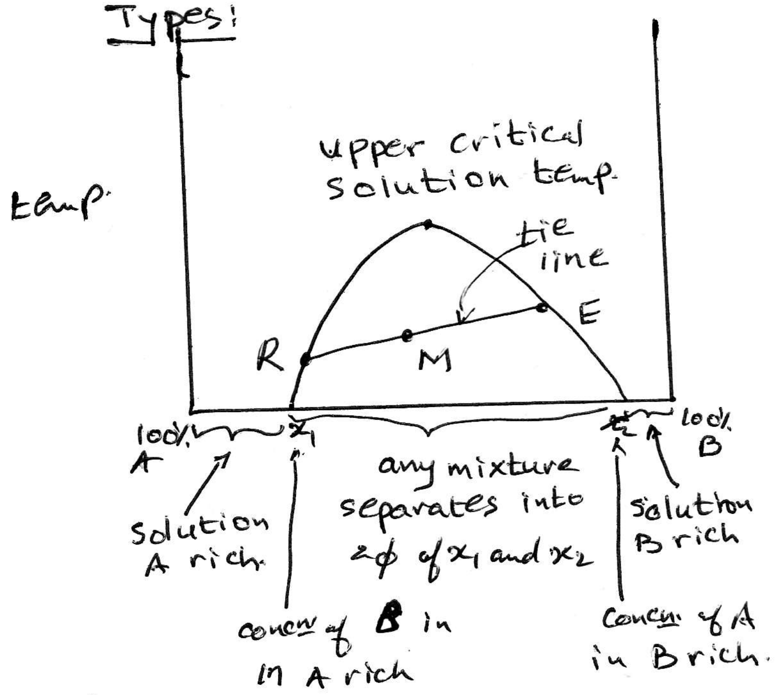
Liquid - Liquid Systems:

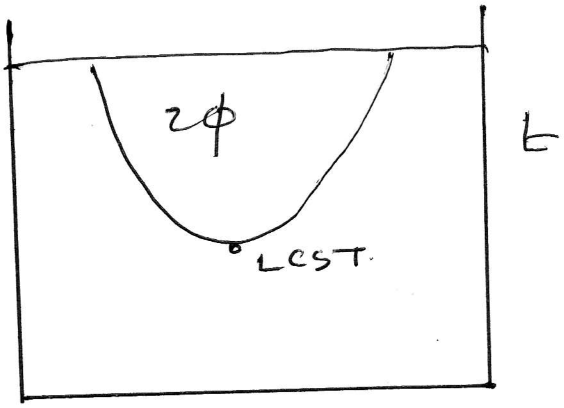
- In reality all liquids are soluble in each other to a limited extent [Hand book of solvent extraction]
- only systems that exhibit partial miscibility are of interest.
- From a practical point of view, some systems may be considered as completely immiscible over wide temperature ranges.
- In extraction systems, at least three components are involved. They are called "Ternary Systems".

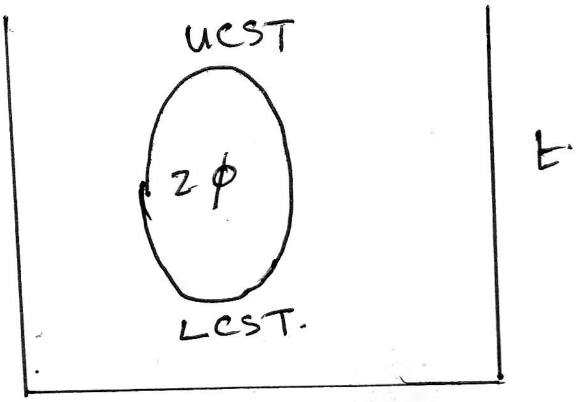
Binary systems:

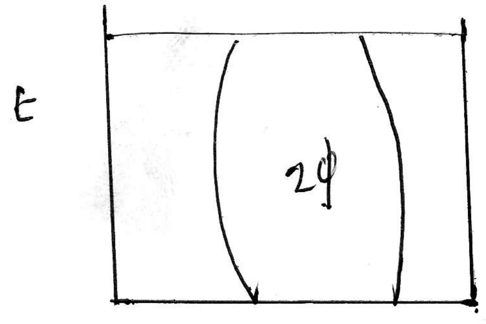


Types:









Effect of pressure is negligible.

