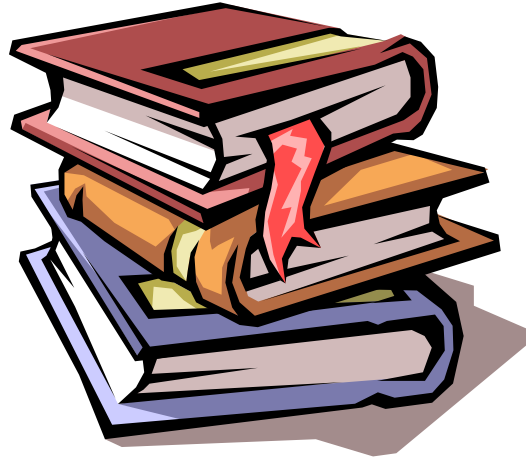# Cryogenic Engineering

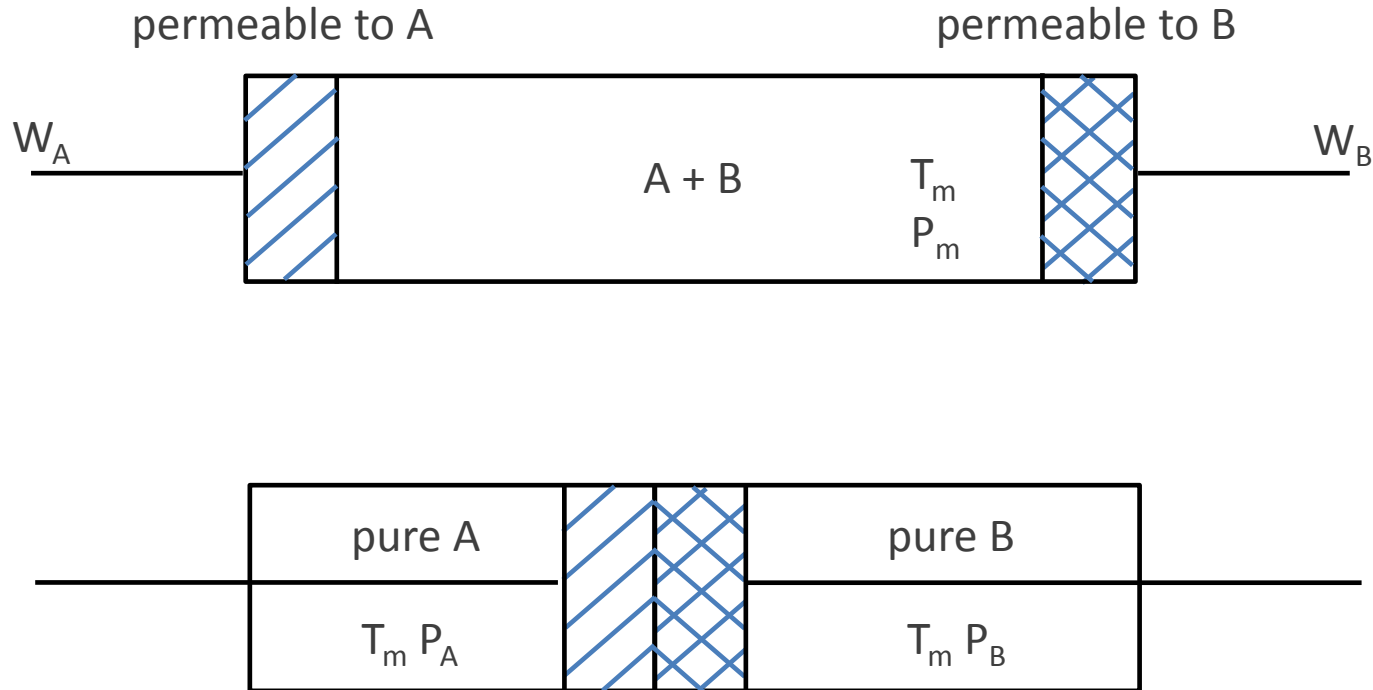**2015 Fall Semester**

Min Soo, Kim

Chapter 4.

Separation and Purification Systems

4.1 Thermodynamically Ideal Separation

※ reversible mixing/unmixing – semipermeable membrane
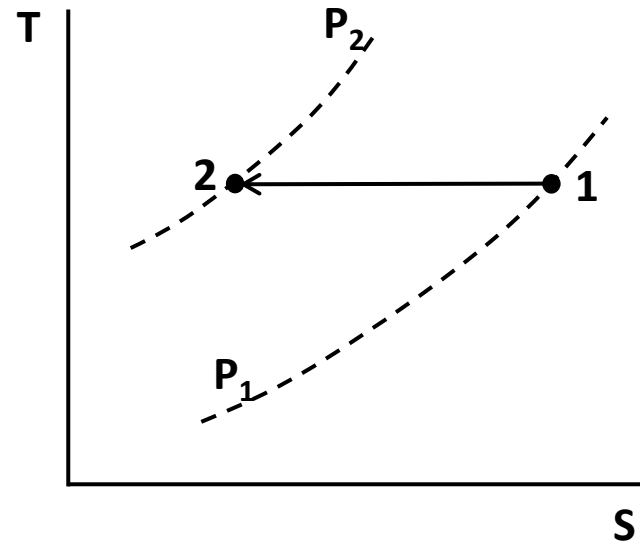(free passage for one gas)

permeable to A   permeable to B

W_A A + B T_m W_B
                                        P_m

pure A   pure B

$T_m\ P_A$ $T_m\ P_B$

4.1 Thermodynamically Ideal Separation

- **reversible isothermal work**

$$-\frac{W_i}{m} = T_m(s_1 - s_2) - (h_1 - h_2)$$

1 – before separation
2 – after separation

$$-\frac{W_i}{m_m} = -\frac{W_{ia}}{m_a}\frac{m_a}{m_m} - \frac{W_{ib}}{m_b}\frac{m_b}{m_m}$$

$$= \{T_m(s_{1a} - s_{2a}) - (h_{1a} - h_{2a})\}\left(\frac{m_a}{m_m}\right) + \{T_m(s_{1b} - s_{2b}) - (h_{1b} - h_{2b})\}\left(\frac{m_b}{m_m}\right)$$

4.1 Thermodynamically Ideal Separation

■ Ideal work of separation for an ideal gas mixture

For an ideal gas,
$$pV = mRT$$
$$h = C_p T$$
$$s = C_p \ln T - R \ln p$$

$$\therefore \; -\frac{W_i}{m_m} = T_m R_a \left(\ln \frac{P_m}{P_{1a}} \right) \frac{m_a}{m_m}$$
$$+ T_m R_b \left(\ln \frac{P_m}{P_{1b}} \right) \frac{m_b}{m_m}$$

$$\frac{P_m}{P_{1a}} = \frac{m_m R_m T_m / V_m}{m_a R_a T_m / V_m} = \frac{m_m R_m}{m_a R_a}$$

4.1 Thermodynamically Ideal Separation

Since $\quad mR = n\bar{R} = m\bar{R}/M$

$$\frac{P_m}{P_{1a}} = \frac{n_m}{n_a} = \frac{1}{y_a} \qquad y_a: \text{mole fraction of gas A}$$

- Work requirement per unit mole of mixture

$$-\frac{W_i}{n_m} = \bar{R}T_m \left(y_a \ln\frac{1}{y_a} + y_b \ln\frac{1}{y_b} \right)$$

$$= \bar{R}T_m \sum_j y_j \ln\frac{1}{y_j}$$

4.1 Thermodynamically Ideal Separation

■ **Ideal work of separation of gas mixtures**

Table 4.1. Ideal work of separation of gas mixtures. The mixture is assumed to be separated into two parts: the desired gas, which has the given mole fraction in the original mixture, and the remainder of the gas mixture. The mixture is to be separated at 300 K (80°F)

Gas	Mole Fraction	Work per Mole of Mixture		Work per Unit Mass of Separated Gas	
		J/mol	Btu/lbmole	J/g	Btu/lb$_m$
Nitrogen	0.78084	1312	564	60.0	25.8
Oxygen	0.20946	1280	550	191.0	82.1
Argon	0.00934	132.1	56.8	353.9	152.2
Carbon dioxide	0.00033	7.42	3.19	511.0	219.7
Neon	1.818×10^{-5}	0.540	0.232	1472.5	633.1
Krypton	1.14×10^{-6}	0.0404	0.0174	438.1	188.4
Xenon	8.60×10^{-8}	0.00370	0.001593	328.1	141.0
Hydrogen deuteride	3.12×10^{-4}	7.06	3.035	7483	3217
Deuterium	1.56×10^{-4}	3.80	1.634	6090	2618
Helium-3	1.00×10^{-7}	0.00427	0.00184	14 222	6114

4.2 General characteristics of mixtures

- For a single substance in a single phase, we need only 2 independent thermodynamic properties are required to Specify thermodynamic state

■ **Gibbs phase rule**

The Gibbs Phase Rule

- **The phase rule** is

$$f = c - p + 2$$

Where

f = degrees of freedom

c = number of components

p = number of phases

at equilibrium for a system of any composition.

4.2 General characteristics of mixtures

- **Gibbs phase rule**

The Gibbs Phase Rule

- **Degree of freedom (f)**: It is the number of external variables that can be changed *independently* without disturbing the number of phases in equilibrium. These are pressure, temperature and composition.
- **Component**: a chemically independent constituent of a system
- **number of components (c)**: the minimum number of independent species necessary to define the composition of all the phase present in the system
- **Phase**: a state of matter that is uniform throughout in chemical composition and physical state.

4.2 General characteristics of mixtures

■ **Phase diagram**

   - Temperature-composition diagram
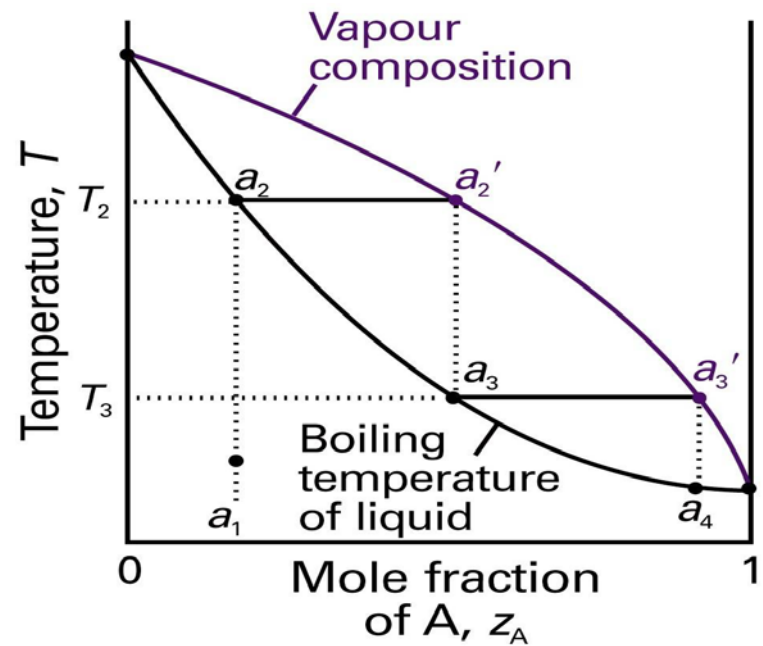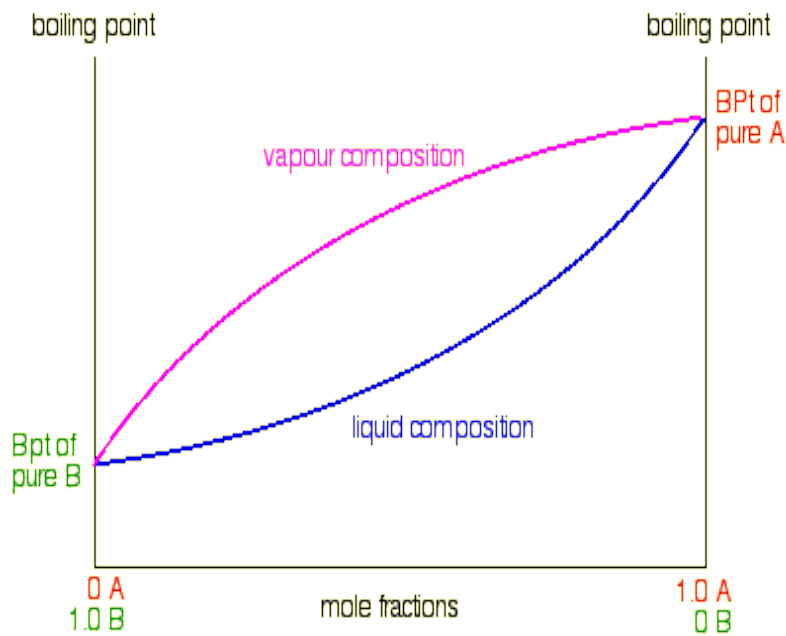
Figure 6-14
Atkins Physical Chemistry, Eighth Edition
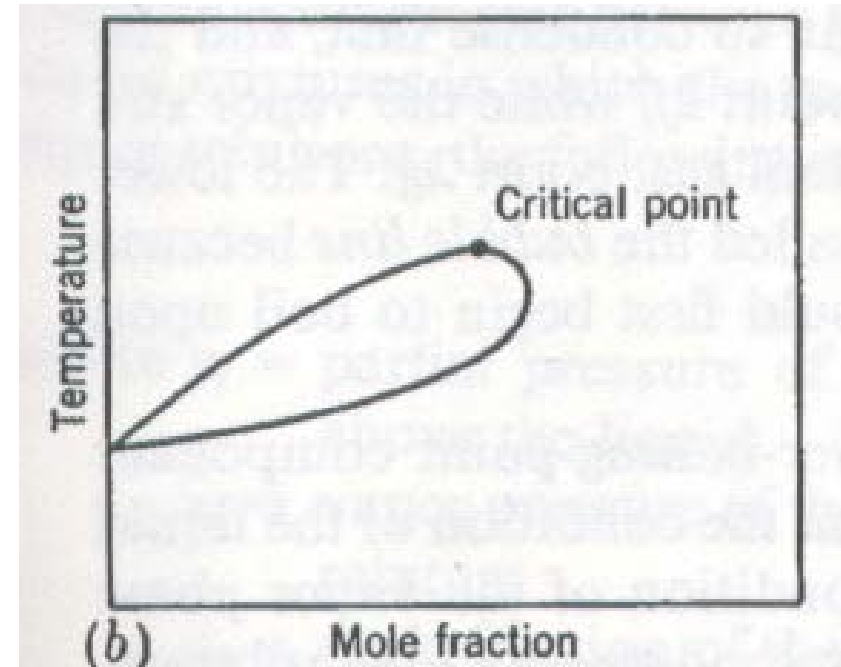© 2006 Peter Atkins and Julio de Paula

4.2 General characteristics of mixtures

■ **Typical temperature-composition diagrams for binary mixtures**
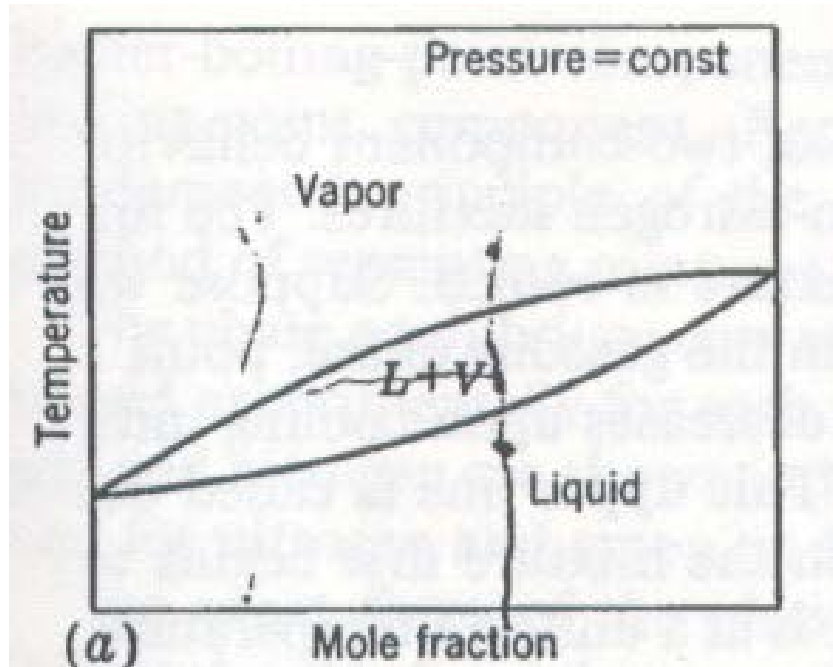
(a) Typical curve for pressures less than the critical pressure for both components

(b)Typical curve for pressures less than the critical pressure for one component, but above the critical pressure for the other component

4.2 General characteristics of mixtures

■ **Azeotrope**

not boil change

Azeotrope is a particular mixture (two or more miscible liquids) which does not change the composition during the distillation.
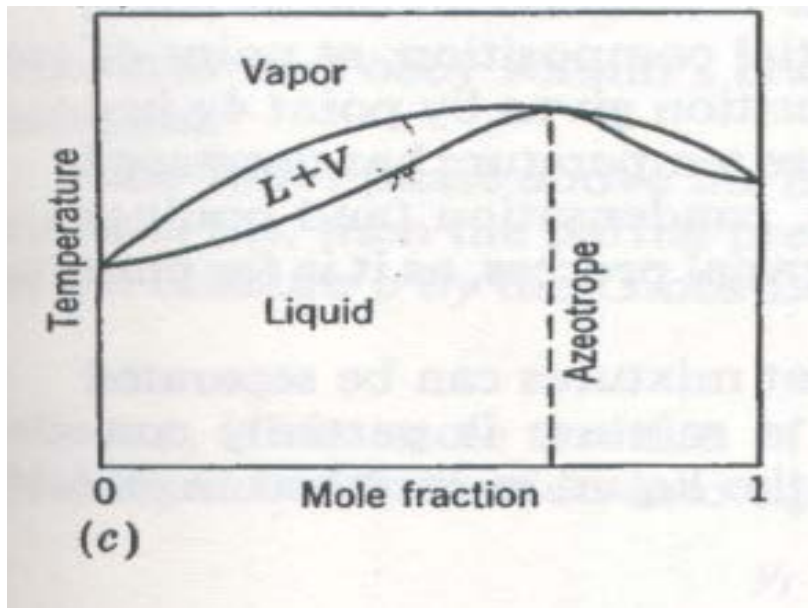
(c) Azeotropic mixture
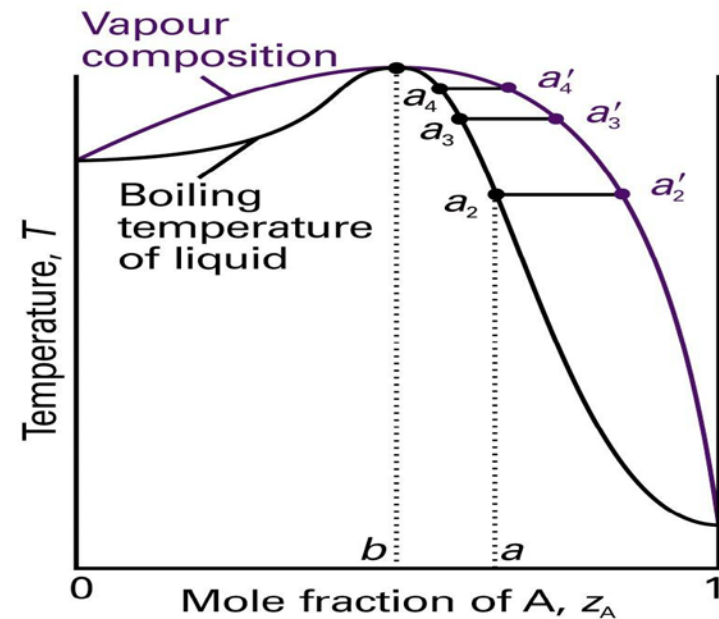
Figure 6-16
Atkins Physical Chemistry, Eighth Edition
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4.2 General characteristics of mixtures

▪ **Water-alchol distillation**

• An-dong soju(안동소주) : 23~45% alcohol

4.2 General characteristics of mixtures

- **Water-alchol distillation**

  - Vodka : 40% alcohol

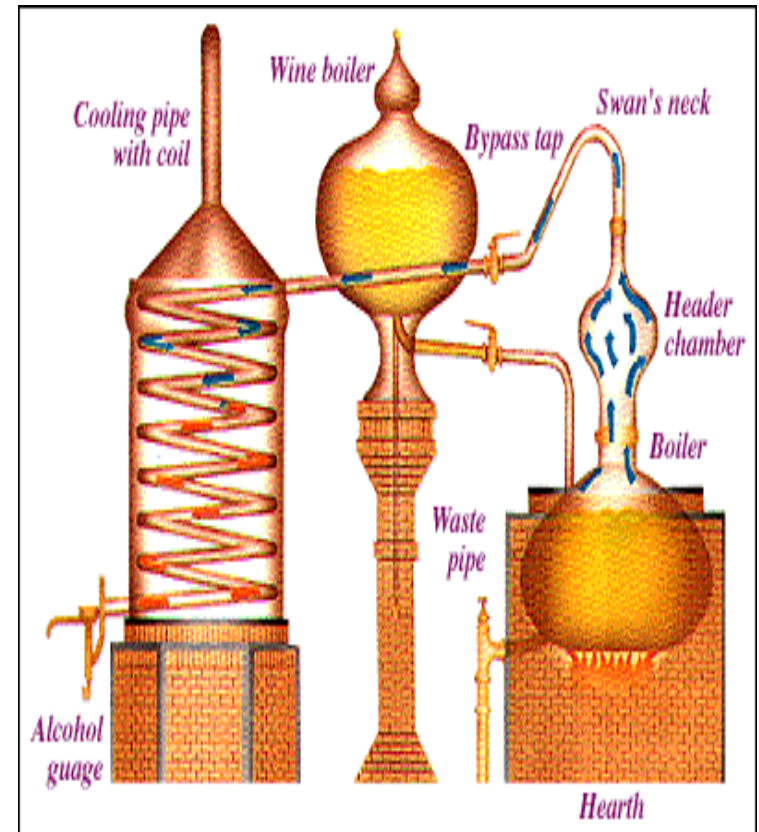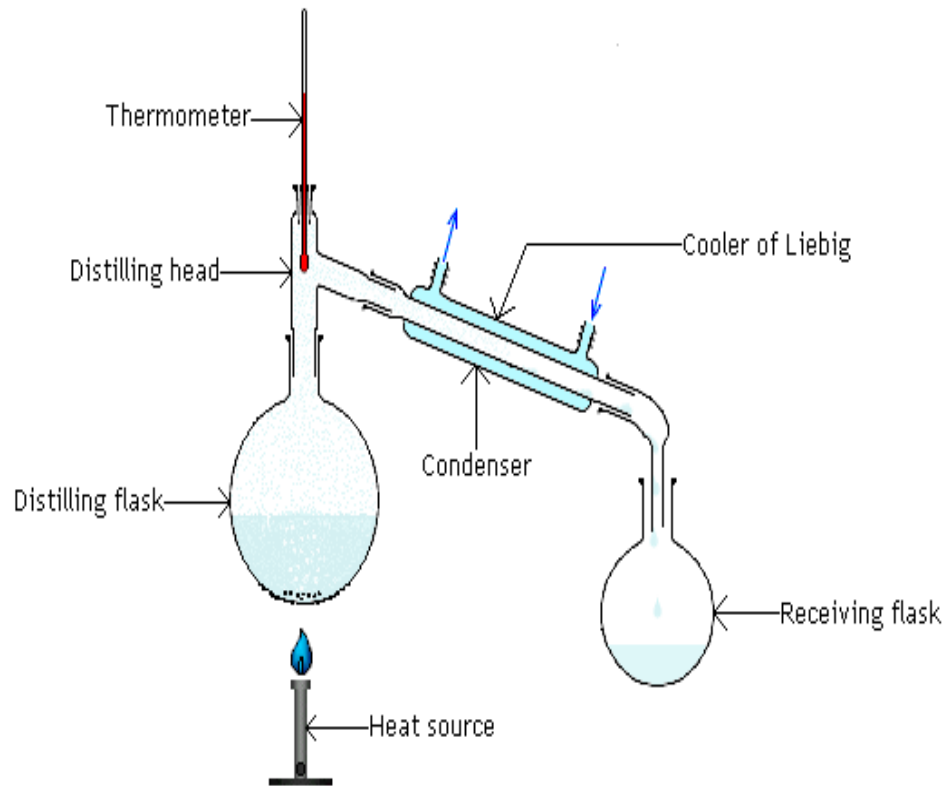# 4.2 General characteristics of mixtures

- **Distillation apparatus**

4.2 General characteristics of mixtures

■ **Distillation apparatus**
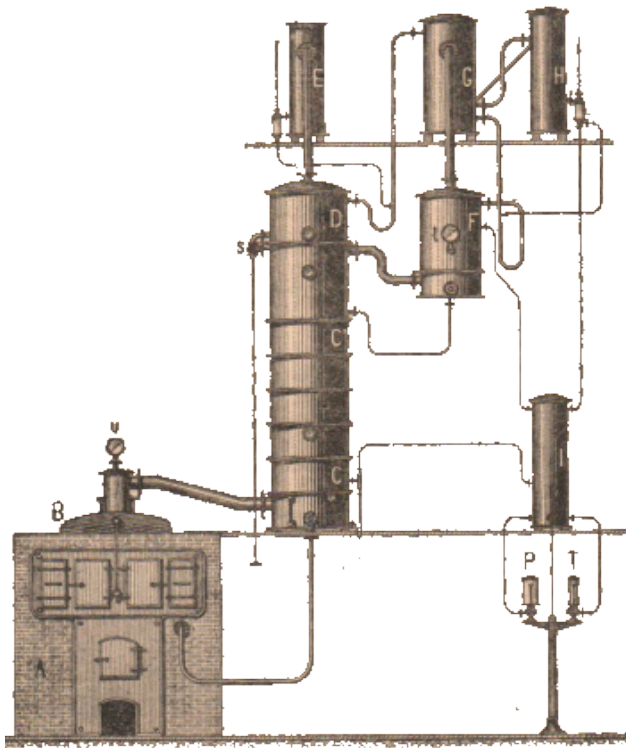
4.2 General characteristics of mixtures

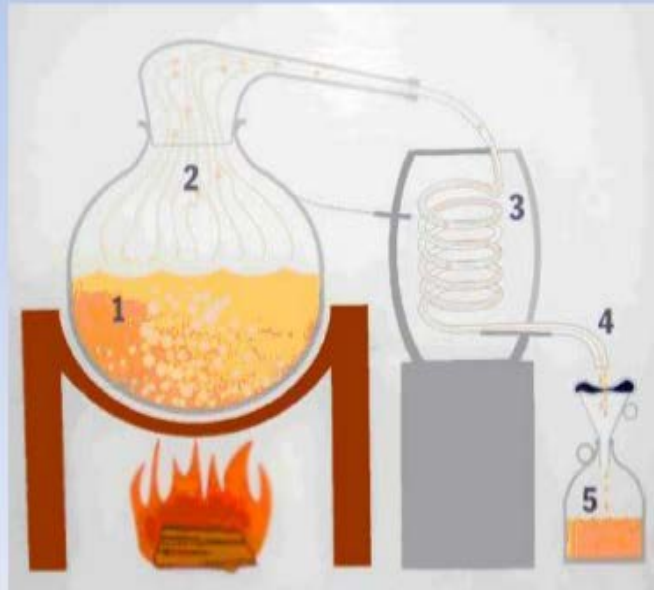▪ **The basics of distilling alcohol**

4.2 General characteristics of mixtures

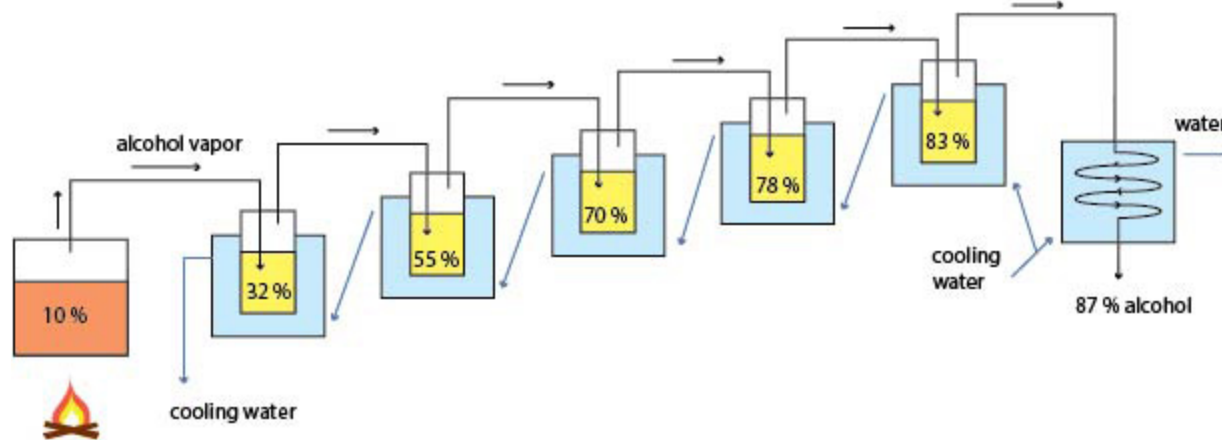▪ **How Alcohol distillation works**

How a pot still works

1. Mixture with alcohol.
2. Vapors from the boiling alcohol after heating to 173ºF.
3. The captured vapors pass through coiled copper tubing which is submerged in cold water.
4. The coiled tubing and cold water cool the vapors back to a liquid form.
5. The resulting liquid is much higher in alcohol content than the previous mixture.

