ChE-310

Fundamentals of Separation Processes

Moodle & course syllabus

All information available on Moodle https://moodle.epfl.ch/course/view.php?id=15847

Summary

Students will learn the fundamentals concepts related to molecular separations in industrial processes. Students will employ these concepts to design equilibrium-stage and rate-limited processes for the separation of homogeneous mixture.

Intended Learning Outcome

By the end of the course, students should be able to

- Use of energy separating agent (ESA) and mass separating agent (MSA) for separating chemical mixtures.
- Calculate composition of streams leaving a separation process using the concepts of mass and energy balances, phase equilibria, mass transfer and diffusion.
- Design equilibrium-stage separation process (number of stages, concentration of streams entering or leaving the processes) for the desired outlet concentration from a given feed.

Course Content

Mass and Energy Balances
Thermodynamics of Separations/Phase Equilibria/Degree of Freedom
Flash Distillation
Column Distillation
Multicomponent Distillation
Absorption and Stripping
Liquid-Liquid Extraction
Diffusion and Mass Transfer
Adsorption Processes
Membrane Processes

Intended Learning Outcome

1. Introduction to separation processes, and why it is important for chemical engineers.

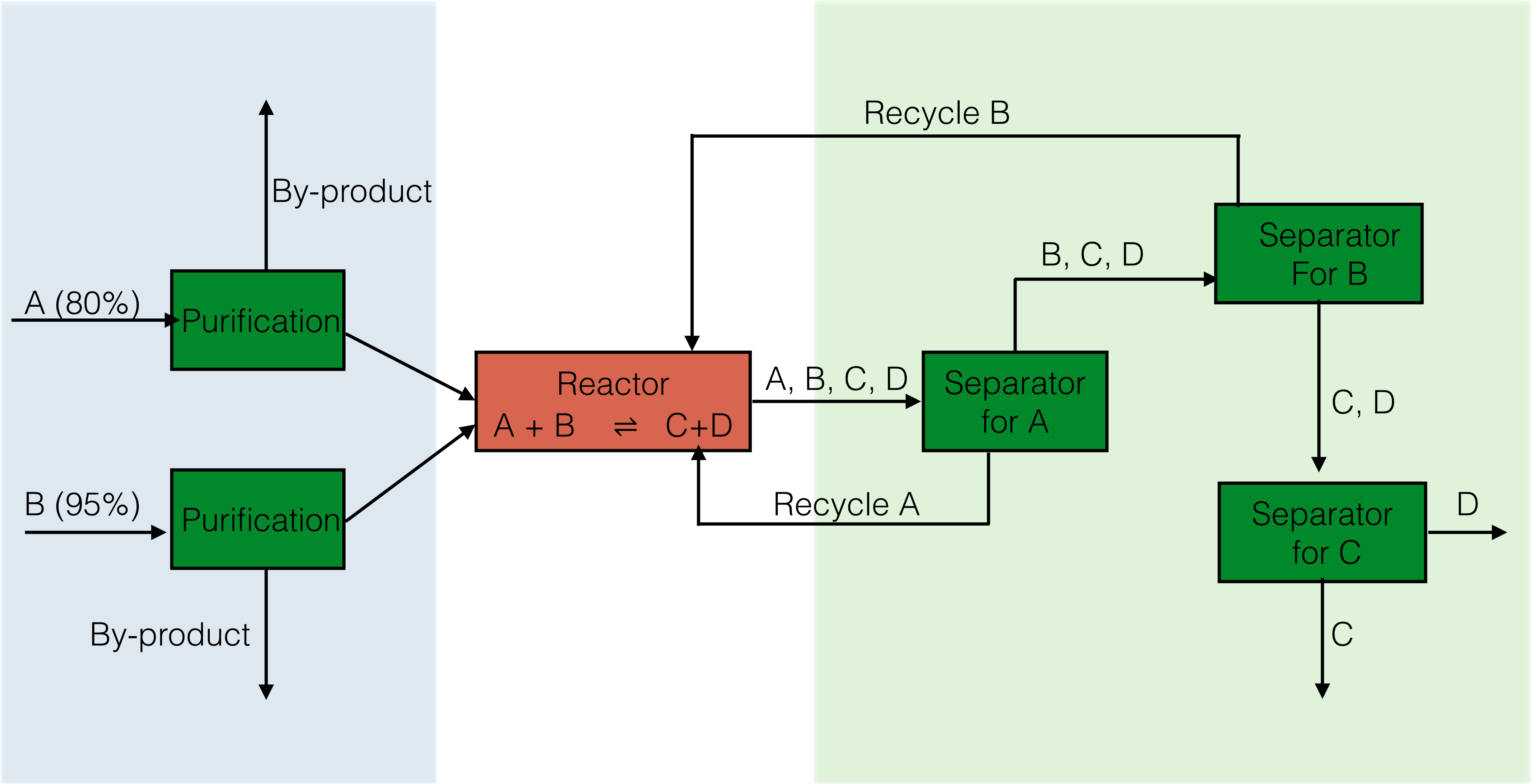
2. Equilibrium driven separation: The concept of phase equilibria.

3. Composition-temperature, composition-pressure, composition-enthalpy based phase diagrams.

Separation processes consume energy. In a chemical industry where there are typically many processes (for example chemical reactors), what fraction of the total energy use comes from the separation processes.

A. ≤ 10 %
B. 10-25%
C. 25-40%
D. ≥ 40%

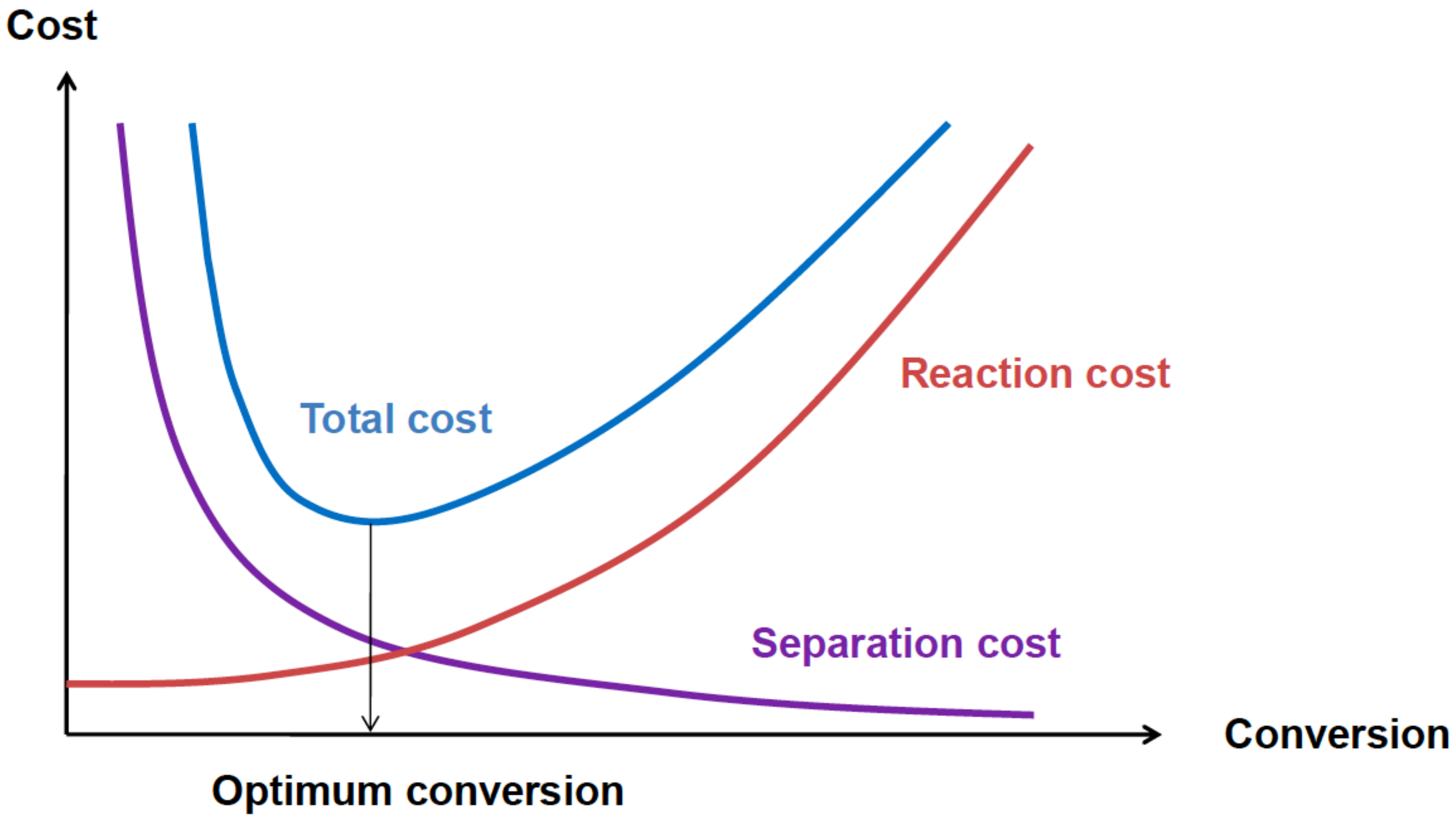
Importance of separation in chemical industry



Upstream of reactor

Downstream of reactor

Overall process economics



DOW Chemicals: Olefin production via steam cracking of naphtha followed by cryogenic distillation

The separation of the $C_2 - C_4$ paraffin/olefin mixtures by cryogenic distillation is one of today´s indispensable and most energy-intensive processes in the refinery industry, consuming up to 85% of the total energy needed for the entire production process.

Van Miltenburg…
Adsorptive separation of light olefin/paraffin mixtures,
Chem. Engin. Res. & Design 84 (2006) 350

Importance of separation for environment: Carbon capture

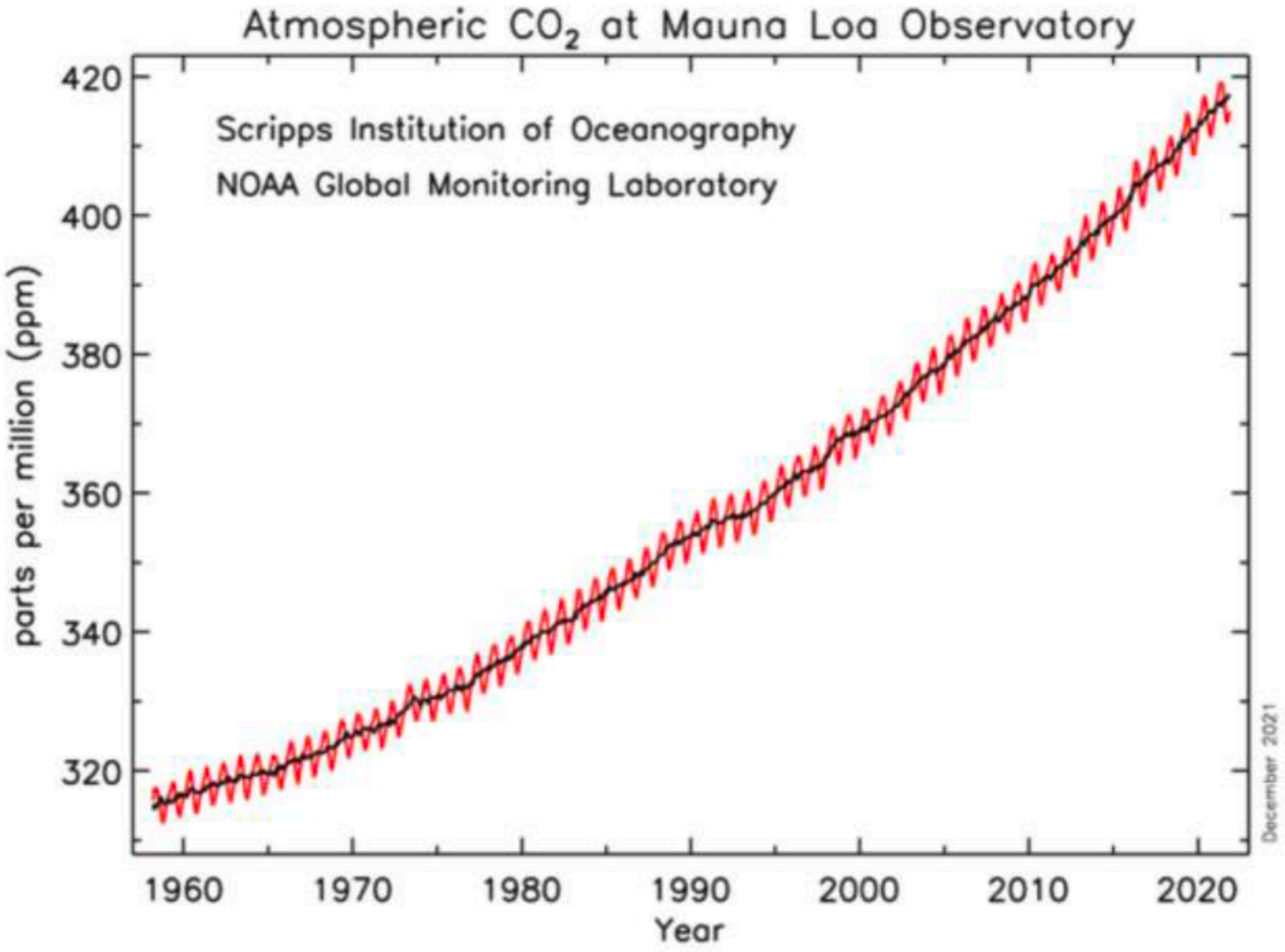
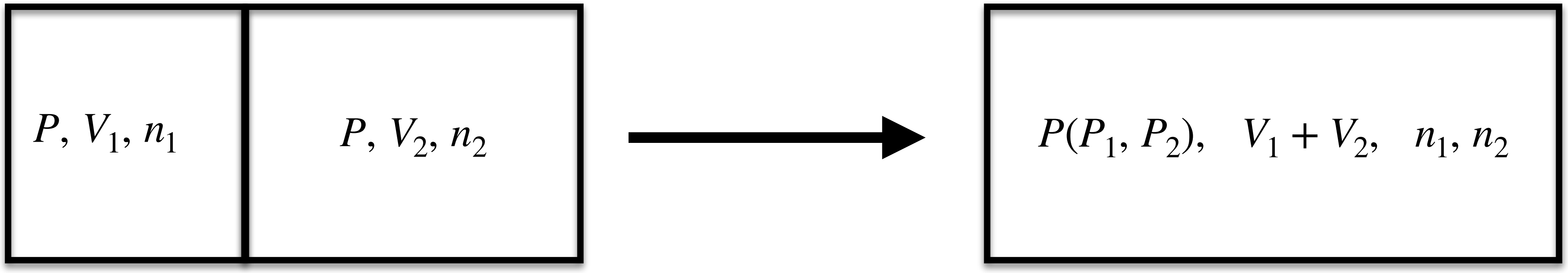


