

CRYOGENIC ENGINEERING



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Lecture No - **22**

Earlier Lecture

- In the earlier lecture, we have studied Dalton's Law, Raoult's Law and Gibbs – Dalton's Law.
- These Laws relate vapor and liquid fractions of a component in a mixture at a given temperature and pressure.
- Distribution Coefficient (**K**) is a constant and it depends on temperature and pressure.
- **K** is meaningful and defined only in two phase region of a mixture.

Outline of the Lecture

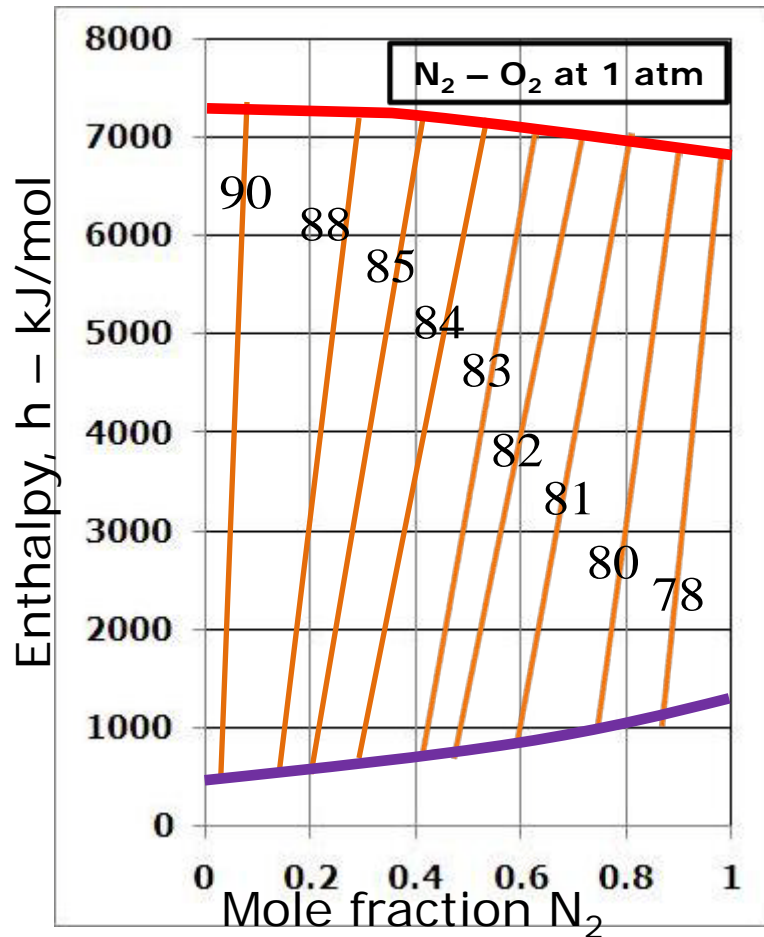
Topic : Gas Separation (contd)

- Enthalpy composition diagrams
- Rectification Column
- Murphree efficiency
- Tutorial

Introduction

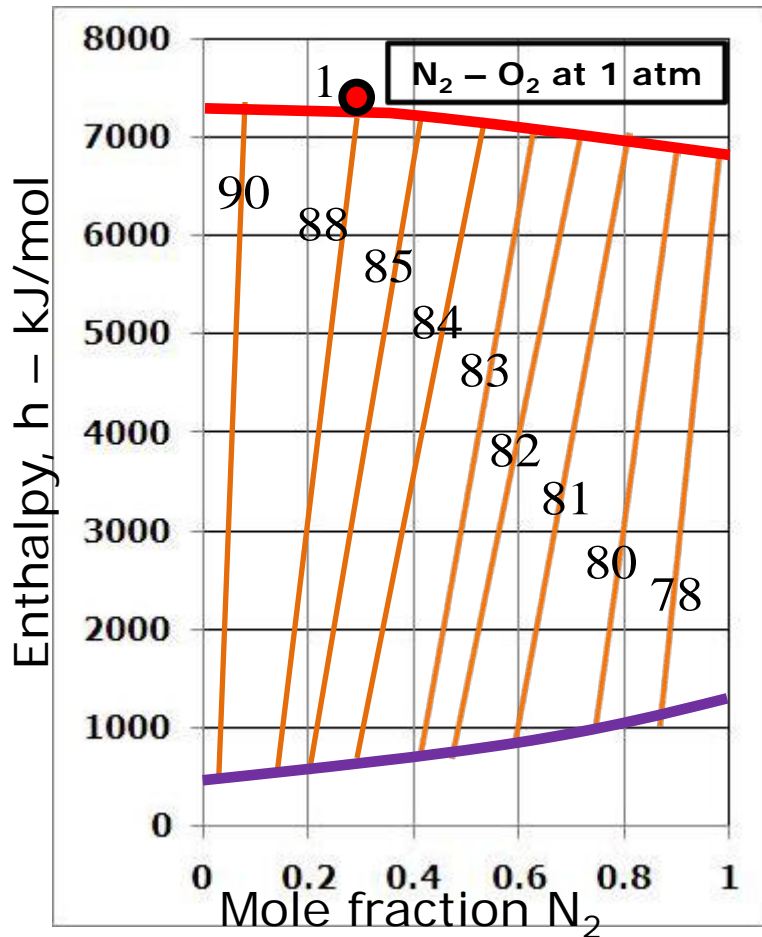
- In the earlier lecture, we have studied the temperature composition diagrams and their importance in gas separation.
- The enthalpies of the vapor and the liquid fractions are dependent on the
 - Temperature of the mixture.
 - Relative mole fractions of the component.
- In a mixture, the enthalpy calculations for liquid and vapor mole fractions are done using the **Enthalpy composition diagrams**.

Enthalpy Composition Diagram



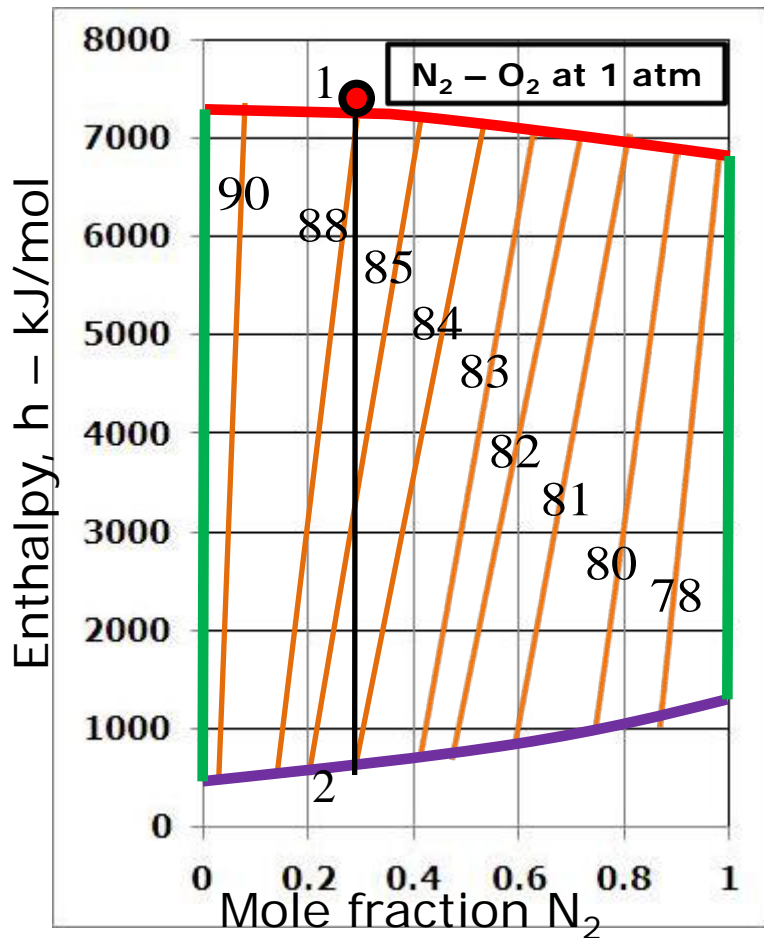
- Consider a mixture of N_2 and O_2 at 1 atm pressure.
- The variation of enthalpy with the mole fraction of N_2 is as shown.
- The **Red** and the **Violet** curves are the **Dew** and the **Bubble** lines respectively.

Enthalpy Composition Diagram



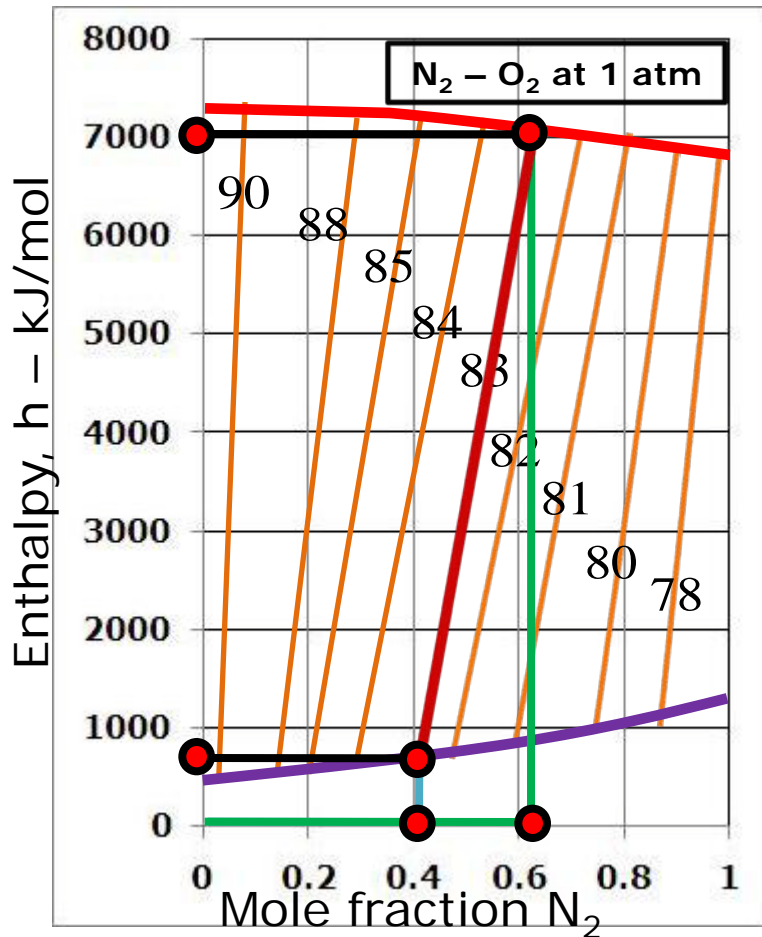
- The figure shows the **isotherms** (constant temperature lines) between the **Dew** and **Bubble** lines.
- These isotherms have finite slope specifying that the condensation or boiling of the mixture is a non – isothermal process.
- Let the state of the mixture be on **Dew** line (point **1**).