Water out
Steam conduit
Spiral cooling tube
50cm
Digital temperature display
Valve
Water in
Alcohol out
Handle
36CM
304 stainless steel
33L
5mm thick bottom of barrel
36CM

4.2 General characteristics of mixtures

▪ **Multistage Distillation Principle**

| Stage	The beginning	The end
1	11% (base alcohol, for example wine)	32%
2	32%	55%
3	55%	70%
4	70%	78%
5	78%	83%

4.2 General characteristics of mixtures

▪ Two different shapes of temperature-composition diagrams

As shown below, in case of the narrow diagram, a substance cannot be purified quickly, so more steps are required to get purer substance in liquid composition

(a)

(b)
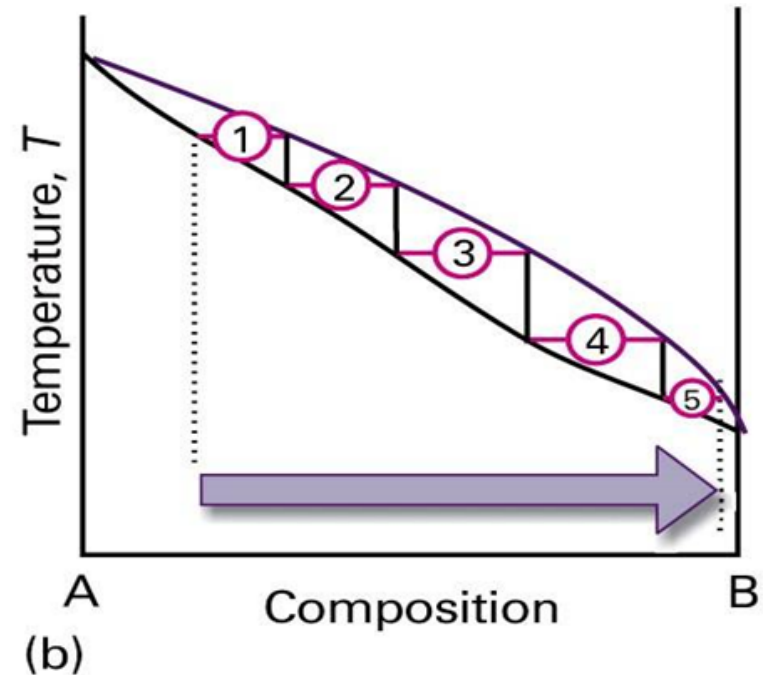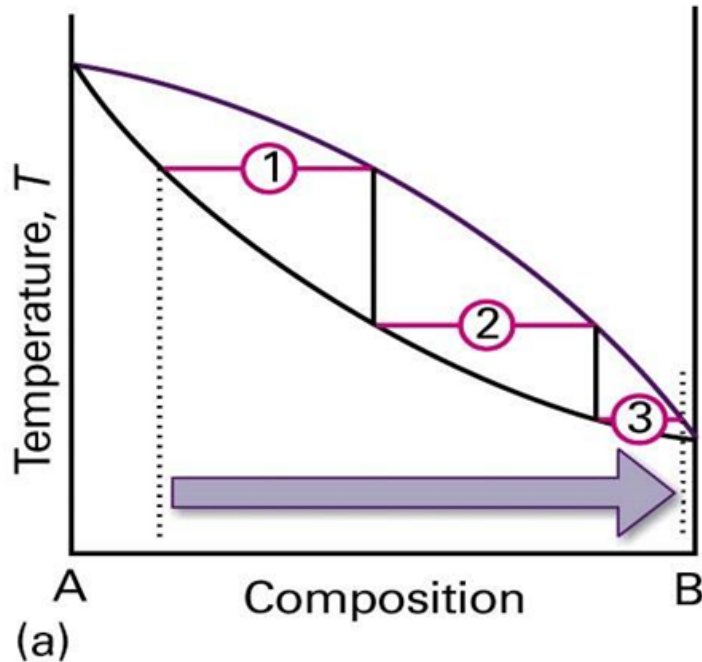
4.5 Enthalpy-composition diagrams
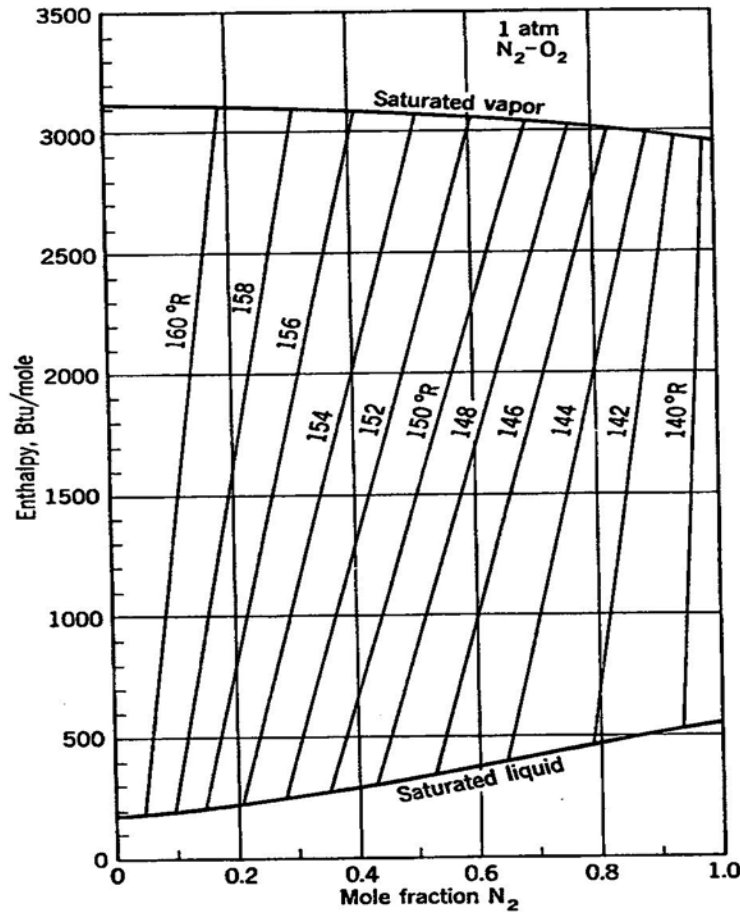
- Another set of thermodynamic curves important in the study of mixtures

Fig. Enthalpy-composition for nitrogen-oxygen mixtures at 101.3kPa
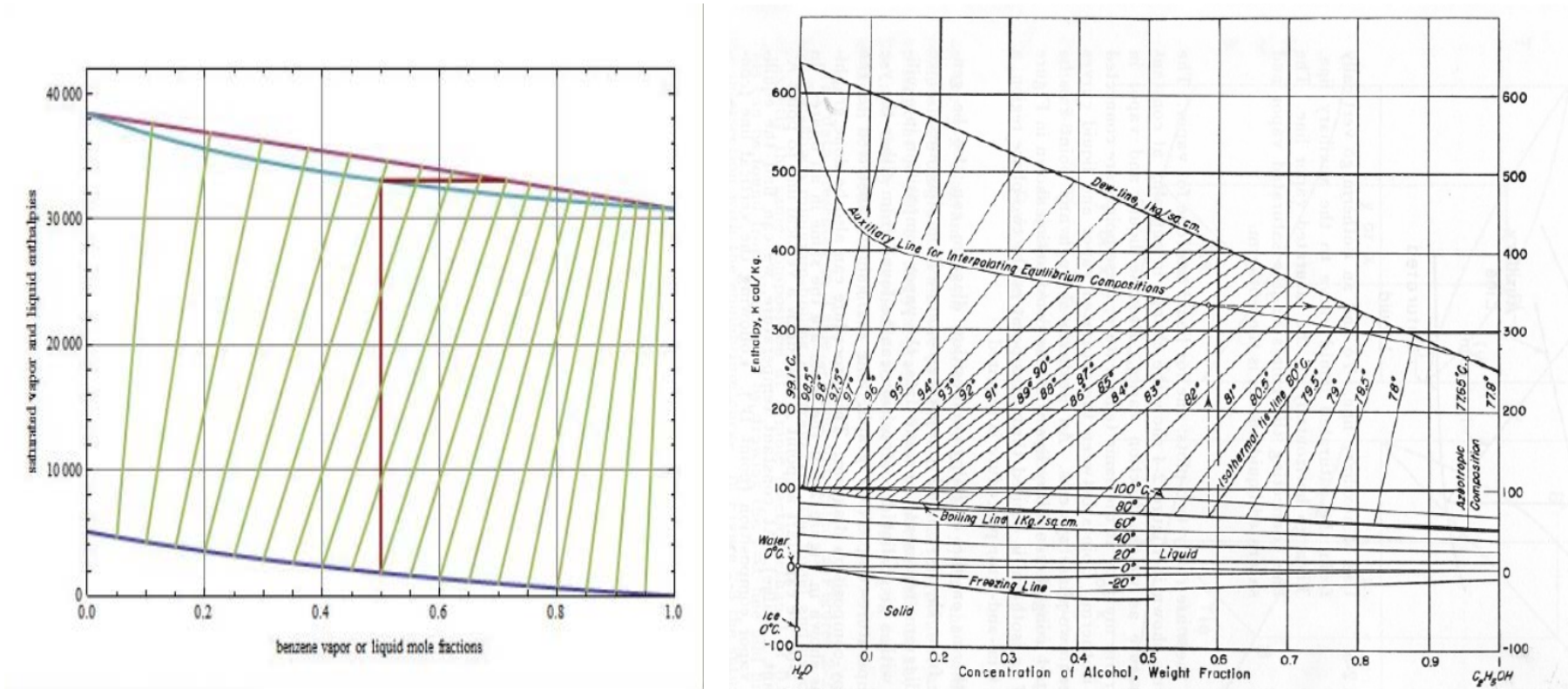
4.5 Enthalpy-composition diagrams

Fig. Enthalpy-composition diagrams

4.5 Enthalpy-composition diagrams

Mole Fraction N_2	101.3 kPa (1 atm)				506.6 kPa(5atm)			
	Temp. (K)		h	H	Temp. (K)		h	H
	Liquid	Vapor	J/mol	J/mol	Liquid	Vapor	(J/mol)	(J/mol)
0.00	90.2	90.2	419	7252	108.9	108.9	1315	7536
0.10	87.7	89.5	461	7231	106.3	107.9	1403	7507
0.20	85.7	88.7	519	7210	104.2	106.7	1499	7478
0.30	84.1	87.7	599	7185	102.5	105.6	1591	7448
0.40	82.5	86.7	682	7151	100.9	104.3	1675	7415
0.50	81.3	85.6	779	7118	99.7	103.0	1758	7377
0.60	80.4	84.3	879	7084	98.5	101.5	1851	7339
0.70	79.6	83.1	984	7042	97.4	100.0	1947	7298
0.80	78.8	81.5	1084	6992	96.5	98.4	2052	7252
0.90	78.1	79.7	1181	6933	95.6	96.6	2152	7201
1.00	77.4	77.4	1273	6871	94.2	94.2	2248	7147

Table. Enthalpy of nitrogen-oxygen mixtures. h= enthalpy of the saturated liquid at the bubble point; H= enthalpy of the saturated vapor at the dew point

# 4.6 Simple condensation or evaporation

- Rectification is synonymous with countercurrent distillation. This special distillation separation process enables the individual components of a mixture to be separated with a high purity combined with a good yield, even when their boiling points are relatively close to each other.

Distillation column in a cryogenic Air separation plant

4.6 Simple condensation or evaporation
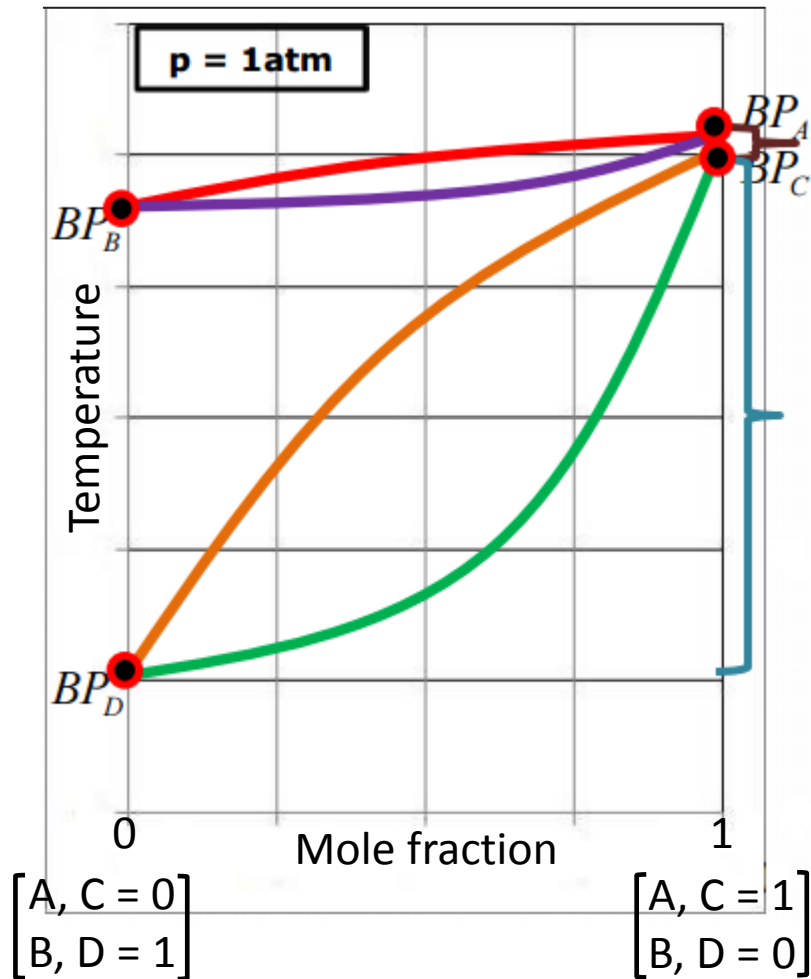
- Consider two mixtures **AB** and **CD** at 1 atm whose temperature-composition diagrams are as shown.
  - **Gas A** + **Gas B**
  - **Gas C** + **Gas D**

- The respective boiling points of each gas are as shown.

- The boiling point difference of the mixture **AB** is less than that of the mixture **CD**.

4.6 Simple condensation or evaporation
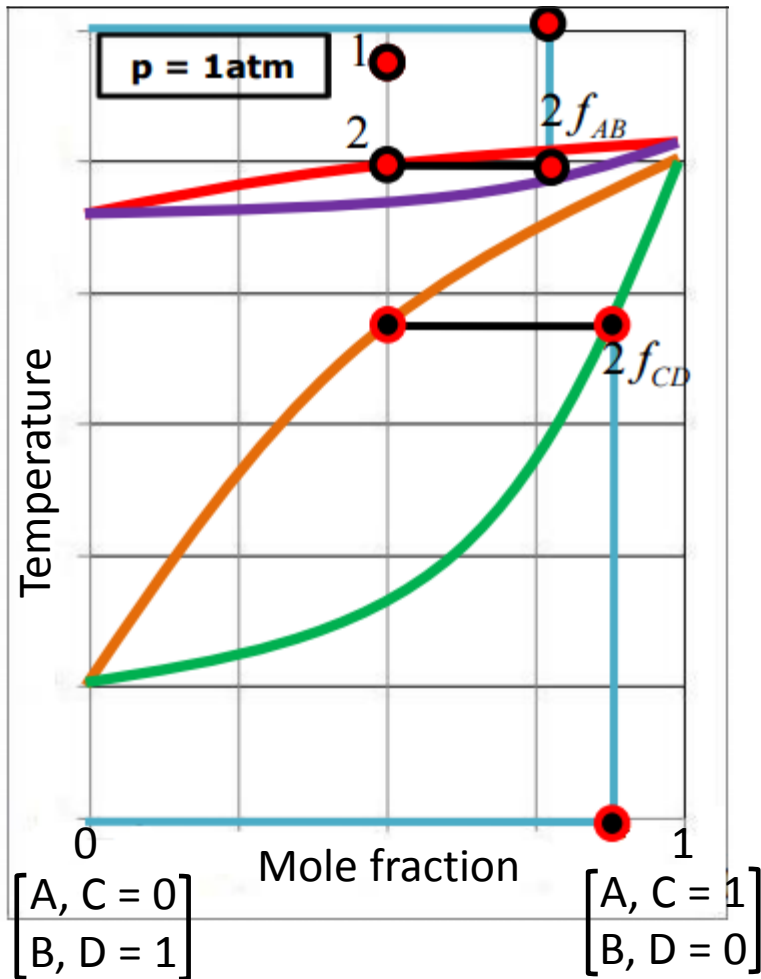
- Let us consider a mixture with composition at state 1 as shown.

- If this mixture is rectified on **AB** diagram at 2, we have

$$y_{liq} = 2f_{AB}$$

- Again, if this mixture is rectified on **CD** diagram, we have
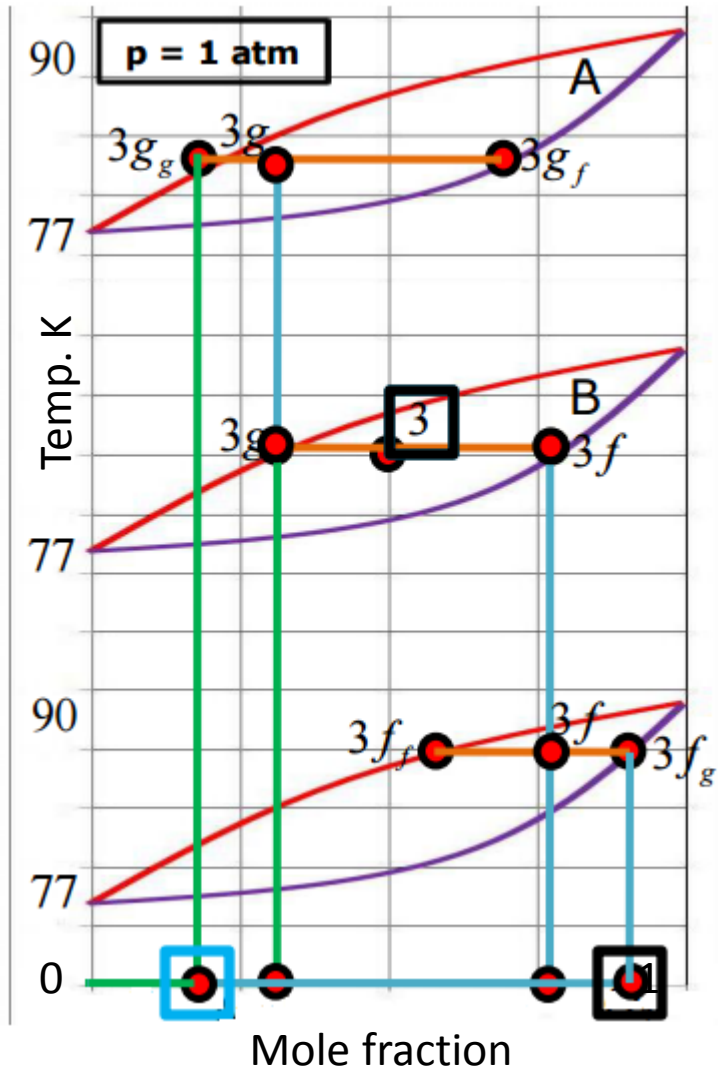
$$y_{liq} = 2f_{CD}$$

4.6 Simple condensation or evaporation
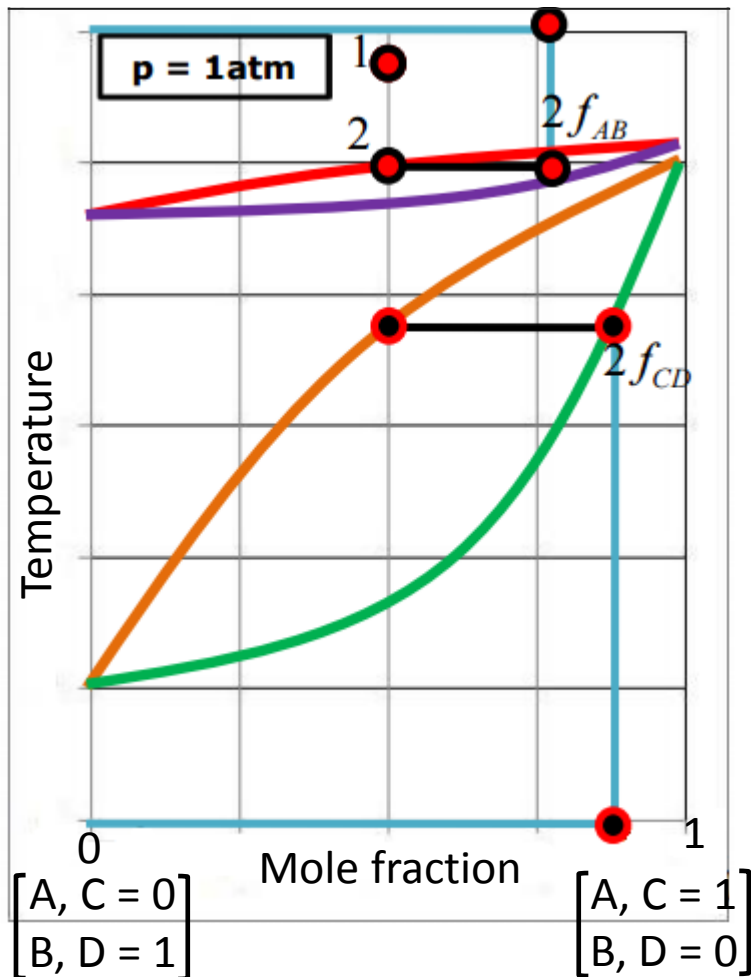
- The separation is more effective when the difference in the boiling points is more.

- For such mixtures, almost pure product is obtained in one or two condensations.

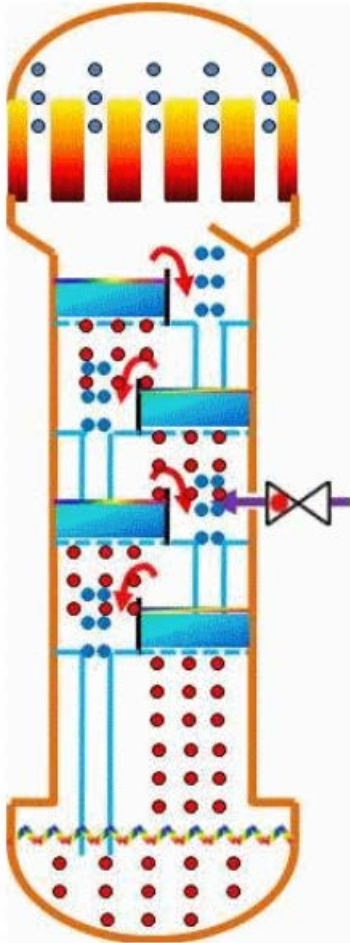# 4.6 Simple condensation or evaporation

- As done earlier, rectification of this mixture at point 3.

    - Vapor is enriched in low boiling point component (N_2)
    - Liquid is enriched in high boiling point component (O_2)

- This process forms the fundamental step for the rectification column.
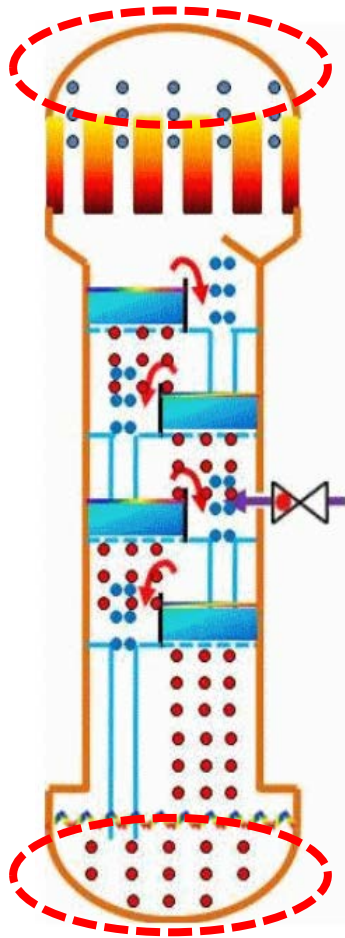
4.7 Principles of rectification

■ **Rectification Column**

- As mentioned earlier, gas separation is a process of repeated rectification.

- The equipment which carries out these processes is called as a **Rectification column**.

- The figure shows the schematic of a Rectification column.