Figure 2. Monthly mean carbon dioxide measured at Mauna Loa Observatory, Hawaii (Source: National Oceanic and Atmospheric Administration)

Mixing vs. Separation

Explain using thermodynamic principles, why mixing to form a homogeneous mixture is a spontaneous process, while separation of that mixture is not.

Consider the case of isothermal mixing



P, V_1, n_1

P, V_2, n_2

$P(P_1, P_2), \quad V_1 + V_2, \quad n_1, n_2$

$$G = n\left(\mu^0 + RT \ln \frac{P}{P^0}\right)$$

Change in gibbs free energy = $\Delta \mathrm{G} = \mathrm{G}_{\text{final}} - \mathrm{G}_{\text{initial}}$

$$\Rightarrow \Delta G = \left[n_1\left(\mu_1^0 + RT \ln \frac{P_1}{P_1^0}\right) + n_2\left(\mu_2^0 + RT \ln \frac{P_2}{P_2^0}\right)\right] - \left[n_1\left(\mu_1^0 + RT \ln \frac{P}{P_1^0}\right) + n_2\left(\mu_2^0 + RT \ln \frac{P}{P_2^0}\right)\right]$$

$$\Rightarrow \Delta G = n_1 RT \ln\left(\frac{P_1}{P}\right) + n_2 RT \ln\left(\frac{P_2}{P}\right)$$

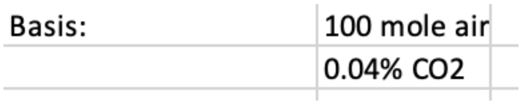
$$\Rightarrow \Delta G = (n_1 + n_2)(RT)\left(\frac{n_1}{n_1 + n_2} \ln x_1 + \frac{n_2}{n_1 + n_2} \ln x_2\right)$$

$$\Rightarrow \Delta G = (n_1 + n_2)RT(x_1 \ln x_1 + x_2 \ln x_2)$$

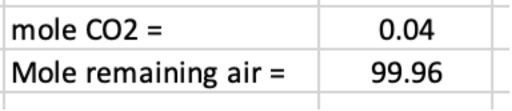
$\Rightarrow \Delta G \leq 0$ **Mixing is spontaneous**

Find the theoretical energy penalty (kJ/kgCO$_2$) for separating CO$_2$ (0.04% in air) from air. Direct air capture industries quotes energy penalty which is at least 8 MJ/kgCO$_2$. What is their energy efficiency?

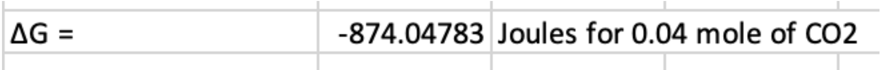
$$\Delta G = (n_1 + n_2)RT(x_1 \ln x_1 + x_2 \ln x_2)$$



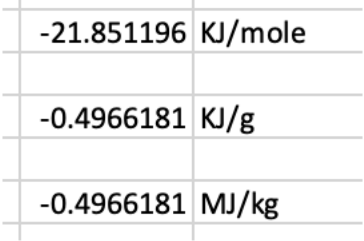
Basis:	100 mole air
	0.04% CO2



mole CO2 =	0.04
Mole remaining air =	99.96



ΔG =	-874.04783	Joules for 0.04 mole of CO2

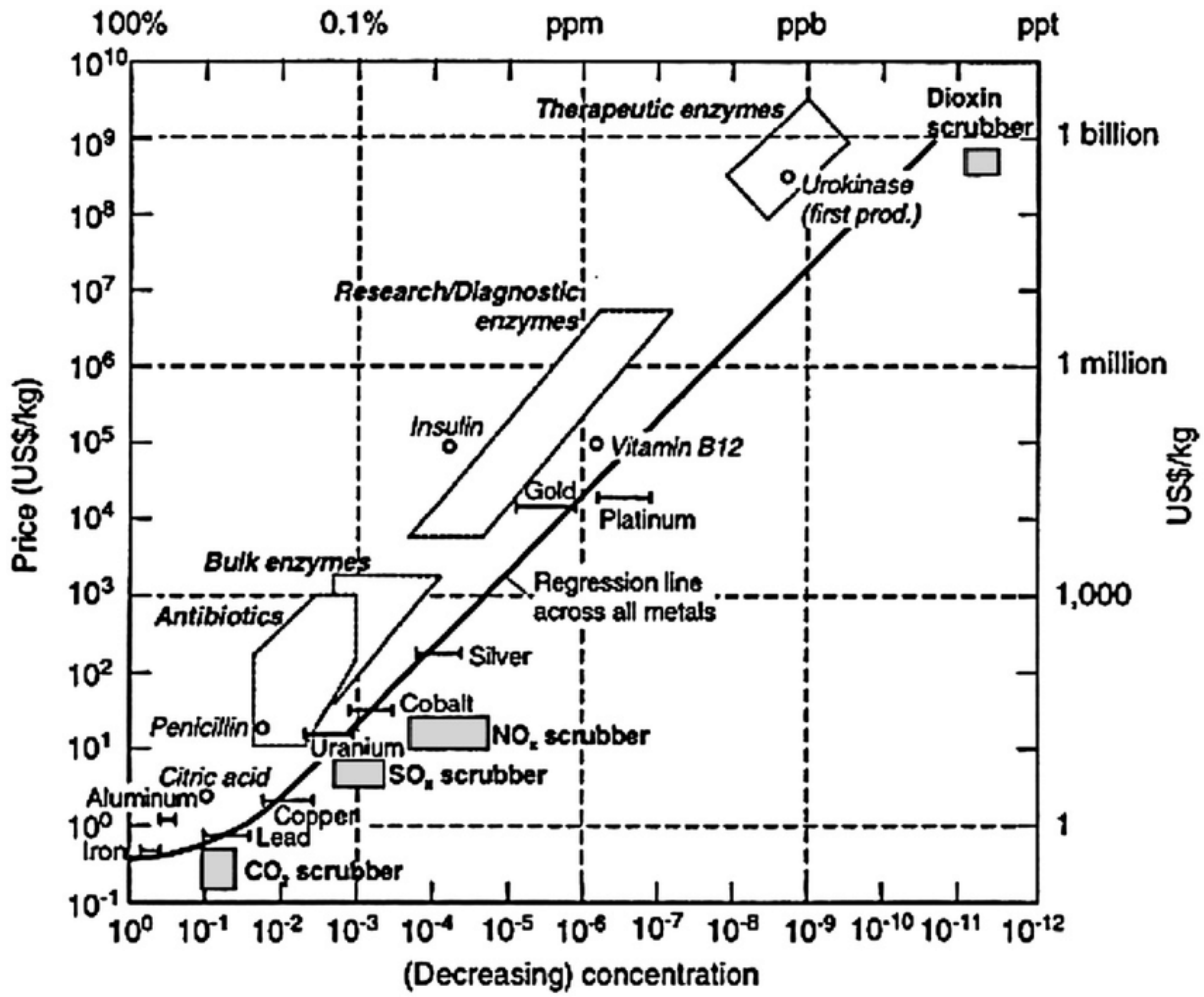


-21.851196	KJ/mole
-0.4966181	KJ/g
-0.4966181	MJ/kg

Efficiency of commercial process = 0.5/8 = 6.25%

In most cases, the cost/energy needed for separation decides the chemical cost

Sherwood plot



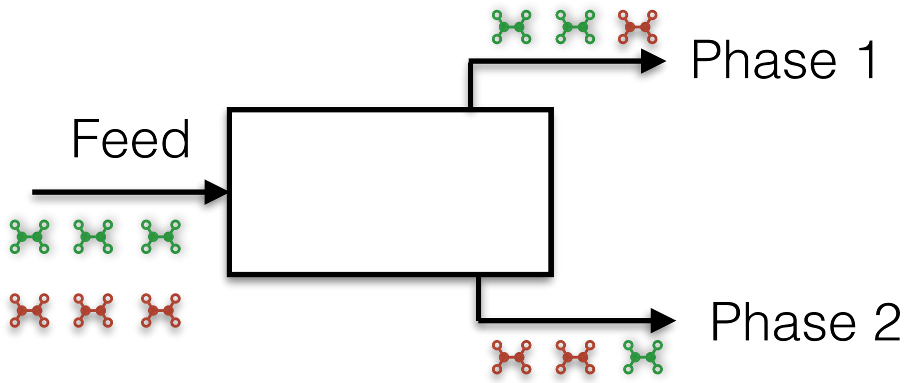
A Grübler, Technology and Global Change (Cambridge Univ Press, Cambridge, UK, 1998).

Separation process exploit differences in the chemical and the physical properties

Type	Examples	Properties
Solid-Solid	Powder mixtures	Size, density, binding
Solid-Liquid	Colloidal suspensions	Size, density, binding
Dissolved solid (ions) - Liquid	Seawater	Ionic size, solubility
Liquid-Liquid	Crude oil	Relative volatility, solubility
Gas-Liquid	Dissolved CO_2	Solubility (pressure, temperature)
Gas-Gas	Air	Boiling point, molecular size, binding

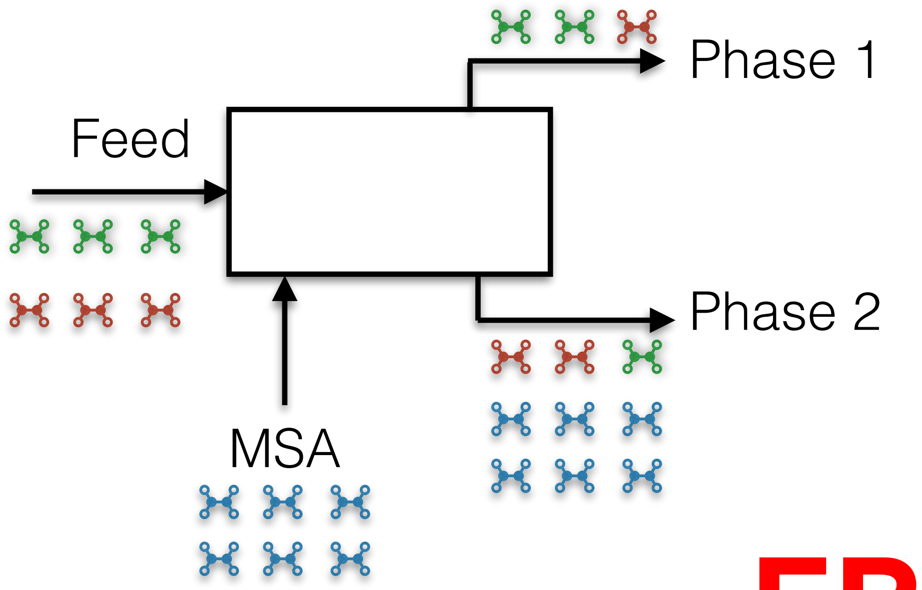
Type of separation process

(1) **Phase creation by adding/withdrawing energy separating agent (ESA)**
(change in temperature, pressure)