Ternary Systems:

Presentation of ternary Equilibrium data:

Notations:

A and B : Insoluble liquids.
C : Solute distributed between A and B

A+C is a mixture of which C is to be extracted by B.

Concentrations:

x : mass fraction of solute (C) in "A" rich liq
y : mass fraction of solute (c) in "B" rich liq

Distillation
x in liq
y in vap.

solute free concentrations (C-free)

$$x' = \frac{x}{1-x}$$

$$y' = \frac{y}{1-y}$$

Solvent free concentrations: (B-free)

$$X = \frac{\text{mass } C}{\text{Mass}(A+C)} \qquad \text{A rich}$$

$$Y = \frac{\text{mass } C}{\text{mass}(A+C)} \qquad \text{B rich.}$$

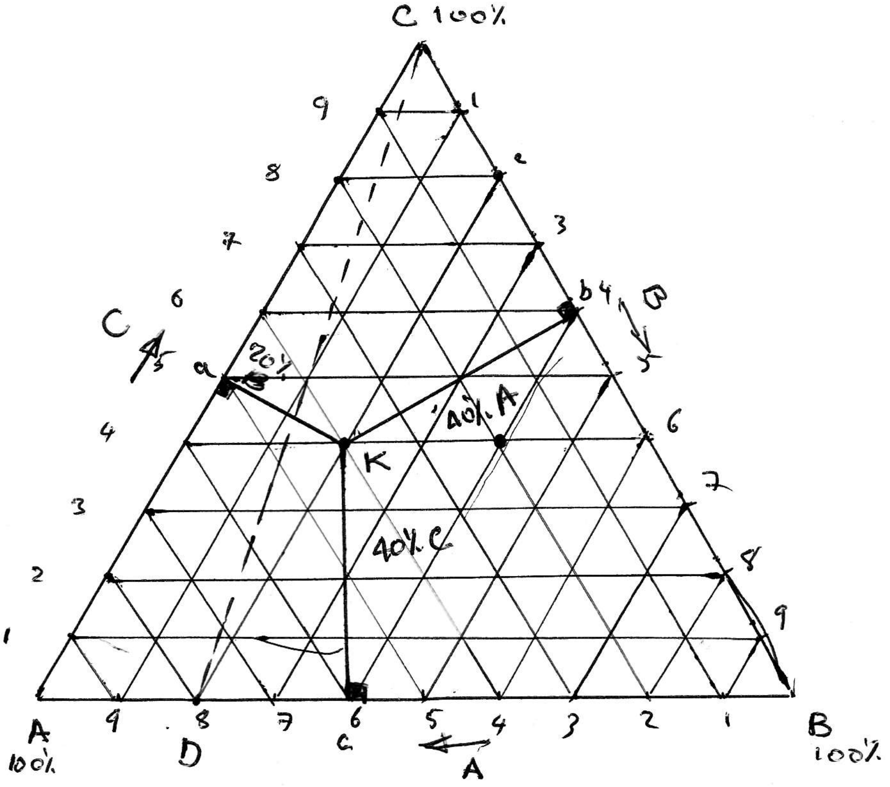
N = mass fraction of B on B-free basis

$$= \frac{\text{mass } B}{\text{mass}(A+C)}$$

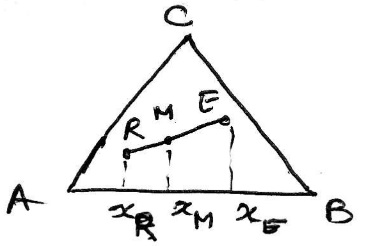
phase Diagrams:

Triangular diagrams

Ternary phase equilibrium data are most simply represented on an equilateral triangular diagram at constant temperature and pressure.