Enthalpy Composition Diagram



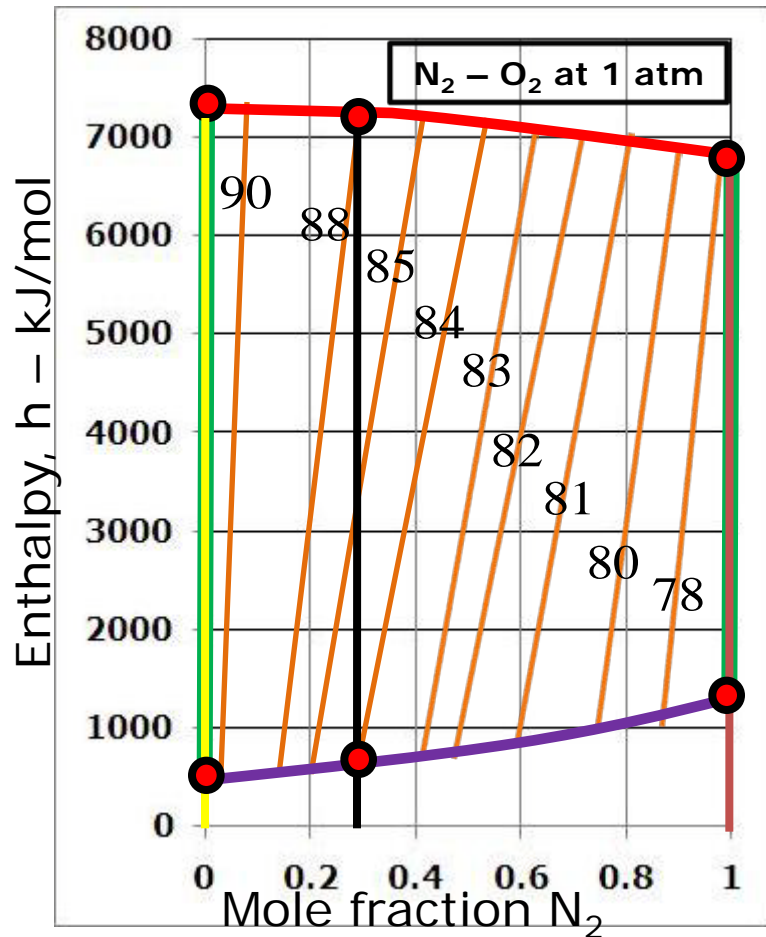
- If it is cooled to **Bubble** line (point **2**), the temperature of the mixture changes from 88 K to 84 K.
- On the other hand, consider pure **N₂** or **O₂**, the isotherms (**77.36 K** or **90.2 K**) are vertical as there is no change in temperature during condensation or boiling.

Enthalpy Composition Diagram



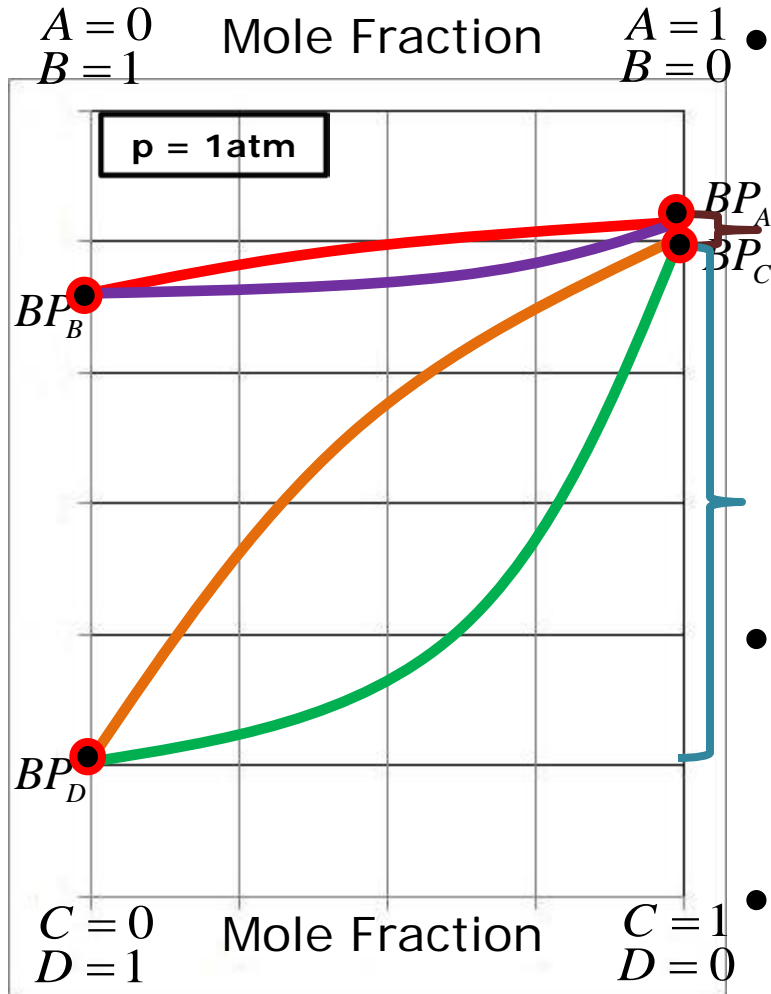
- At any temperature, say 83 K, the mole fraction of N_2 in liquid and vapor is given by
 - y_{Liq}
 - y_{Vap}
- Also, the corresponding enthalpies are
 - Liquid content $(h) = 656$ kJ/mol
 - Vapor content $(H) = 7000$ kJ/mol

Enthalpy Composition Diagram



N ₂	T. (K)		1 atm	
y	Liq	Vap	h	H
0.0	90.2	90.2	419	7252
0.1	87.7	89.5	461	7231
0.2	85.7	88.7	519	7210
0.3	84.1	87.7	599	7185
0.4	82.5	86.7	682	7151
0.5	81.3	85.6	779	7118
0.6	80.4	84.3	879	7084
0.7	79.6	83.1	984	7042
0.8	78.8	81.5	1084	6992
0.9	78.1	79.7	1181	6933
1.0	77.4	77.4	1273	6871

Gas Separation

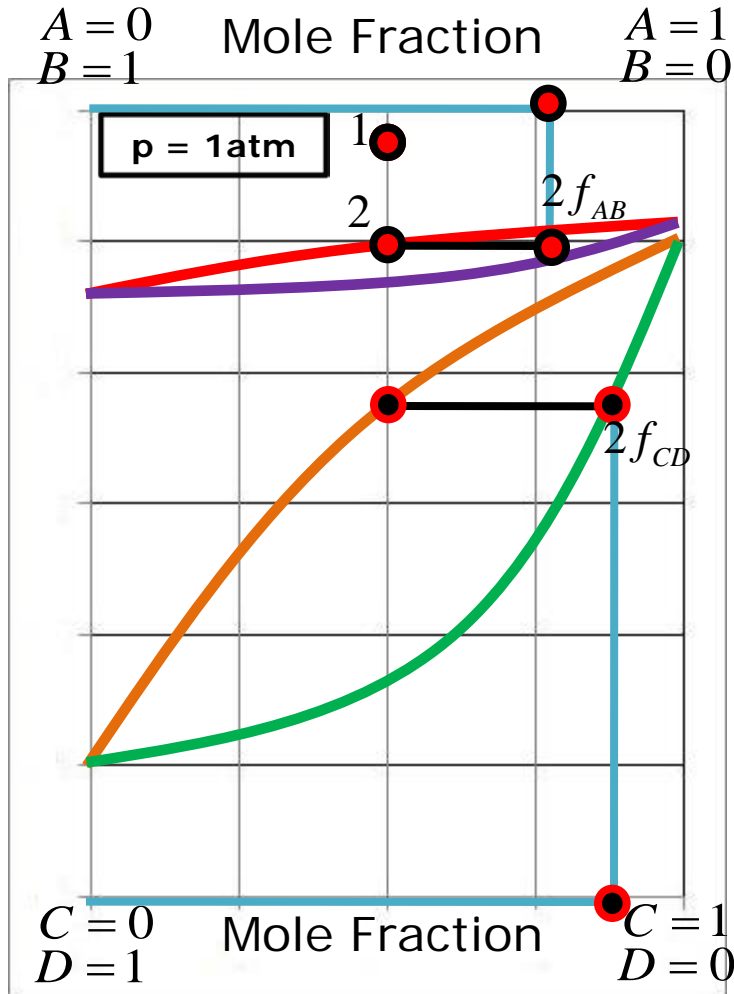


Consider two mixtures **AB** and **CD** at 1 atm whose temperature – composition diagrams are as shown.

- **Gas A** + **Gas B**
- **Gas C** + **Gas D**

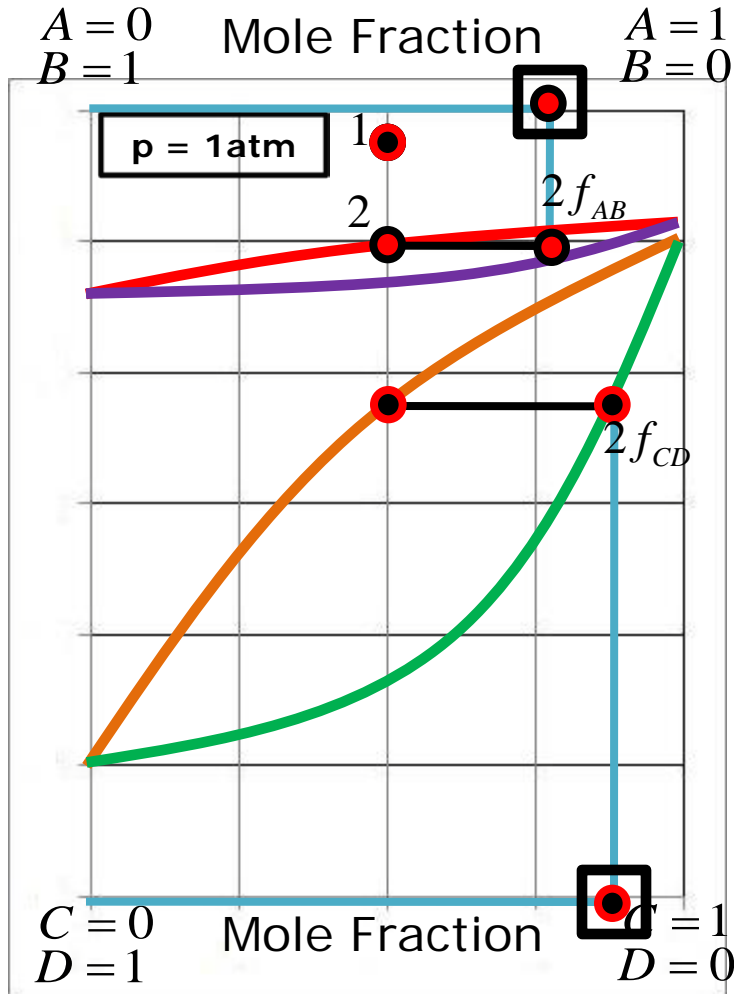
- The respective boiling points of each gas are as shown.
- The boiling point difference of the mixture **AB** is less than that of the mixture **CD**.