4.7 Principles of rectification

▪ Rectification Column

- It is vertical column which is closed by spherical domes, both at the top and at the bottom.

- Theses are spherical in shape in order to minimize surface area(less heat in-leak) and accommodate high pressures(1~5 atm)

- The column is well insulated because, it is usually operated at cryogenic temperatures.

4.7 Principles of rectification

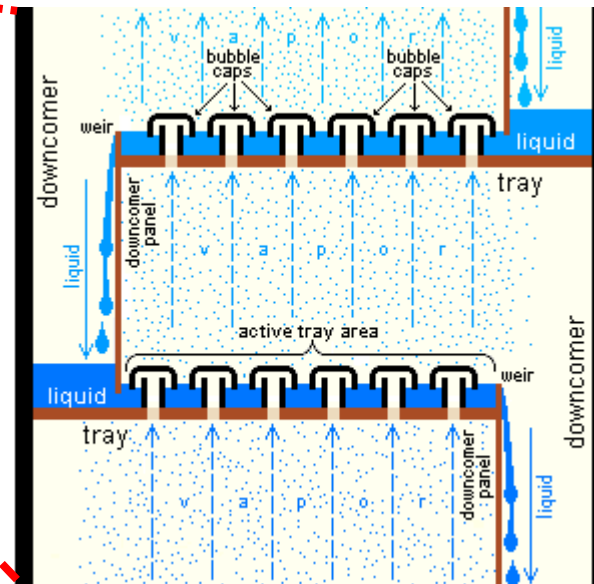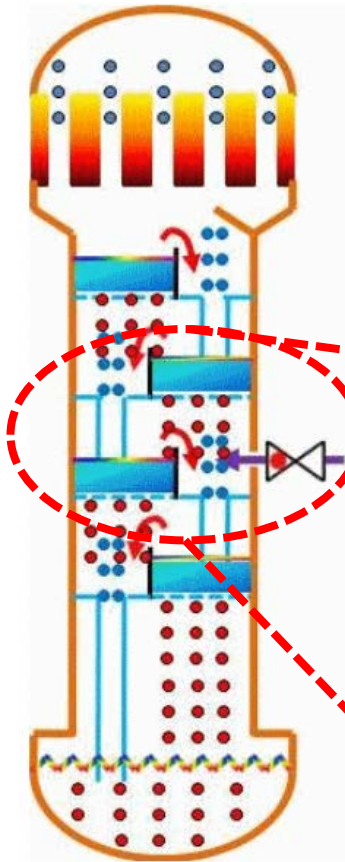■ **Rectification Column**

Condenser
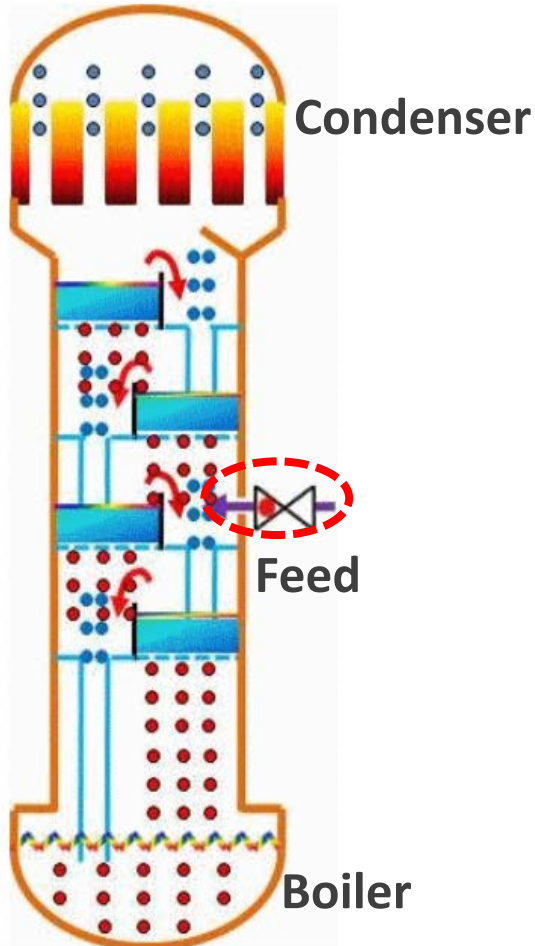
Feed

Boiler

- The top dome houses a **Condenser** and the bottom done houses a **Boiler**.

- The two phase mixture is first expanded isenthalpically. It can be **liquid** or **liquid + vapor** or **vapor**.

- This expanded product is introduced into the column as **Feed**.
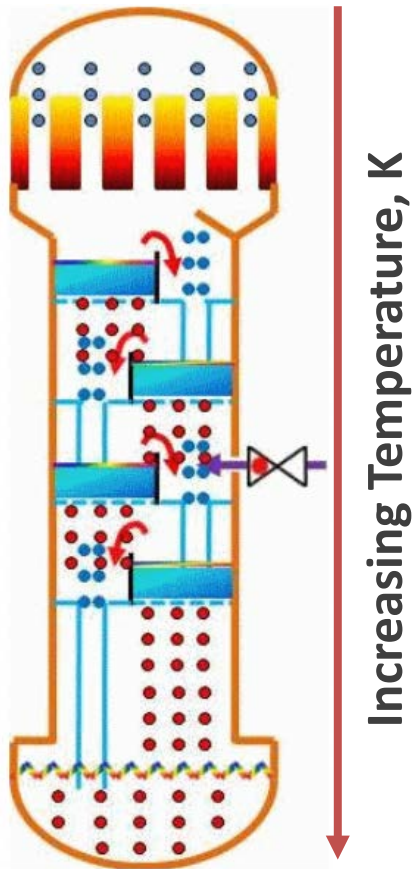
4.7 Principles of rectification

▪ **Rectification Column**

- The rectification of the mixture occurs across each **Plate** and **Downcomer** assembly as shown in the figure.

- These **Plates** have **holes** for the vapor mixture to pass through and ultimately reach the condenser.

- Similarly, the **Downcomer** takes the mixture in liquid phase towards the boiler.
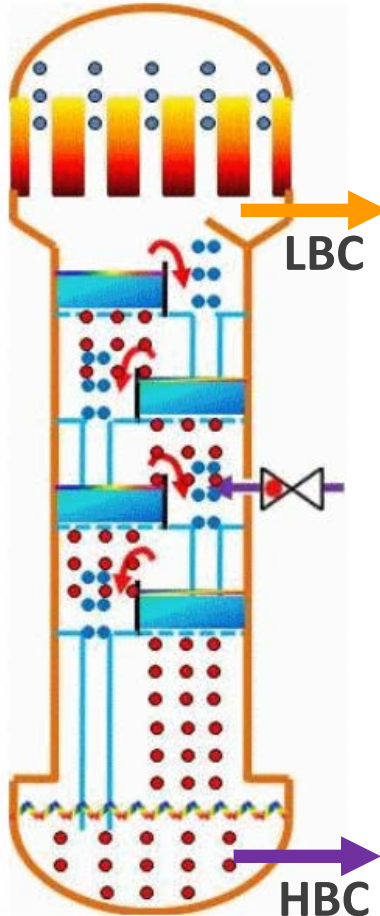
4.7 Principles of rectification

▪ Rectification Column

Increasing Temperature, K

- During this motion, vapor and liquid flow in opposite directions and exchange heat in a counter-flow manner.

- Hence, there is a temperature gradient across the length of the column.

4.7 Principles of rectification

■ **Rectification Column**

LBC

HBC

- The low boiling component(LBC) is condensed in the **Condenser** and the high boiling component(HBC) is evaporated in the **Boiler**.

- The low and high boiling components are collected at the top and bottom respectively.
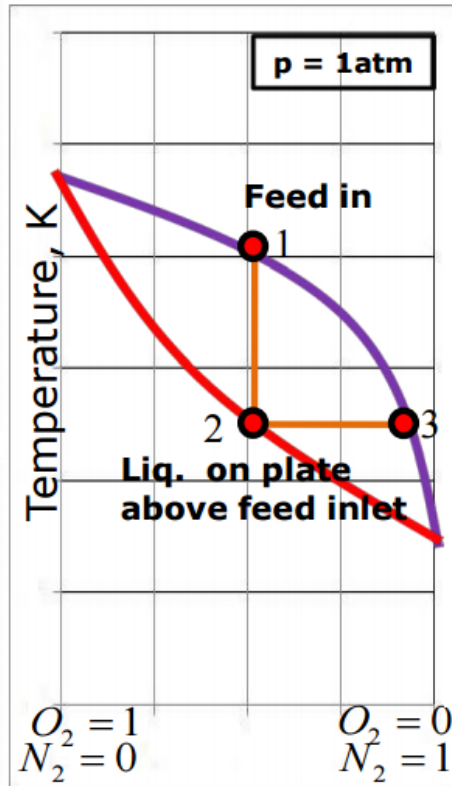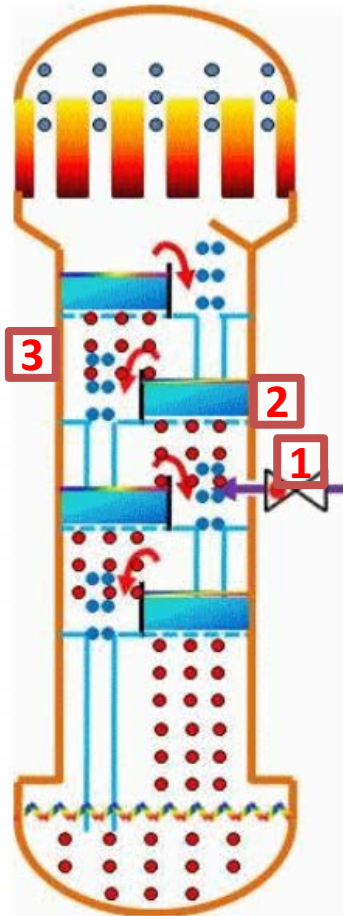
4.7 Principles of rectification
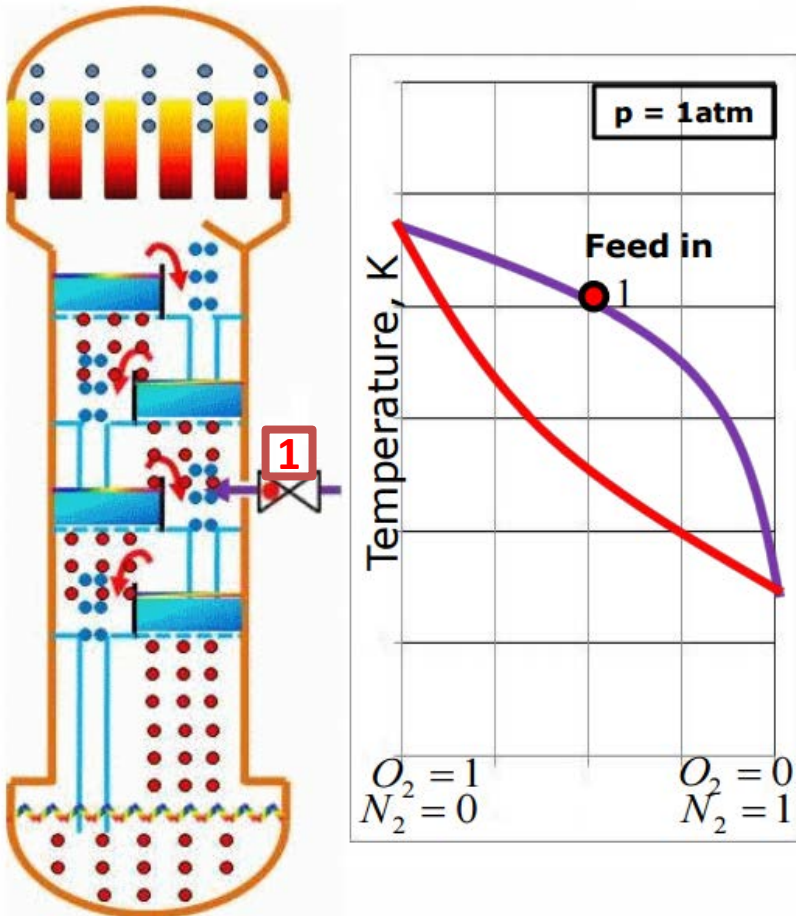
- For the ease of understanding, consider a mixture of N_2 and O_2 at 1 atm.

- Let the Feed in saturated vapor condition enter the column at 1, as shown in figure.

- Let us assume a steady state and an ideal operation of column.

- When the mixture condenses or evaporates, its composition remains constant.
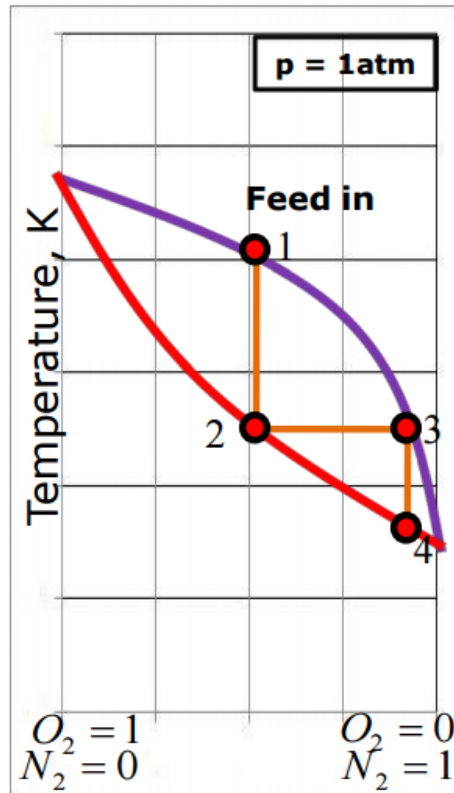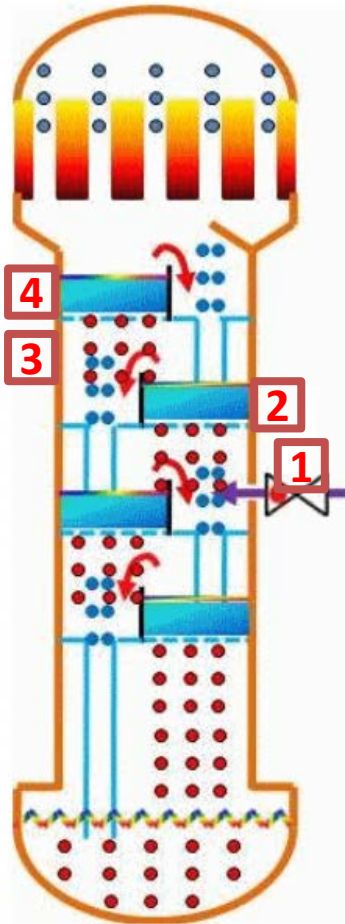
4.7 Principles of rectification
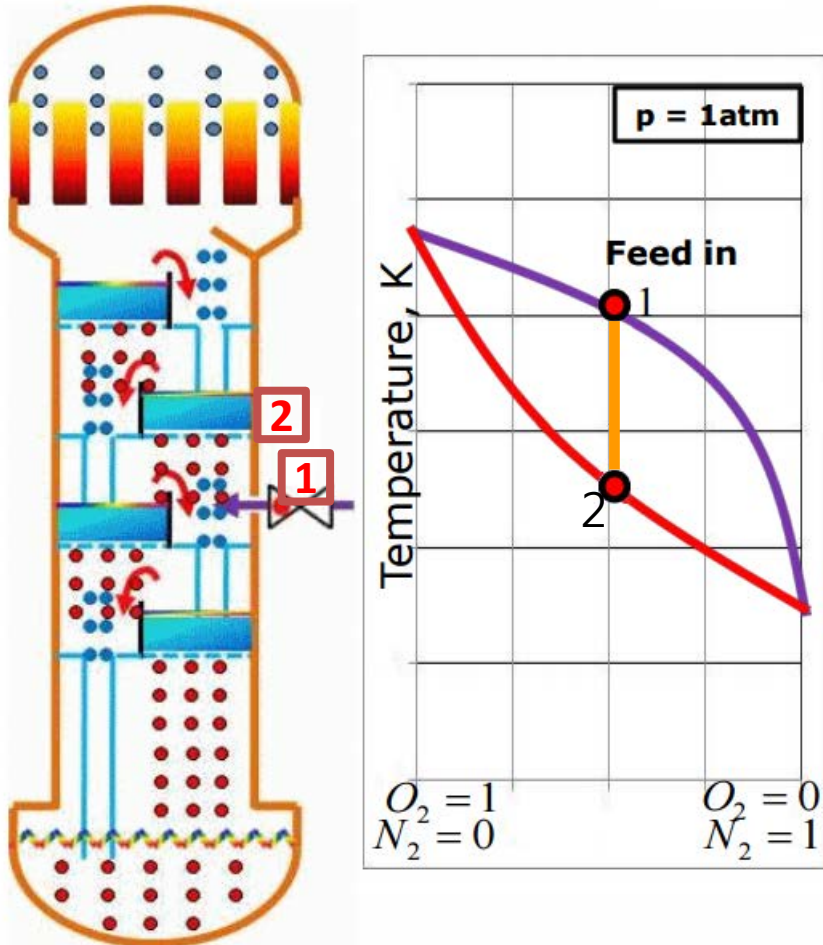
- Hence for any plate, the vapor rising and the liquid on the plate have same molar composition, although the liquid is at lower temperature.

- Hence, the liquid on the plate above the feed inlet(point 2) has same composition as the vapor.

- Therefore, extending a constant composition line about point1, we have point 2.

4.7 Principles of rectification

p = 1atm

Feed in

Liq. on plate above feed inlet
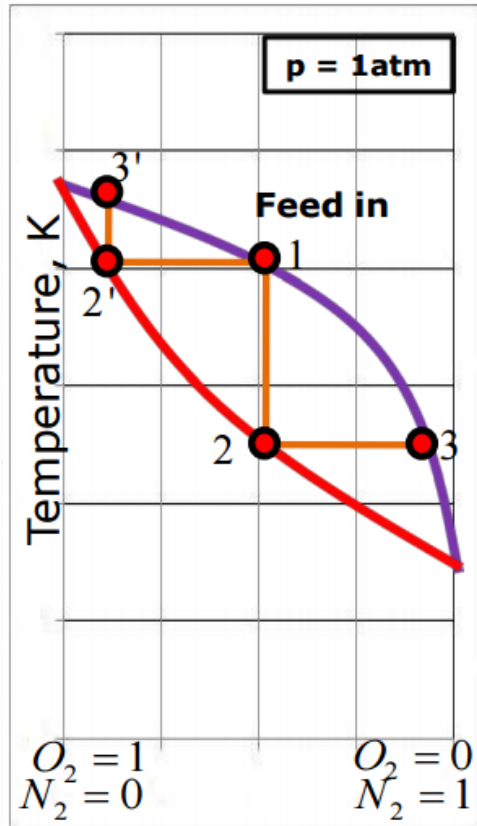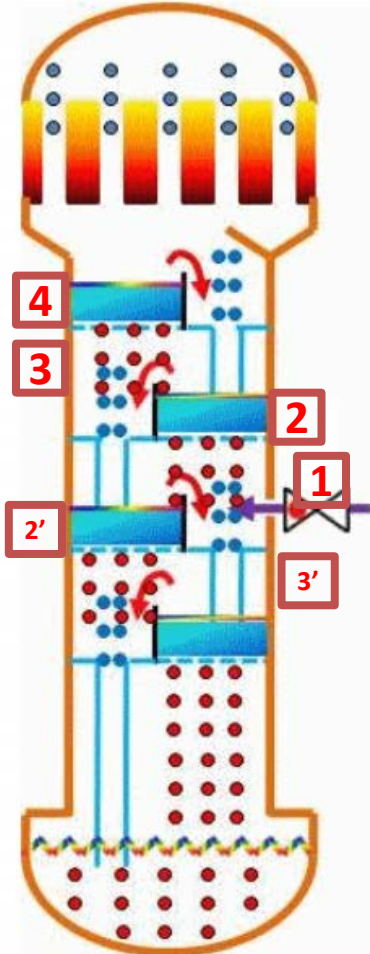
$O_2 = 1$
$N_2 = 0$

$O_2 = 0$
$N_2 = 1$

Temperature, K

- Also, the vapor leaving point 3 is in thermal equilibrium with liquid at 2. (same plate)

- Extending an isotherm about the point2, we have the point 3.

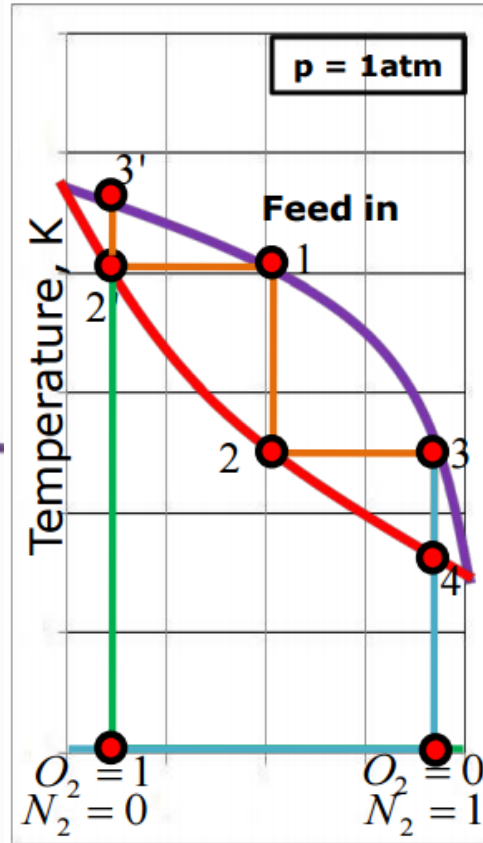# 4.7 Principles of rectification

- Similarly, liquid at point 4 has same composition as point3.

- Extending a constant composition line about 3, we have point 4

4.7 Principles of rectification

- On the other hand, we have the points 1, 2' and 3' as shown in the figure.

- The point 1 and 2' are in thermal equilibrium(same plate).

- Also, liquid at point 2' has same composition as point 3' and liquid is at lower temperature.

4.7 Principles of rectification
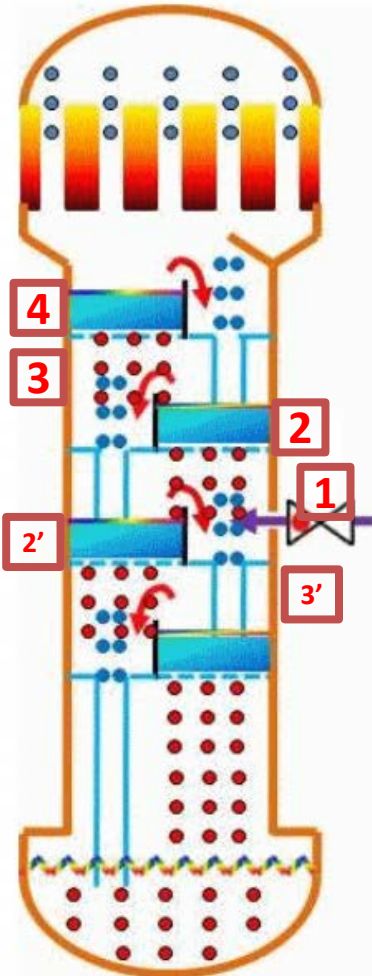
- Therefore, the liquid moving down is enriched in high boiling point component(O_2).

- On the other hand, the vapor moving up is enriched in low boiling point component(N_2).
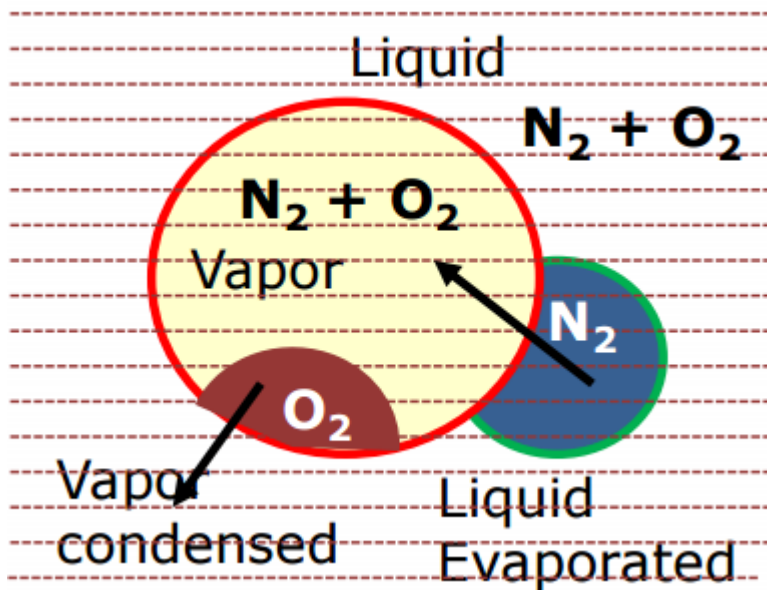
4.7 Principles of rectification
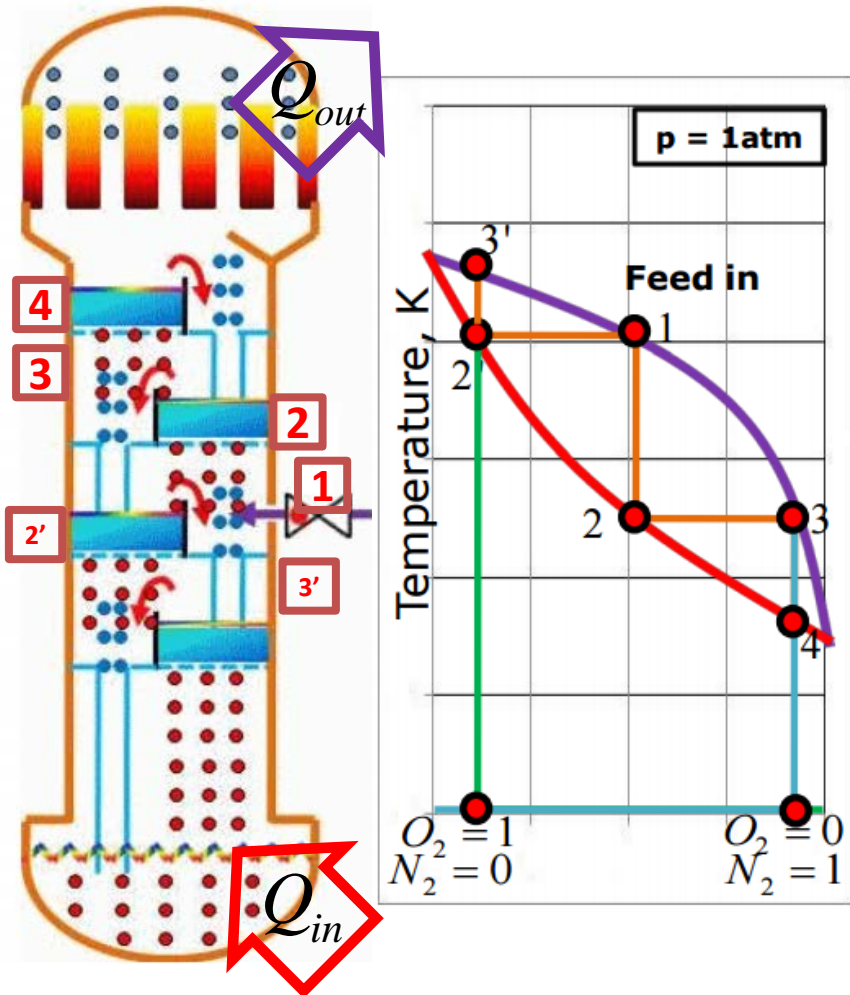
- In order to keep the process running, some heat is supplied to the boiler, to continuously evaporate the high boiling component.