Examples:
1. Flash vaporization
2. Partial vaporization
3. Partial condensation
4. Distillation
5. Crystallization

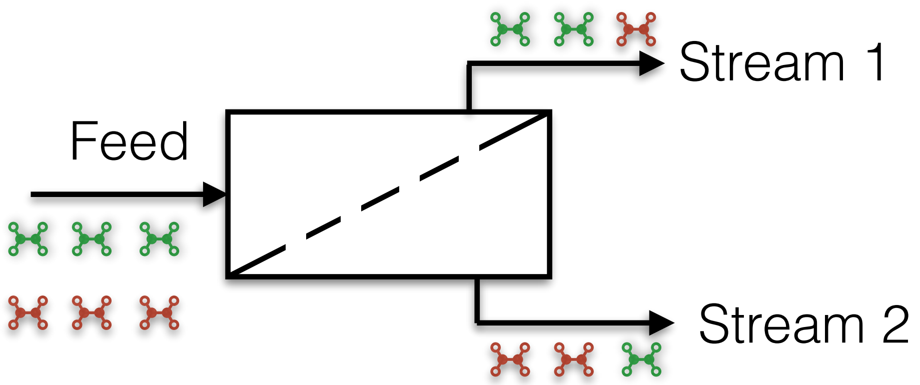
(2) **Phase creation by adding mass separating agent (MSA)**



Examples:
1. Absorption
2. Liquid-Liquid Extraction
3. Adsorption

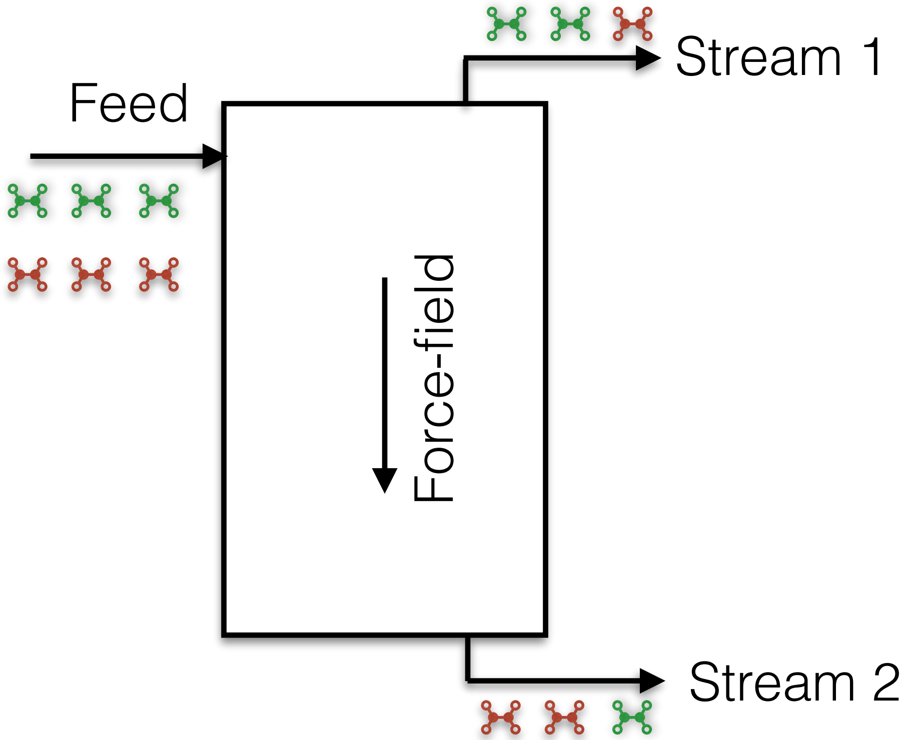
Type of separation process

(3) **Separation using size difference (selective barrier)**



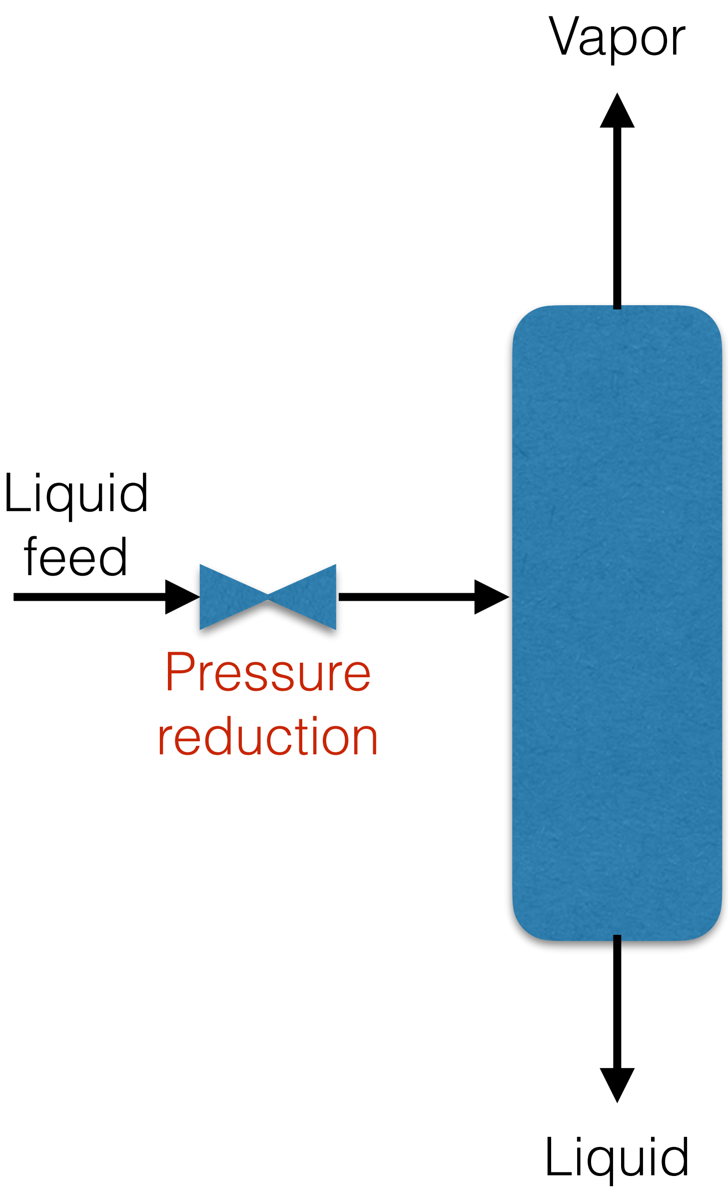
Example: Membranes

(4) **Separation using force-field**



Example:
1) Centrifugation (colloids)
2) Electrophoresis (proteins)

Phase creation by energy separating agent (ESA)