Gas Separation



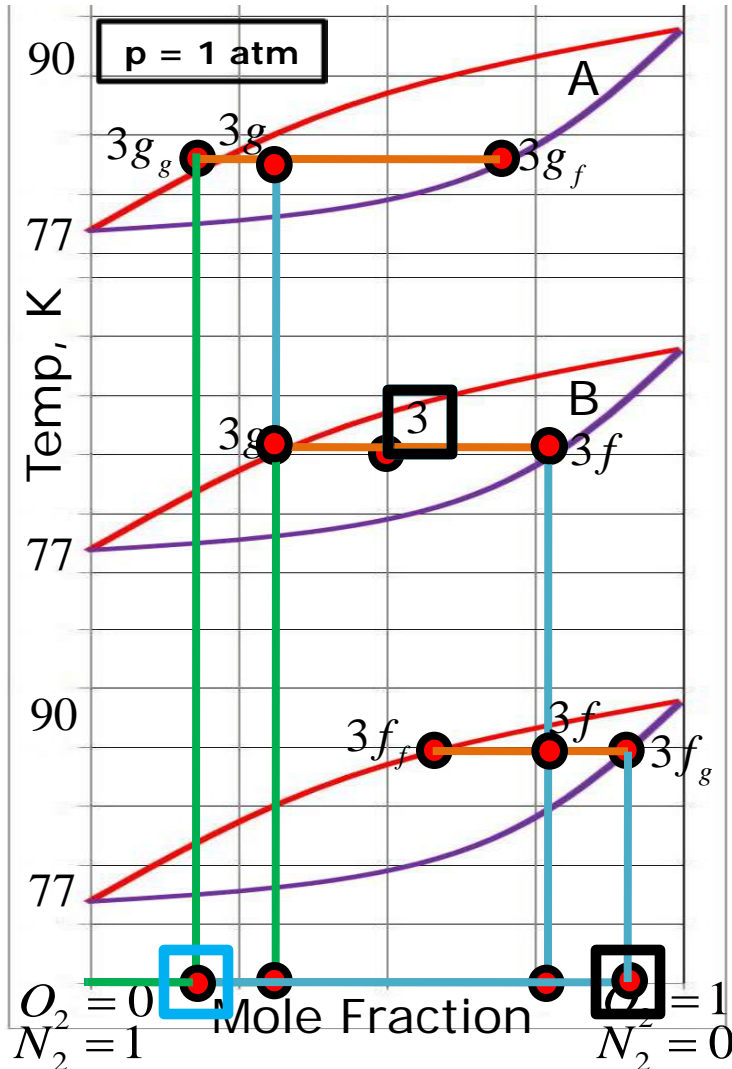
- Let us consider a mixture with composition at state **1** as shown.
- If this mixture is rectified on **AB** diagram at **2**, we have
 - $y_{\text{liq}} = 2f_{AB}$
- Again, if this mixture is rectified on **CD** diagram, we have
 - $y_{\text{liq}} = 2f_{CD}$

Gas Separation



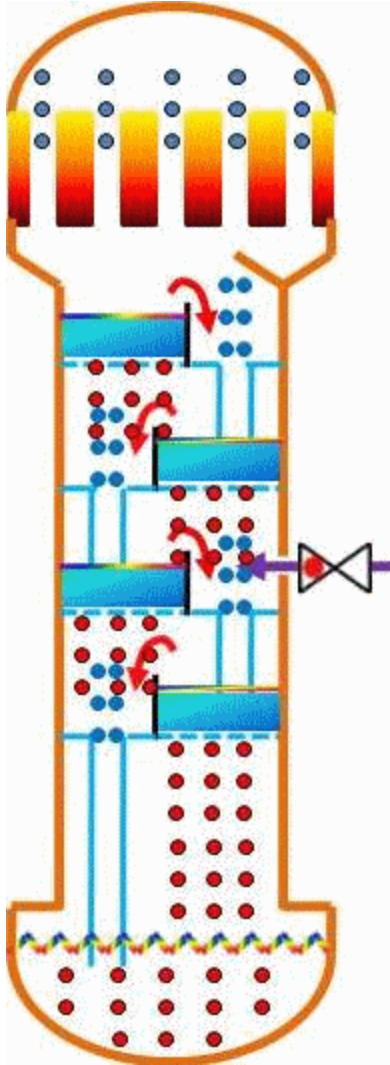
- The separation is more effective when the difference in the boiling points is more.
- For such mixtures, almost pure product is obtained in one or two condensations.

Gas Separation



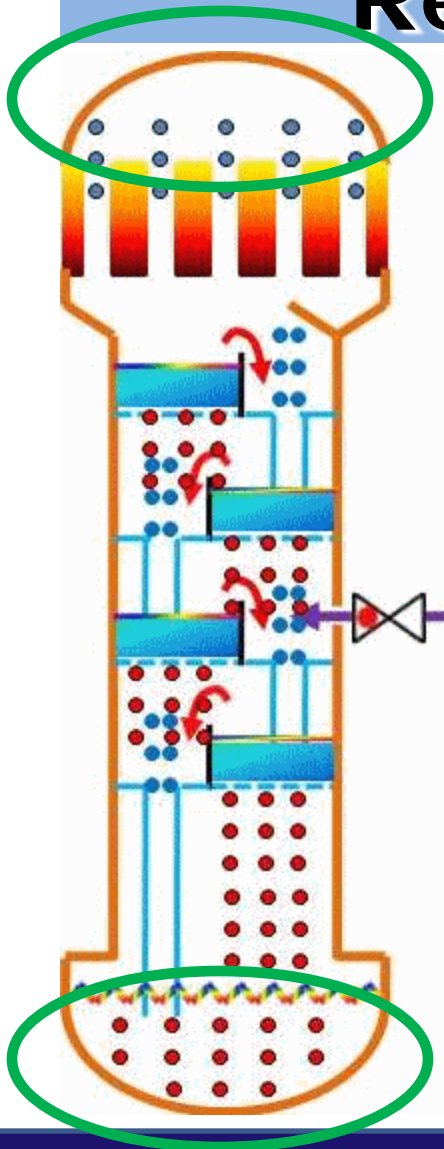
- As done earlier, rectification of this mixture at point **3**
 - Vapor is enriched in low BP component (N_2).
 - Liquid is enriched in high BP component (O_2).
- This process forms the fundamental step for the rectification column.

Rectification Column



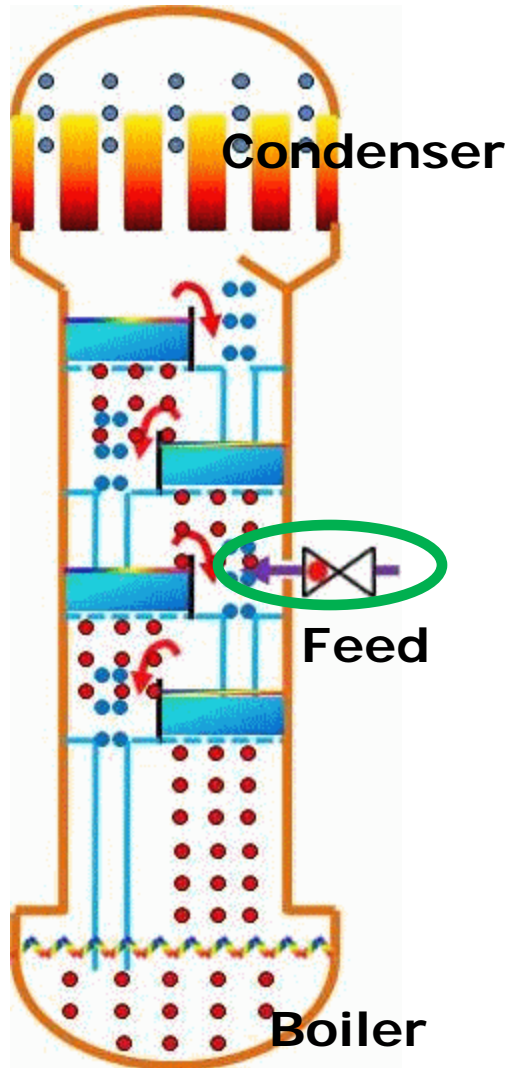
- As mentioned earlier, gas separation is a process of repeated rectification.
- The equipment which carries out these processes is called as a **Rectification Column**.
- The figure shows the schematic of a Rectification column.