- Similarly, some heat is withdrawn from the condenser to condense the low boiling component.

# 4.7 Principles of rectification

- **Condensation and Evaporation in bubble.**

- The heat exchange between the liquid and vapor fractions is explained as follows.

- The vapor is at high temperature as compared to that of liquid.

- When vapor bubbles through the liquid layer, the high temperature vapor transfers heat to the liquid.

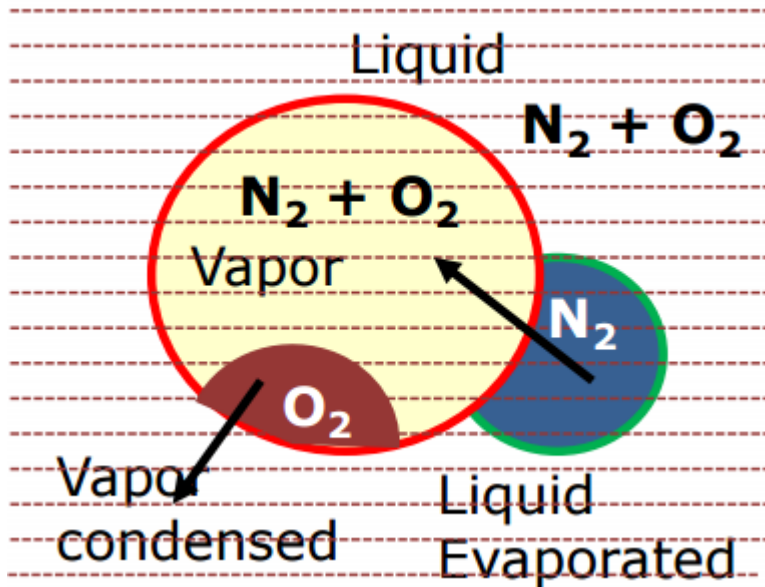# 4.7 Principles of rectification

▪ **Condensation and Evaporation in bubble.**
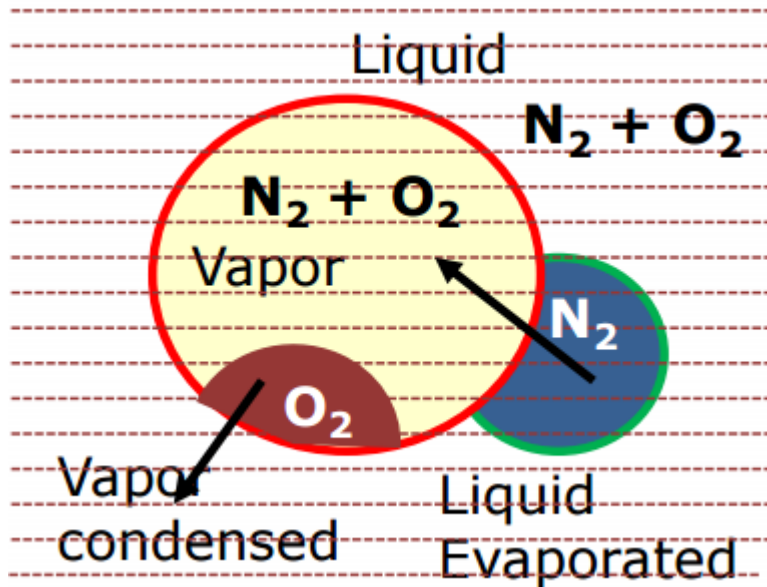
- Heat transfer from vapor bubble results in condensation of as little bit of high boiling point component(here, O_2) from bubble.

- Also this heat exchange causes an evaporation of a little bit of low boiling point component(here, N_2) from the bulk liquid.

4.7 Principles of rectification

- **Condensation and Evaporation in bubble.**

- Thus as the vapor bubble moves up, it becomes richer in low boiling point component, that is N_2.

- And as liquid moves down, it gets richer and richer in high boiling point component, that is O_2.

4.7 Principles of rectification

- **Real Rectification Column.**

  - In an ideal rectification column, the vapor and the liquid are in thermal equilibrium.

  - But in actual rectification columns, the vapor does not leave the plate as the same temperature of the liquid.

  - To ensure the required heat exchange, more number of plates are required than the theoretical prediction.

  - Hence, there is a need to study efficiency of an actual system with respect to and ideal system.

4.7 Principles of rectification
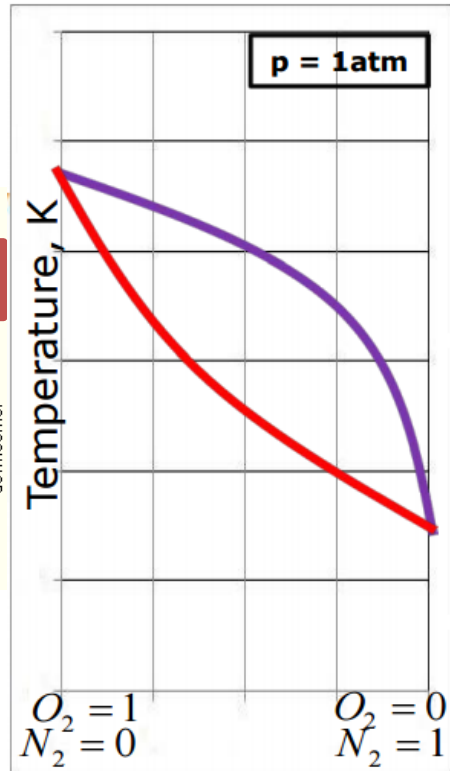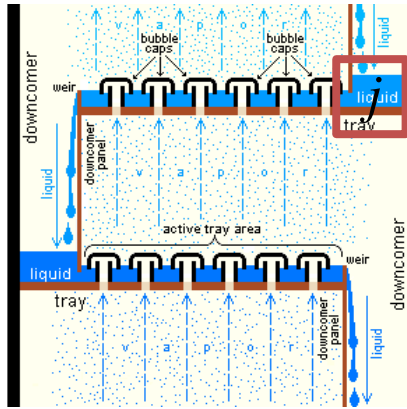
- Let the mixture of N_2 and O_2 at 1 atm be subjected to rectification.

- Consider a jth plate of the rectification column as shown in the figure.

- Across this plate, the vapor mixture rises up and the liquid mixture flows down.

4.7 Principles of rectification
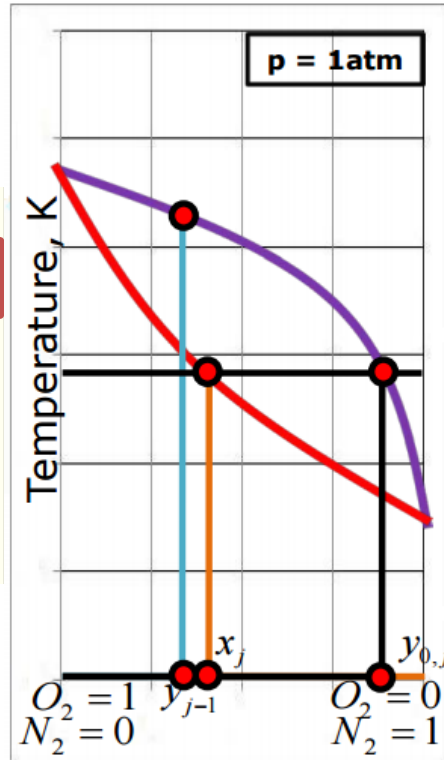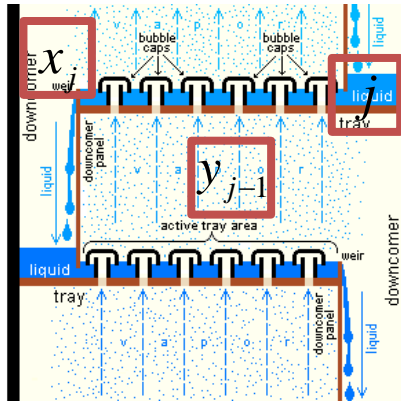
- Let y_{j-1} be the mole fraction of LBC in vapor phase rising to the jth plate.

- The composition of liquid at this plate is given by x_j

- In thermal equilibrium, the mole fraction of LBC in vapor phase leaving the jth plate is $y_{0,j}$

4.7 Principles of rectification
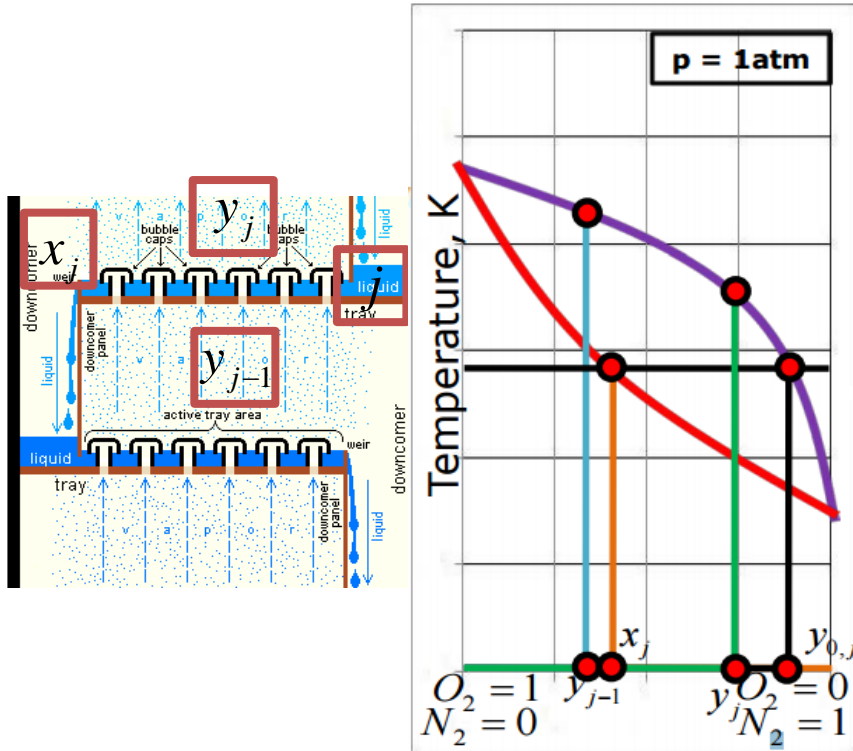
- But due to the non-ideality, the mole fraction of LBC in vapor phase leaving the jth plate is y_j .

- Hence, the maximum possible and the actual change in mole fractions are
  - $y_{0,j} - y_{j-1}$
  - $y_j - y_{j-1}$

4.7 Principles of rectification

▪ **Murphree efficiency**
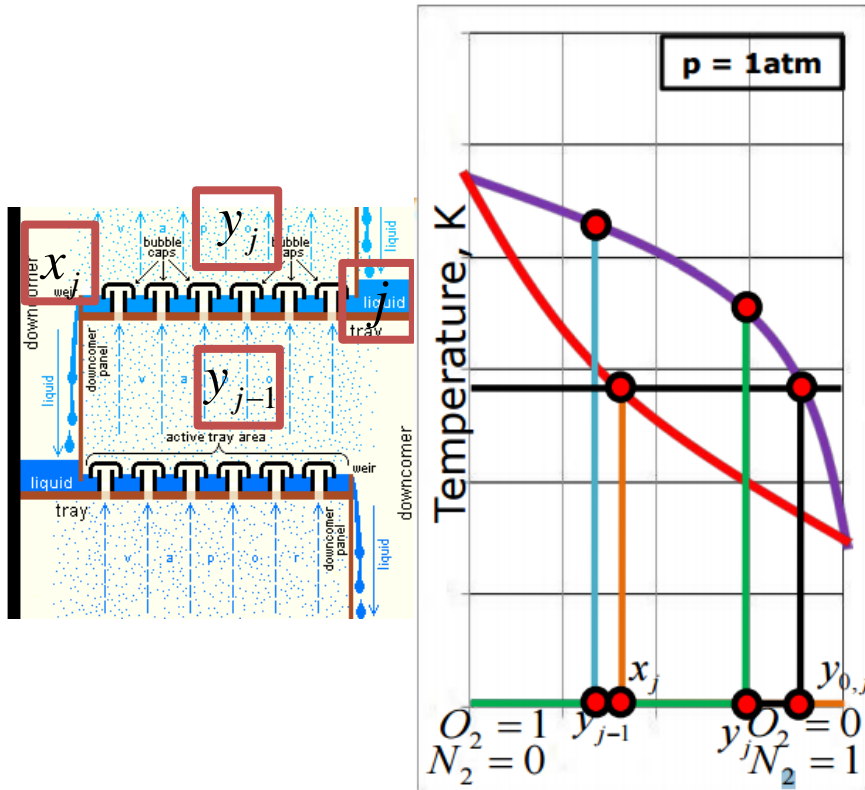
- Murphree efficiency of a plate is defined as the ratio of actual change in mole fraction to the maximum possible change that can occur.

- Mathematically,

$$\eta_M = \frac{y_j - y_{j-1}}{y_{0,j} - y_{j-1}}$$

4.7 Principles of rectification

- **Murphree efficiency**

- Heat and mass transfer analysis between the vapor and the bulk fluid is important to understand the underlying physics.

- In order to achieve high Murphree efficiency, the following conditions are required.
    - Small bubbles
    - Long time of contact
    - Large values of the overall mass and heat transfer coefficients.

4.8 Flash calculations
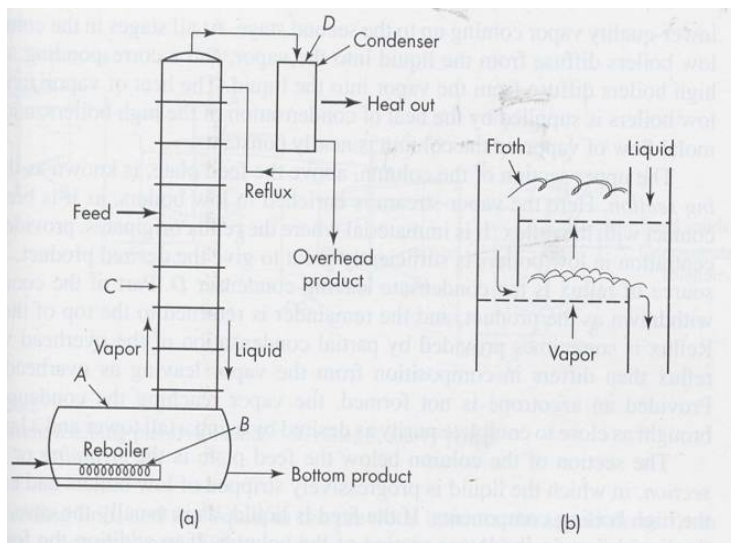
Fig. rectification column

- When the feed stream is introduced into a rectification column, it is important to determine the condition of the feed stream if the stream enters the column as a two-phase fluid. Flash calculation is used to solve this type of problem.

4.8 Flash calculations

Applying a mass balance for component j, we obtain

$$x_{Fj}F = y_jV + x_jL = y_j(F - L) + x_jL$$

The mole fraction of the jth component in the liquid phase $x_j = y_j/K_j$, so
We may solve the mole fraction y_j

$$y_j = \frac{x_{Fj}}{1 + \frac{L}{F}\left(\frac{1}{K_j} - 1\right)}$$

4.8 Flash calculations

If we apply an energy balance to the system, we obtain

$$h_F F = hL + HV = hL + H(F - L)$$

$$\frac{L}{F} = \frac{H - h_F}{H - h}$$
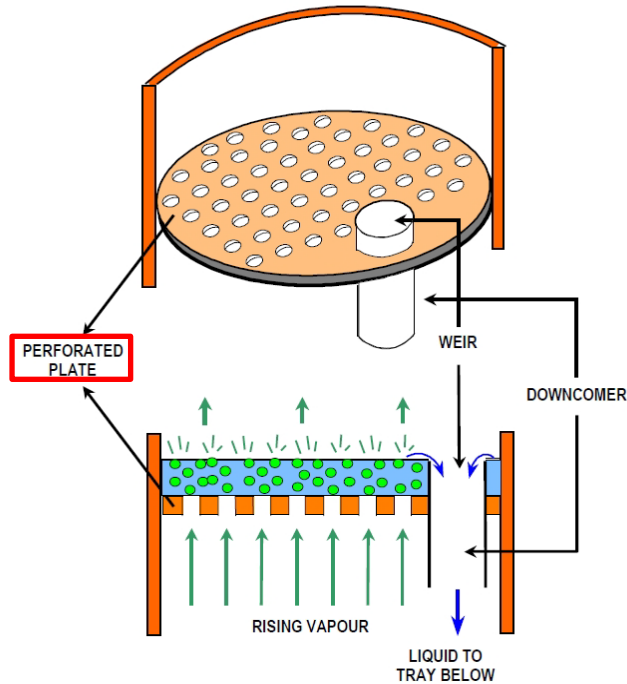
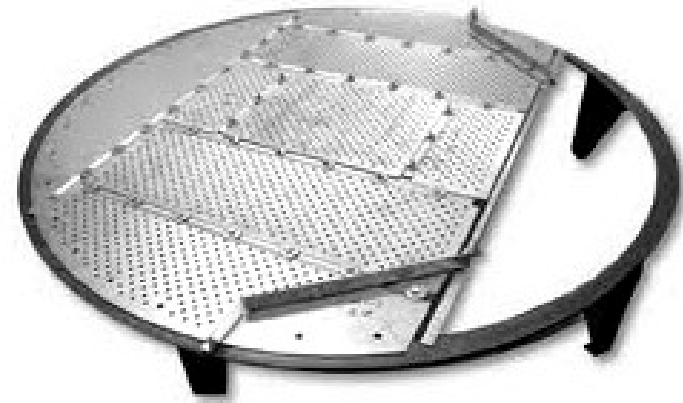The sum of the mole fractions for the vapor phase is equal to unity.

$$\sum_j y_j = 1 = \sum_j \frac{x_{Fj}}{1 + \frac{L}{F}\left(\frac{1}{K_j} - 1\right)}$$

4.9 Theoretical plate calculations for columns

Rectification column

Perforated plate

Two basic methods used to determine the number of theoretical plates

- Ponchon (1921) and Savarit (1922)

- McCabe and Thiele (1925)

4.9 Theoretical plate calculations for columns

■ **Ponchon (1921) and Savarit (1922) method**

- Rigorous and capable of handling all distillations, but requires detailed enthalpy data

    for its application

- Simultaneous material and energy balance calculations

- Detailed calculations of equilibrium conditions

- More accurate, but difficult to use

- Largely superseded by rigorous computer simulation calculations

- **Requires detailed enthalpy data in its application**

4.9 Theoretical plate calculations for columns

▪ **McCabe and Thiele (1925) method**

- Less rigorous, enthalpy data not required.

- Adequate for many applications, more commonly use because of its simplicity

- Uses graphical solution for binary mixture on equilibrium diagram (x-y plot).

- Provides the number of theoretical (ideal) trays required for a given separation.

- Pressure is assumed constant throughout the entire column.

- **Less general, but it requires only equilibrium concentration data in its application**

4.9 Theoretical plate calculations for columns

- **Upper enriching section**
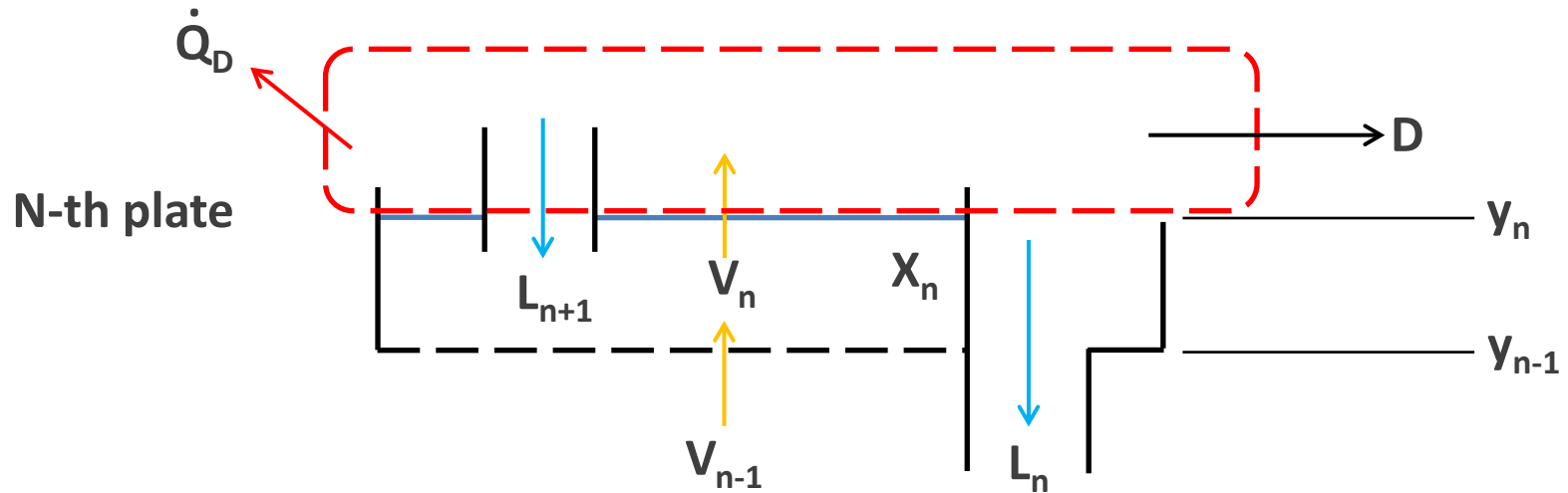
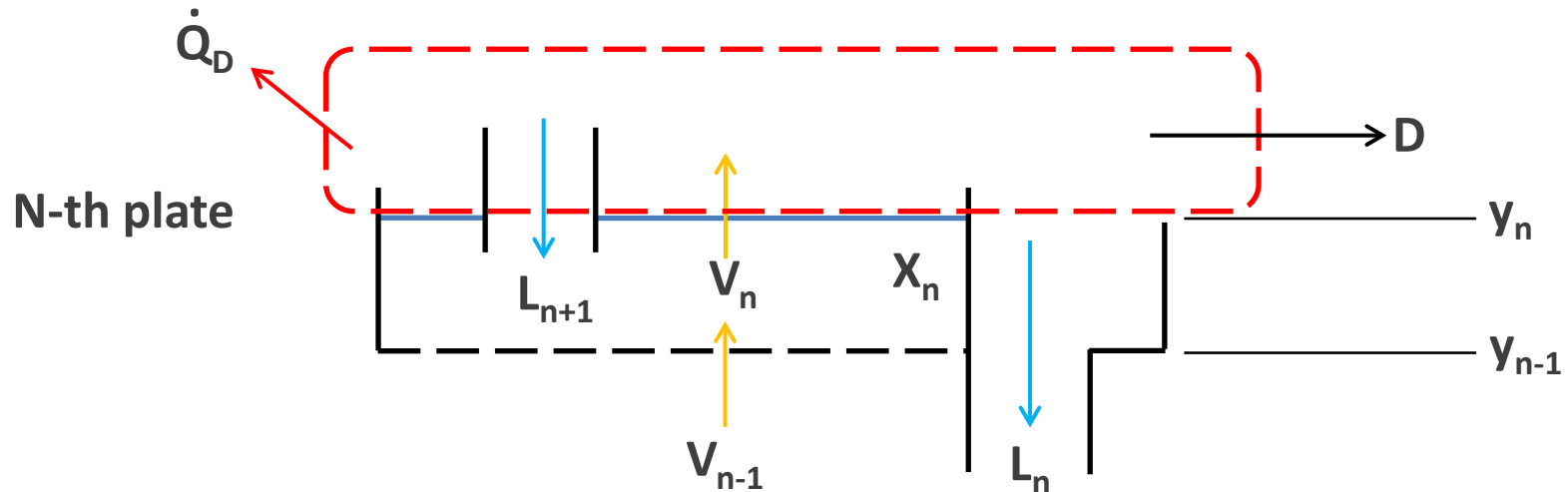Conservation of Mass Principle $\quad V_n = L_{n+1} + D$ $\qquad$ (4.38)

4.9 Theoretical plate calculations for columns

▪ **Upper enriching section (suppose a two-component mixture for simplicity)**

$\dot{Q}_D$

N-th plate

L_{n+1} V_n X_n D

y_n

V_{n-1} L_n

y_{n-1}

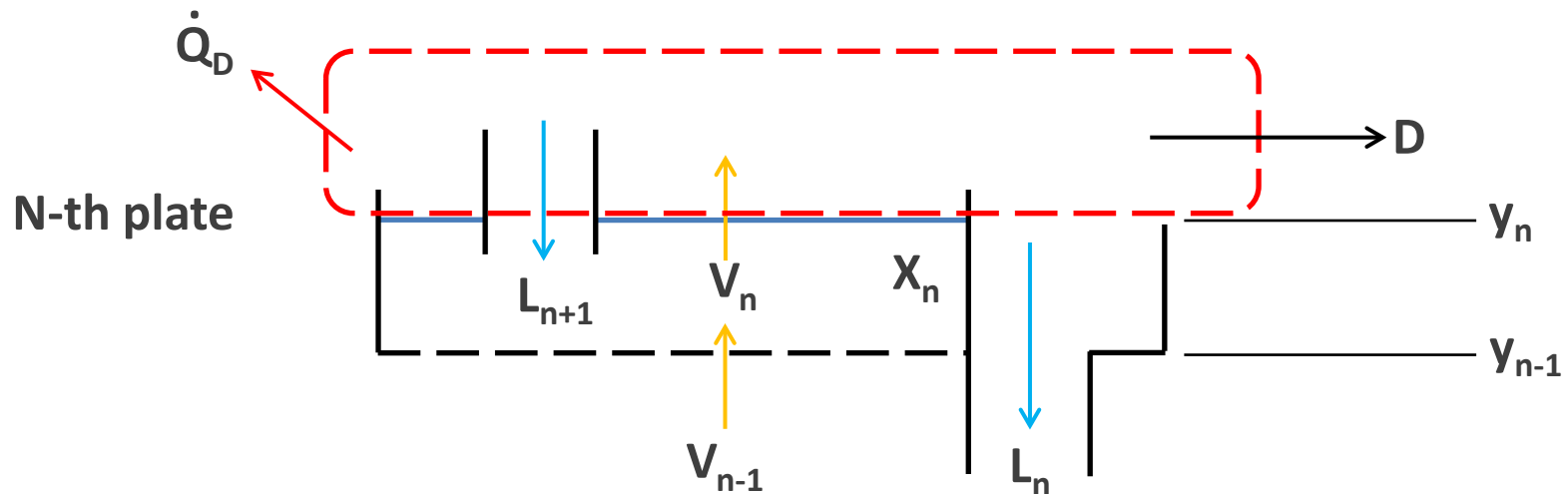Conservation of Mass Principle $y_n V_n = x_{n+1} L_{n+1} + x_D D$ **(4.39)**