- Altitude of triangle = sum of perpendicular distances from any point inside triangle to the sides
  ≡ 100% composition
- Each corner represents pure component (A, B, C)
- points on one side represent binary mixture (D: 80% A, 20% B)
- points inside represent ternary mixtures (K: 40% A, 40% C, 20% B)
- points on lines such as CD represent mixtures of A and B in the same ratio.
- lever rule applies for mixing or removal of material.



$$\frac{R}{E} = \frac{EM}{RM} = \frac{x_E - x_M}{x_M - x_R}$$

Distribution Diagrams:

y vs x

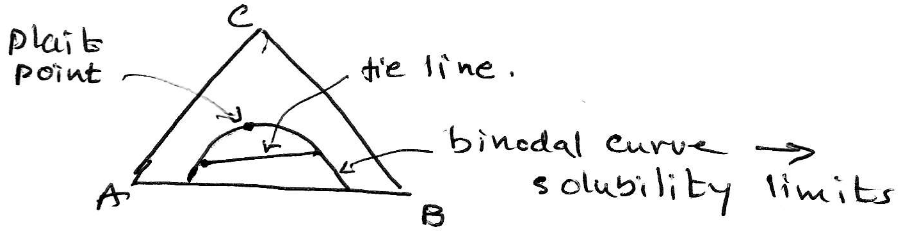
Y vs X

Types of Ternary systems:

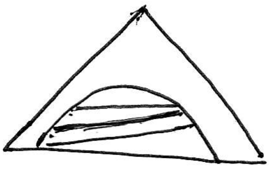
Ternary systems are broadly classified into four types:

TYPE I:- "one partially miscible binary pair. Also referred to as closed system"

- Most important for liquid/liquid extraction. It includes 75% of ternary systems on which experimental data are available.

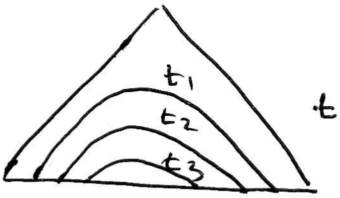


- The orientation of tie lines indicates which phase the solute favors (above it favors B). In most cases the orientation of tie lines changes in the same direction but never changes sign.

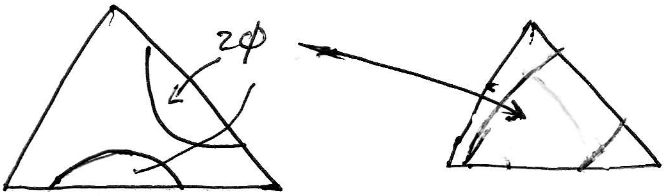


in cases where it changes sign, the system is termed "solutropic"

- The effect of temperature is to increase the solubility and thus diminish the two phase region.

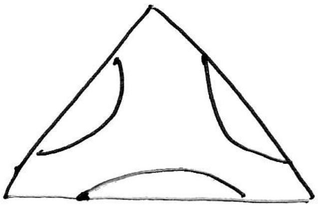


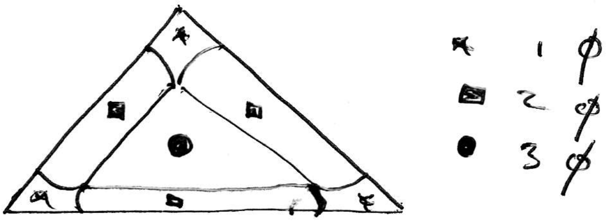
TYPE II :- "Two partially miscible binary pairs". Also referred to as an open system.



- Increase in temperature generally increases the mutual solubility of the two liquid phases, and at a temperature above the critical solution temperature of one of the liquid systems the system is closed and becomes similar to type I.

TYPE III : "contains three partially miscible binary pairs"





TYPE IV : "contains a solid"

TYPES III and IV are of little interest and should be avoided where possible

Selectivity:

The effectiveness of the solvent may be expressed by comparing the ratio of solute to liquid A in B rich phase to that in the A-rich phase at equilibrium. This is defined as the "selectivity" of the solvent or the "separation factor" (similar to relative volatility in distillation).

$$\beta = \frac{(\text{mass fraction of C in B rich}) / (\text{mass fraction of A in B rich})}{(\text{mass fraction of C in A rich}) / (\text{mass fraction of A in A rich})}$$

E: B rich R: A rich.