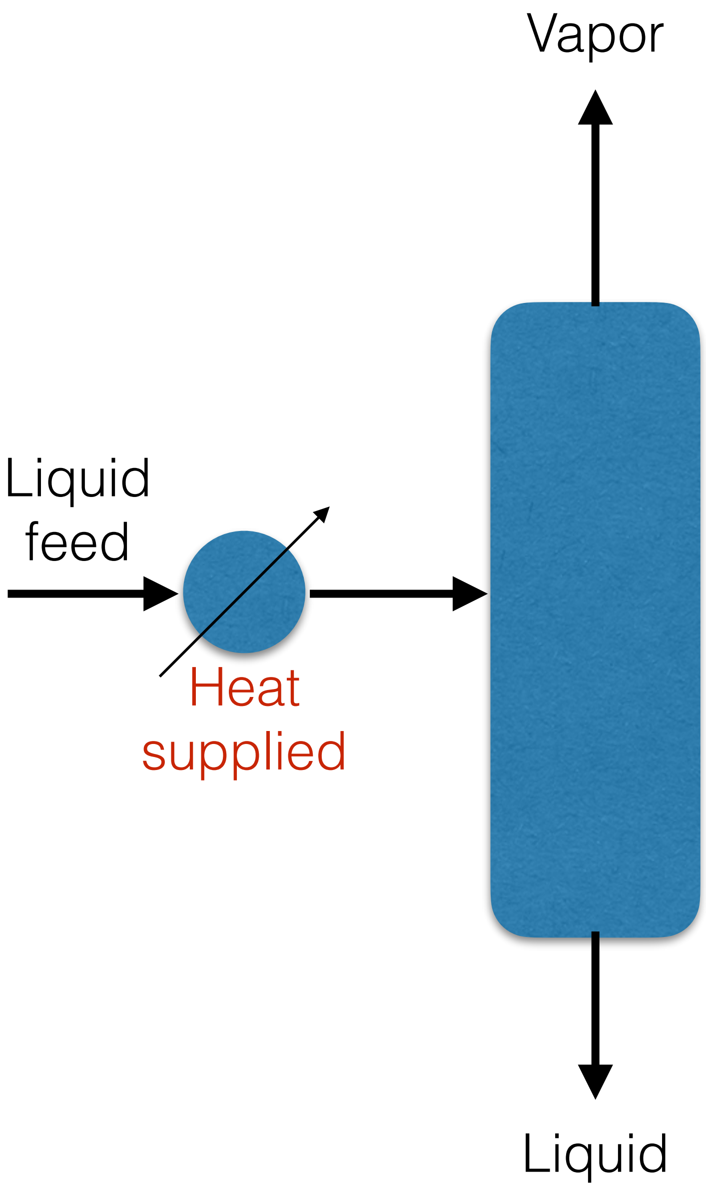
Vapor

Liquid
feed

Pressure
reduction

Liquid

Flash vaporization



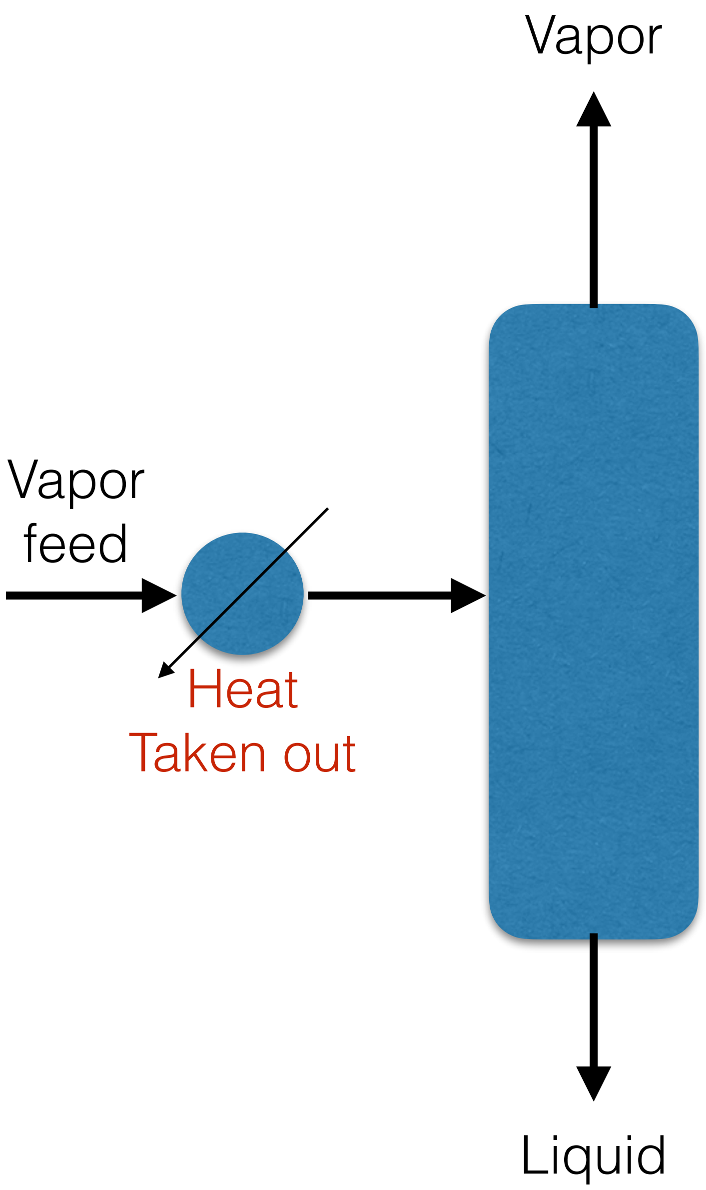
Vapor

Liquid
feed

Heat
supplied

Liquid

Partial vaporization



Vapor

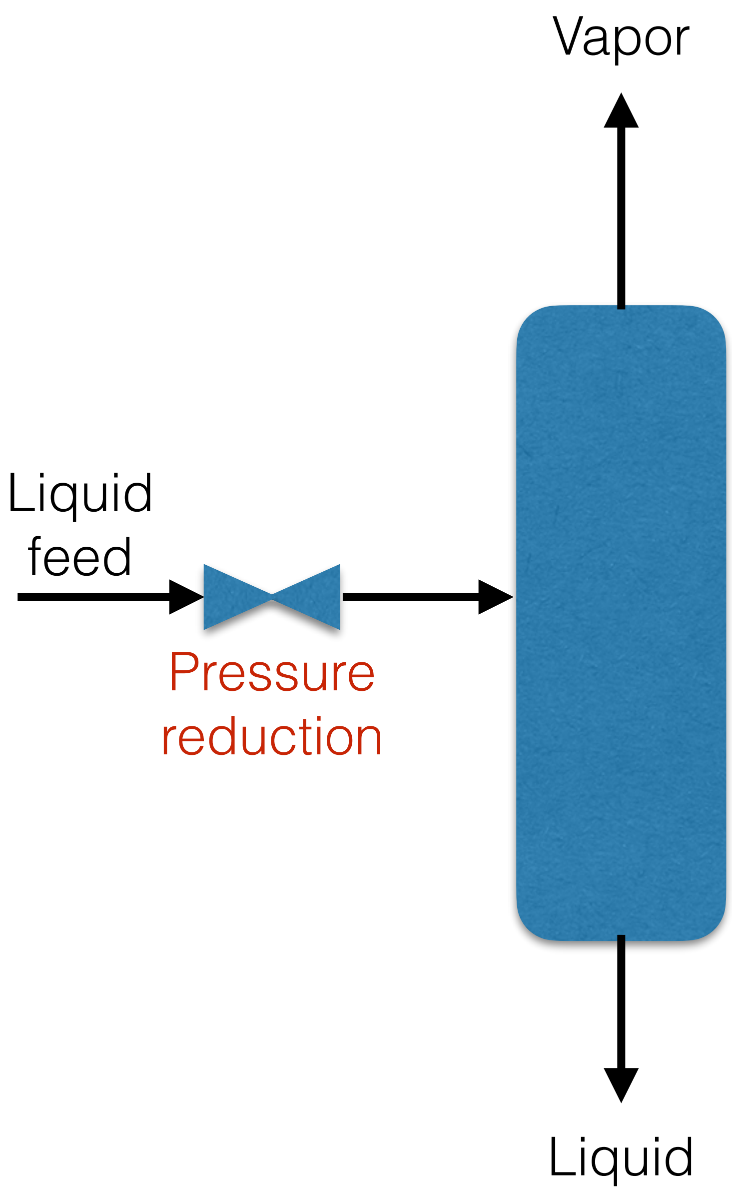
Vapor
feed

Heat
Taken out

Liquid

Partial condensation

What do we need to know to design these ??

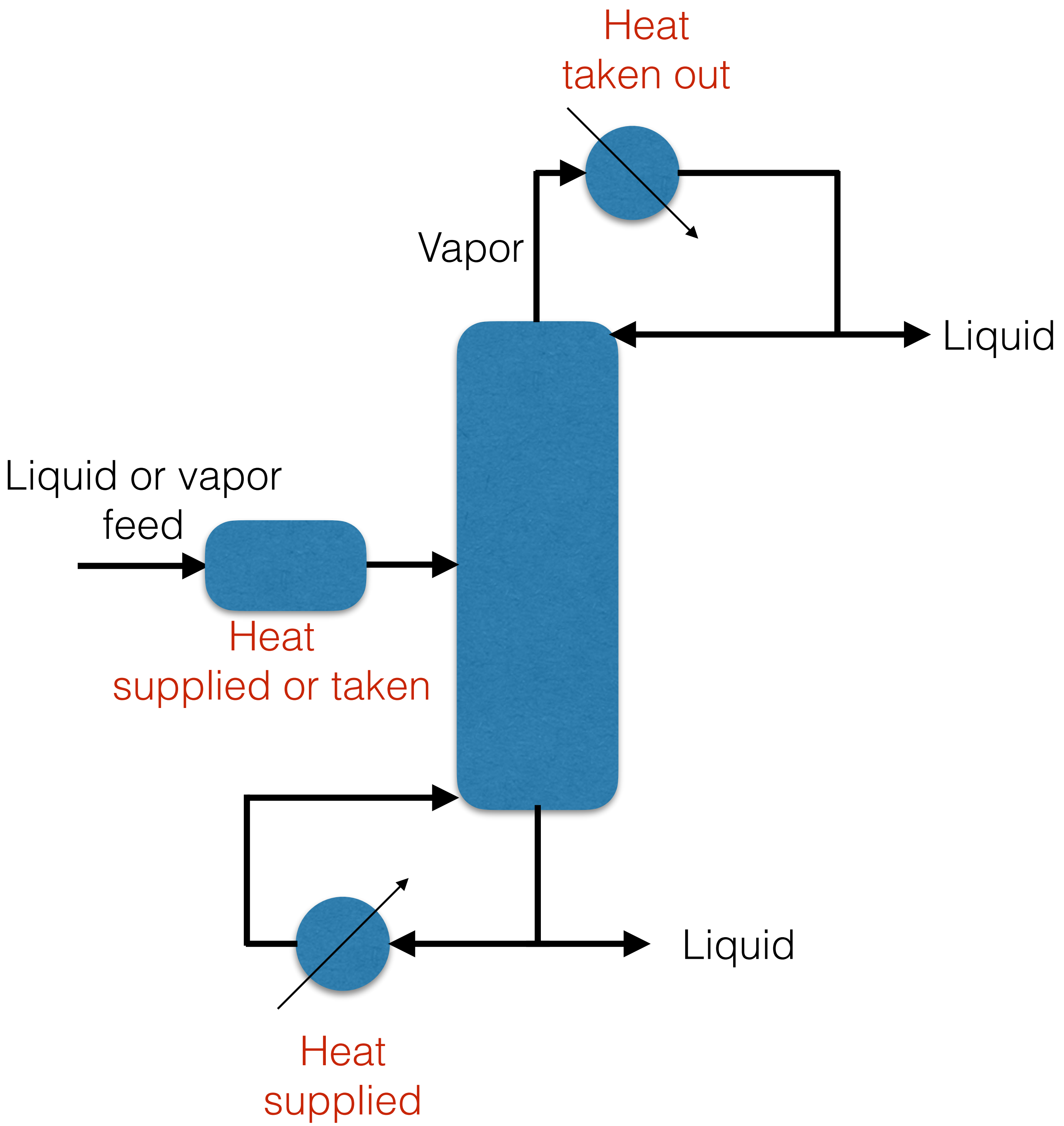


Flash vaporization

What is the relationship between liquid and vapor concentrations at a given pressure and temperature ???

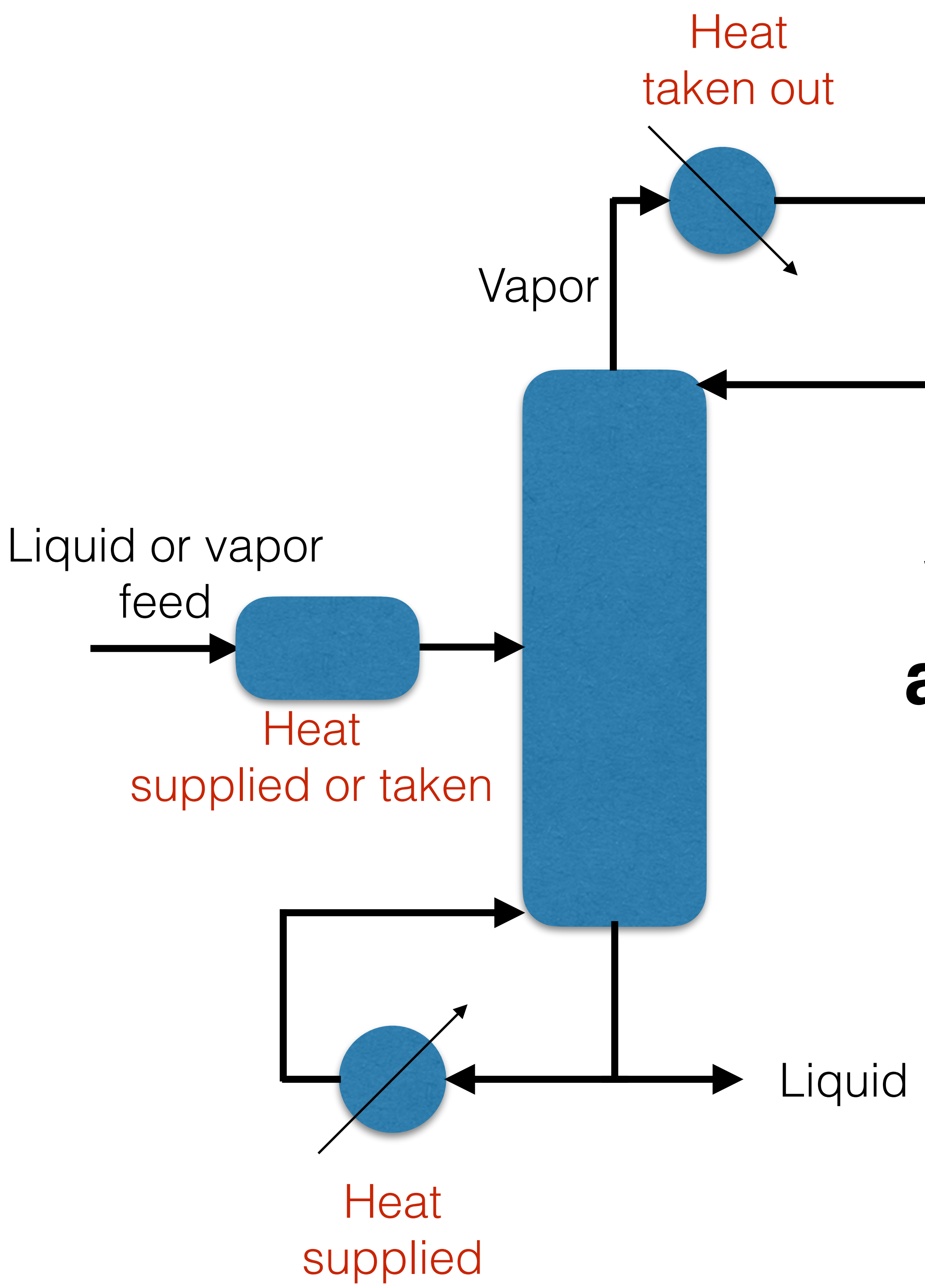
Phase equilibria
Mass balance

Phase creation by energy separating agent (ESA)



Distillation column

What do we need to know to design these ??



Distillation column

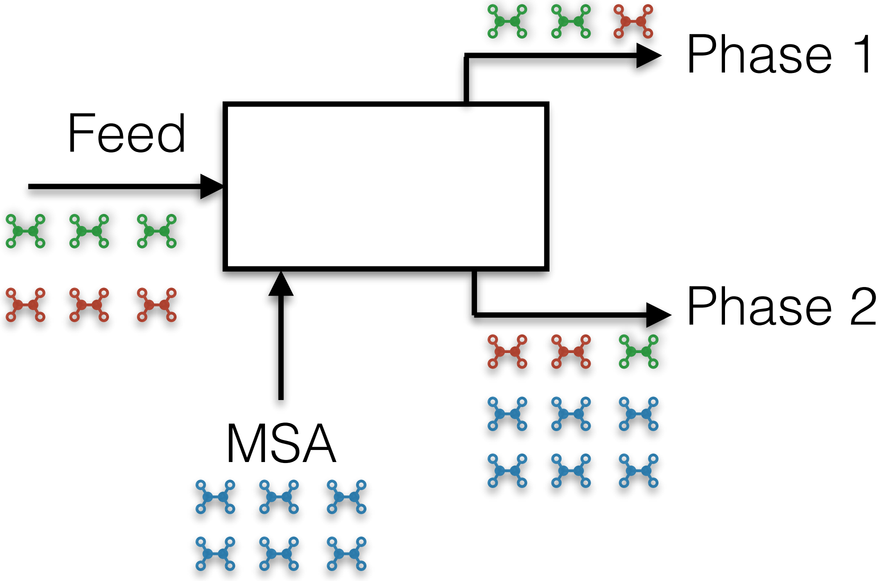
What is the relationship between liquid and vapor concentrations as we change pressure and temperature at several stages of the column ??