4.9 Theoretical plate calculations for columns

▪ **Upper enriching section (suppose a two-component mixture for simplicity)**

- First Law of Thermodynamics

Assuming
1. no heat inleaks from ambient
2. no work transfer
3. steady-state operation
4. negligible changes in kinetic and potential energies

4.9 Theoretical plate calculations for columns

- **Upper enriching section (suppose a two-component mixture for simplicity)**

$$\cancel{\dot{E}} = \dot{Q} - \cancel{\dot{W}} + \sum \dot{m}_i(h_i + \frac{1}{2}v_i^2 + gz_i) - \sum \dot{m}_e(h_e + \frac{1}{2}v_e^2 + gz_e)$$

③   ②

$$= \cancel{\dot{Q}}_{in} - \dot{Q}_{out} + \dot{m}_i(h_i + \frac{1}{2}\cancel{v_i^2} + g\cancel{z_i}) - \dot{m}_e(h_e + \frac{1}{2}\cancel{v_e^2} + g\cancel{z_e})$$

①   ④   ④   ④   ④

$$= \dot{Q}_{out} + \dot{m}_i h_i - \dot{m}_e h_e$$

Assuming
1. no heat inleaks from ambient
2. no work transfer
3. steady-state operation
4. negligible changes in kinetic and potential energies

4.9 Theoretical plate calculations for columns

- **Upper enriching section (suppose a two-component mixture for simplicity)**

$$= \dot{Q}_{out} + \dot{m}_i h_i - \dot{m}_e h_e$$

$$= -\dot{Q}_D + V_n H_n - L_{n+1} h_{n+1} - h_D D$$

$$\boldsymbol{V_n H_n = h_{n+1} L_{n+1} + h_D D + \dot{Q}_D} \qquad \text{(4.40)}$$

Assuming
1. no heat inleaks from ambient
2. no work transfer
3. steady-state operation
4. negligible changes in kinetic and potential energies

4.9 Theoretical plate calculations for columns

▪ **Upper enriching section (suppose a two-component mixture for simplicity)**

$$V_n H_n = h_{n+1} L_{n+1} + hDD + \dot{Q}_D \qquad (4.40)$$

$$V_n H_{n}/D = h_{n+1} L_{n+1}/D + hD + \dot{Q}_D/D$$

$$\frac{V_n H_n}{D} = \frac{h_{n+1}(V_n - D)}{D} + hD + \frac{\dot{Q}_D}{D}$$

$$\frac{V_n}{D}(H_n - h_{n+1}) = \frac{\dot{Q}_D}{D} + h_D - h_{n+1} \qquad (4.41)$$

4.9 Theoretical plate calculations for columns

▪ **Upper enriching section (suppose a two-component mixture for simplicity)**

$$\frac{V_n}{D}(H_n - h_{n+1}) = \frac{\dot{Q}_D}{D} + h_D - h_{n+1} \qquad (4.41)$$

$$\frac{D}{V_n} = \frac{H_n - h_{n+1}}{(\dot{Q}_D/D) + h_D - h_{n+1}} \qquad (4.42)$$
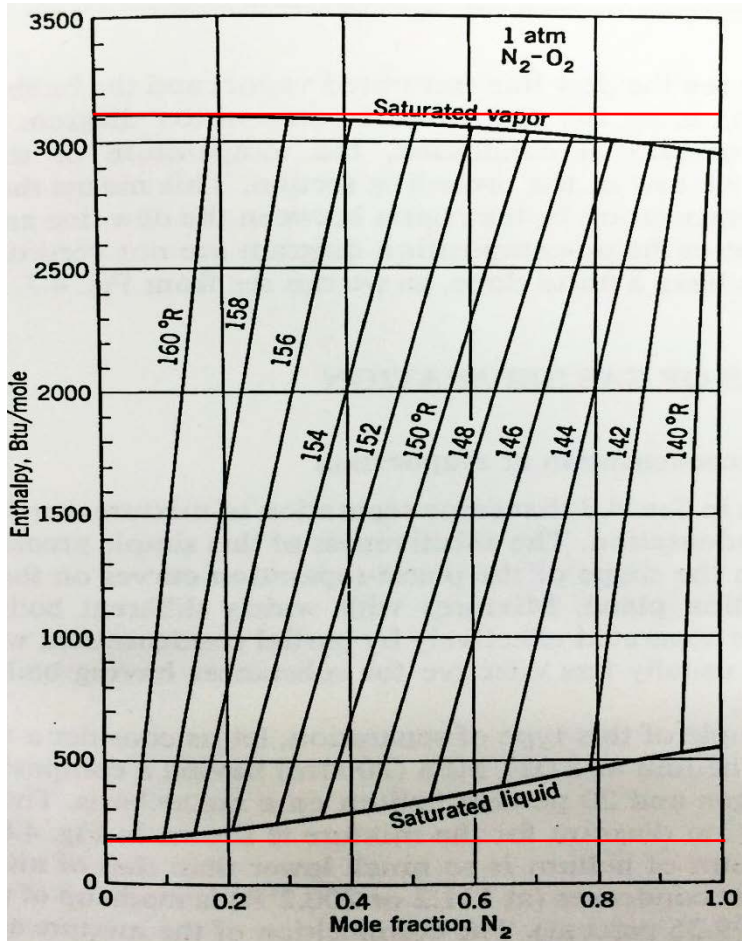
Using eqn. (4.38) $\qquad V_n = L_{n+1} + D \quad \longrightarrow \quad L_{n+1}/V_n = 1 + (D/V_n) \qquad (4.43)$

Using eqn. (4.39) $\qquad y_n V_n = x_{n+1} L_{n+1} + x_D D \longrightarrow y_n = \frac{L_{n+1}}{V_n} x_{n+1} + \frac{D}{V_n} x_D \qquad (4.44)$

4.9 Theoretical plate calculations for columns

■ **Operating line (upper enriching section)**

Enthalpy-composition for nitrogen-oxygen mixtures at 1atm

The bubble line and the dew line

$\downarrow$

If,

1. The molar heat of vaporization for the two pure components were identical

2. The enthalpy of mixing were negligible

$\downarrow$

Then,
Exactly horizontal lines

$\downarrow$

h_{n+1} and H are constans
for a particular column

4.9 Theoretical plate calculations for columns

▪ **Operating line (upper enriching section)**

$$\frac{D}{V_n} = \frac{H_n - h_{n+1}}{(\dot{Q}_D/D) + h_D - h_{n+1}} = constant \qquad \text{(4.42)}$$

$$L_{n+1}/V_n = 1 + (D/V_n) = constant \qquad \text{(4.43)}$$

4.9 Theoretical plate calculations for columns

- **Operating line (upper enriching section)**

$$\frac{D}{V_n} = \frac{H_n - h_{n+1}}{(\dot{Q}_D/D) + h_D - h_{n+1}} = constant \qquad \text{(4.42)}$$

$$L_{n+1}/V_n = 1 + (D/V_n) = constant \qquad \text{(4.43)}$$

The operating line

$$y_n = \frac{L_{n+1}}{V_n} x_{n+1} + \frac{D}{V_n} x_D \qquad \text{(4.44)}$$

slope   intercept

4.9 Theoretical plate calculations for columns

▪ **Operating line (upper enriching section)**

The operating line

$$y_n = \boxed{\frac{L_{n+1}}{V_n}} x_{n+1} + \boxed{\frac{D}{V_n} x_D} \qquad (4.44)$$

slope   intercept

$$= \frac{L_{n+1}}{V_n} x_D + \frac{D}{V_n} x_D = (L_{n+1} + D)\frac{x_D}{V_n} = x_D$$

The y-intercept value (at x=0, y=$x_D D/V_n$) may be used to construct the operating line for the enriching section of the column
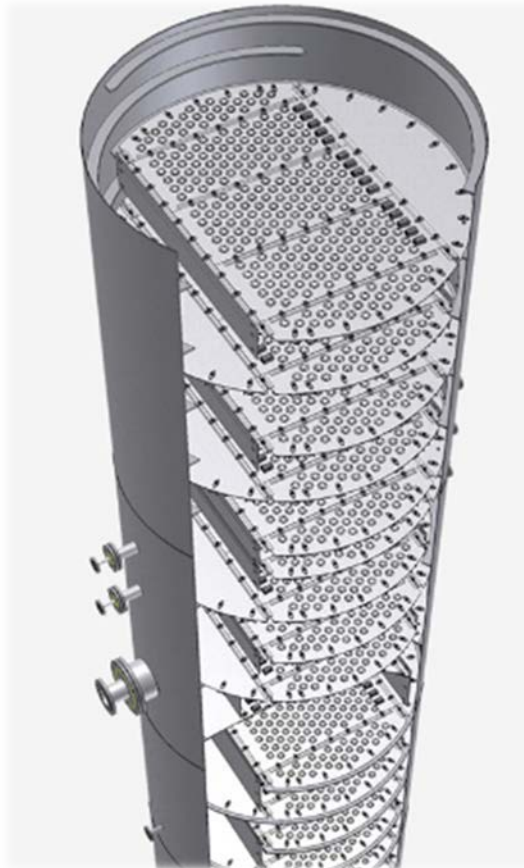
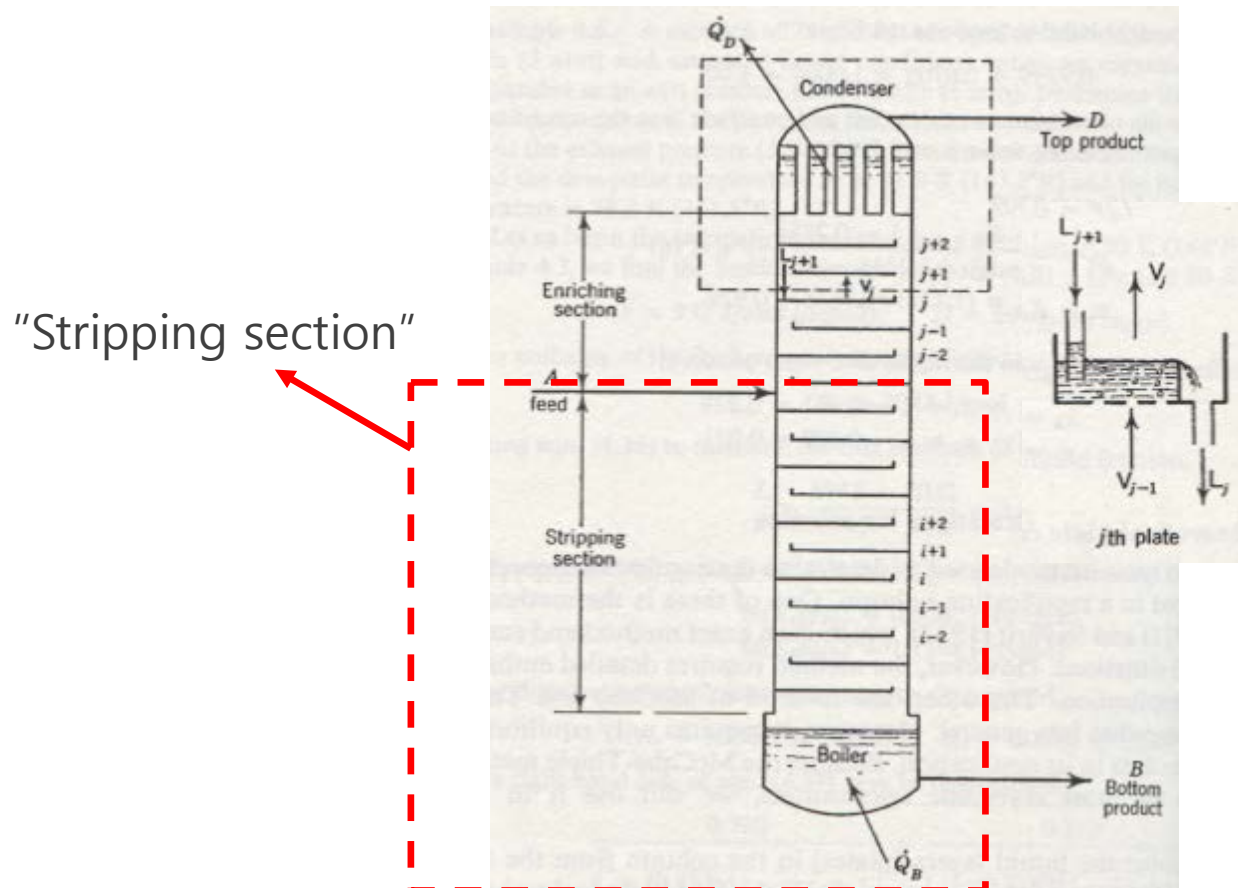# 4.9 Theoretical plate calculations for columns

■ **Rectification columns**

<Bubble-cap trays>

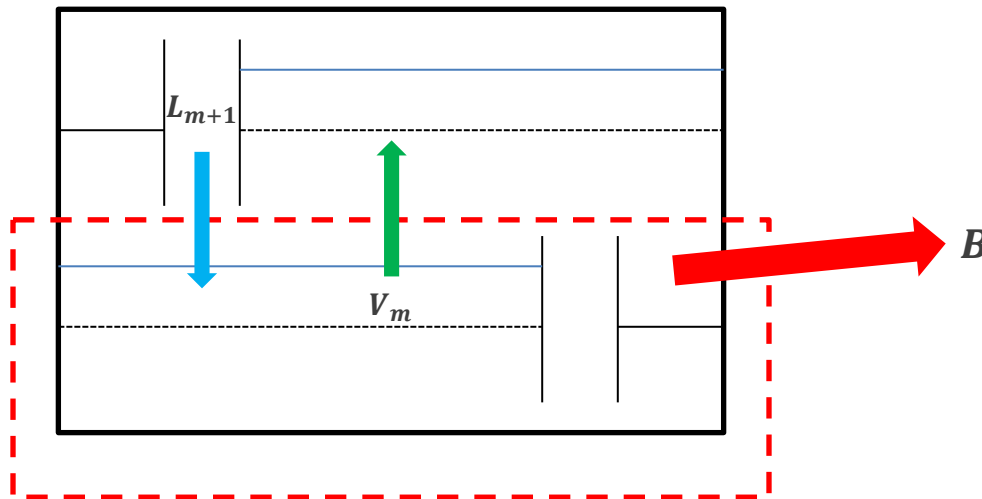<Rectification column>

4.9 Theoretical plate calculations for columns

■ **Lower (stripping section)**

"Stripping section"

4.9 Theoretical plate calculations for columns

▪ **Similar analysis applied to the stripping section**

Conservation of mass principle,

<Control volume for the stripping section>

$$L_{m+1} = V_m + B$$

4.9 Theoretical plate calculations for columns

■ **Similar analysis applied to the stripping section**

Applying lower boiling-point components yields,

$$x_{m+1}L_{m+1} = y_m V_m + x_B B$$

$(x_B = mole\ fraction\ of\ the\ lower-boiling-point\ component\ in\ the\ bottom\ product)$

4.9 Theoretical plate calculations for columns

■ **Similar analysis applied to the stripping section**

Applying First law of thermodynamics,

$$h_{m+1}L_{m+1} + \dot{Q}_B = H_m V_m + h_B B$$

$(h_B = the\ enthalpy\ of\ the\ bottom\ product\ stream)$

4.9 Theoretical plate calculations for columns

■ **Similar analysis applied to the stripping section**

Operating line for the lower or stripping section of the column,

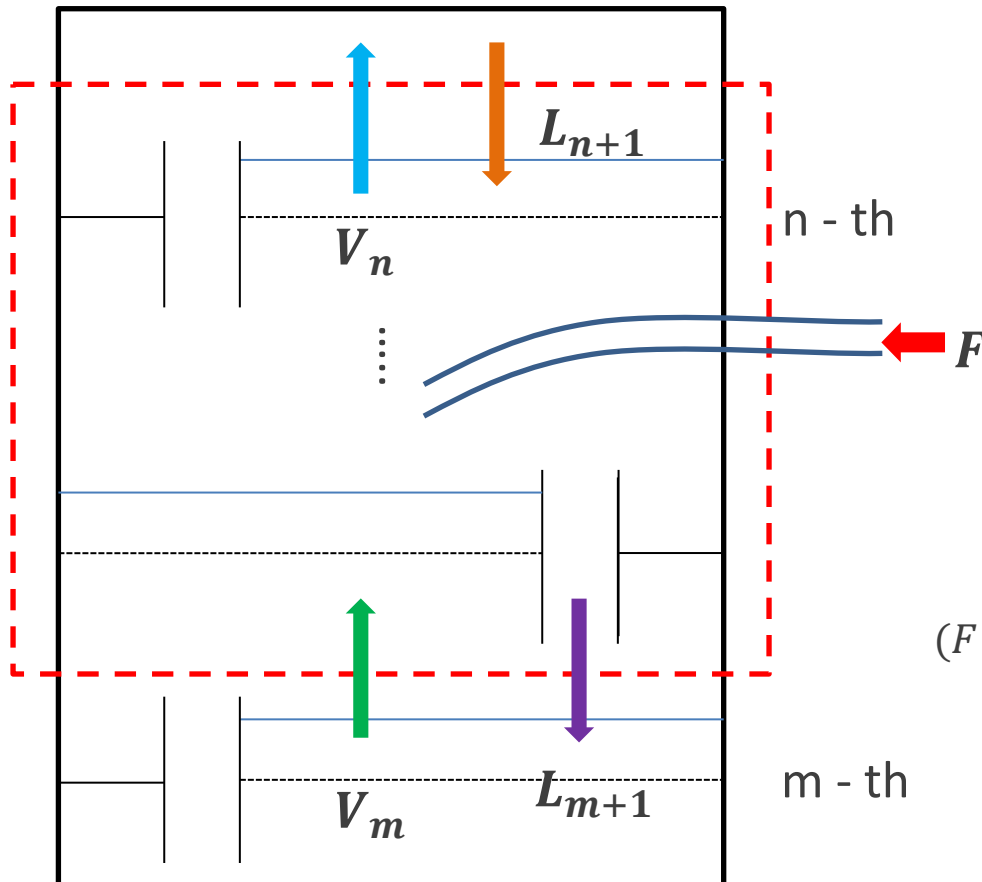$$y_m = \left(\frac{L_{m+1}}{V_m}\right) x_{m+1} - (\frac{B}{V_m}) x_B$$

$$\frac{B}{V_m} = \frac{H_m - h_{m+1}}{\left(\frac{\dot{Q}_B}{B}\right) - h_B + h_{m+1}}$$

$$\frac{L_{m+1}}{V_m} = 1 + (\frac{B}{V_m})$$

4.9 Theoretical plate calculations for columns

Finding intersection of the operating lines for the upper and lower sections,

$$F = V_n - V_m + L_{m+1} - L_{n+1}$$

$(F = mole\ flow\ rate\ of\ feed\ into\ the\ column)$

4.9 Theoretical plate calculations for columns

Define parameter q = the ratio of the difference in liquid flow between the upper and lower column sections to the feed flow

$$q = (L_{m+1} - L_{n+1})/F$$

4.9 Theoretical plate calculations for columns

Combine equations,

$$F = V_n - V_m + L_{m+1} - L_{n+1} , \qquad q = (L_{m+1} - L_{n+1})/F$$

The difference in vapor flows,

$$V_n - V_m = (1 - q)F$$

4.9 Theoretical plate calculations for columns

Using upper vapor flow and lower vapor flow equations, we can obtain the intersection of the two operating lines

$$y_n = \left(\frac{L_{n+1}}{V_n}\right) x_{n+1} + \left(\frac{D}{V_n}\right) x_D \quad \text{(upper section)}$$

$$y_m = \left(\frac{L_{m+1}}{V_m}\right) x_{m+1} + \left(\frac{D}{V_m}\right) x_B \quad \text{(lower section)}$$

$$V_n - V_m = (L_{n+1} - L_{m+1})\left(\frac{x}{y}\right) + \frac{(x_D D + x_B B)}{y} = (1-q)F$$

4.9 Theoretical plate calculations for columns

For the column as a whole,

$$x_F F = x_D D + x_B B$$

Therefore,

$$-qF\left(\frac{x}{y}\right) + \frac{x_F F}{y} = (1-q)F$$

4.9 Theoretical plate calculations for columns

The locus of the intersection of the two operating lines is,

$$y = \frac{x_F}{1 - q} - \frac{q}{1 - q}x$$

4.9 Theoretical plate calculations for columns

Determine q value,

$$h_F F = V_n H_n - V_m H_m + L_{m+1} h_{m+1} - L_{n+1} h_{n+1}$$

Vapor and liquid enthalpies are assumed to be independent of composition,

$$H_n = H_m = H \quad and \quad h_{m+1} = h_{n+1} = h$$

4.9 Theoretical plate calculations for columns

And,

$$h_F F = (V_n - V_m)H + (L_{m+1} - L_{n+1})h$$

And, we also can obtain,

$$h_F = (1 - q)H + qh$$

4.9 Theoretical plate calculations for columns

The value of q may be determined from the feed stream enthalpy h_F and the saturated vapor enthalpy H and saturated liquid enthalpy h

$$q = \frac{H - h_F}{H - h}$$

4.9 Theoretical plate calculations for columns

The value of the parameter q is as follows, depending upon the condition of the feed stream,
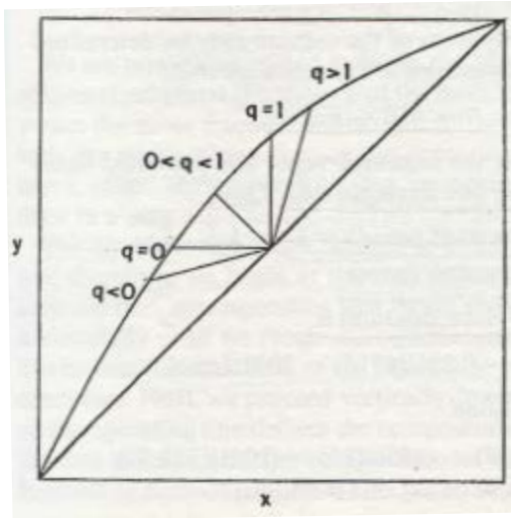
ⅰ) Sub-cooled liquid feed : $q > 1$
ⅱ) Saturated liquid feed : $q = 1$
ⅲ) Two-phase mixture feed : $0 < q < 1$
ⅳ) Saturated vapor feed : $q = 0$
ⅴ) Superheated vapor feed : $q < 0$

4.9 Theoretical plate calculations for columns

Example 4.7 – Determine the number of theoretical plates required!

① Top product : 98% nitrogen
② Bottom product : 5% nitrogen, 95% oxygen
③ Feed stream : 79% nitrogen, 21% oxygen
④ Feed stream liquid Molar fraction : 0.831 mol liquid/mol mixture
⑤ The bottom, top product streams leave as sat.liquid
⑥ Bottom product flow rate : 25 mol/s
⑦ Heat removed at the top : 1071 kW
⑧ Mean pressure : 101.3 kPa (1atm)

4.9 Theoretical plate calculations for columns

Example 4.7 – Determine the number of theoretical plates required!

ⅰ) Find flow rates of the feed and top product – Conservation of mass!

$$F = B + D = 25 + D$$
$$x_F F = x_B B + x_D D$$

Substituting in the numerical values,

$$0.79F = (0.05)(25) + 0.98D = 1.25 + 0.98(F - 25)$$

Solving for the feed stream flow rate,

$$F = \frac{(24.5 - 1.25)}{(0.98 - 0.79)} = 122.37 \; mol/s$$

$$D = F - B = 122.37 - 25 = 97.37 \; mol/s$$

4.9 Theoretical plate calculations for columns

Example 4.7 – Determine the number of theoretical plates required!

ⅱ) Applying the First law of thermodynamics to the entire column,

$$\dot{Q}_B = \dot{Q}_D + h_D D + h_B B - h_F F$$

$$h = 1050\,J/mol\ (saturated\ liquid) = h_D = h_B$$
$$H = 6916\,J/mol\,(saturated\ vapor)$$

The enthalpy of the feed stream(two-phase mixture) is,

$$h_F = (0.831)(1050) + (1 - 0.831)(6916) = 2041\,J/mol$$

Using the values in the First law equation,

$$\dot{Q}_B = 1,071,000 + (1050)(97.37) + (1050)(25) - (2041)(122.37)$$
$$\dot{Q}_B = 949,731\,W = 949.731\,kW$$

4.9 Theoretical plate calculations for columns

**Example 4.7 – Determine the number of theoretical plates required!**

ⅲ) Determine the operating line equations

$$\frac{D}{V_n} = \frac{6916 - 1050}{(1{,}071{,}000/97.37) + 1050 - 1050} = 0.5336$$

The reflux ratio,

$$\frac{L_{n+1}}{V_n} = 1 - 0.5336 = 0.4664$$

Operating line for the upper section,

$$y_n = 0.4664 x_{n+1} + (0.5336)(0.98) = 0.4664 x_{n+1} + 0.5229$$

4.9 Theoretical plate calculations for columns

Example 4.7 – Determine the number of theoretical plates required!

$$\frac{B}{V_m} = \frac{6916 - 1050}{(949{,}731/25) - 1050 + 1050} = 0.1544$$

The reflux ratio,

$$\frac{L_{m+1}}{V_m} = 1 + 0.1544 = 1.1544$$

Operating line for the lower section,

$$y_m = 1.1544x_{m+1} - (0.05)(0.1544) = 1.1544x_{m+1} - 0.00772$$

4.9 Theoretical plate calculations for columns

Example 4.7 – Determine the number of theoretical plates required!

The equation for the feed line,

$$q = \frac{6916 - 2041}{6916 - 1050} = 0.831$$

We obtain feed line,

$$y = \frac{0.79}{1 - 0.831} - \frac{0.831}{1 - 0.831}x = 4.6746 - 4.9172x$$

4.9 Theoretical plate calculations for columns

Example 4.7 – Determine the number of theoretical plates required!