$$\beta = \frac{y_{CE} / y_{AE}}{x_{CR} / x_{AR}}$$

$$= \frac{y_{CE}}{x_{CR}} \cdot \frac{x_{AR}}{y_{AE}}$$

For $K_c = \frac{y_{CE}}{x_{CR}}$; $K_A = \frac{y_{AE}}{x_{AR}}$

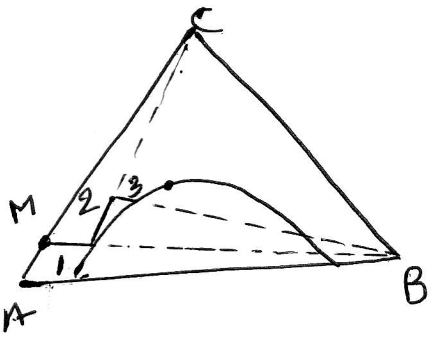
$$\boxed{\beta = \frac{K_c}{K_A}}$$

Experimental determination of data:

Solubility (binodal curve or demixing curve or solubility limit)

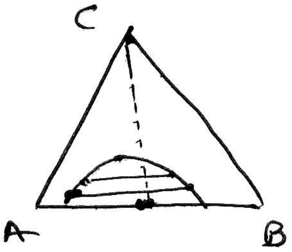
An isothermal binodal curve is determined as follows:

1. Start with a known mixture of A and C in the miscible range - Point M.
2. Add component B by titration until mixture becomes turbid (cloud point) point 1
3. Add known amount of C to obtain point 2 in the miscible range.
4. Add more B to obtain point 3
5. Continue to obtain the complete binodal curve



Tie line determination:

1. Starting with a suitable overall composition of A and B in the immiscible range, component C is added by titration
2. The two phases are then intimately contacted until equilibrium is reached and then they are left to settle.
3. Small samples of each phase are withdrawn and analysed in order to determine tie line data
4. The above procedure is repeated until a homogeneous phase is obtained



Tie line correlations:

Generally the published equilibrium data is presented in the form of solubility data with a limited number of tie line data, and for process calculations it is necessary to interpolate or extrapolate to cover the full range of interest. If sufficient data is available the distribution curve may be used.

Alternatively, tie line correlation or conjugation curves may be constructed. by drawing lines parallel to the sides of the triangle from the ends of available tie lines. The points of intersection of these lines lie on the conjugate curve. This curve can then be used to locate other tie lines.