Rectification Column



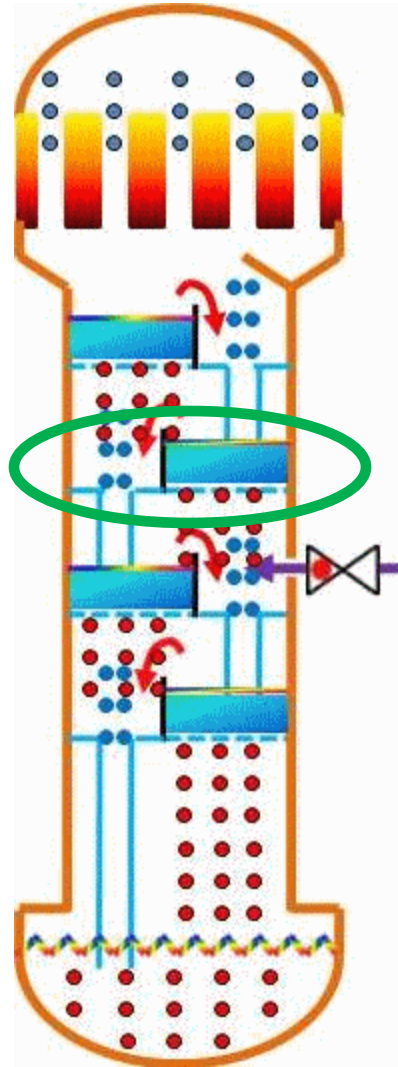
- It is a vertical column which is closed by spherical domes, both at the top and at the bottom.
- These are spherical in shape in order to minimize surface area (less heat in - leak) and accommodate high pressures (1 – 5 atm).
- The column is well insulated because, it is usually operated at cryogenic temperatures.

Rectification Column



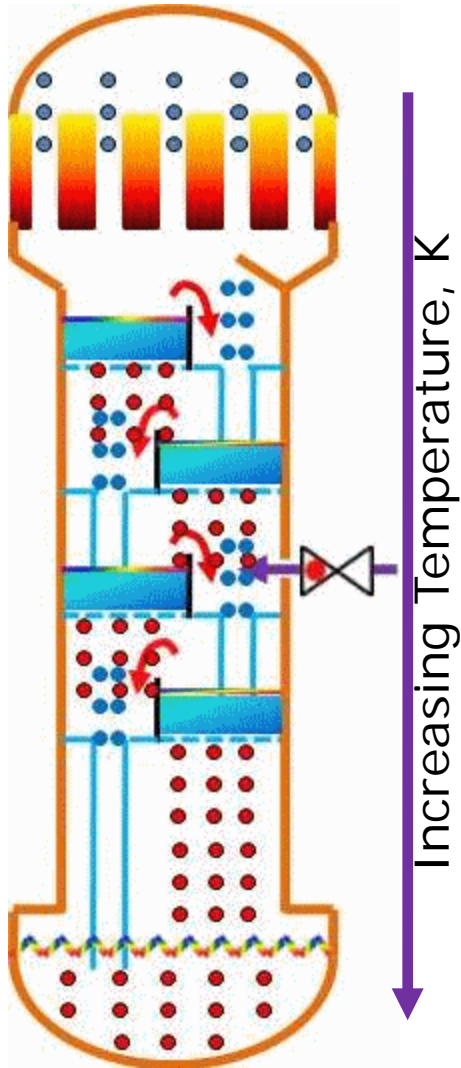
- The top dome houses a **Condenser** and the bottom dome houses a **Boiler**.
- The two phase mixture is first expanded isenthalpically. It can be **liquid** or **liquid + vapor** or **vapor**.
- This expanded product is introduced into the column as **Feed**.

Rectification Column



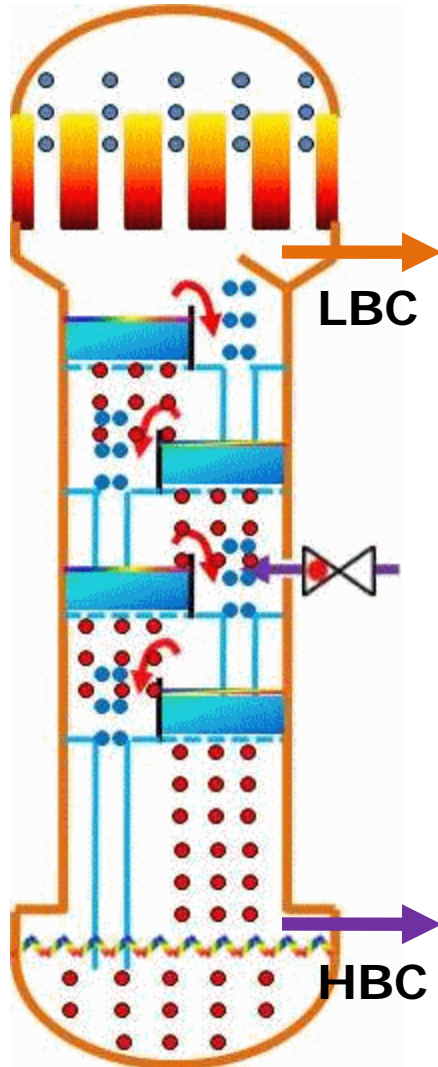
- The rectification of the mixture occurs across each **Plate** and **Downcomer** assembly as shown in the figure.
- These **Plates** have **holes** for the vapor mixture to pass through and ultimately reach the condenser.
- Similarly, the **Downcomer** takes the mixture in liquid phase towards the boiler.

Rectification Column



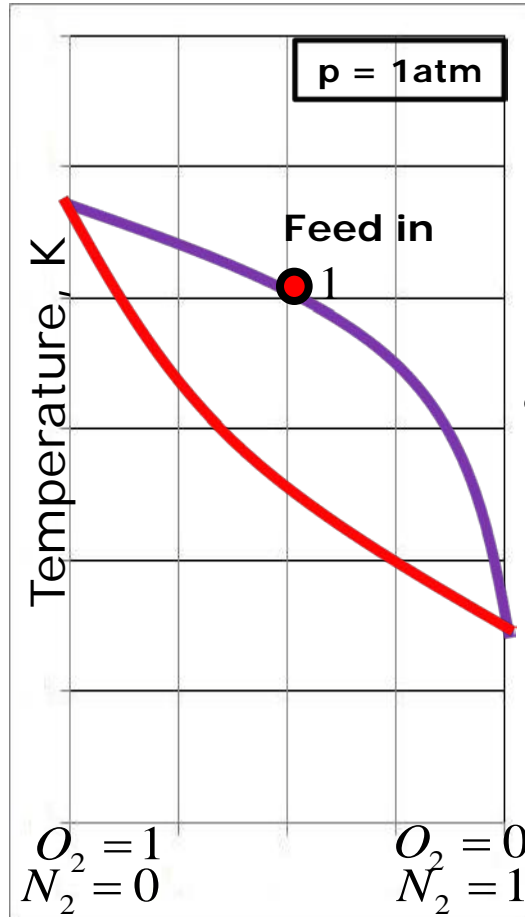
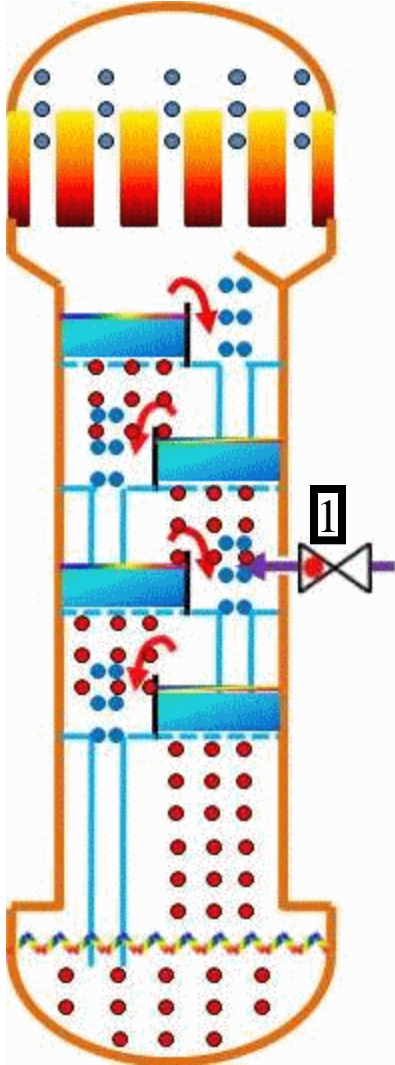
- During this motion, vapor and liquid flow in opposite directions and exchange heat in a counter – flow manner.
- Hence, there is a temperature gradient across the length of the column.

Rectification Column



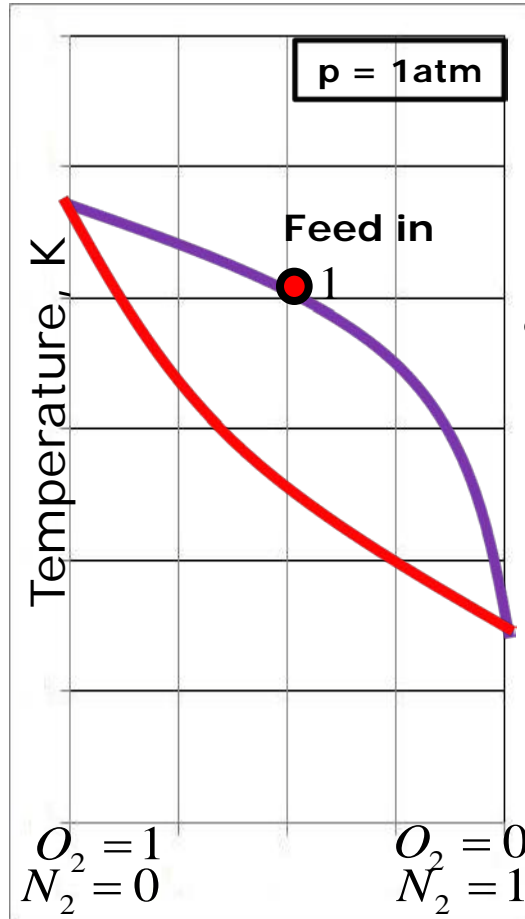
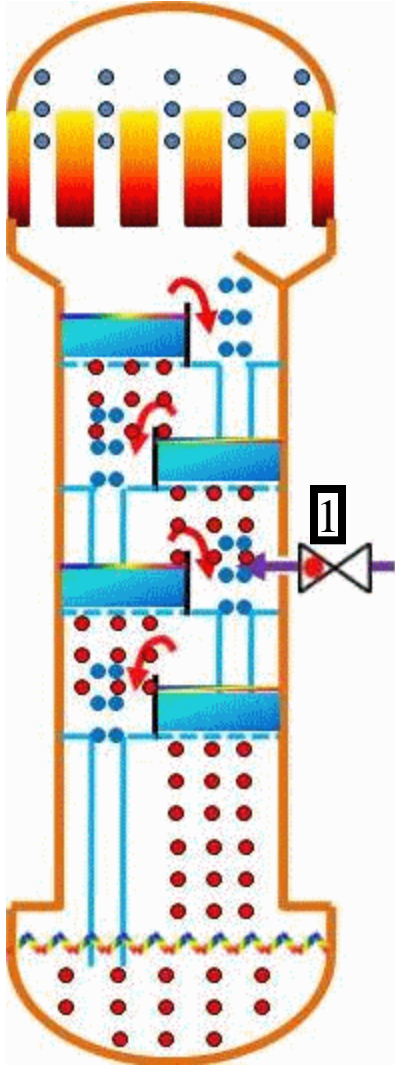
- The low boiling component is condensed in the **Condenser** and the high boiling component is evaporated in the **Boiler**.
- The low and high boiling components are collected at the top and bottom respectively.