Phase equilibria
Mass balance

Type of separation process

(2)

Phase creation by adding mass separating agent (MSA)

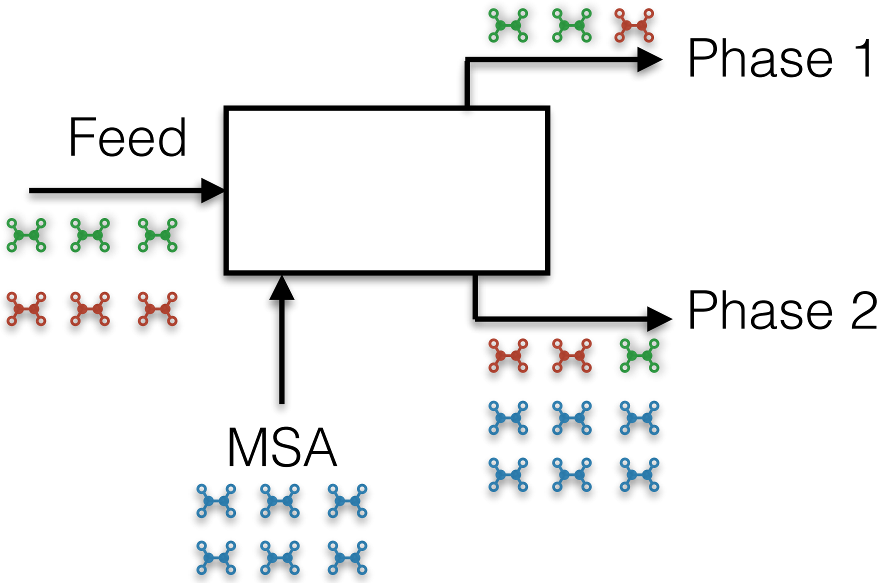


Examples:

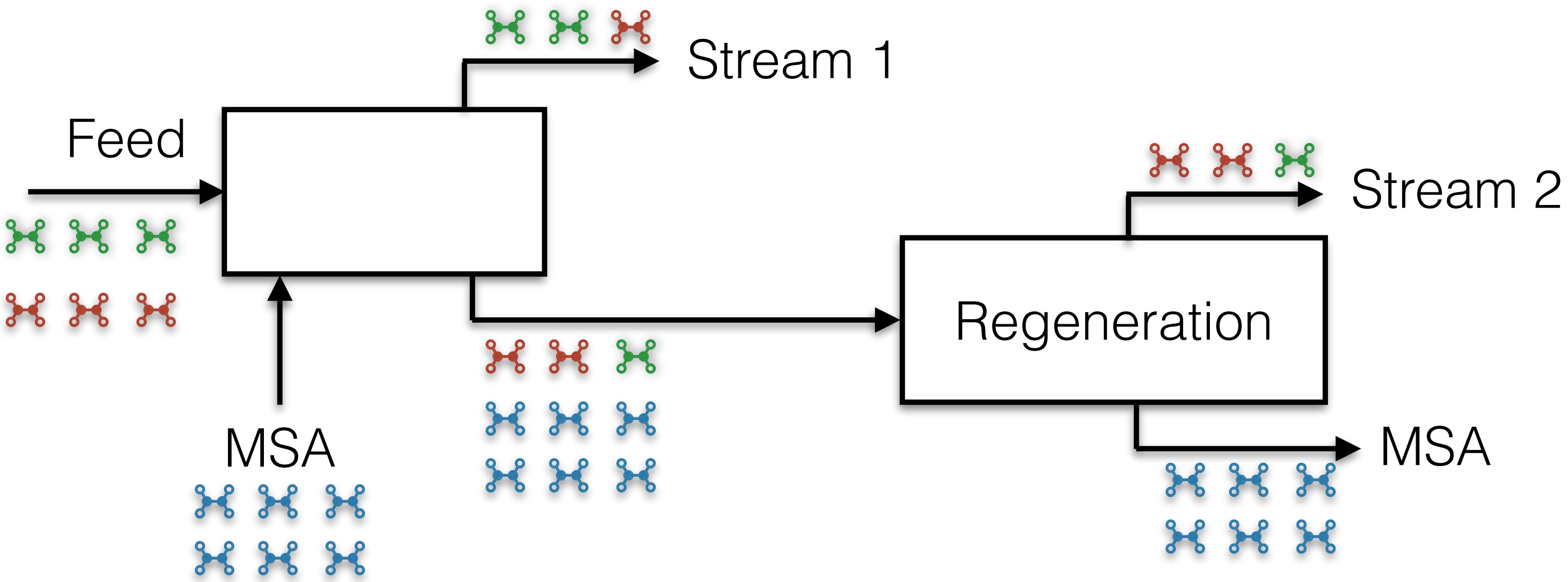
1. Absorption
2. Liquid-Liquid Extraction
3. Adsorption

Is the job of separation finished here ?

Phase creation by adding mass separating agent (MSA)



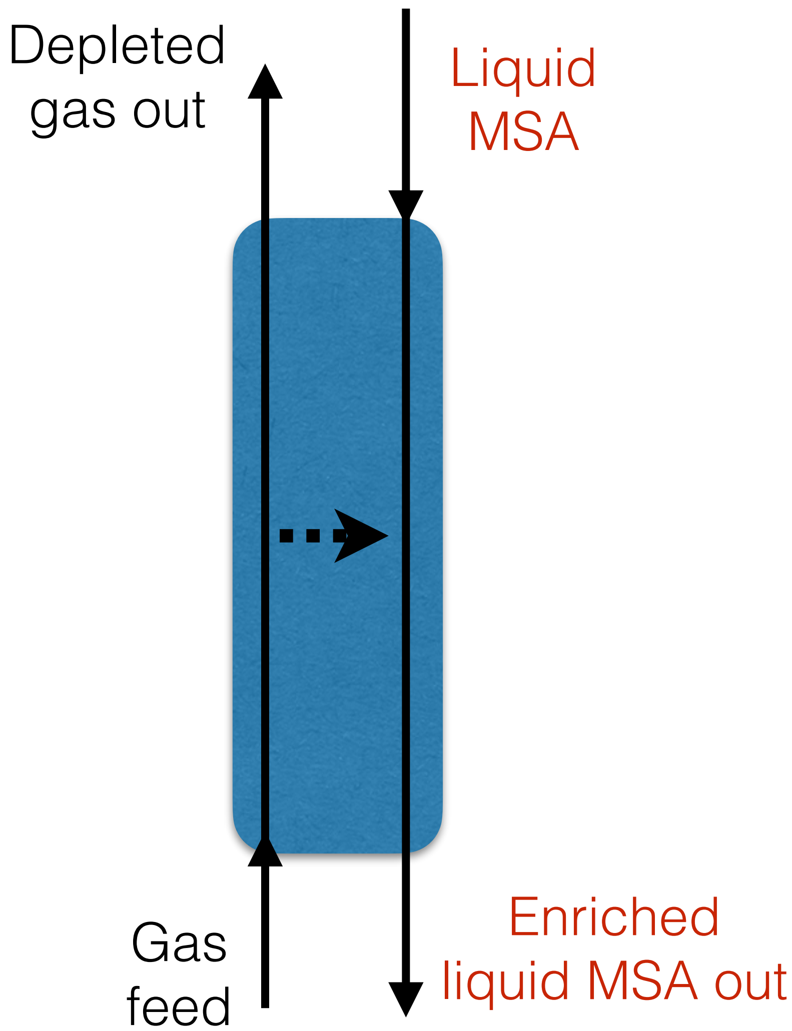
Regeneration step



Usually regeneration step is the more expensive step

Potential issues
1. MSA contamination
2. MSA loss
3. MSA degradation

Phase creation by adding MSA



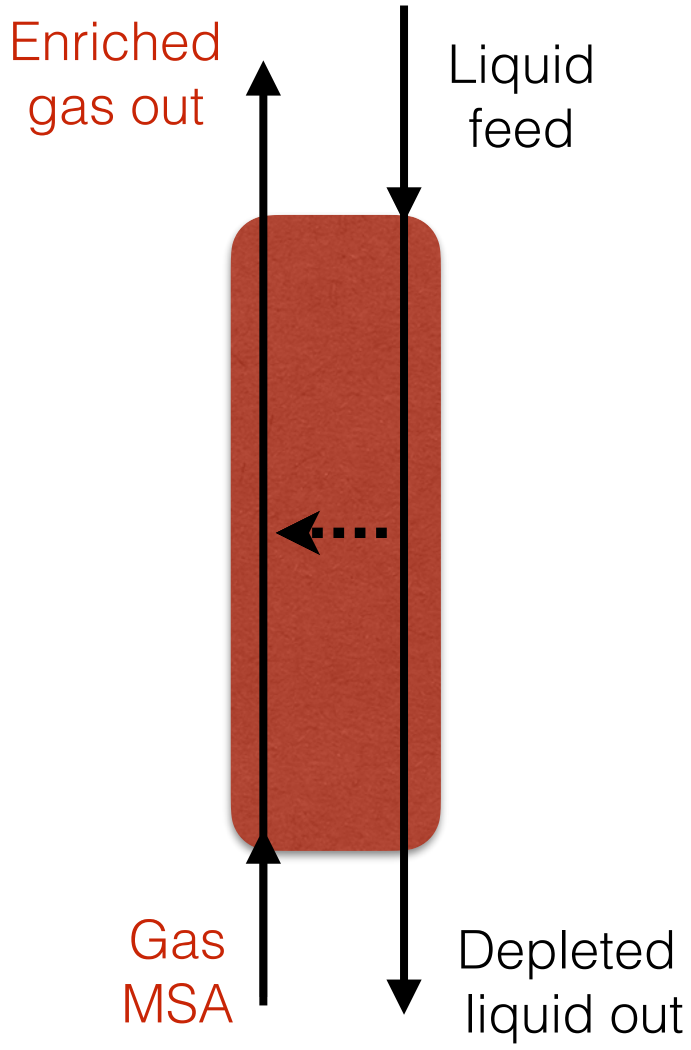
Depleted gas out

Liquid MSA

Gas feed

Enriched liquid MSA out

Absorption



Enriched gas out

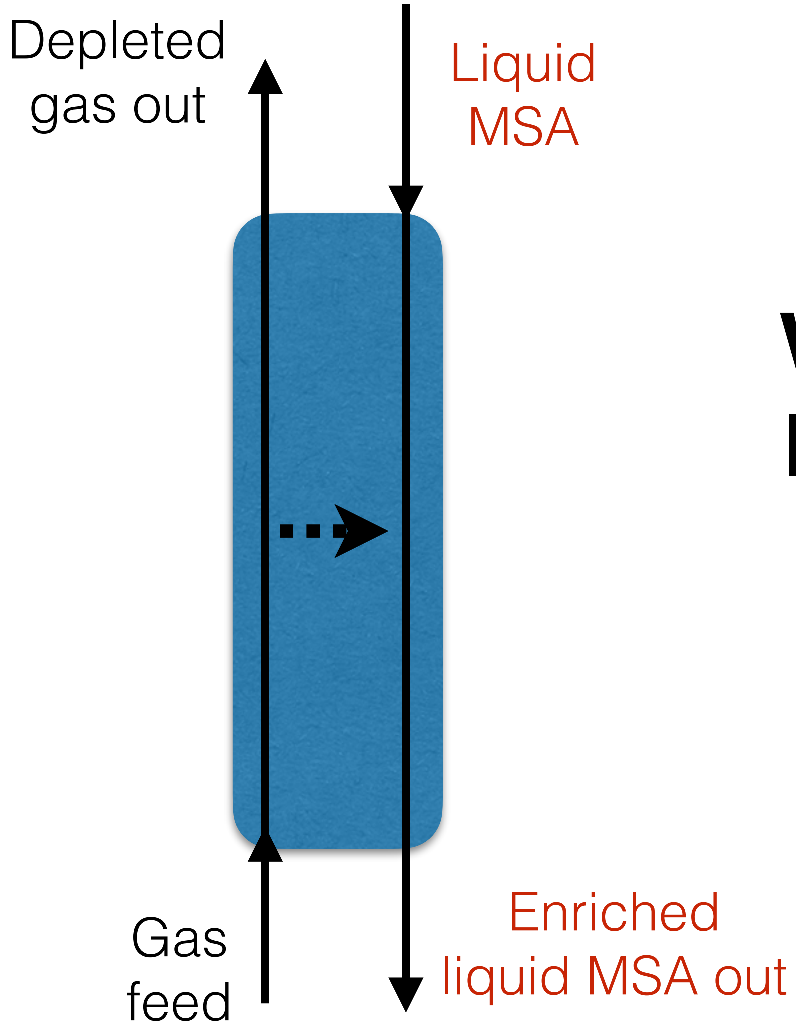
Liquid feed

Gas MSA

Depleted liquid out

Stripping

What do we need to know to design these ??