The equation for the feed line,

$$q = \frac{6916 - 2041}{6916 - 1050} = 0.831$$

We obtain feed line,

$$y = \frac{0.79}{1 - 0.831} - \frac{0.831}{1 - 0.831}x = 4.6746 - 4.9172x$$

4.10 Minimum # of theoretical plates
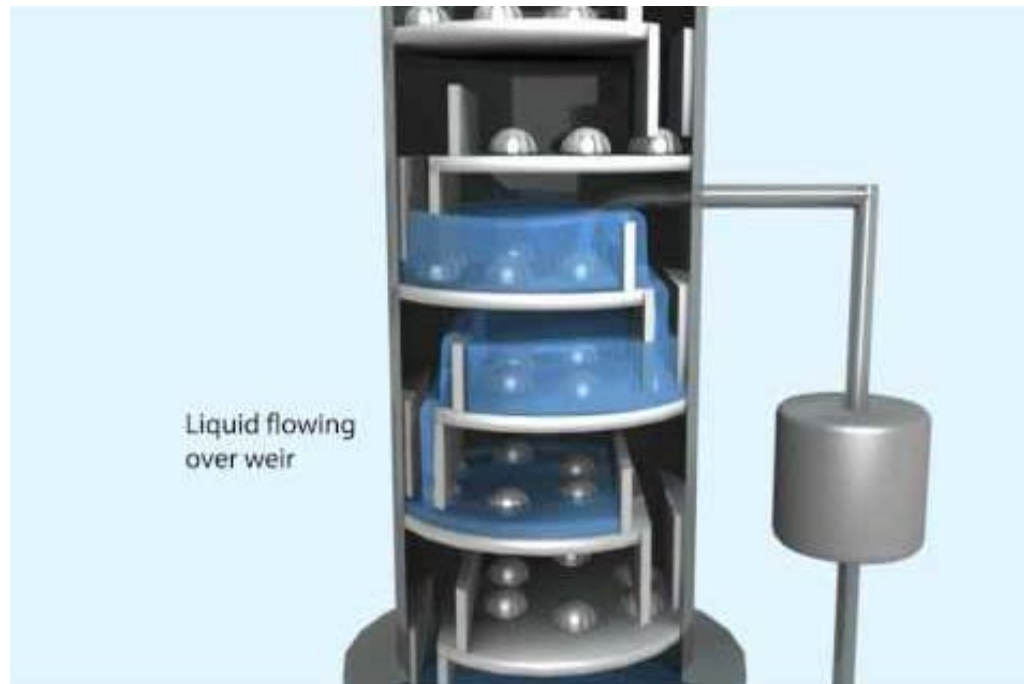
Rectification column

4.10 Minimum # of theoretical plates
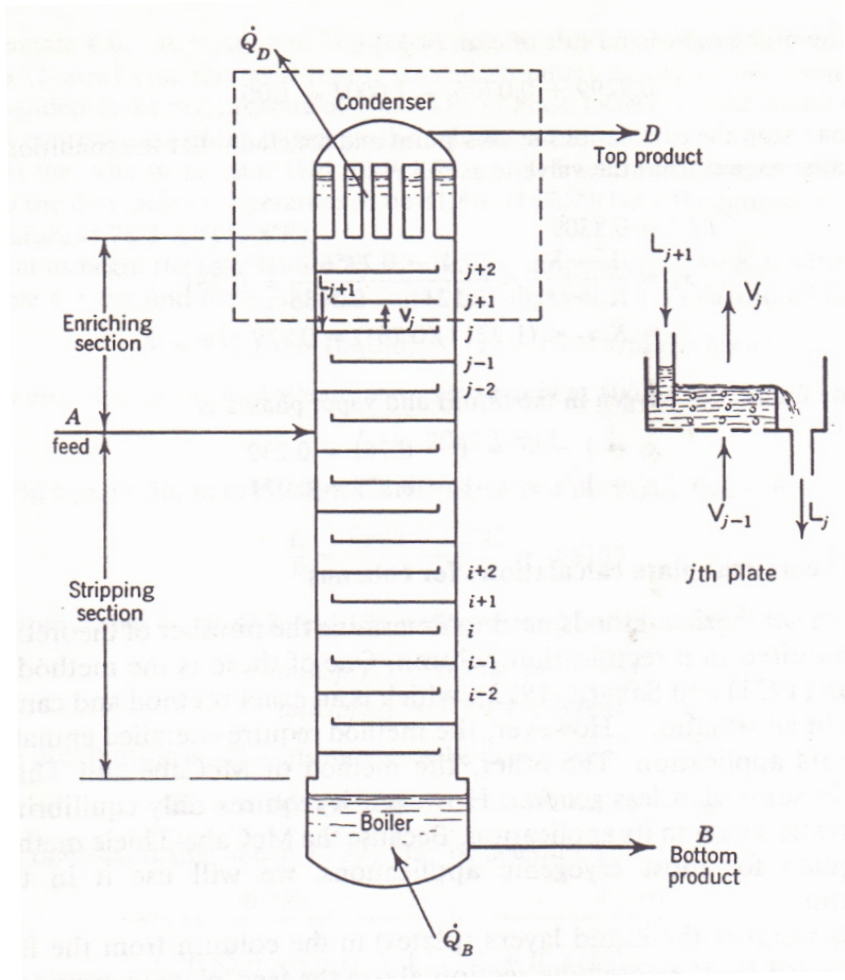
System used in the development of the theoretical-plate equations. The flow rate of vapor *leaving* the nth plate is denoted by V_n and the flow rate of the liquid *leaving* the nth plate is denoted by L_n

4.10 Minimum # of theoretical plates

Minimum number of theoretical plates
→ when the slope of the operating lines approach unity

Upper operating line

$$y_n = \frac{L_{n+1}}{V_n} x_{n+1} + \frac{D}{V_n} x_D$$

Lower operating line

$$y_m = \frac{L_{m+1}}{V_m} x_{m+1} - \frac{B}{V_m} x_B$$

4.10 Minimum # of theoretical plates
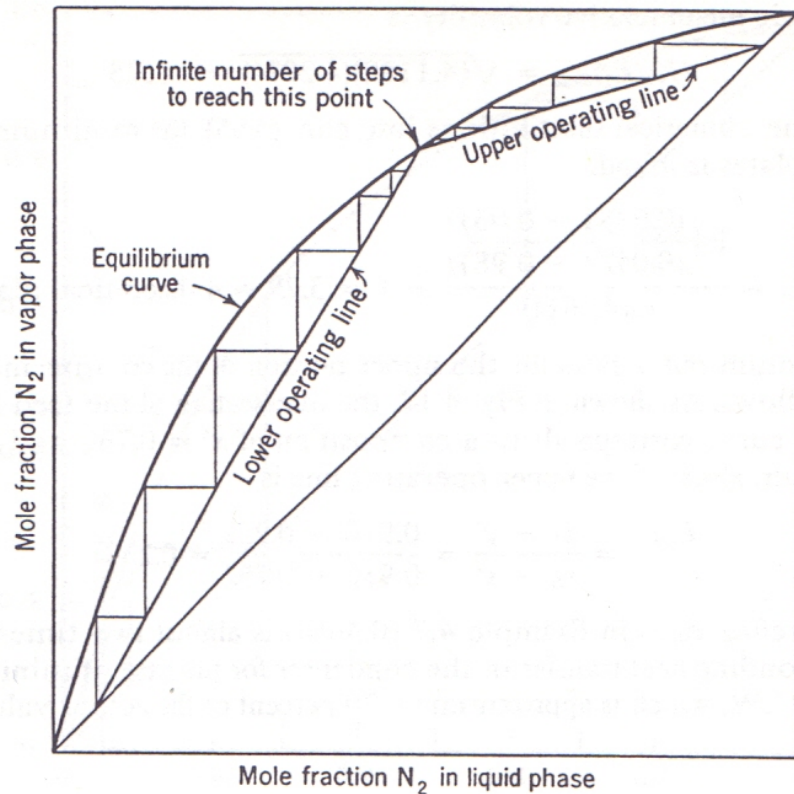
Minimum refrigeration
$$Q_D \downarrow$$
Requirement of an infinite number of theoretical plates

4.11 Types of rectification columns

- **Packed column**

-Cylinders filled with a packing material such as metallic rings and wire gauze

-The packing material provides a large surface area

-This type of column is not so frequently used in cryogenic systems

ex) diffuser

4.11 Types of rectification columns

▪**Plate column**

-Several plates to allow the vapor to bubble through the

liquid on the plate

-Small holes

-Fine mesh

-Bubble cap

4.11 Types of rectification columns
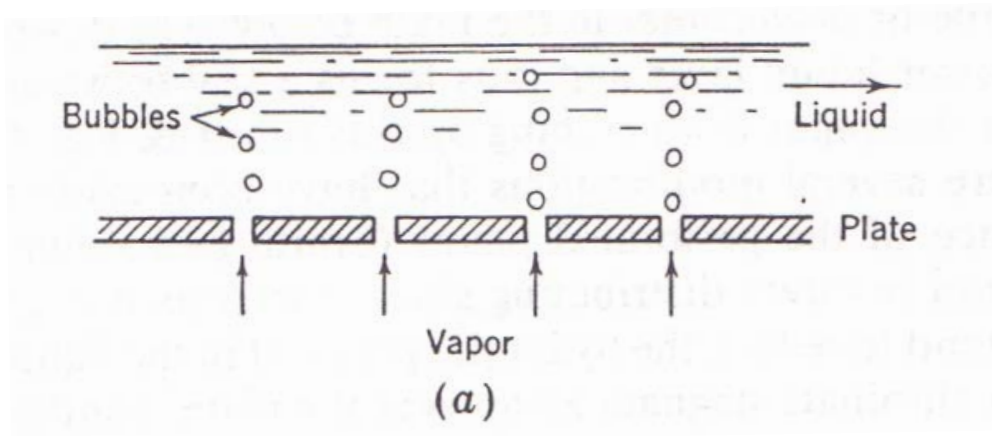
(a) Perforated plate

4.11 Types of rectification columns
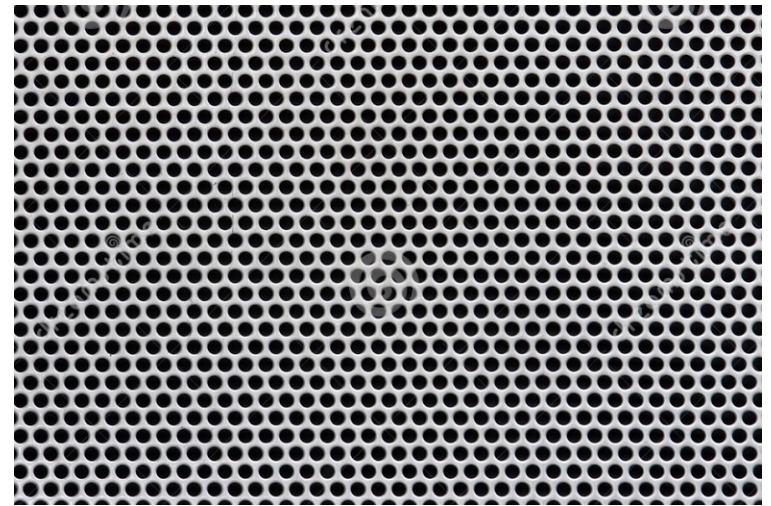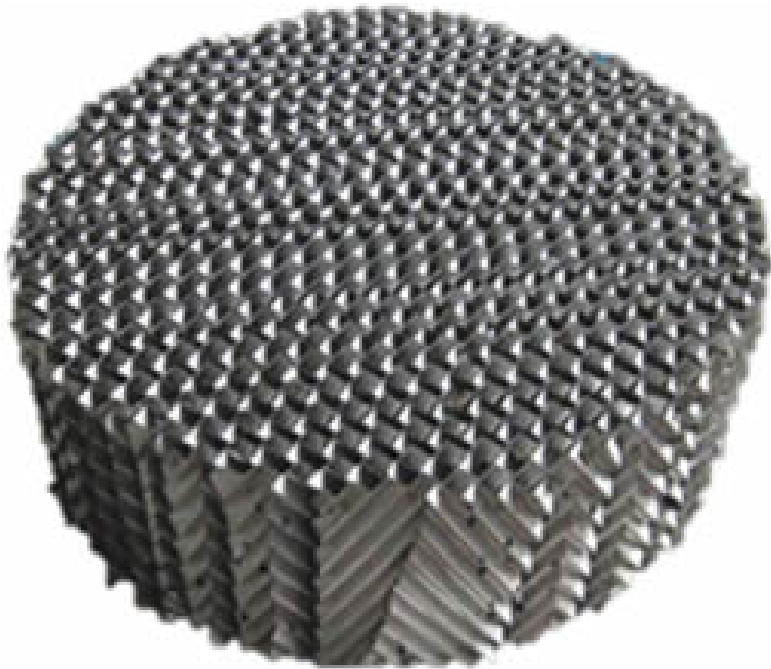
Perforated plates

4.11 Types of rectification columns
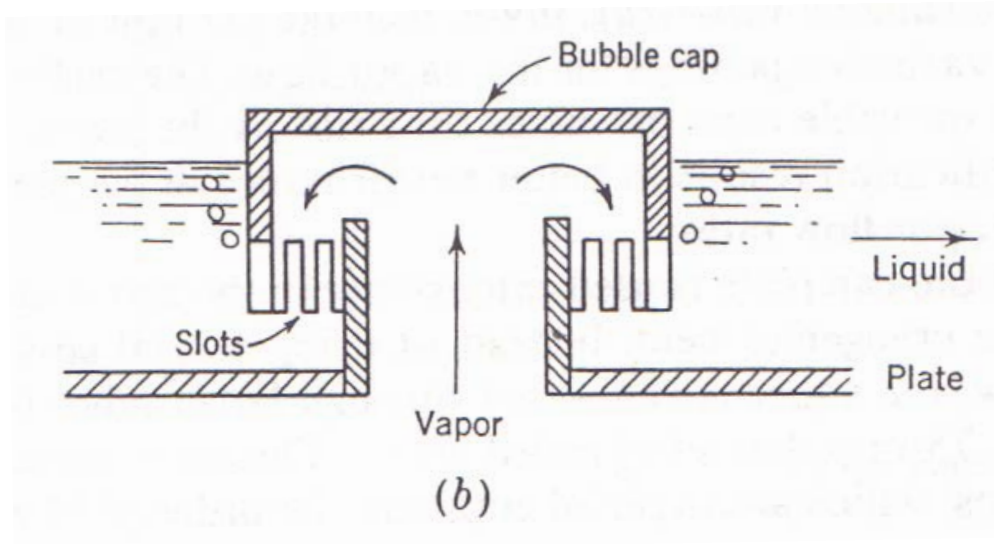
(b) bubble-cap plate

4.11 Types of rectification columns

Bubble-cap trays

4.12 Linde single-column system
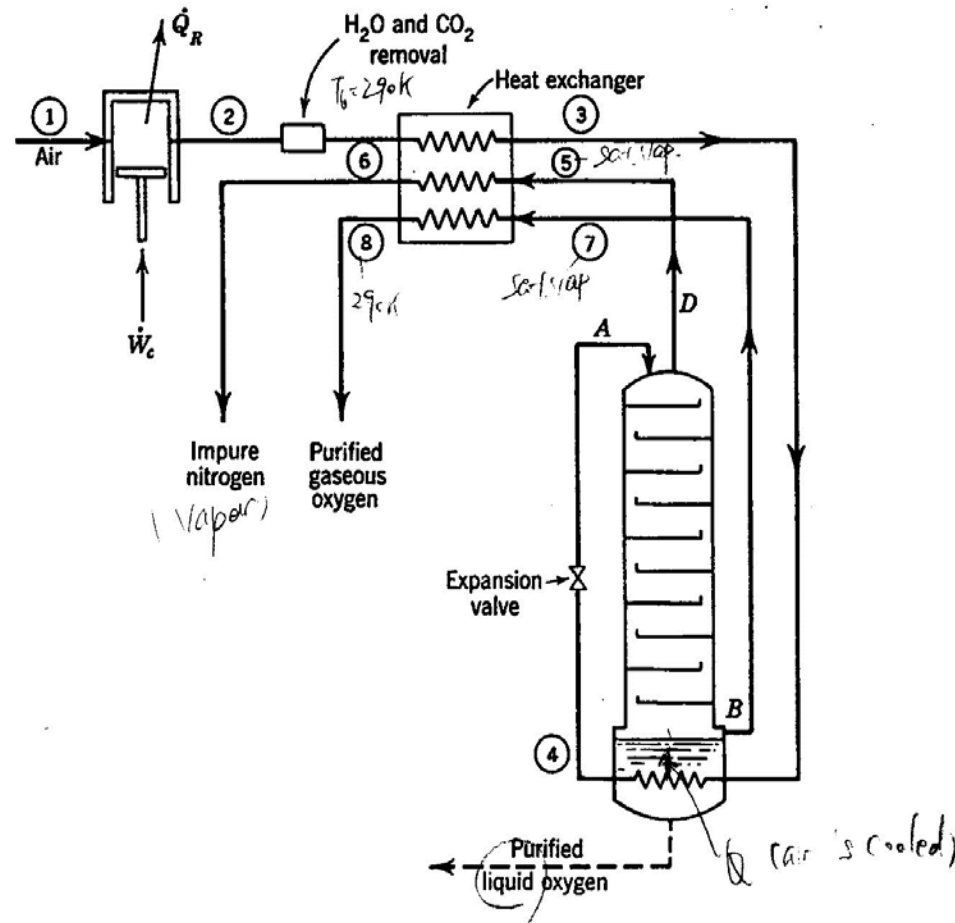
Fig. Linde single-column gas-separation system

4.13 Linde double-column system
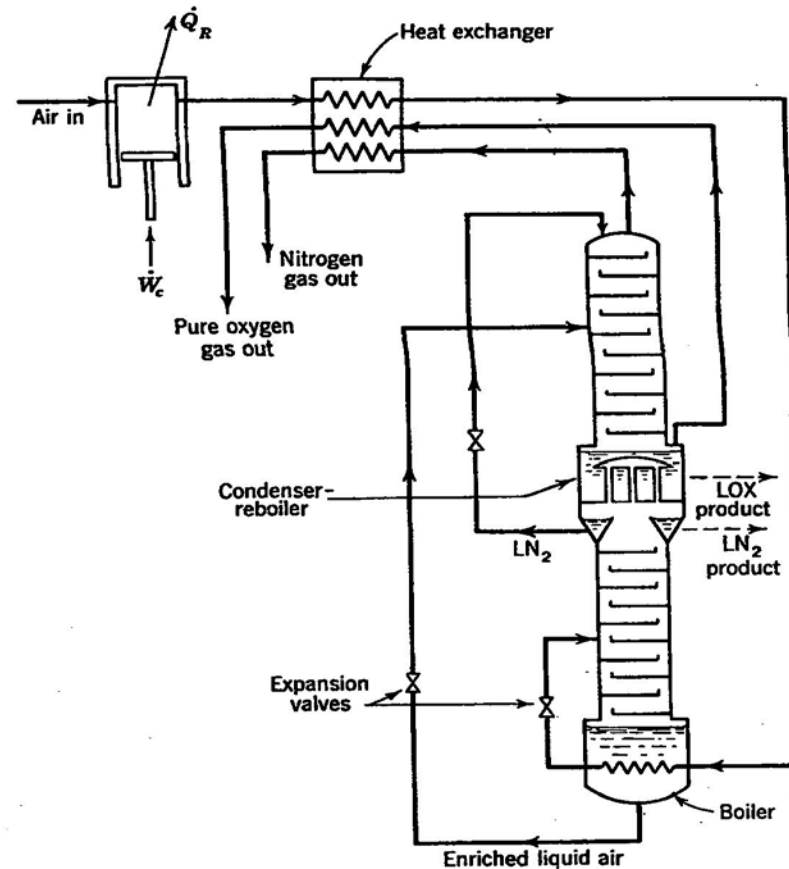
Fig. Linde double-column gas-separation system. If the product were desired in the liquid phase, the heat exchanger would be a two-channel heat exchanger, and The stream marked "pure oxygen gas out" would not be present

4.13 Linde double-column system

- The Linde single-column system has two serious disadvantages.

  1. Only pure oxygen can be produced

  2. Large quantities of oxygen are wasted in the impure nitrogen exhaust gas

4.14 Linde-Frankl system
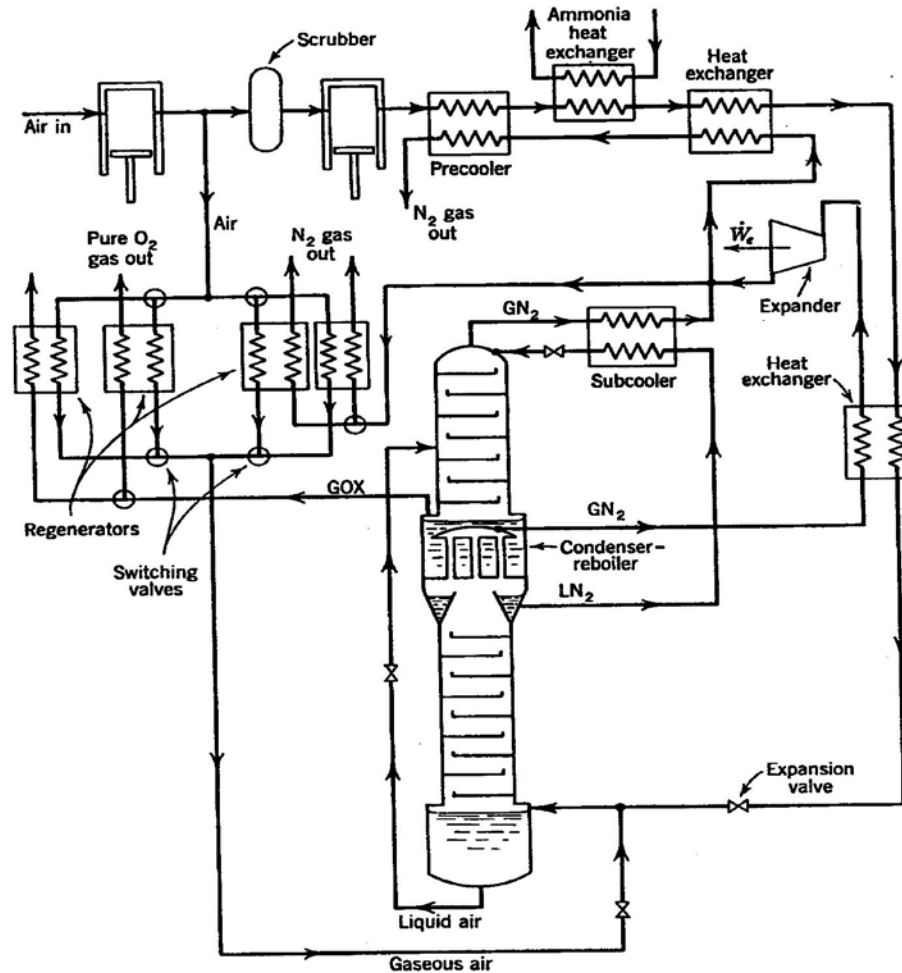
Fig. Linde-Frankl gas-separation system

4.15 Heylandt system
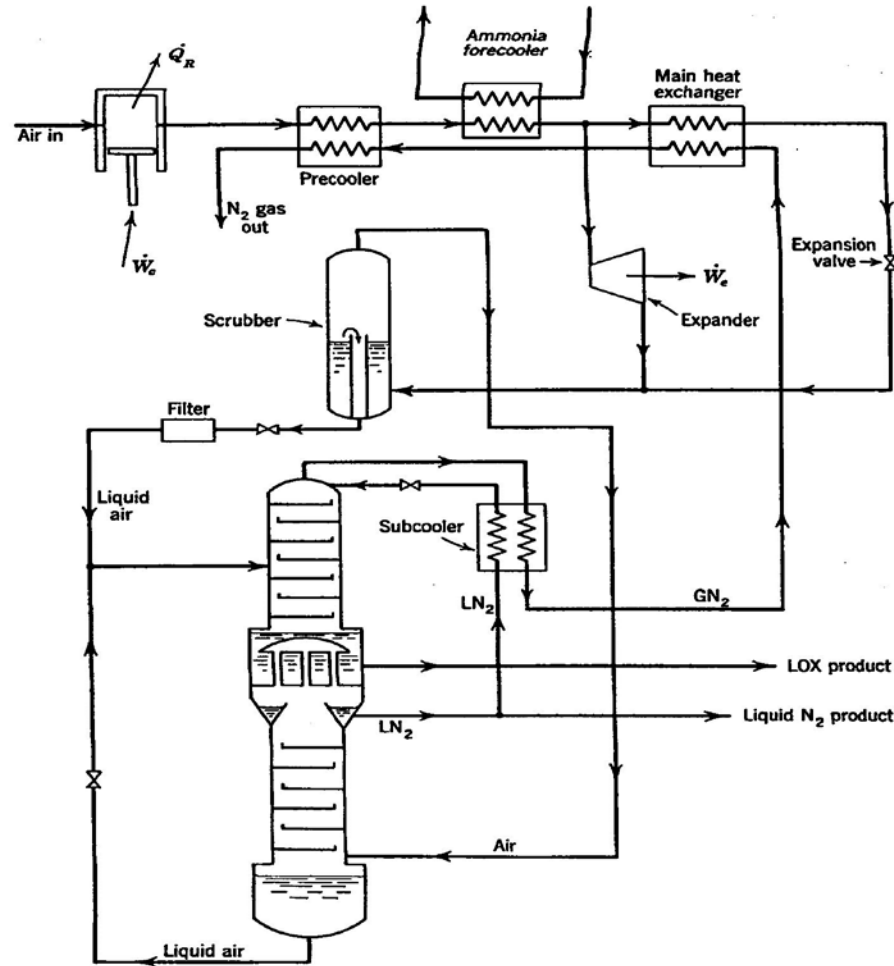
Fig. Heylandt gas-separation system

4.15 Heylandt system

● Schematics and pictures of Air separation systems
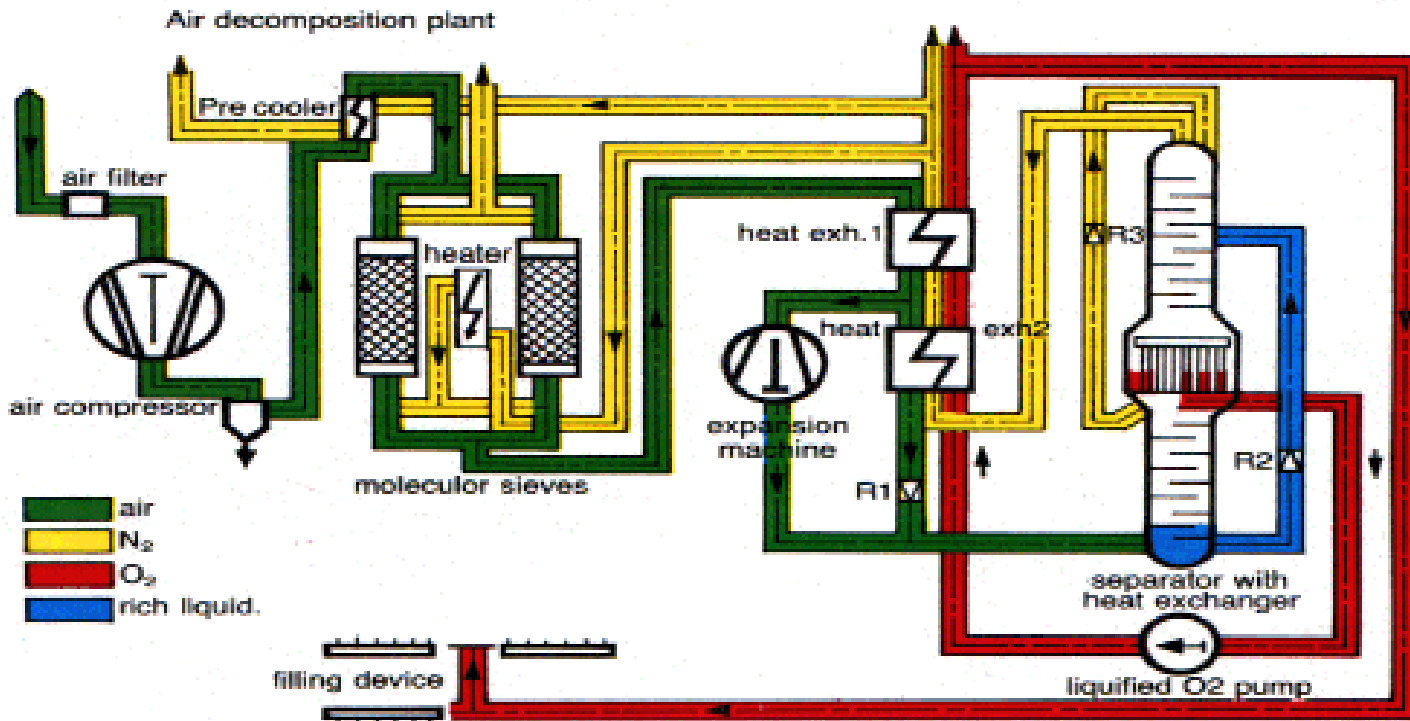
Fig. Air separation plant