Rectification Column



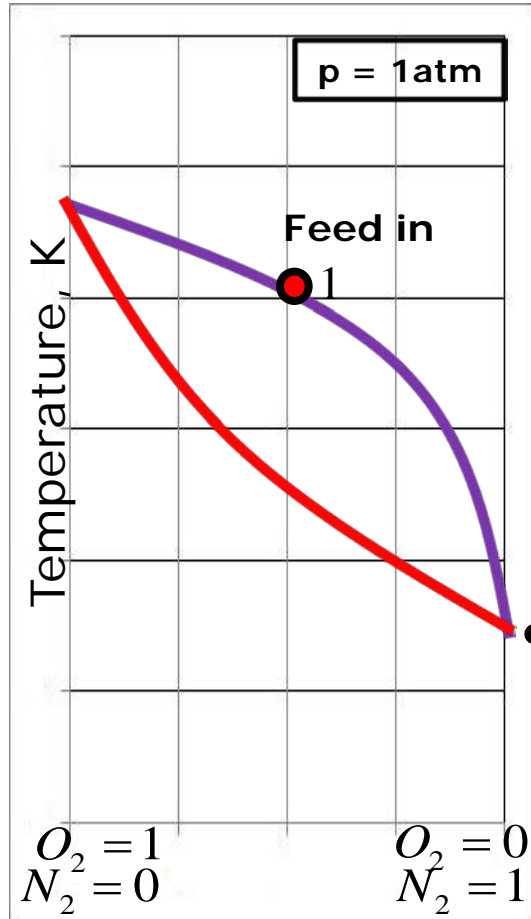
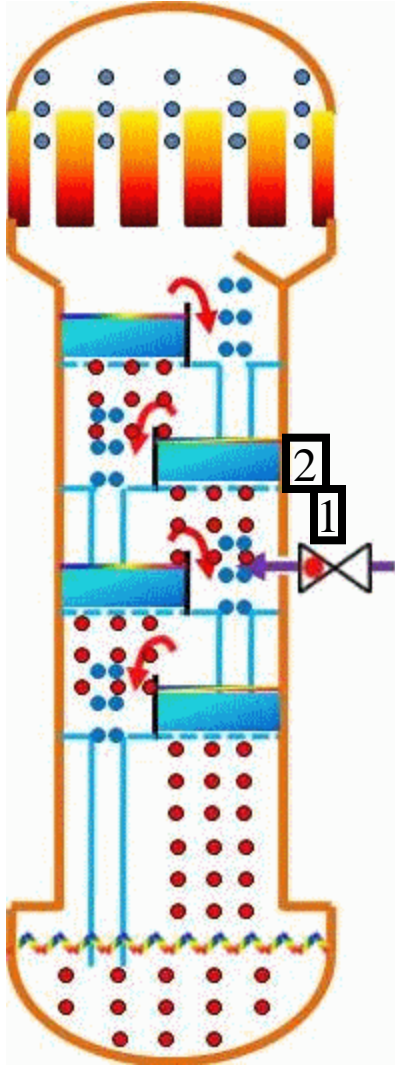
- For the ease of understanding, consider a mixture of N_2 and O_2 at 1 atm.
- Let the **Feed** in saturated vapor condition enter the column at **1**, as shown in figure.

Rectification Column



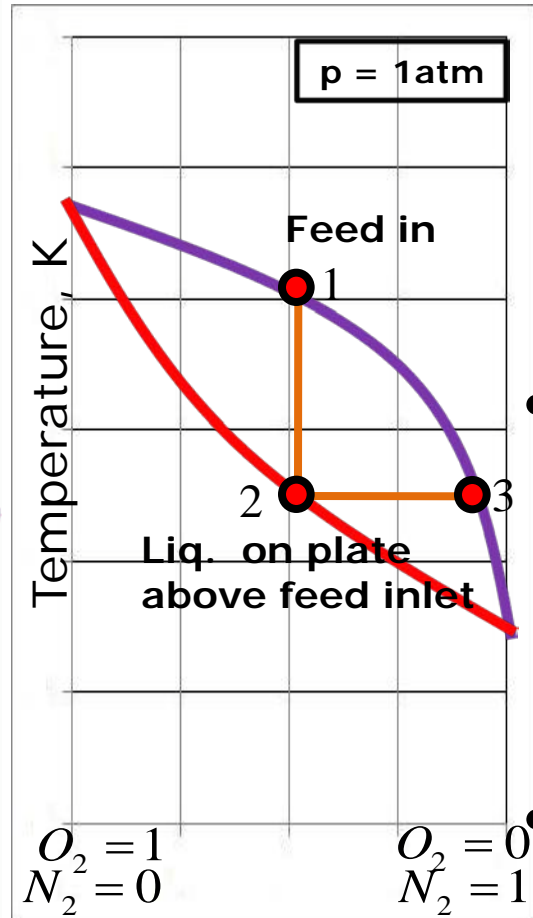
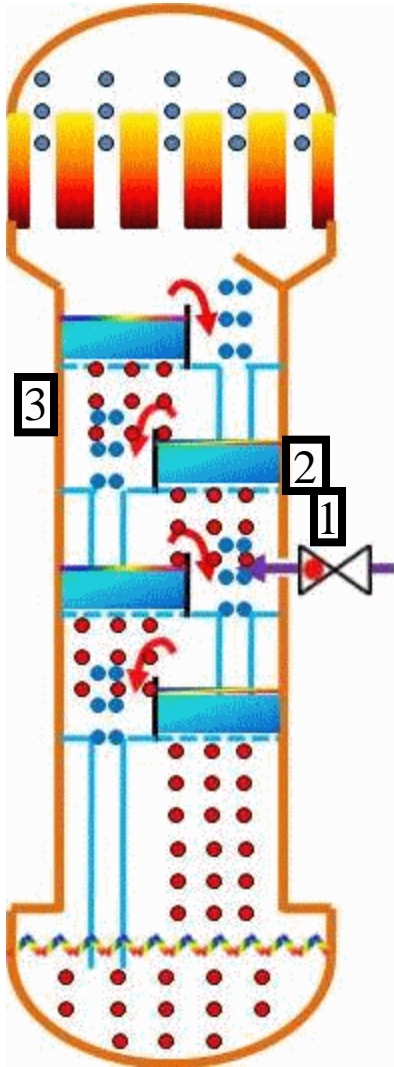
- Let us assume a steady state and an ideal operation of column.
- When the mixture condenses or evaporates, its composition remains constant.

Rectification Column



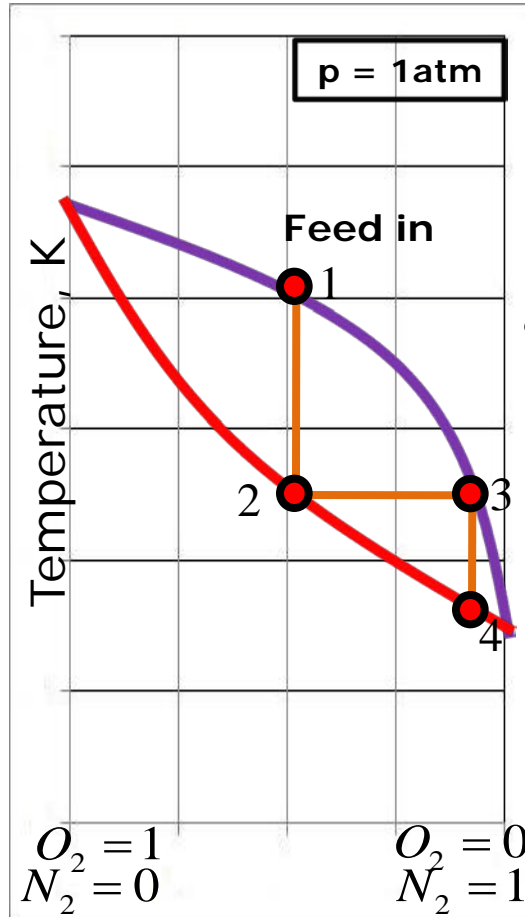
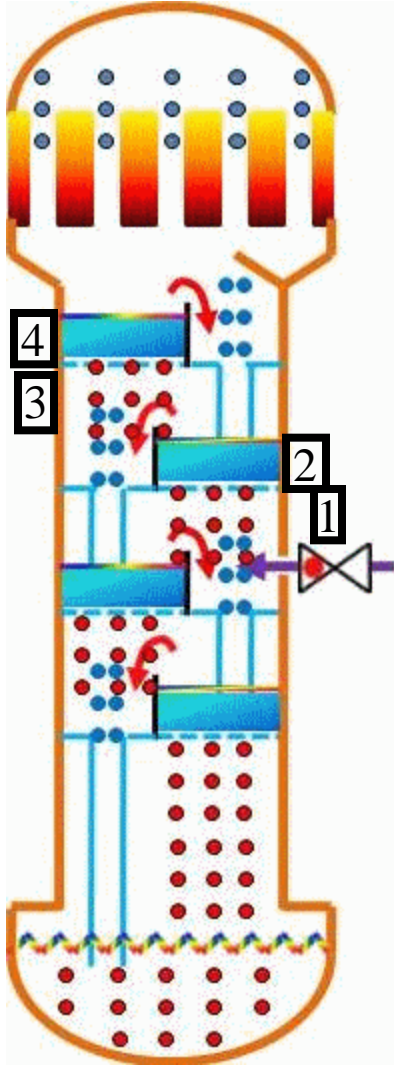
- Hence for any plate, the vapor rising and the liquid on the plate have same molar composition, although the liquid is at lower temperature.
- Hence, the liquid on the plate above the feed inlet (point **2**) has same composition as the vapor.