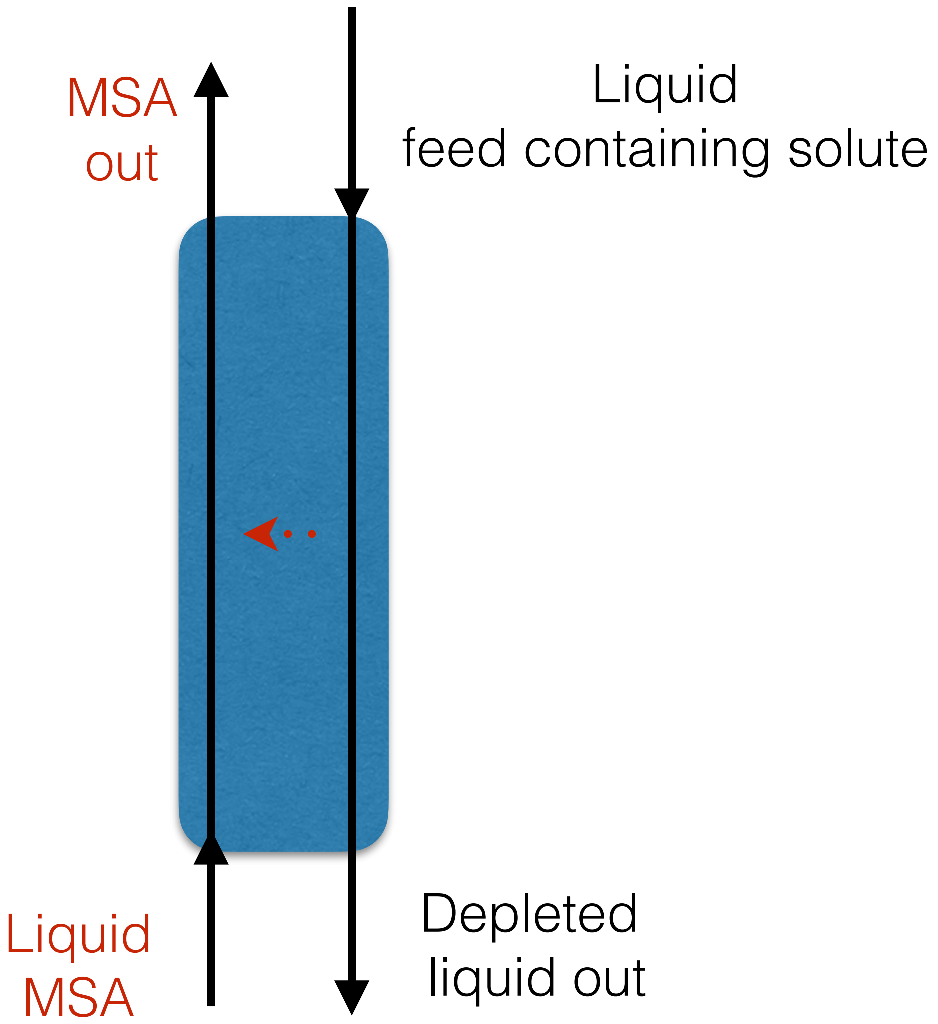


Absorption

What is the relationship between gas and liquid concentrations at a given pressure and temperature ???

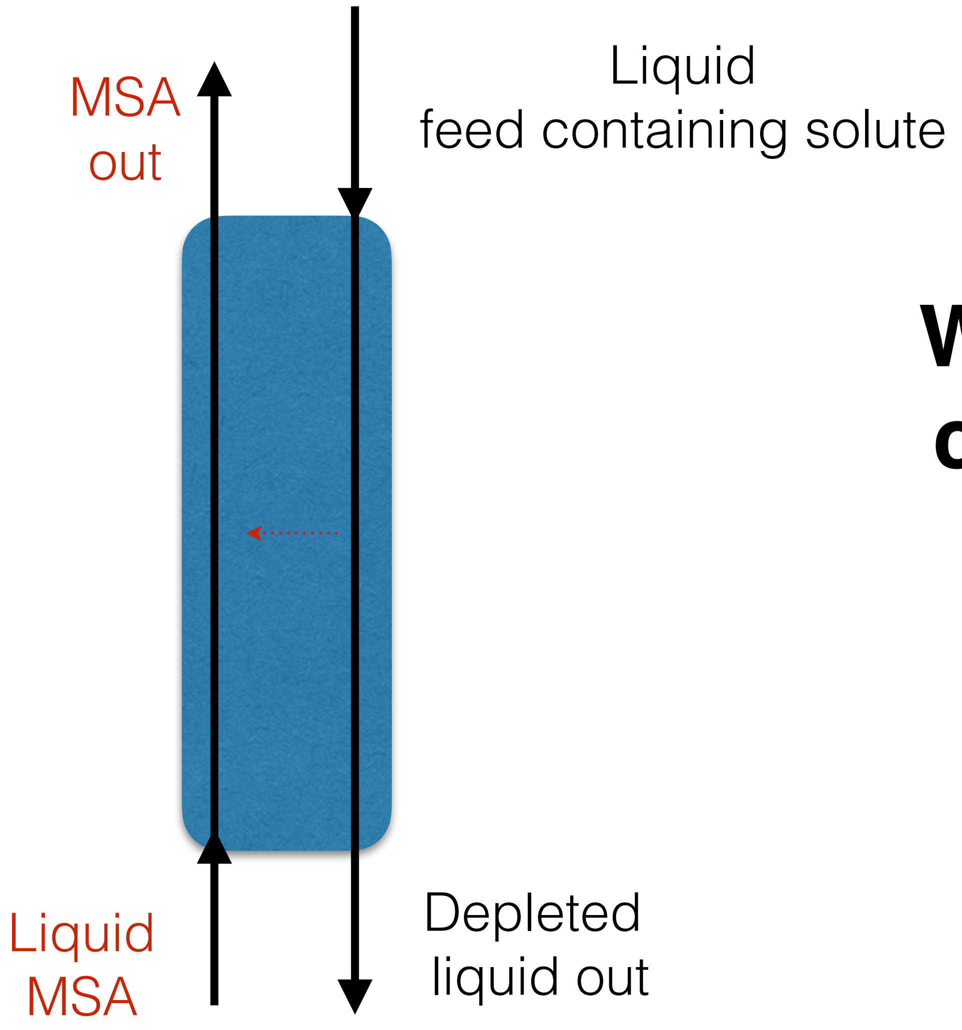
Solubility data (equilibria)
Mass balance

Phase creation by adding MSA



Liquid-Liquid Extraction

What do we need to know to design these ??

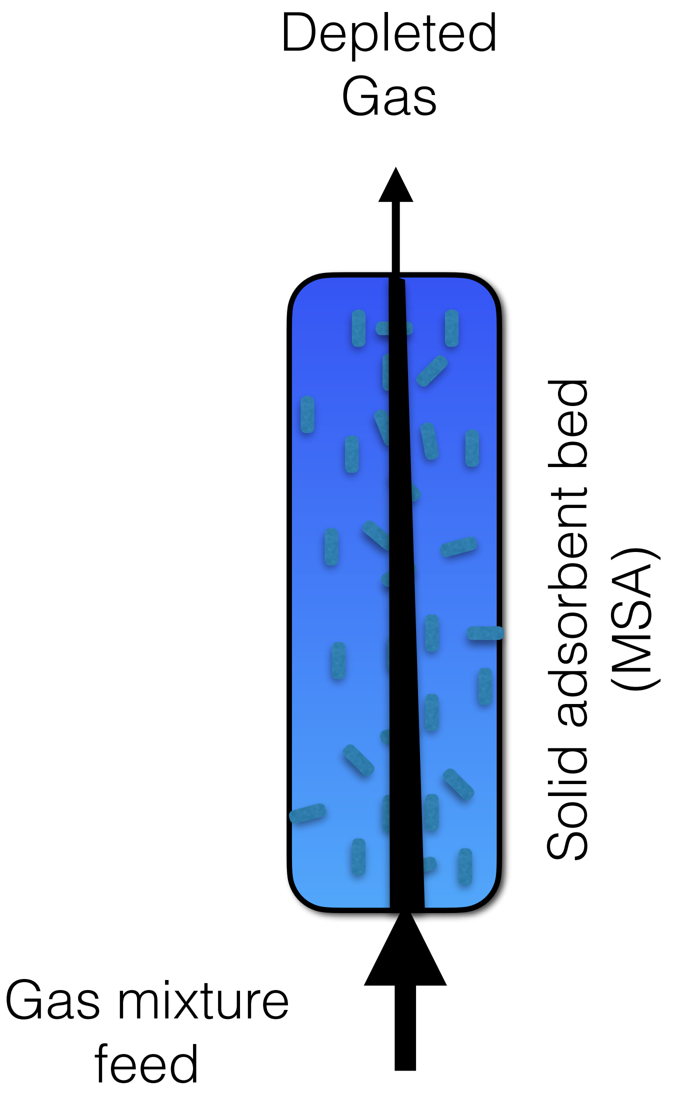


Liquid-Liquid Extraction

What is the relationship between solute concentration in two liquid phases at a given pressure and temperature ???

Solubility data (equilibria)
Mass balance

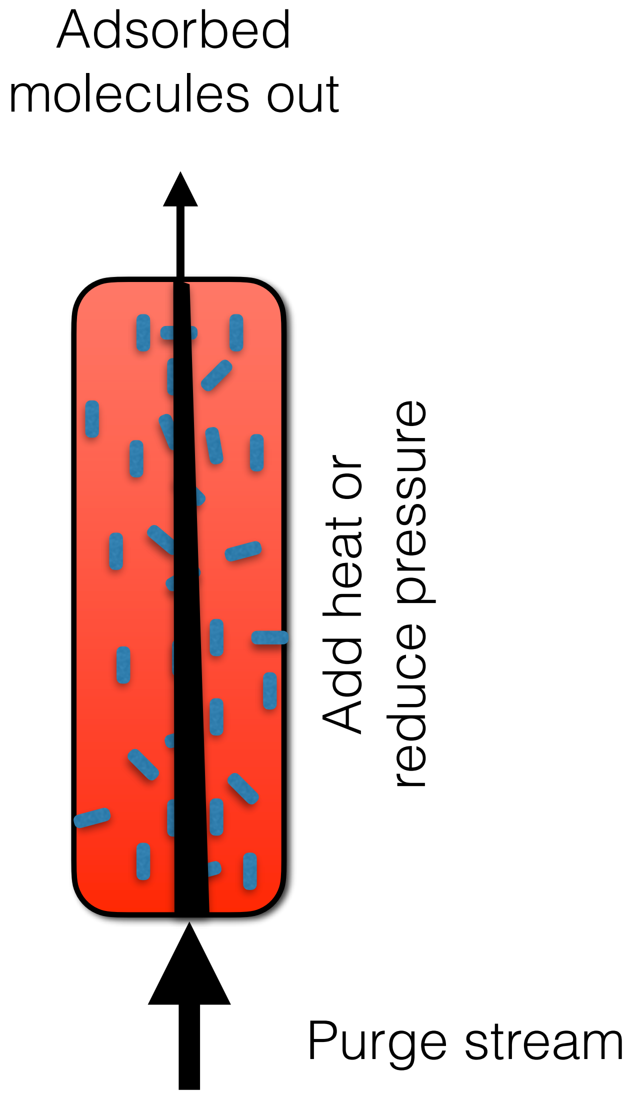
Phase creation by adding MSA


Depleted Gas

Solid adsorbent bed (MSA)

Gas mixture feed

Adsorption in porous adsorbents

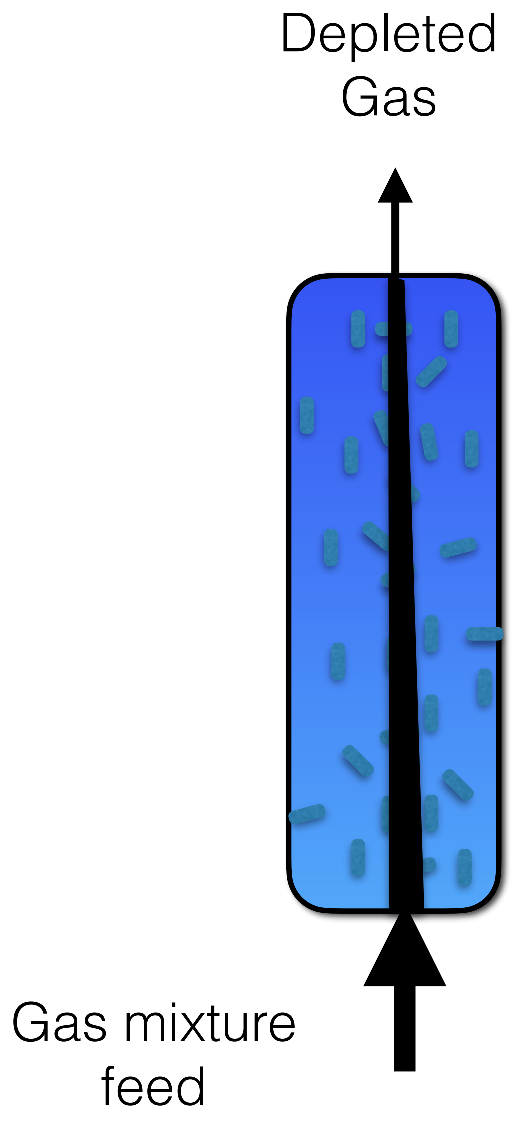

Adsorbed molecules out

Add heat or reduce pressure

Purge stream

Desorption

What do we need to know to design these ??