4.15 Heylandt system

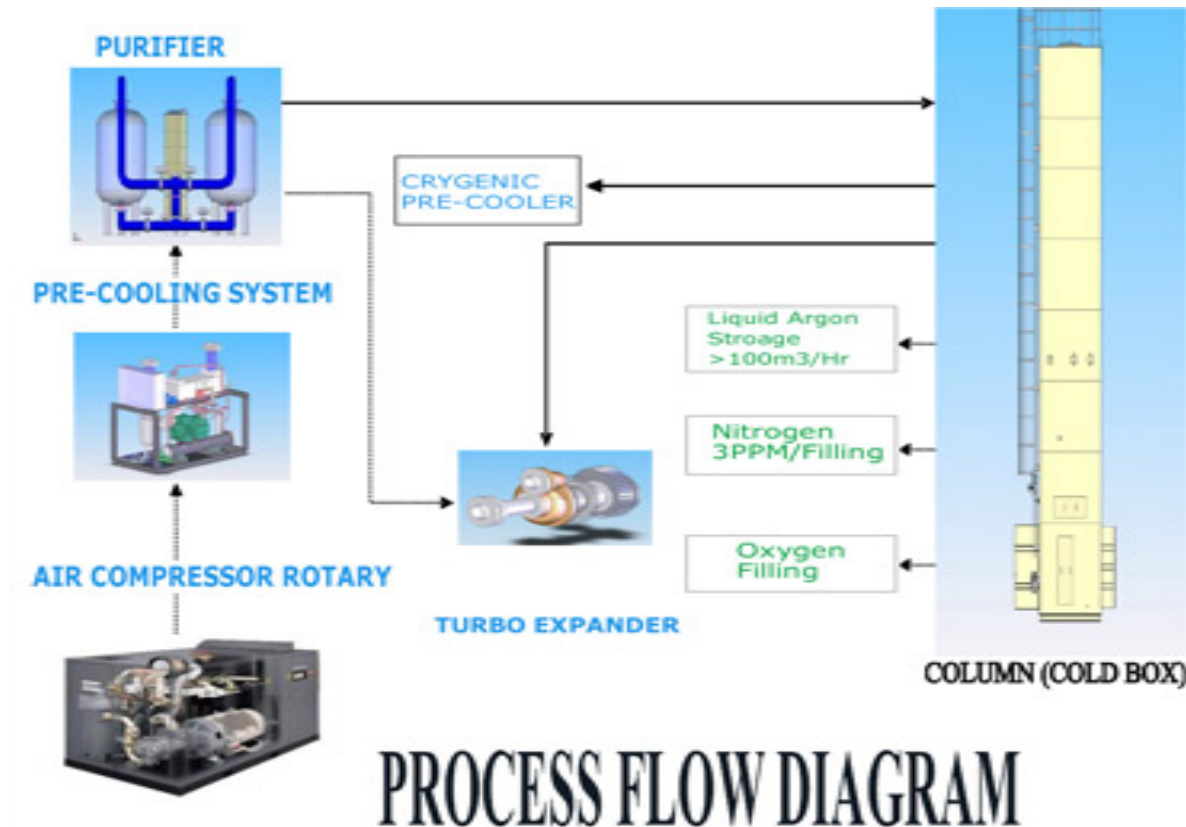● Schematics and pictures of Air separation systems
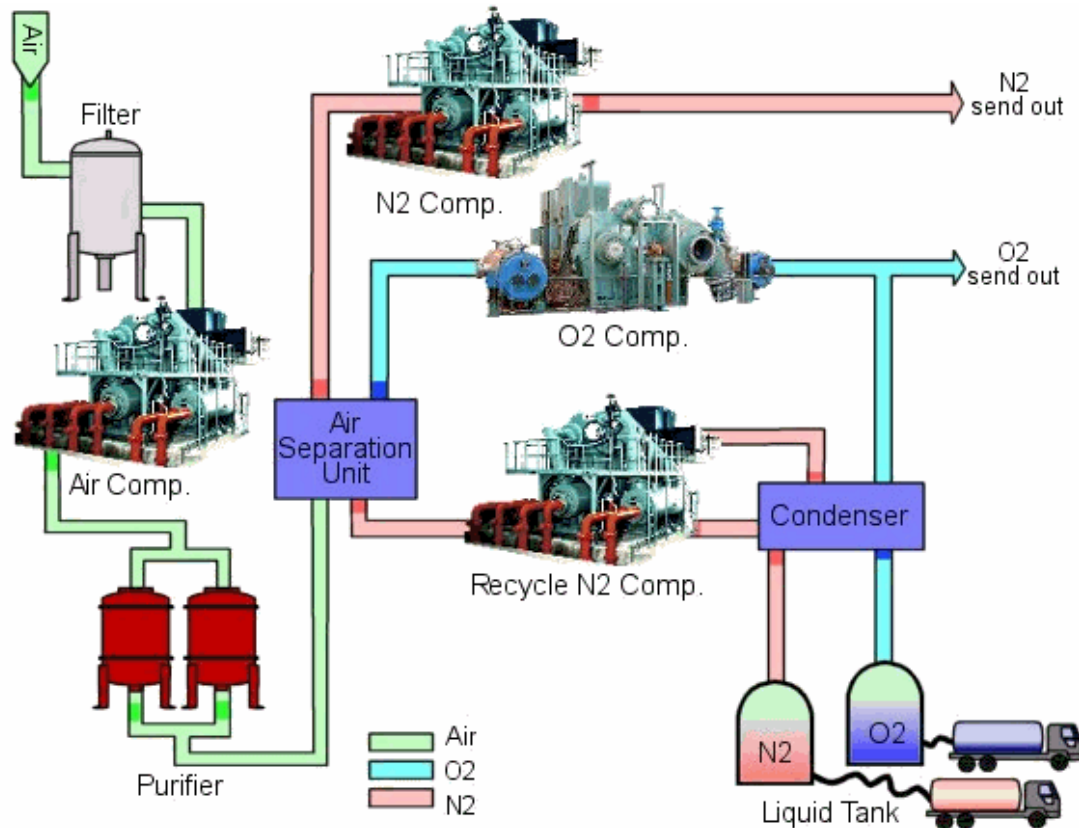
Fig. Air separation plant

4.15 Heylandt system

● Schematics and pictures of Air separation systems

Fig. Air separation process flow diagram

4.15 Heylandt system

■ Schematics and pictures of Air separation systems

Fig. Real pictures of air separation systems

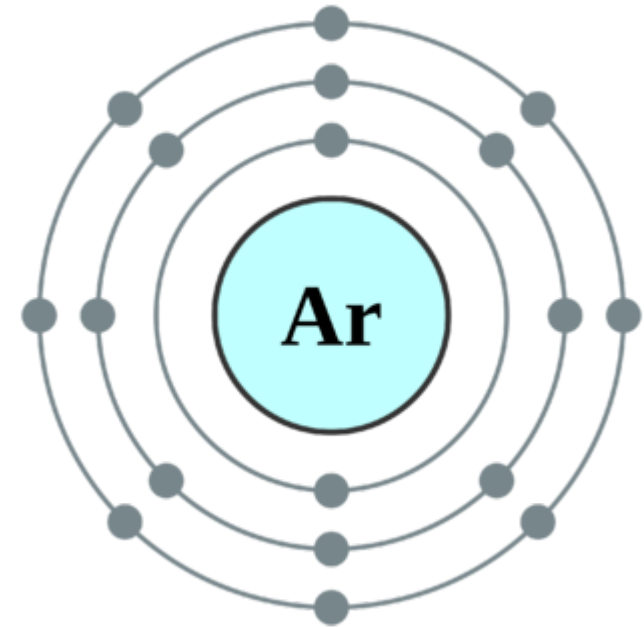# 4.16 Argon-separation system

▪ Introduction to Argon
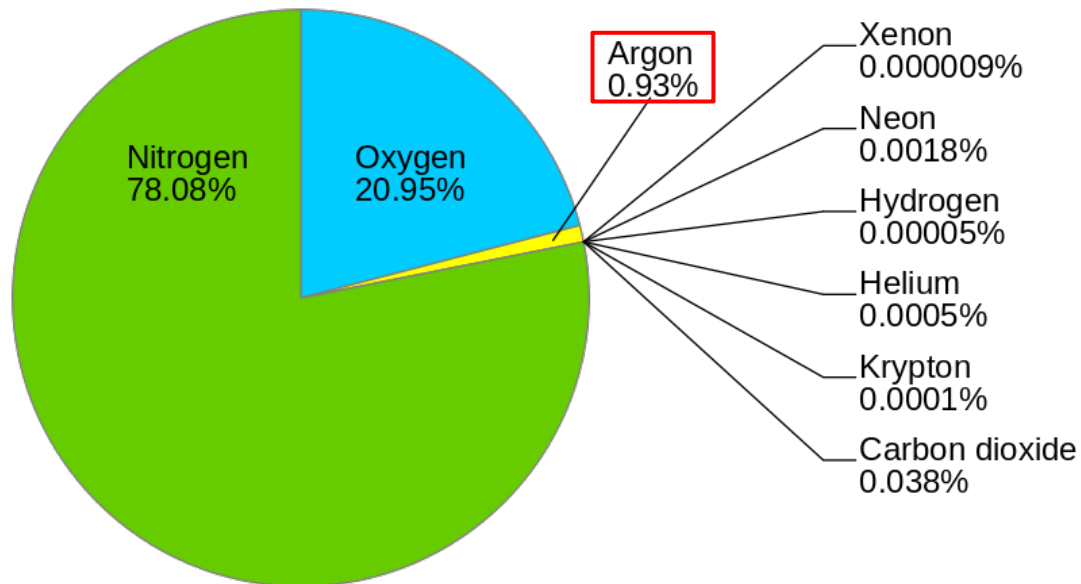
Fig. Composition of dry atmospheric air

Argon

• NBP: 87.302K at 1atm

4.16 Argon-separation system

- **The argon-separation system usually consists of two basic parts**

  - **A recovery subsystem**

  - **The purification subsystem**

    - **The catalytic-combustion system**

    - **The adsorption system**

Fig. Air separation system for Argon
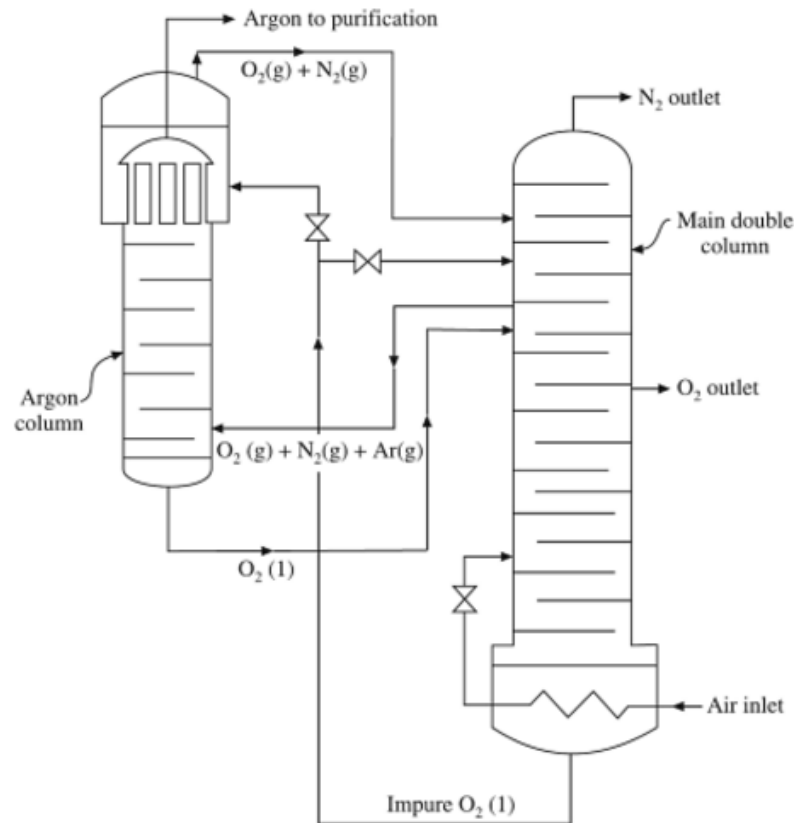
4.16 Argon-separation system

- **A Recovery Subsystem**

Fig. Argon recovery subsystem

4.16 Argon-separation system

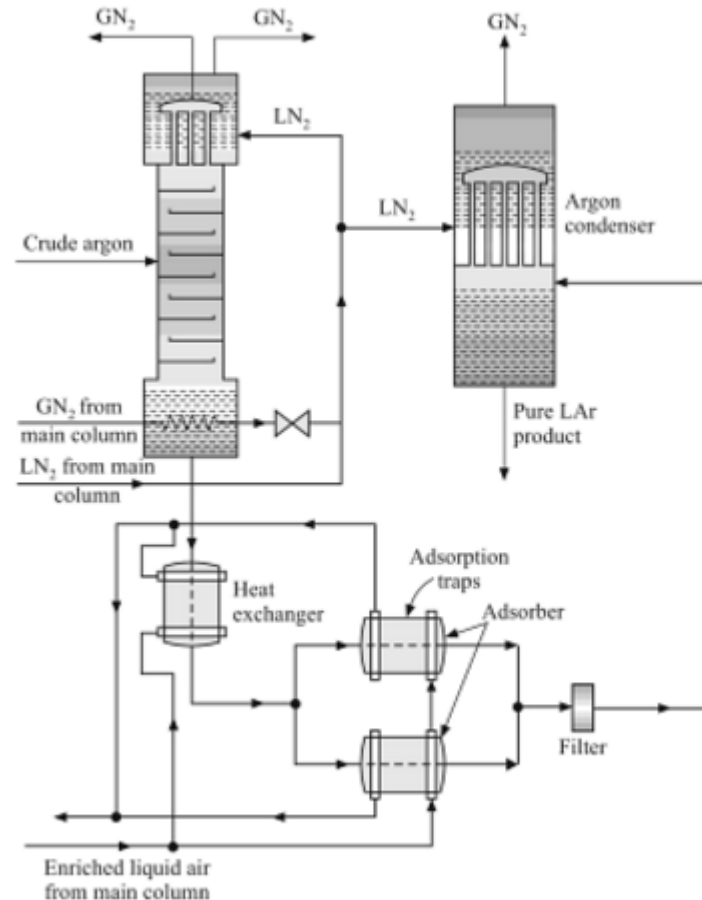▪ **The purification system (adsorption system)**

Fig. Argon purification subsystem using an absorption trap to remove the oxygen

4.16 Argon-separation system

▪ **The purification system (catalytic-combustion system)**
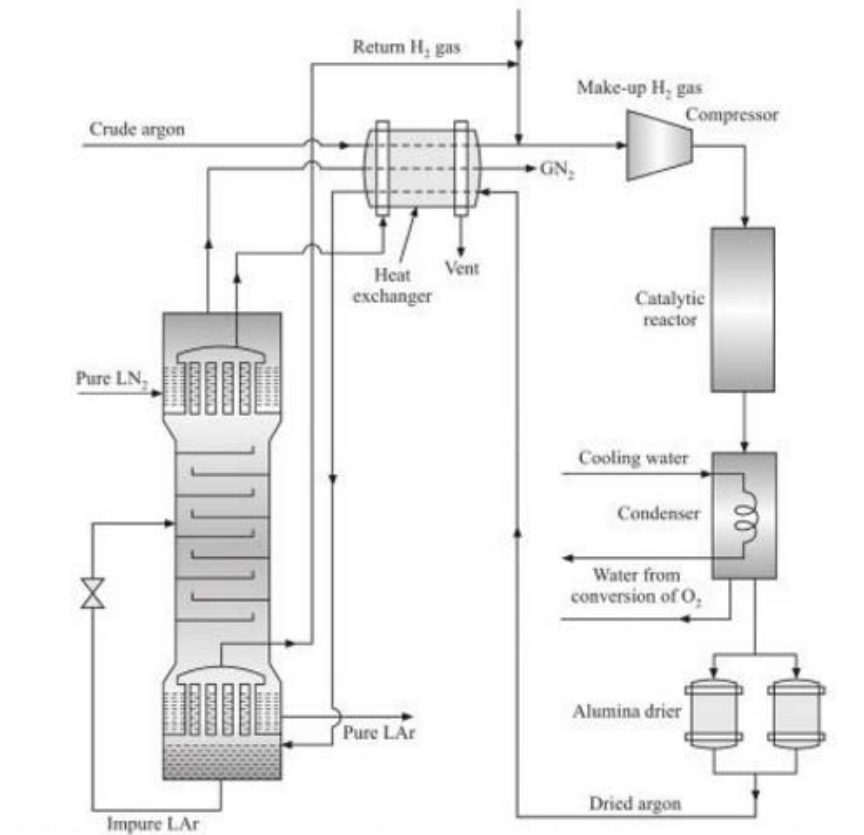

Fig. Argon-purification subsystem using catalytic combustion with hydrogen
    to remove the oxygen
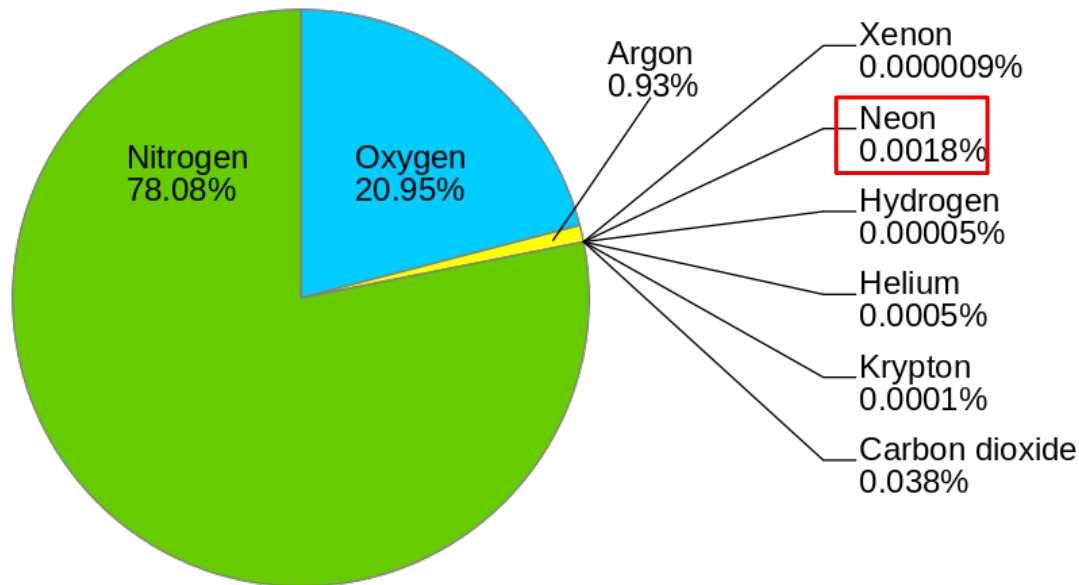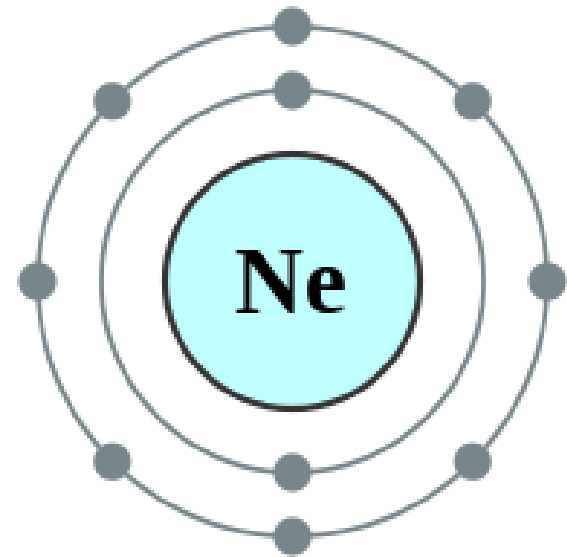
4.17 Neon-separation system

■ Introduction to Neon

Fig. Composition of dry atmospheric air

Neon

- NBP: 27.3K at 1atm

4.17 Neon-separation system

■ The neon-separation system usually consists of two basic parts

- A recovery subsystem
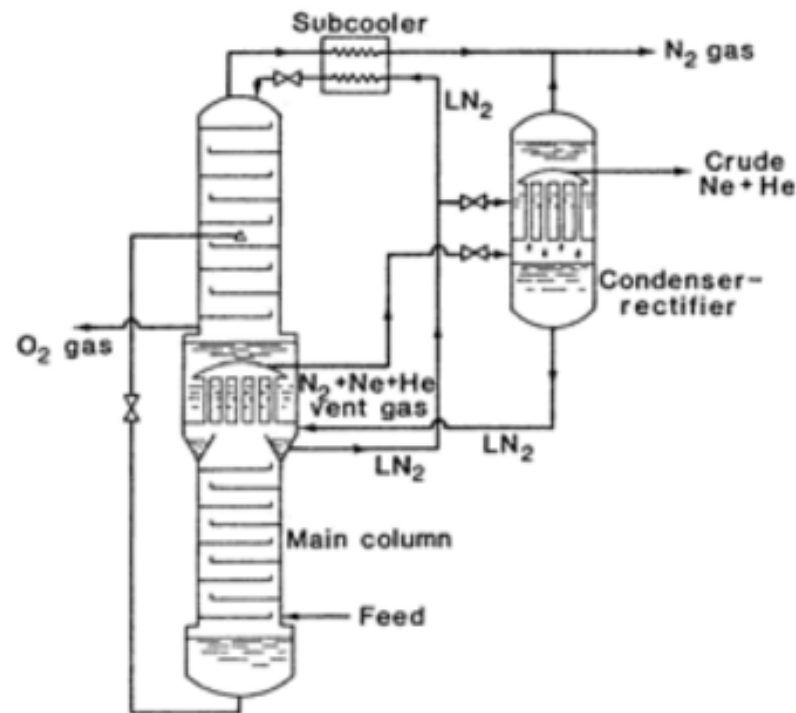
- The purification subsystem

Fig. Neon-recovery subsystem
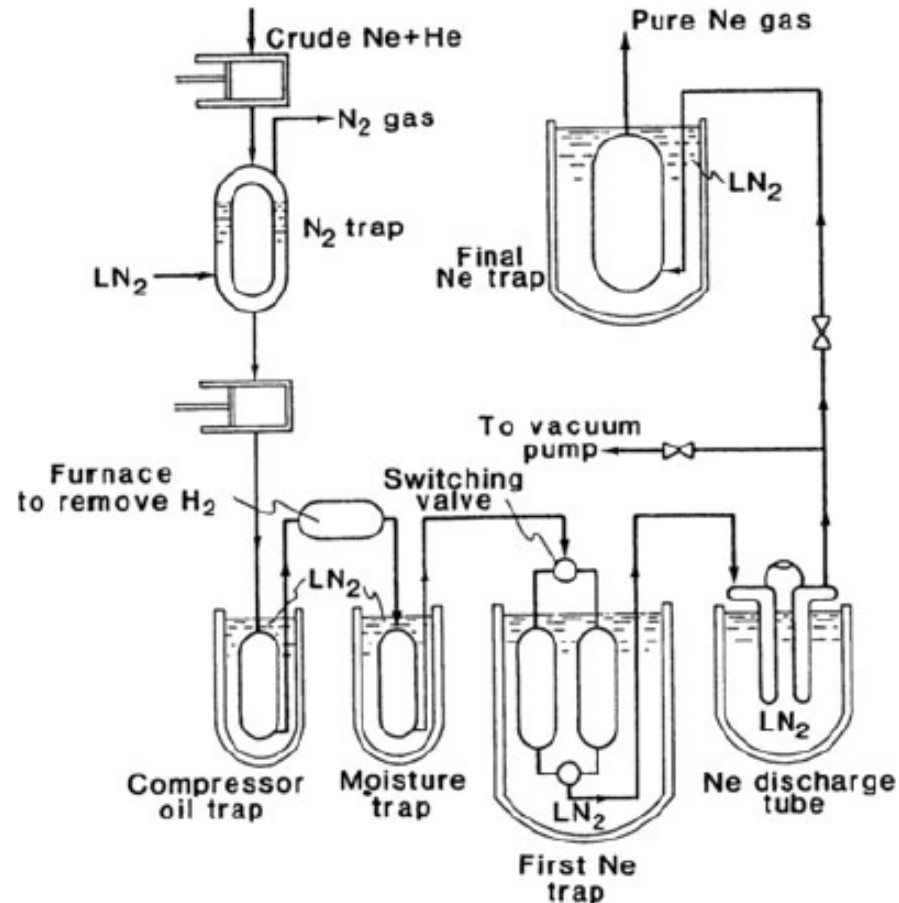
4.17 Neon-separation system