Rectification Column



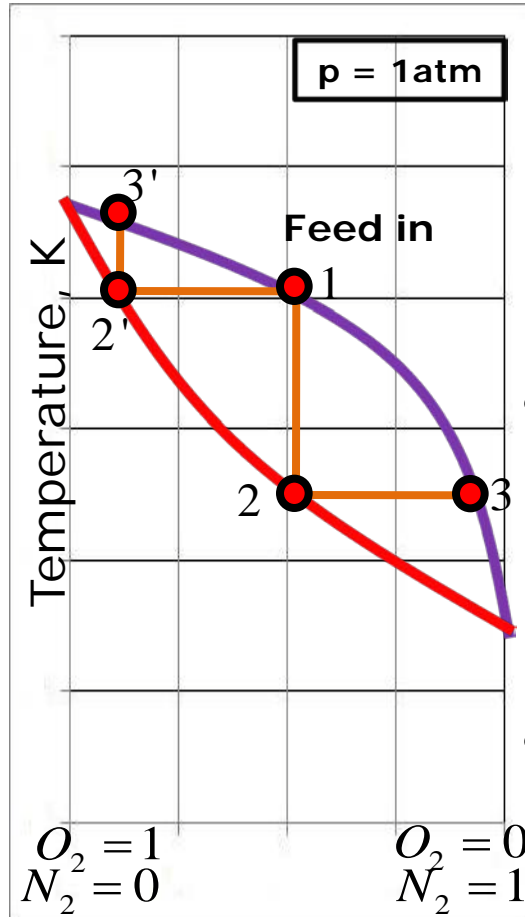
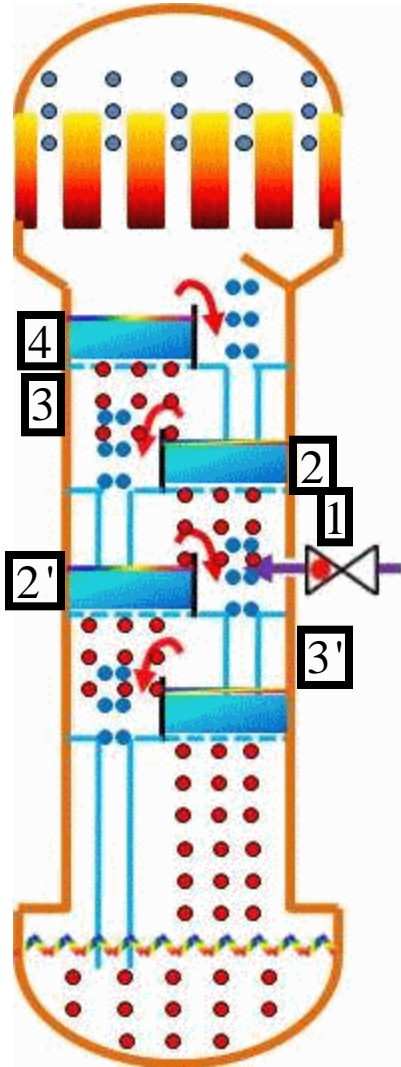
- Therefore, extending a constant composition line about point **1**, we have point **2**.
- Also, the vapor leaving point **3** is in thermal equilibrium with liquid at **2**. (same plate).
- Extending an isotherm about the point **2**, we have the point **3**.

Rectification Column



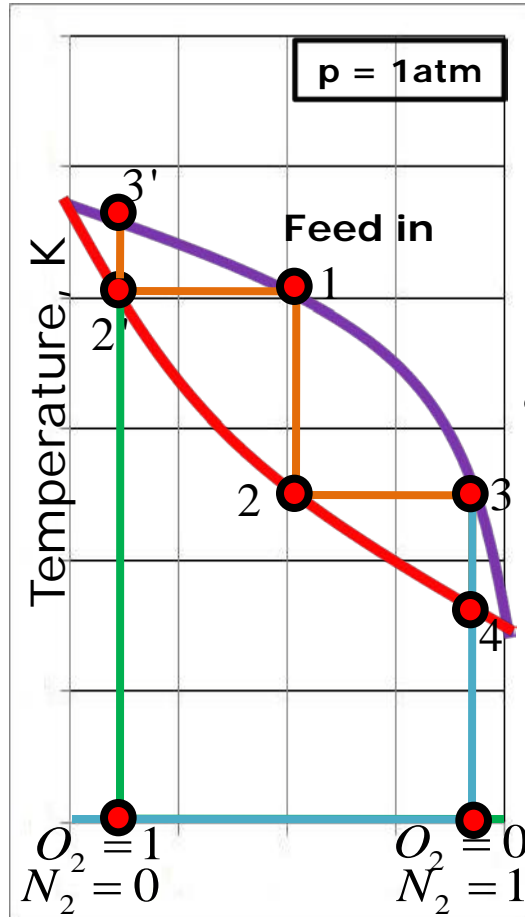
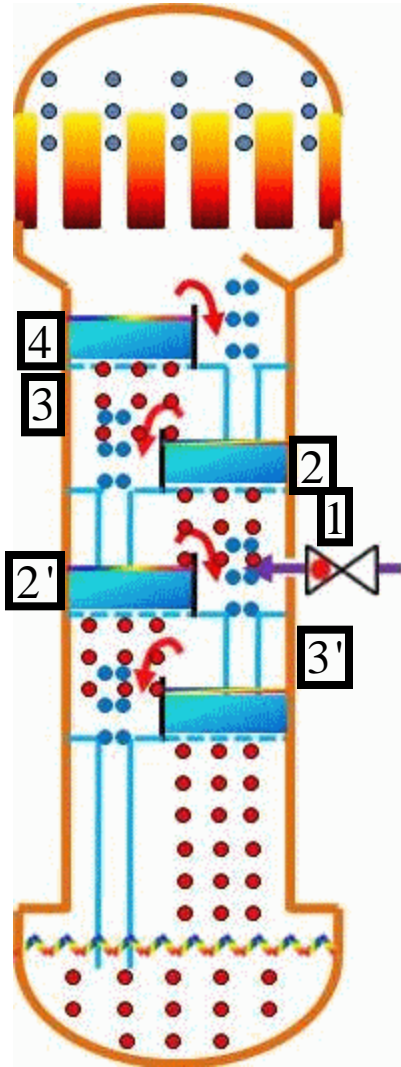
- Similarly, liquid at point **4** has same composition as point **3**.
- Extending a constant composition line about **3**, we have point **4**.

Rectification Column



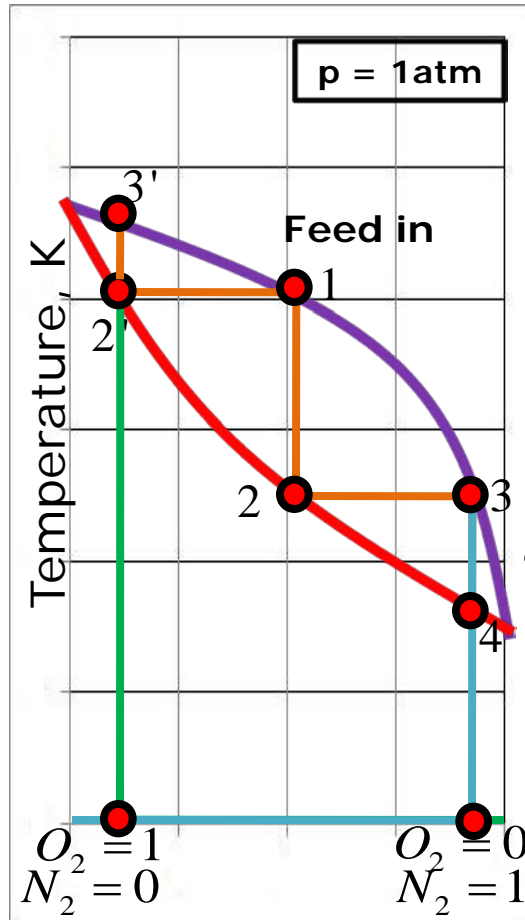
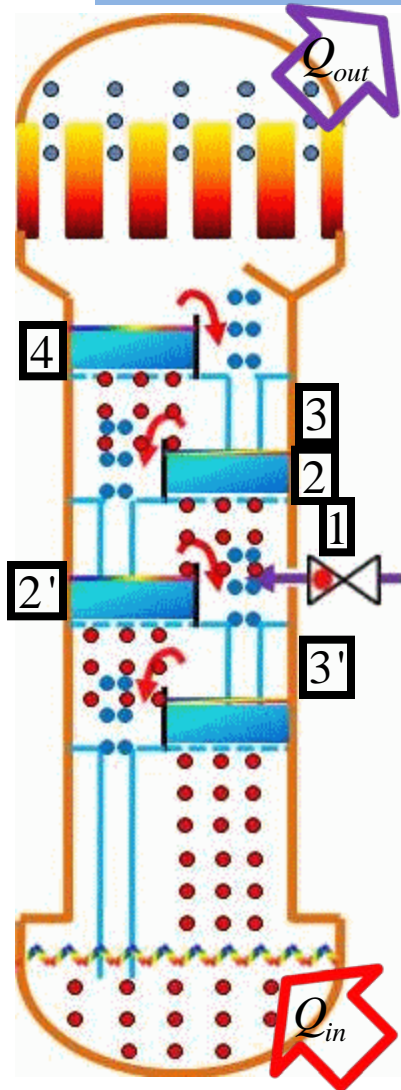
- On the other hand, we have the points **1**, **2'** and **3'** as shown in the figure.
- The point **1** and **2'** are in thermal equilibrium (same plate).
- Also, liquid at point **2'** has same composition as point **3'** and liquid is at lower temperature.

Rectification Column



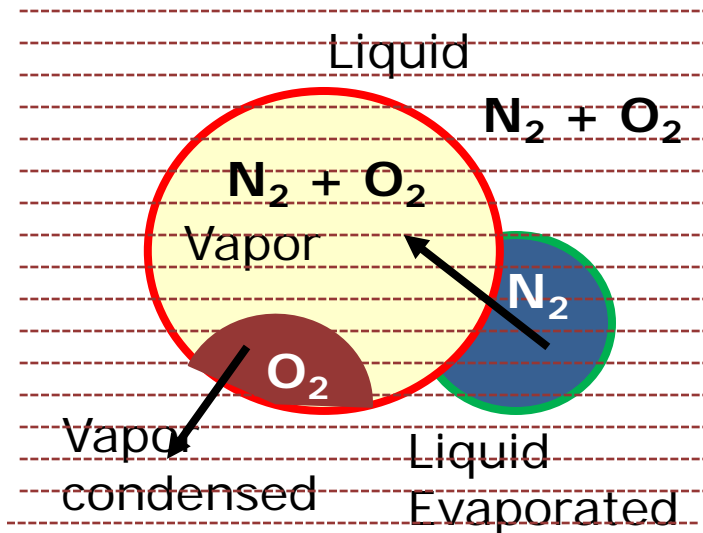
- Therefore, the liquid moving down is enriched in high BP component (O_2).
- On the other hand, the vapor moving up is enriched in low BP component (N_2).