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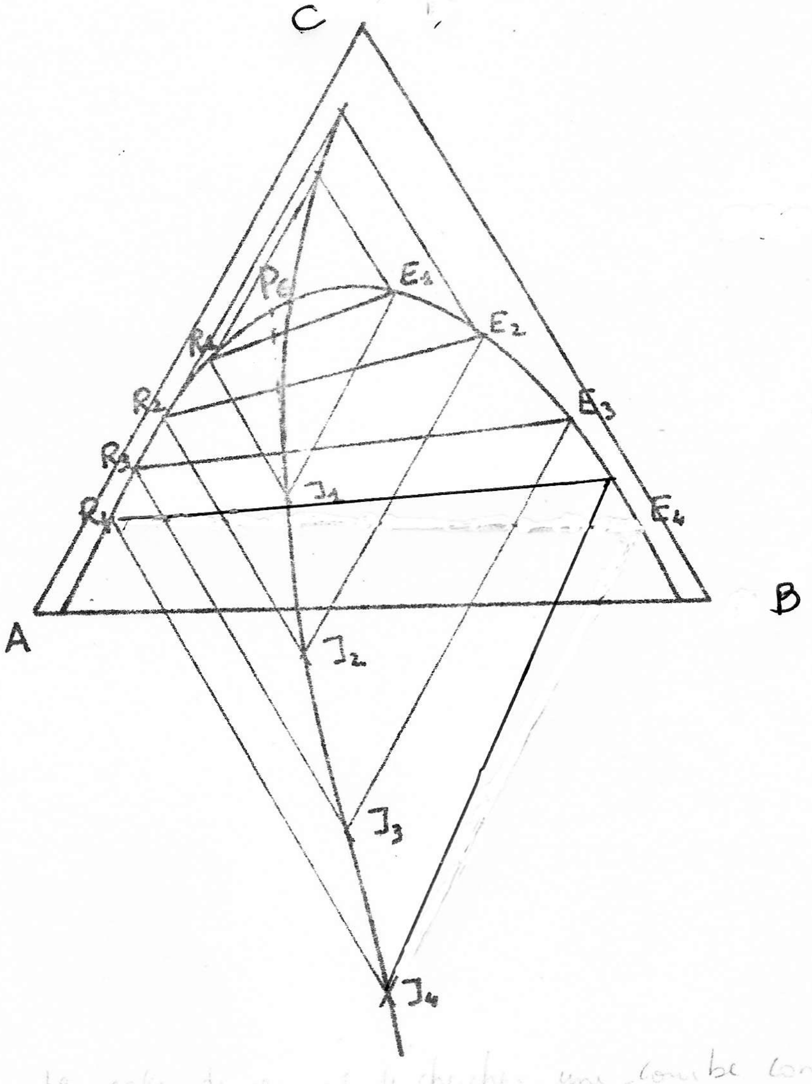
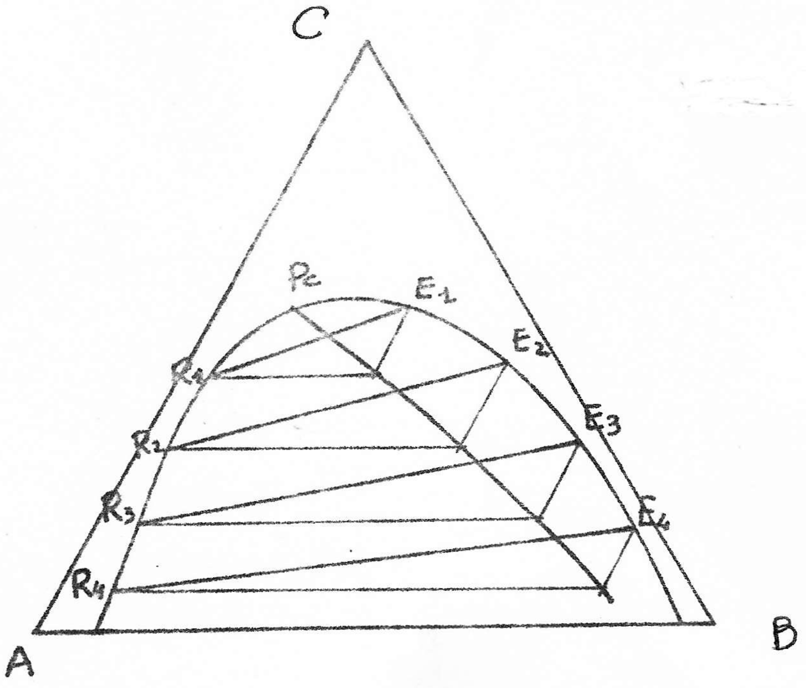


La règle de jeu est de chercher une courbe conjuguée



Types of Contactors:

- Mode of contact
  - continuous (differential)
  - stagewise
    - Discontinuous (single stage)
    - Mixer settlers
      - Horizontal
      - Vertical.
- Agitation
  - Agitated – MS, RDC, pulsed columns
  - non agited – spray columns
- Separation of phases
  - By gravity
  - by centrifugal force
    - compactness
    - high throughput
    - very low residence time

Choice of Solvent:

1. High selectivety for solute or separation factor β
2. Separation after mixing must occur quickly. i e reasonable differential density, interfacial tension and viscosity prevent emulsification.
3. low viscosity reduces pumping cost
4. Low pressure to avoid high pressure operation
5. Check toxicity, inflammability and cost.

Basic Extraction Calculations:

General:

All extraction systems are partially miscible to some extent; some systems can be considered as completely immiscible (Benzen and water)

For immiscible systems, flow rates of carriers (A and B ≡ R and E) can be considered constant and McCabe-Thiele type analysis or Kremser equations are used for the extraction calculations.

For partially miscible systems, a calculation method which allows for the variable flow rates must be used.

In the following, calculation procedures will be limited to isothermal ternary systems for the following arrangements:

- Single stage
- Cross flow
- Countercurrent multistage.

The solution may be handled in two ways

- Stage wise calculations
- graphical determination.

For ternary systems, the following sets of equations may be used:

- 3 independent mass balance equations
- 1 composition equation $\Sigma \text{con}^{\underline{n}} = 1$
- 1 eqm relationship for each stage.