▪ **The purification system**

Fig. Neon-purification subsystem utilizing charcoal adsorption

4.18 Hydrogen-separation systems

■ **Several methods for obtaining hydrogen gas**

- Cryogenic treatment of coke-oven gas or other hydrogen-rich by-product stream
- Reforming natural gas
- Partial oxidation of crude oil
- Electrolysis of water
- Ammonia dissociation
- Passing steam over heated iron
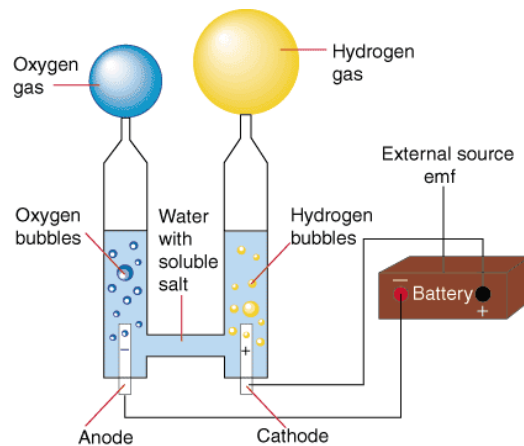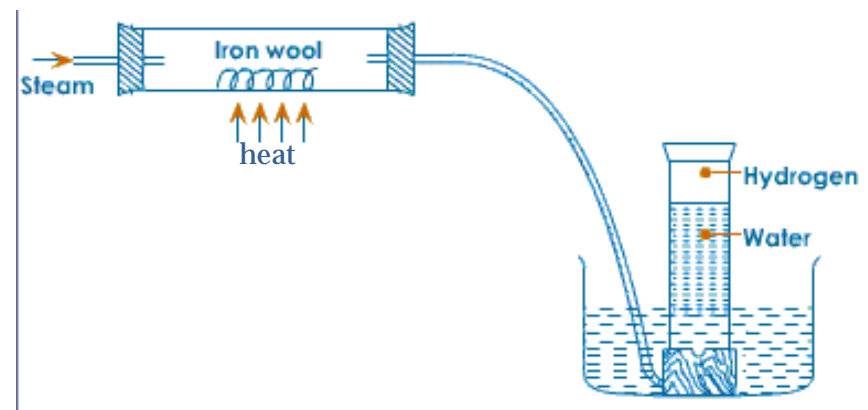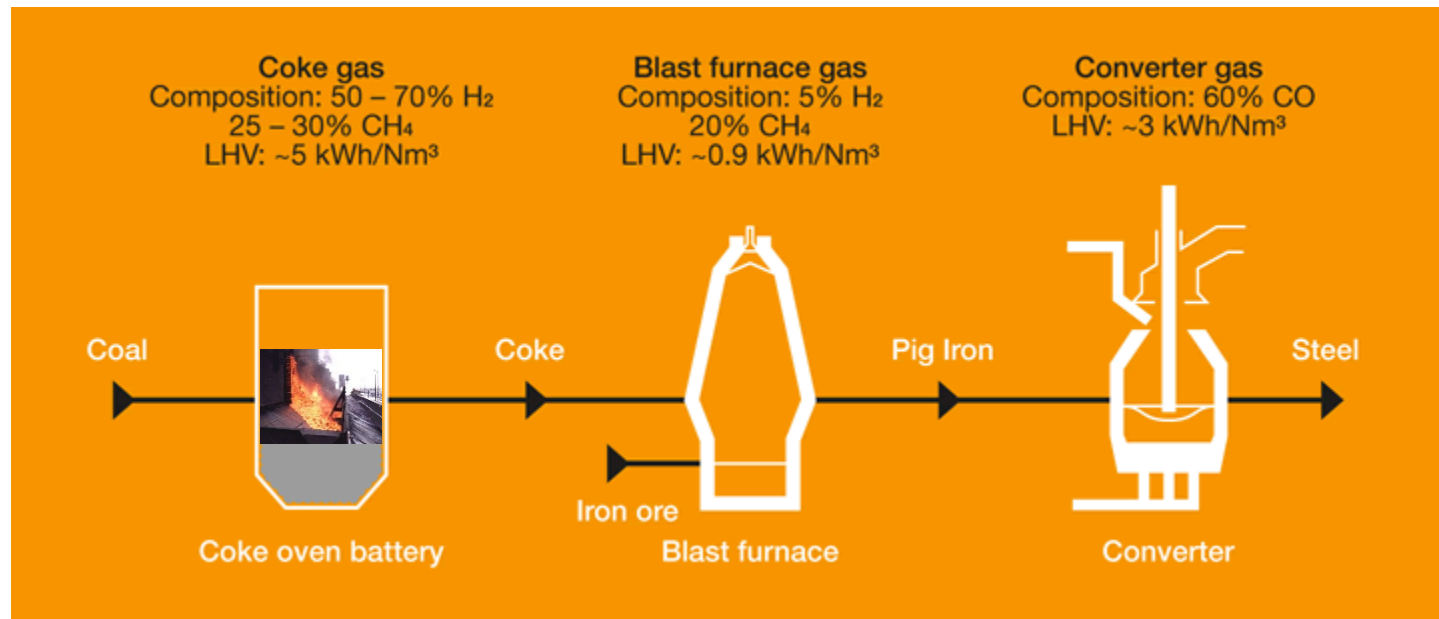- Thermal decomposition of hydrocarbons

Fig. Electrolysis of water   Fig. Passing steam over heated iron

4.18 Linde-Bronn system

▪ Coke-oven gas

Coke-oven gas is a fuel gas having a medium calorific value that is produced during the manufacture of metallurgical coke by heating bituminous coal to temperatures of 900°C to 1000°C in a chamber from which air is excluded. The main constituents are, by volume, about 50% hydrogen, 30% methane and 3% higher hydrocarbons, 7% carbon monoxide, 3% carbon dioxide and 7% nitrogen. The gas has a heating value of about 20,000 kJ/m3.

Coke gas
Composition: 50 – 70% H_2
25 – 30% CH_4
LHV: ~5 kWh/Nm³

Blast furnace gas
Composition: 5% H_2
20% CH_4
LHV: ~0.9 kWh/Nm³

Converter gas
Composition: 60% CO
LHV: ~3 kWh/Nm³

Coal   Coke   Pig Iron   Steel

Iron ore

Coke oven battery   Blast furnace   Converter

4.18 Linde-Bronn system

▪ **Chemical composition of some common gaseous fuels**

	Composition (Percent by Volume)									
Fuel	Carbon Dioxide (CO_2)	Carbon Monoxide (CO)	Methane (CH_4)	Butane (C_4H_{10})	Ethane (C_2H_6)	Propane (C_3H_8)	Hydrogen (H_2)	Hydrogen Sulfide (H_2S)	Oxygen (O_2)	Nitrogen (N_2)
Carbon Mon oxide		100								
Coal Gas	3.8	28.4	0.2				17.0			50.6
Coke Oven Gas	2.0	5.5	32				51.9		0.3	4.8
Digester Gas	30		64				0.7	0.8		2.0
Hydrogen							100			
Landfill Gas	47	0.1	47				0.1	0.01	0.8	3.7
Natural Gas	0 - 0.8	0 - 0.45	82 - 93		0 - 15.8		0-1.8	0 - 0.18	0 - 0.35	0.5 - 8.4
Propane Gas				0.5 - 0.8	2.0 - 2.2	73 - 97				

4.18 Linde-Bronn system
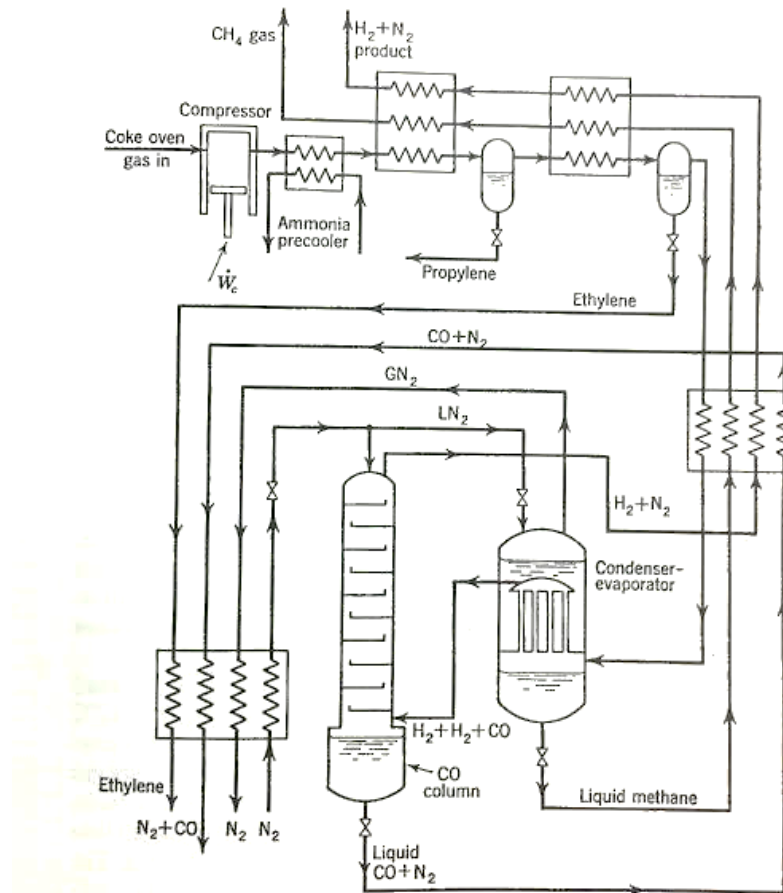
▪ **Linde-Bronn system**

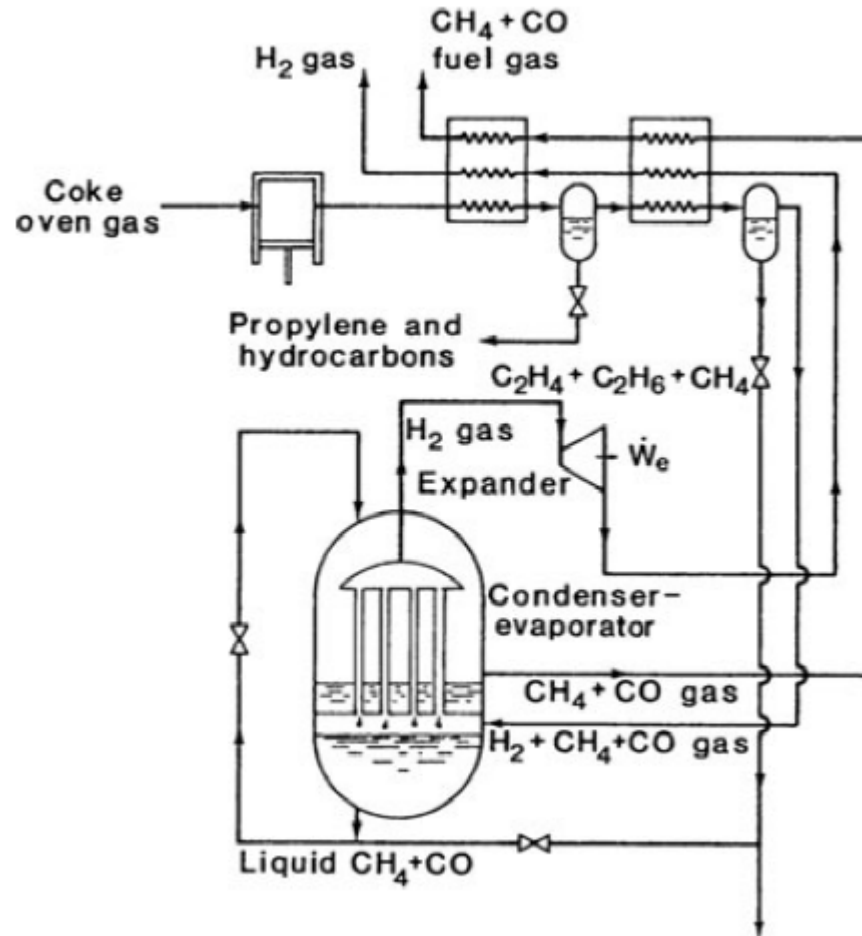
< Linde-Bronn system >

4.19 l'Air Liquide system

■ **The Societe l'Air Liquide system**

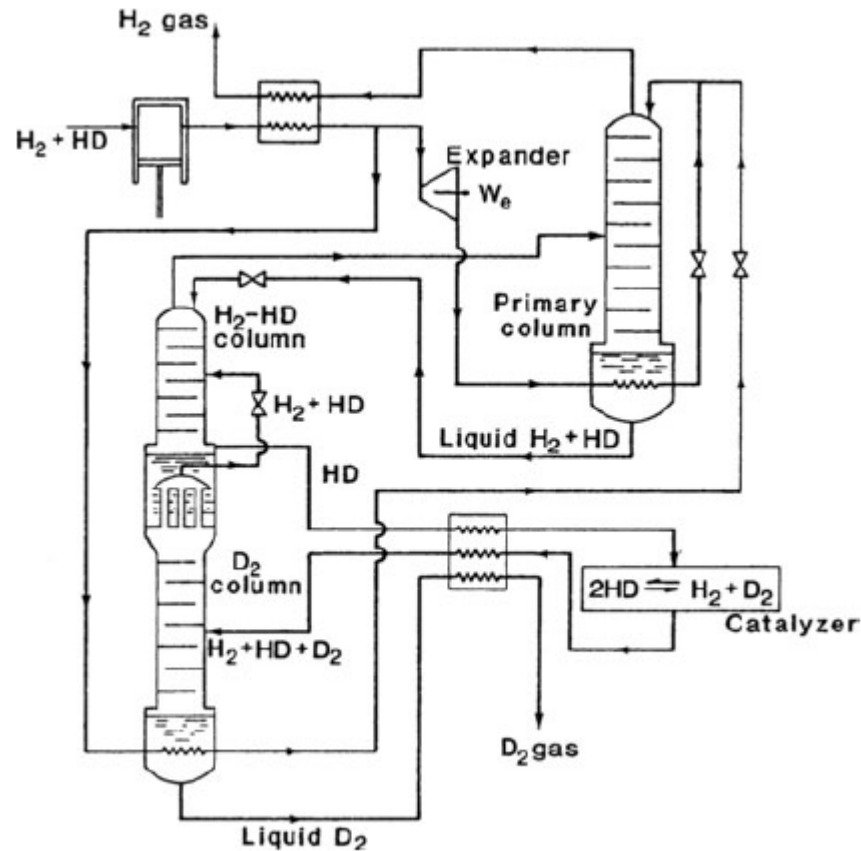< The Societe l'Air Liquide system >

4.20 Hydrogen-deuterium separation systems

▪ **Hydrogen-deuterium separation system**

< Hydrogen-deuterium separation system >

4.21 Helium separation from natural gas

▪ **Uses of helium**
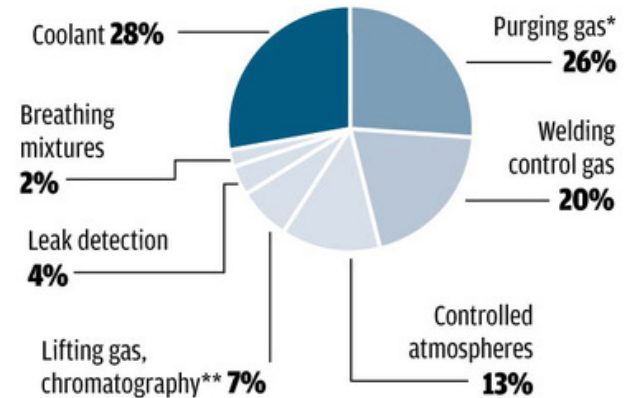
< The uses of helium in industry >

4.21 Helium separation from natural gas

■ **U.S Bureau of Mines for the separation of helium-rich natural gas**
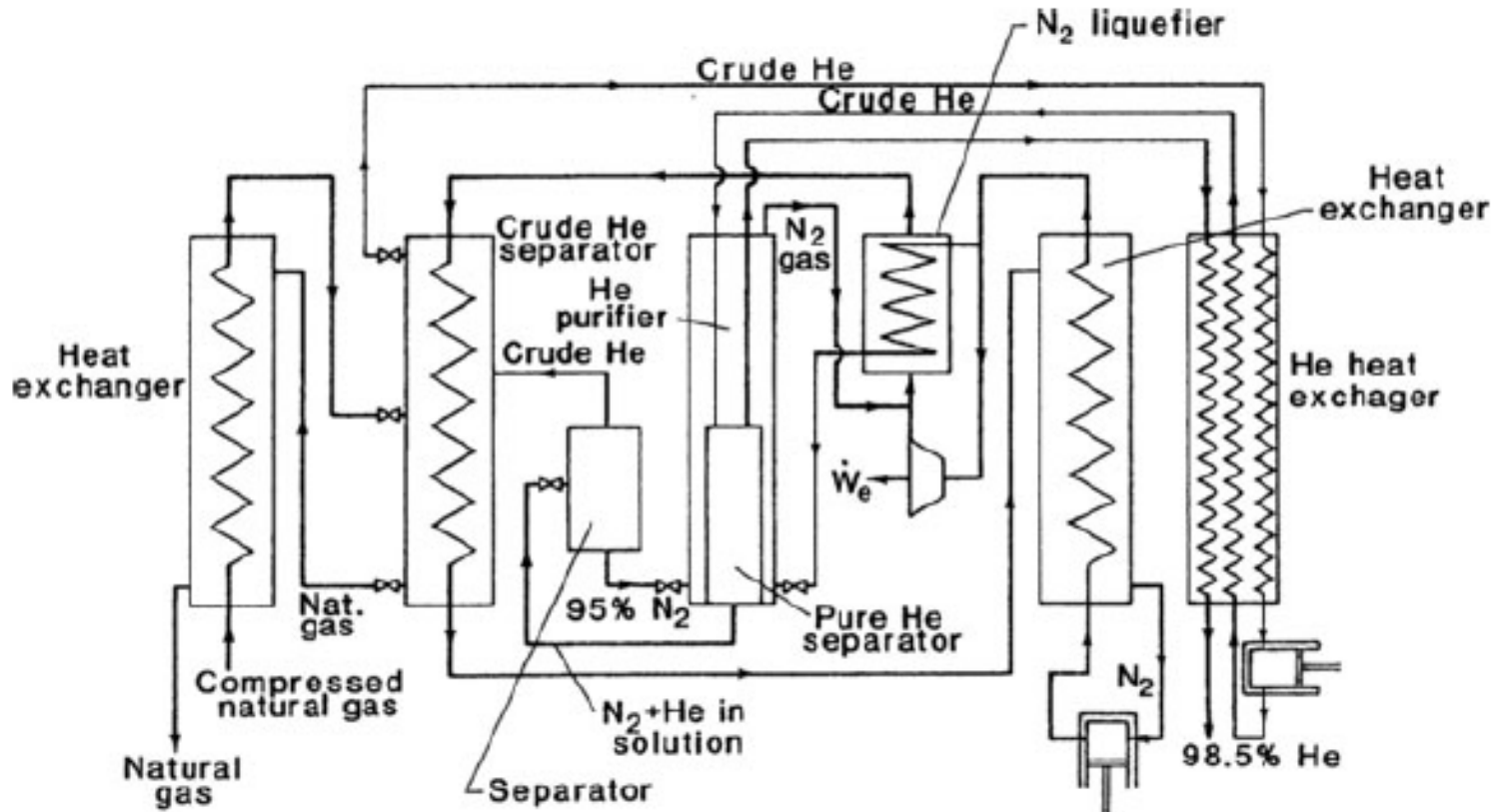
< Schematic diagram of a United States Bureau of Mines helium separation plant >

4.22 Refrigeration purification

▪ **Clapeyron equation**

$$\frac{dp}{dT}\bigg]_{sat} = \frac{s_g - s_f}{v_g - v_f} = \frac{h_{fg}}{T(v_g - v_f)}$$

$v_g = saturated - vapor\ specific\ volume$
$v_f = saturated - liquid\ specific\ volume$
$s_g = saturated - vapor\ entropy$
$s_f = saturated - liquid\ entropy$
$h_{fg} = heat\ of\ vaporization$

$$h_{fg} = A - BT$$

$A, B = constants\ that\ depend\ upon\ the\ substance$

$$v_g = \frac{RT}{p}\ (at\ low\ pressures; ideal\ gas)$$

4.22 Refrigeration purification

▪ **The expression for the vapor-pressure curve**

$$\frac{dp}{dT}\bigg]_{sat} = \frac{P(A - BT)}{RT^2}$$

$$\boxed{\ln\left(\frac{p}{p_0}\right) = C_1 - \frac{C_2}{T} - C_3 \ln T}$$: The expression for the vapor-pressure curve

| Component	C_1	C_2	C_3
Acetylene			
Above 192.4 K	48.02186	3227.716	5.89590
Below 192.4 K	6.61698	2390.926	-1.14947
Ammonia	32.47835	3651.233	3.14837
Butane	39.42435	3998.688	4.41474
Carbon dioxide			
Above 216.6 K	20.23206	2342.869	1.44734
Below 216.6 K	6.09712	2816.149	-1.58721
Carbon monoxide			
Above 68.2 K	18.74780	908.1219	1.73345
Below 68.2 K	48.03457	1357.805	7.10787
Ethane	22.44295	2211.727	2.00404
Ethylene	23.85846	2077.362	2.25908
Methane	14.04585	1119.925	0.84985
Nitrogen	15.07543	795.7286	1.10112
Oxygen	16.45239	967.5537	1.27156
Propane	24.44777	2883.487	2.19931
Water			
Above 273.1 K	46.45934	6731.423	4.79561
Below 273.1 K	19.68116	6233.177	0.34756

4.23 Physical adsorption

▪ **Adsorption**

Adsorption is when one substance just hangs onto the outside of another. Think of people holding onto a car trolley with one hand and leaning off the side. They're along for the ride but not inside.
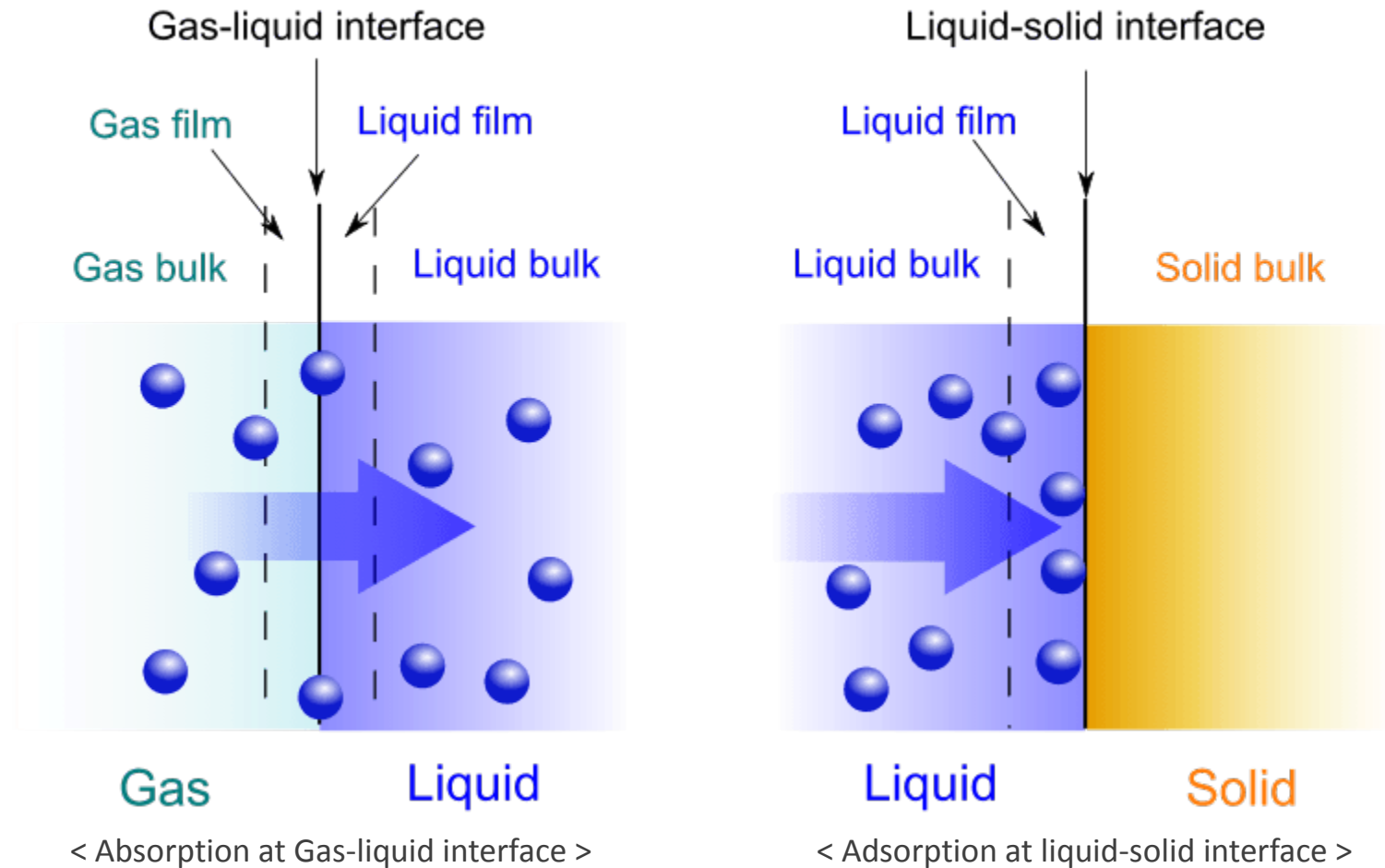
▪ **Absorption**

Absorption is when one substance enters completely into another. Think of people walking into and sitting down in a car trolley.
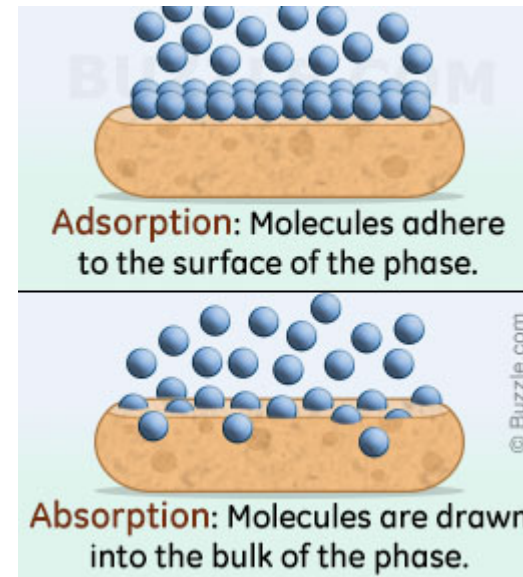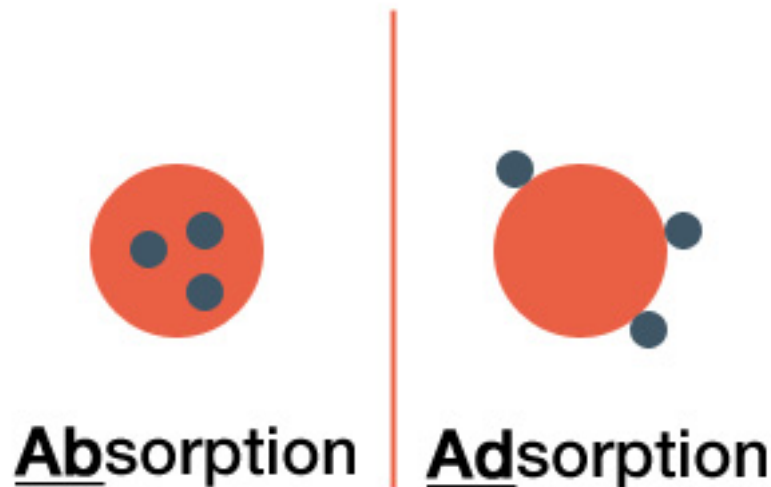
4.23 Physical adsorption

- **Absorption and adsorption at Gas-liquid and liquid-solid interfaces respectively**

< Absorption at Gas-liquid interface >   < Adsorption at liquid-solid interface >

4.23 Physical adsorption

- **Purifier using a refrigeration purifier and an adsorption purifier in series**