Rectification Column



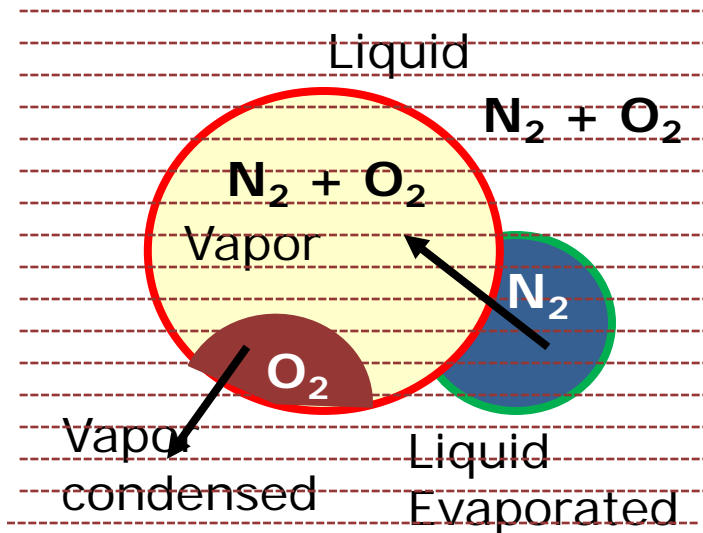
- In order to keep the process running, some heat is supplied to the boiler, to continuously evaporate the high boiling component.
- Similarly, some heat is withdrawn from the condenser to condense the low boiling component.

Rectification Column



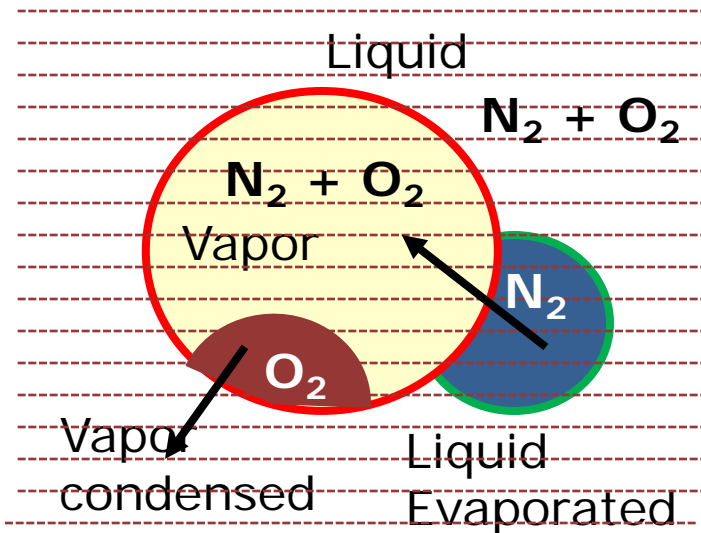
- The heat exchange between the liquid and vapor fractions is explained as follows.
- The vapor is at high temperature as compared to that of liquid.
- When vapor bubbles through the liquid layer, the high temperature vapor transfers heat to the liquid.

Rectification Column



- Heat transfer from vapor bubble results in condensation of a little bit of high BPC (here, O_2) from bubble.
- Also this heat exchange causes an evaporation of a little bit of low BPC (here, N_2) from the bulk liquid.

Rectification Column

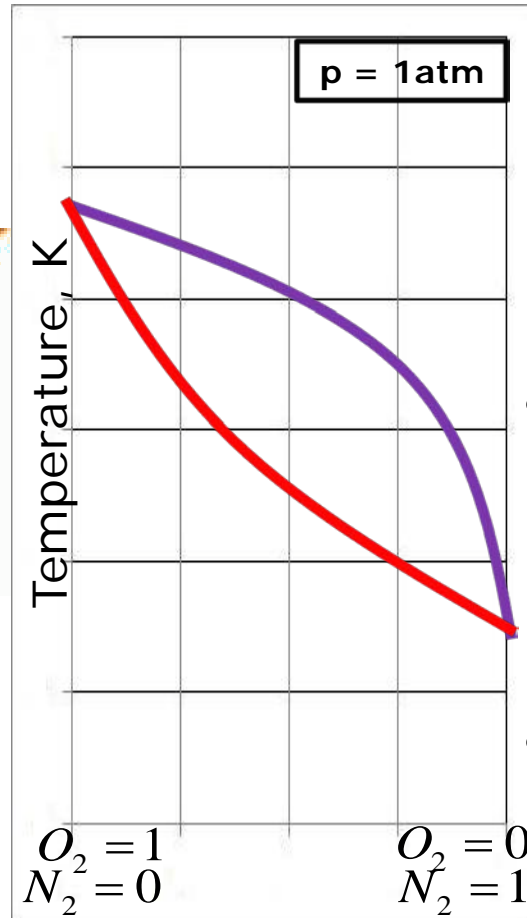
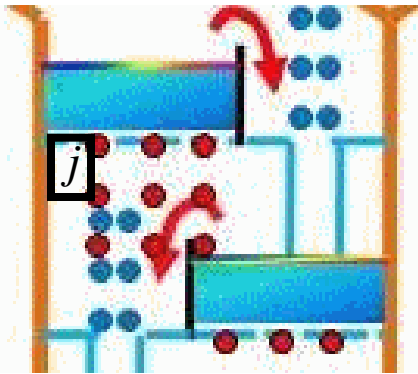


- Thus as the vapor bubble moves up, it becomes richer and richer in low BPC, that is N_2 .
- And as liquid moves down, it gets richer and richer in high BPC, that is O_2 .

Real Rectification Column

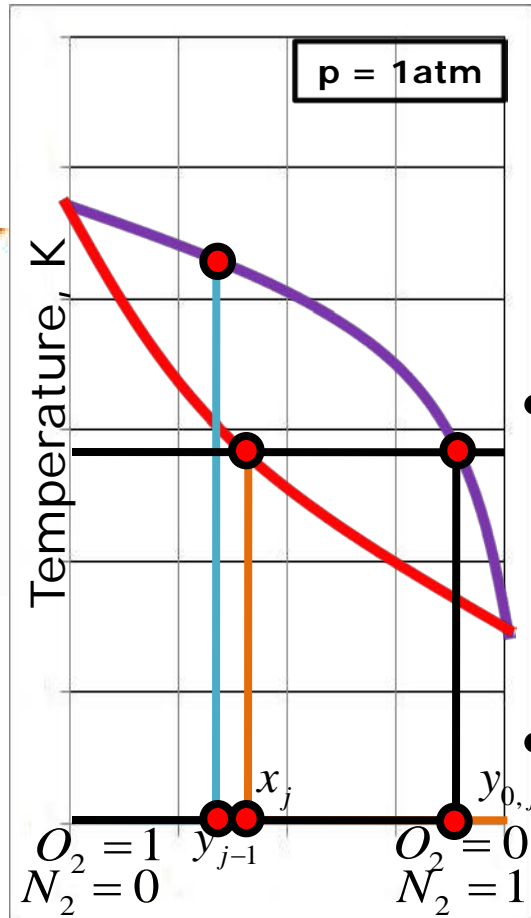
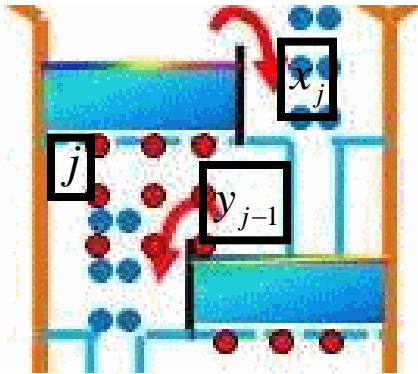
- In an ideal rectification column, the vapor and the liquid are in thermal equilibrium.
- But in actual rectification columns, the vapor does not leave the plate as the same temperature of the liquid.
- To ensure the required heat exchange, more number of plates are required than the theoretical prediction.
- Hence, there is a need to study efficiency of an actual system with respect to an ideal system.

Real Rectification Column



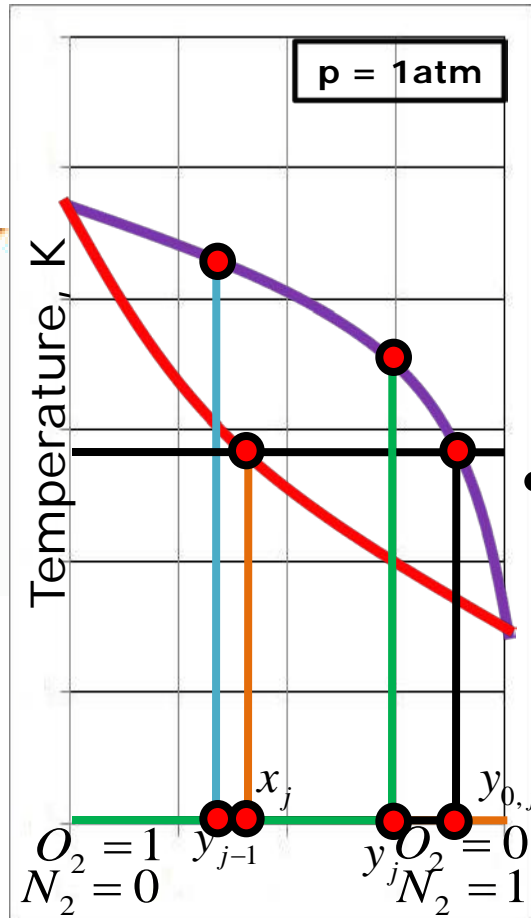
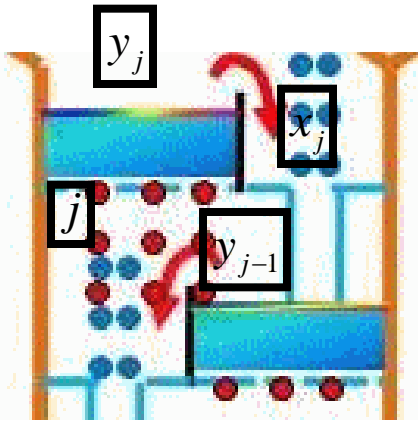
- Let the mixture of N_2 and O_2 at 1 atm be subjected to rectification.
- Consider a j^{th} plate of the rectification column as shown in the figure.
- Across this plate, the vapor mixture rises up and the liquid mixture flows down.