Adsorption

What is the relationship between residence time of two gas components in the column containing porous adsorbent

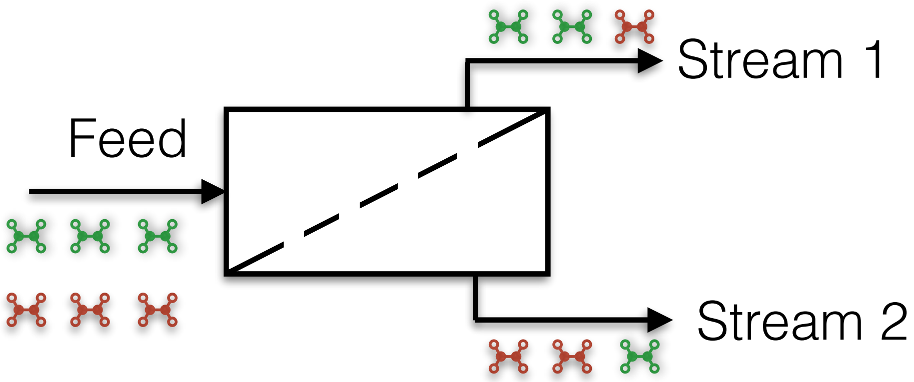
Binding/adsorption data
Velocity data
Mass balance

Types of separation using MSA

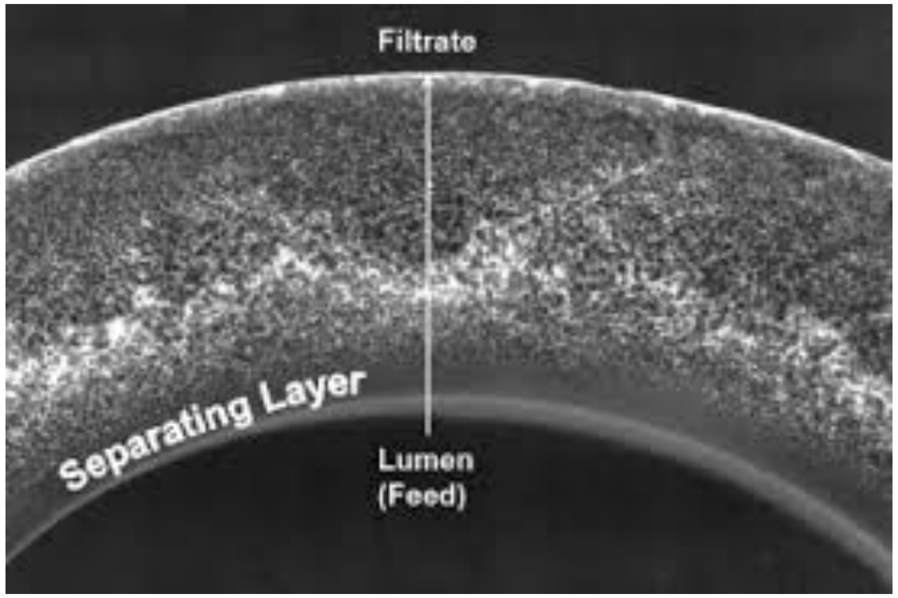
Feed	**MSA**	**Separation**	**Regeneration Step**
Gas	Liquid	Absorption	Stripping
Liquid	Steam	Stripping	Condensation
Solute dissolved in liquid	Liquid solvent	Liquid-Liquid Extraction	Distillation, Stripping, Crystallization
Gas	Porous solid	Adsorption	Desorption

Separation using selective barrier

(3)

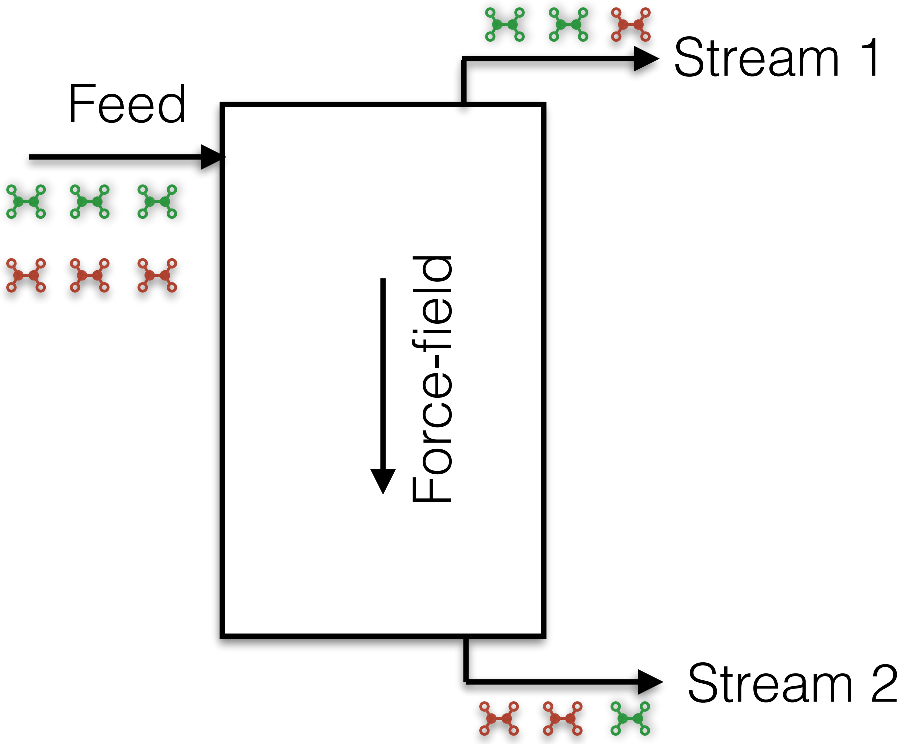


Example: Membranes



Separation using force-field

(4)



Example:

1) Centrifugation (colloids)
2) Electrophoresis (proteins)

Equilibrium vs steady-state

Equilibrium: Thermodynamically balanced properties across interacting system

Thermal Equilibrium

Mechanical Equilibrium

Chemical Equilibrium

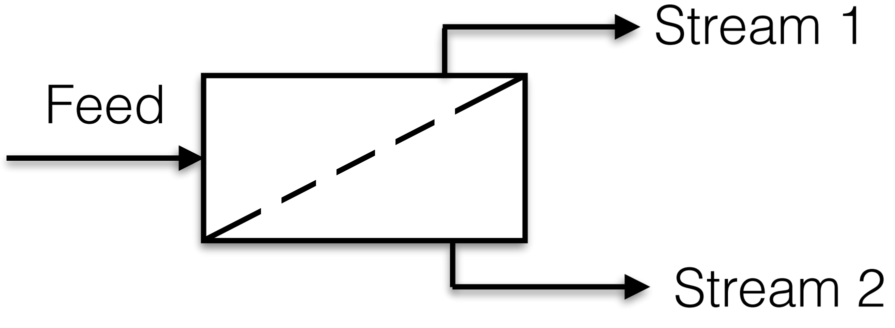
Steady-state: No change in process parameters with respect to time

Distinction of the separation processes

Separation process	Equilibrium-stage	Steady-state
Distillation	Yes	Yes
Absorption	Yes	Yes
Liquid-Liquid Extraction	Yes	Yes
Membranes	No	Yes
Adsorption	No	No

Phase equilibria

What is the relationship between the two streams 1 and 2 in membrane process



A. They are at equilibrium

B. They are at steady-state

C. They are at equilibrium as well as at steady-state

D. They are neither at equilibrium nor at steady-state

A quick recap of thermodynamics

Specific properties: properties per unit mass

$$\hat{X} = \frac{X}{mass}$$

Definition of a phase: A region of space where all properties are uniform.

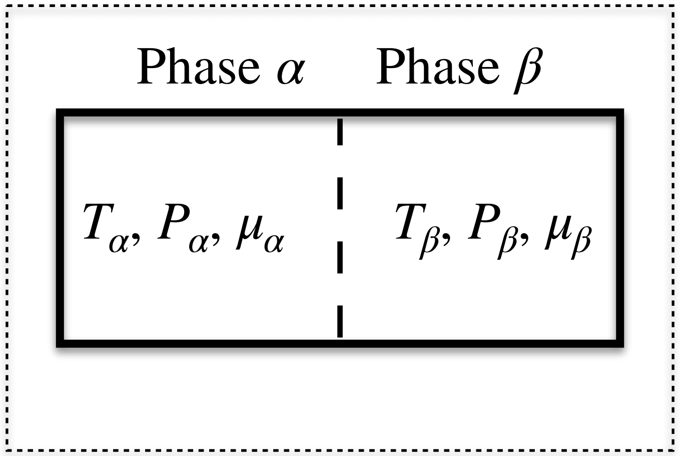
Definition of a steady-state: When properties at a particular point in space do not change with time.

Phase equilibrium: When the temperature, pressure and chemical potential of any component present in one phase is equal to the temperature, pressure and chemical potential of that component in other phase.

$$T_\alpha = T_\beta$$

$$P_\alpha = P_\beta$$

$$\mu_\alpha = \mu_\beta$$



Isolated system

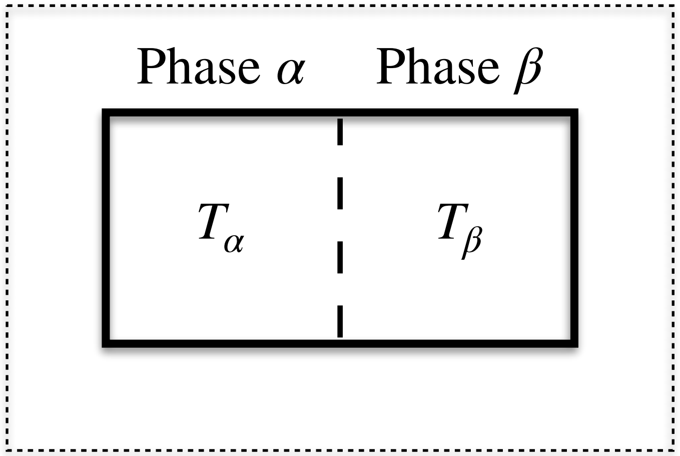
Phase equilibrium: thermal equilibrium

Consider two phases in contact with each other.

The overall system is in isolation.

Temperature of one phase is T_α

Temperature of other phase is T_β



Isolated system

Let's assume that the phases are not in thermal equilibrium $T_\alpha > T_\beta$

As a result a small amount of heat, dq, will flow from phase α to phase β

$$\text{Total entropy change of the system} = dS = -\frac{dq}{T_\alpha} + \frac{dq}{T_\beta} = dq\left(\frac{1}{T_\beta} - \frac{1}{T_\alpha}\right)$$

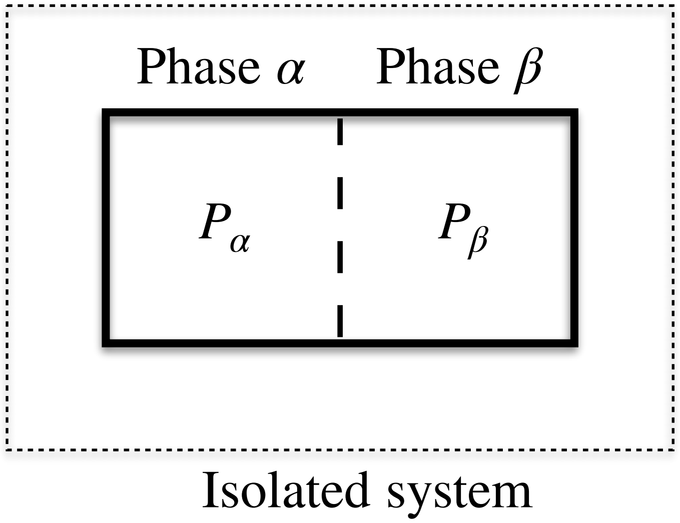
$$\Rightarrow dS > 0$$

$\Rightarrow$ heat flow will be spontaneous until $T_\alpha = T_\beta$

Phase equilibrium: mechanical equilibrium

Consider two phases in contact with each other.

The overall system is in isolation.