Real Rectification Column



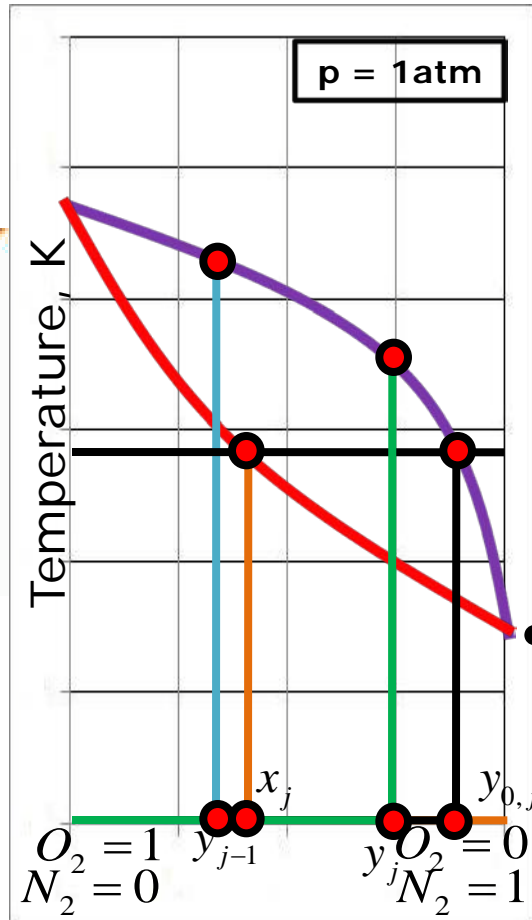
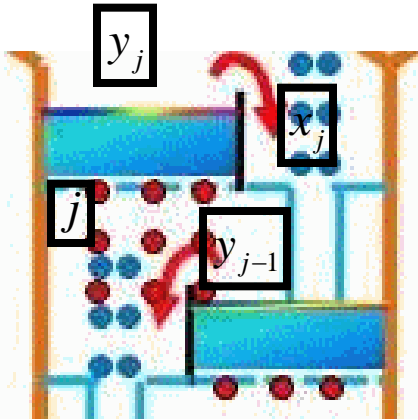
- Let y_{j-1} be the mole fraction of LBC in vapor phase rising to the j^{th} plate.
- The composition of liquid at this plate is given by x_j .
- In thermal equilibrium, the mole fraction of LBC in vapor phase leaving the j^{th} plate is $y_{0,j}$.

Real Rectification Column



- But due to the non-ideality, the mole fraction of LBC in vapor phase leaving the j^{th} plate is y_j .
- Hence, the maximum possible and the actual change in mole fractions are
 - $y_{0,j} - y_{j-1}$
 - $y_j - y_{j-1}$

Real Rectification Column



- **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,

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

Real Rectification Column

- 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 efficiencies, the following conditions are required.
 - Small bubbles.
 - Long time of contact.
 - Large values of the overall mass and heat transfer coefficients.

Tutorial

- Consider a mixture of N_2 and O_2 at 1 atm. Calculate the Murphree efficiency for a plate with liquid at 80 K and the vapor below this plate is at 85 K. Also, it is given that the mole fraction of N_2 leaving this plate in vapor phase is 0.84.
- Use the temperature composition diagram given in the earlier lectures.

Tutorial

Given

Working Pressure : 1 atm

Mixture : $N_2 + O_2$

Liquid temperature : 80 K

Vapor temperature (below) : 85 K

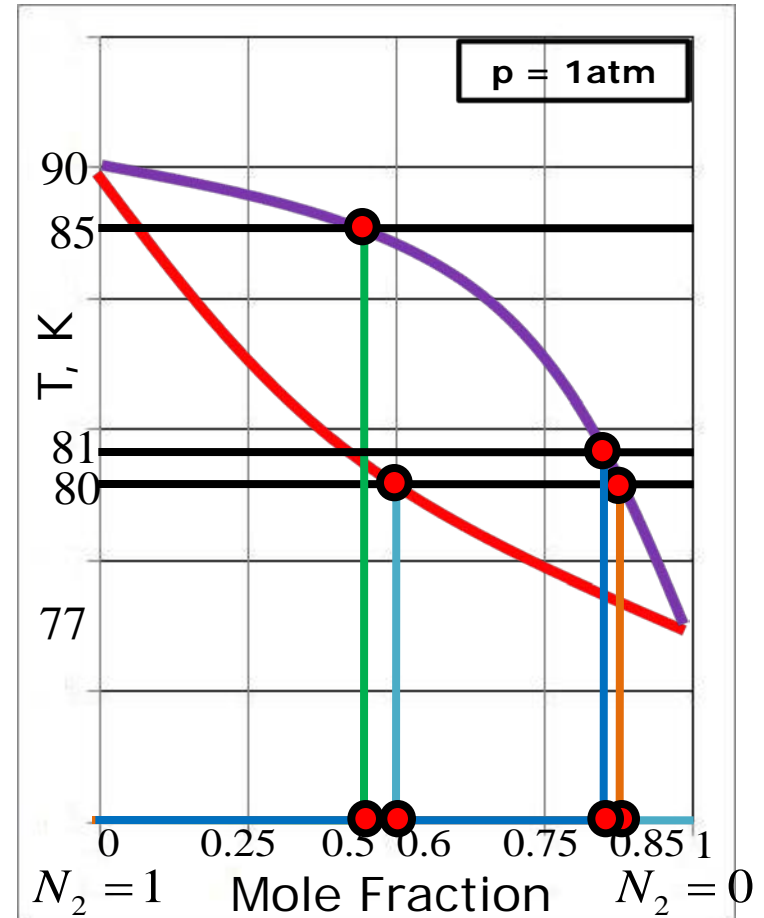
y_{N_2} : 0.84

For above mixture, Calculate

Murphree Efficiency

Tutorial

- **Murphree Efficiency**
- For the ease of understanding, the $T - y$ diagram is enlarged and is not to scale.
- Draw isotherms at 80 and 85 K.
- $y_{j-1} = 0.5$, $x_j = 0.6$, $y_{0,j-1} = 0.85$.
- $y_j = 0.84$ (given)



Tutorial

- Murphree Efficiency

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

Data

$p = 1 \text{ atm}$

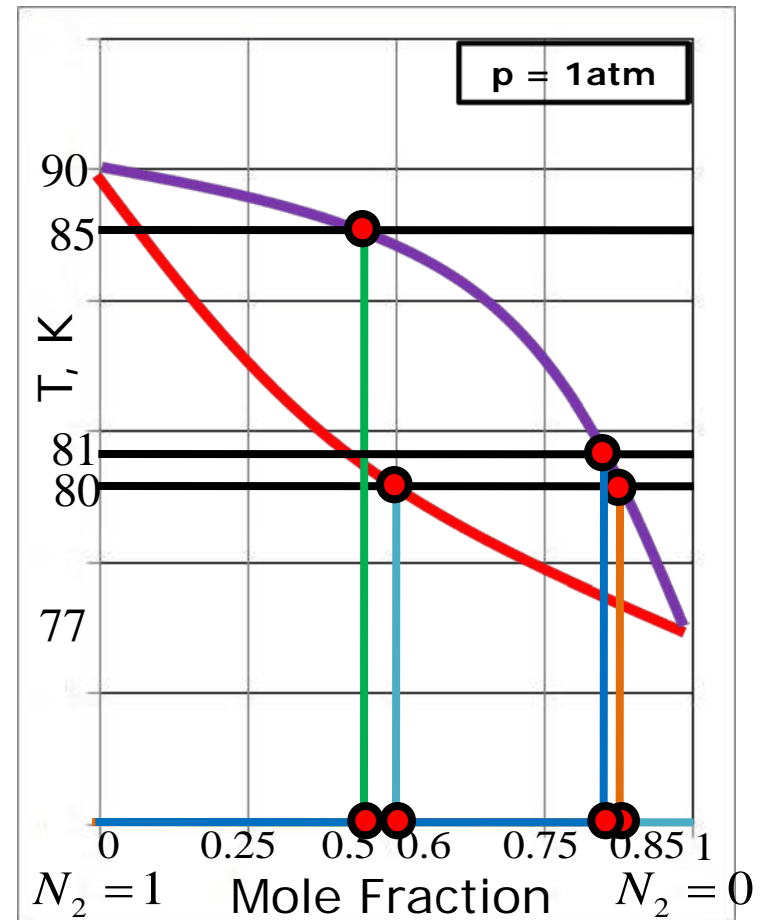
$y_{j-1} = 0.5 \text{ at } 85 \text{ K}$

$x_j = 0.6 \text{ at } 80 \text{ K}$

$y_{0,j-1} = 0.85 \text{ at } 80 \text{ K}$

$y_j = 0.84 \text{ at } 81 \text{ K}$

$$\eta_M = \frac{0.84 - 0.5}{0.85 - 0.5} = 0.97$$



Assignment

- Consider a mixture of N_2 and O_2 at 2 atm. Calculate the Murphree efficiency for a plate with liquid at 89 K and the vapor below this plate is at 94 K. Also, it is given that the mole fraction of N_2 leaving this plate in vapor phase is 0.67.
- Use the temperature composition diagram given in the earlier lectures.

Answers

Data

$$p = 2 \text{ atm}$$

$$y_{j-1} = 0.4 \text{ at } 94 \text{ K}$$

$$x_j = 0.42 \text{ at } 89 \text{ K}$$

$$y_{0,j-1} = 0.72 \text{ at } 89 \text{ K}$$

$$y_j = 0.67 \text{ at } 90 \text{ K}$$

$$\eta_M = 0.843$$

Summary

- The isotherms on Enthalpy – composition diagrams have finite slope indicating that the condensation or boiling of a mixture is a non – isothermal process.
- The separation is more effective when the difference in the boiling points is more.
- In a rectification column, a saturated vapor or saturated liquid or liquid + vapor mixture is introduced as **Feed**.

Summary

- **Murphree efficiency** of a plate is defined as the ratio of actual change in mole fraction to the maximum possible change that can occur.
- In order to achieve high Murphree efficiencies, the conditions are (i) small bubbles, (ii) long time of contact, (iii) large values of the overall mass and heat transfer coefficients.

Thank You!