Pressure of one phase is P_α

Pressure of the other phase is P_β

Let's assume that the phases are not in mechanical equilibrium $P_\alpha > P_\beta$

As a result, the phase α will expand by small volume dV, and phase β will shrink by the $-\mathrm{dV}$

Change in Helmholtz free energy of the entire system $= \mathrm{dA} = \Sigma\left(-\mathrm{SdT} - \mathrm{PdV}\right) = -\Sigma\left(\mathrm{PdV}\right) = -\mathrm{P}_\alpha\mathrm{dV} - \mathrm{P}_\beta(-\mathrm{dV})$

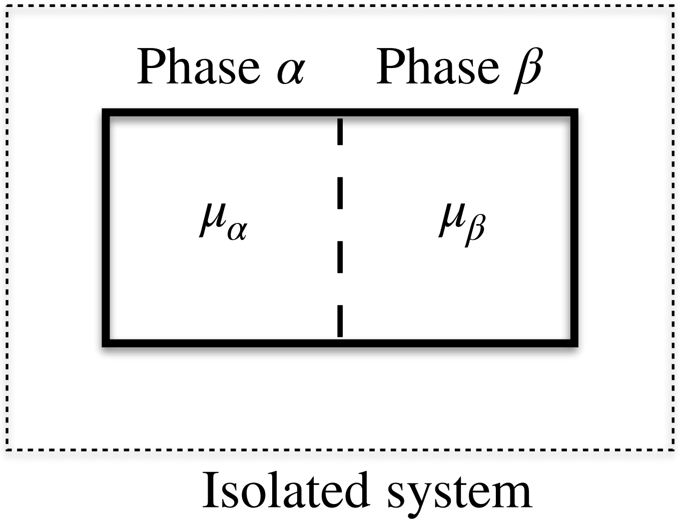
$$\Rightarrow dA = dV\left(P_\beta - P_\alpha\right) < 0$$

$\Rightarrow$ volume expansion will be spontaneous until $\mathrm{P}_\alpha = \mathrm{P}_\beta$

Phase equilibrium: chemical equilibrium

Consider two phases in contact with each other.

The overall system is in isolation.



Chemical potential of one phase is μ_α

Chemical potential of the other phase is μ_β

Let's assume that the phases are not in chemical equilibrium $\mu_\alpha > \mu_\beta$

As a result, a small amount of moles, dN, will transfer from phase α to the phase β

Change in Gibbs free energy of the entire system $= \mathrm{dG} = \Sigma\left(-\mathrm{SdT} + \mathrm{VdP} + \mu\mathrm{dN}\right) = \Sigma\left(\mu\mathrm{dN}\right) = \mu_\alpha(-\mathrm{dN}) + \mu_\beta(\mathrm{dN})$

$$\Rightarrow dG = -dN\left(\mu_\alpha - \mu_\beta\right) < 0$$

$\Rightarrow$ mole transfer will be spontaneous until $\mu_\alpha = \mu_\beta$

Degree of Freedom $\mathscr{F}$

$$\mathscr{F} = \textbf{number of variables} - \textbf{number of equations}$$

Typically, number of variables are more than number of equations.

The knowledge of the degree of freedom for a given system allows us to choose number of independent variables.

$\mathscr{F} = 3$, then one can assign 3 independent variables : P, T, mole fraction

$\mathscr{F} = 2$, then one can assign 2 independent variables : T, mole fraction

$\mathscr{F} = 1$, then one can assign 1 independent variables : mole fraction

It would be nice to have some guideline which can tell us about $\mathscr{F}$

For phase equilibria, Gibbs phase rule : $\mathscr{F} = 2 - N_{\text{phase}} + N_{\text{component}}$

Derivation for Gibbs phase rule

Consider a system with *c* component where several phases (N_{phase}) are in equilibrium with each other.

Phase 1 — c component

Phase 2 — c component

Phase 3 — c component

Phase 4 — c component

Phase $\mathrm{N_{phase}}$ — c component

Total number of variables: P, T, mole fraction of all *c* component in each phase $= 2 + cN_{phase}$

Total number of equations:

Mole fraction in each phase add up to 1

$$\Rightarrow \Sigma_{i=1}^{c}\, x_i^{phase\ k} = 1,\ for\ k = 1,2,3 \ldots, N_{phase}$$

Number of such equation $= \mathrm{N_{phase}}$

Equilibrium relationships

$$x_i^{phase\ 1} = k_{i,12}\, x_i^{phase\ 2}$$

Number of such equation for each component $= \mathrm{N_{phase}} - 1$

Total number of such equations $= \mathrm{c(N_{phase} - 1)}$

Total equations $= \mathrm{N_{phase} + c(N_{phase} - 1)}$

Total number of independent variables $= 2 + \mathrm{cN_{phase}} - \left(\mathrm{N_{phase} + c(N_{phase} - 1)}\right) = 2 - N_{phase} + c$

Vapor-liquid equilibrium (2 component)

$Py_1 = \gamma_1 x_1 P_{1,sat}$ where, $\mathrm{P_{1,sat}} = \mathrm{f(T)}$ $\gamma_1 = g(T, x_1)$

$$k_1 = \frac{\gamma_1 P_{1,sat}}{P}$$

$$\Rightarrow y_1 = k_1 x_1 \qquad \mathbf{y_1 = f(T, P, \gamma_1, x_1)}$$

For ideal solution, $\gamma_1 = 1$

$Py_1 = x_1 P_{1,sat}$ Roult's law

$$k_1 = \frac{P_{1,sat}}{P}$$

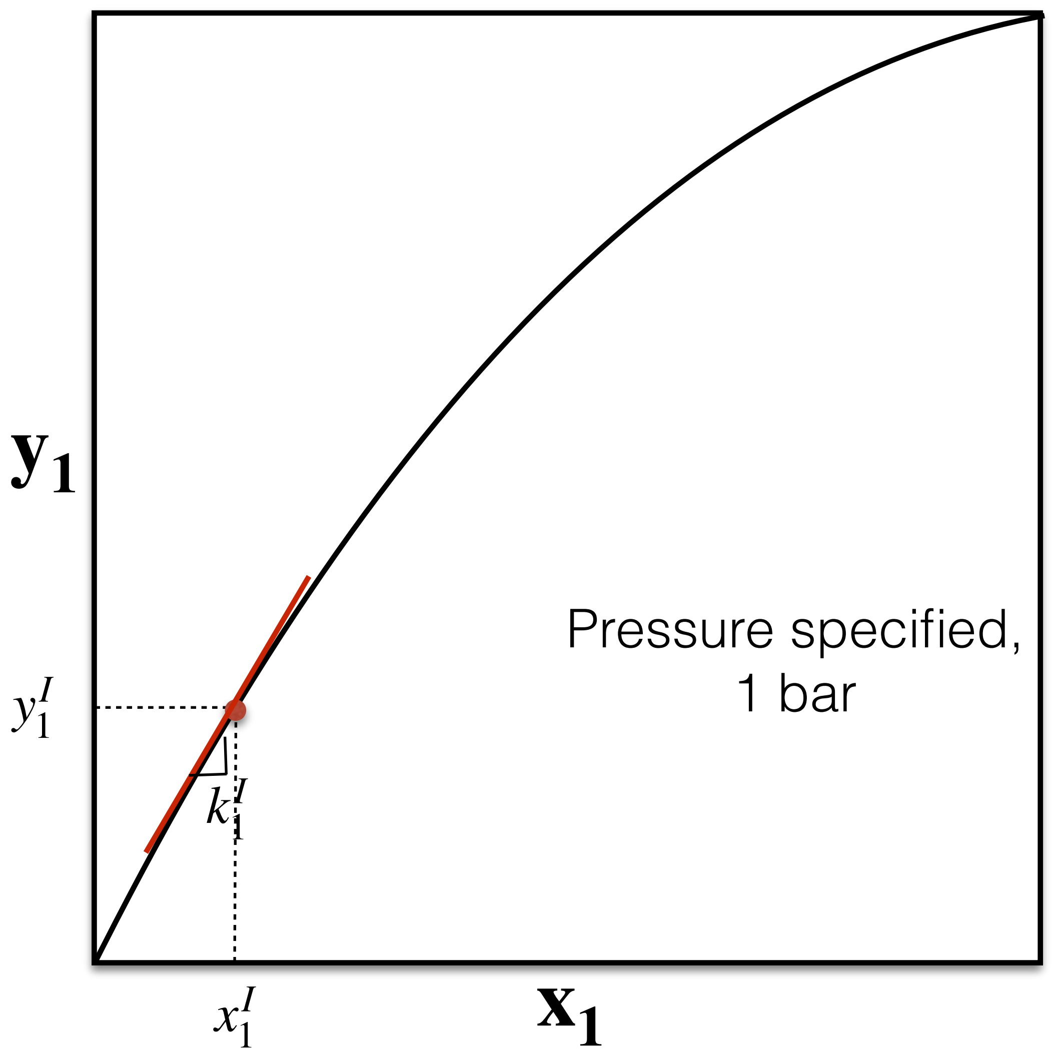
$$y_1 = \frac{P_{1,sat}}{P} x_1$$

$\mathscr{F}$ for 2 component, 2 phase = 2

Any of these set of variables can be specified : $(\mathrm{T}, \mathrm{x}_1)$, $(\mathrm{P}, \mathrm{x}_1)$, (T, P), $(\mathrm{x}_1, \mathrm{y}_1)$

Sometime, instead of temperature/pressure, specific enthalpy is specified

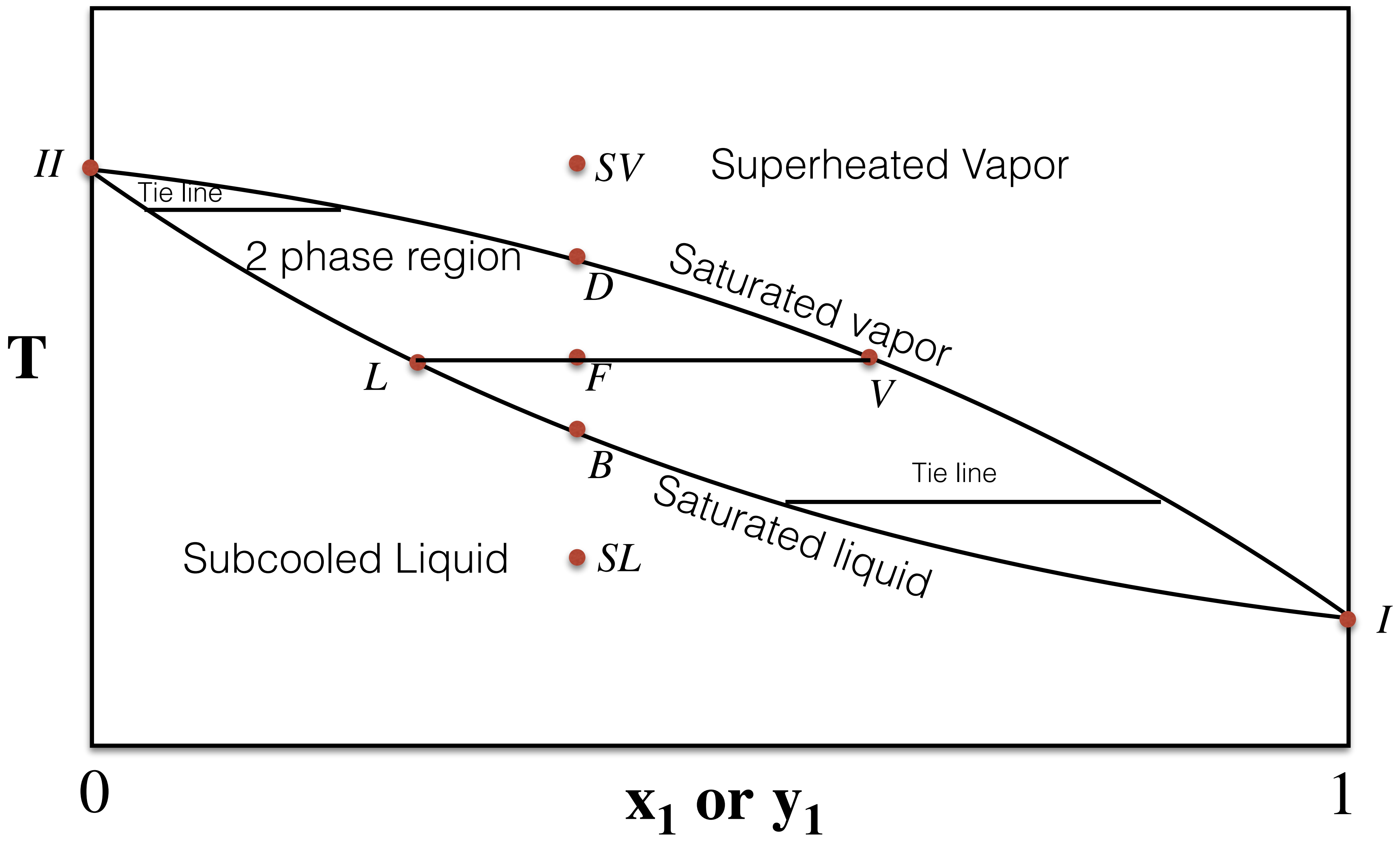
Graphical methods: y-x diagram



$$Py_1 = \gamma_1 x_1 P_{1,sat} \qquad k_1 = \frac{\gamma_1 P_{1,sat}}{P}$$

$$y_1^I = k_1^I \, x_1^I$$

Graphical methods: T-x-y diagram for liquid-vapor phase



T_D = Dew point : temperature at which liquid droplets first appear in saturated vapor

T_B = Bubble point : temperature at which vapor bubbles first appear in saturated liquid

Graphical methods: T-x-y diagram for liquid-vapor phase

What is special about points I and II ?