CRYOGENIC ENGINEERING

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Lecture No - 20

Earlier Lecture

- A mixture composition can be represented by either volume, mass or mole fractions.

- Work of separation is represented by $\mathbf{W_{i,m} / n_m}$, $\mathbf{W_{i,m} / n_A}$ and $\mathbf{W_{i,m} / n_B}$ (for **Gas A** and **B**). Additionally, it is also represented by $\mathbf{W_{i,A} / n_A}$, $\mathbf{W_{i,B} / n_B}$ and $\mathbf{W_{i,C} / n_C}$ (for **Gas A, B** and **C**).

- Ideal work of separation/mole of mixture with **N** constituents is given by

$$\frac{-W_i}{n_m} = \Re T_m \sum_{j=1}^{N} y_j \ln\left(\frac{1}{y_j}\right)$$

  - where $\mathbf{y_j}$ is mole fraction of $\mathbf{j^{th}}$ component.

Outline of the Lecture

Topic : Gas Separation (contd)

- Gibbs Phase Rule
- Phase Equilibrium Curves
- Temperature Composition Diagrams

Introduction

- A mixture can have various components and can exist in various phases in thermal equilibrium.
- For example, a mixture of ice and water is a 1 – component and a two phase mixture.
- If number of components and number of phases in thermal equilibrium are denoted by C and P respectively, then for above mixture $C = 1$ and $P = 2$
- Similarly, boiling **LAir** is **LOX** + **LN_2** + **N_2** +**O_2**. the values of C and P are 2 and 2 respectively.

Introduction

- Every mixture can be uniquely defined by a set of properties called as Thermostatic Properties.
- These properties can either be Intensive (independent of mass) or Extensive (dependent on mass) properties.
- Pressure, temperature, density are examples of Intensive properties and volume, enthalpy, entropy are few examples of Extensive properties.

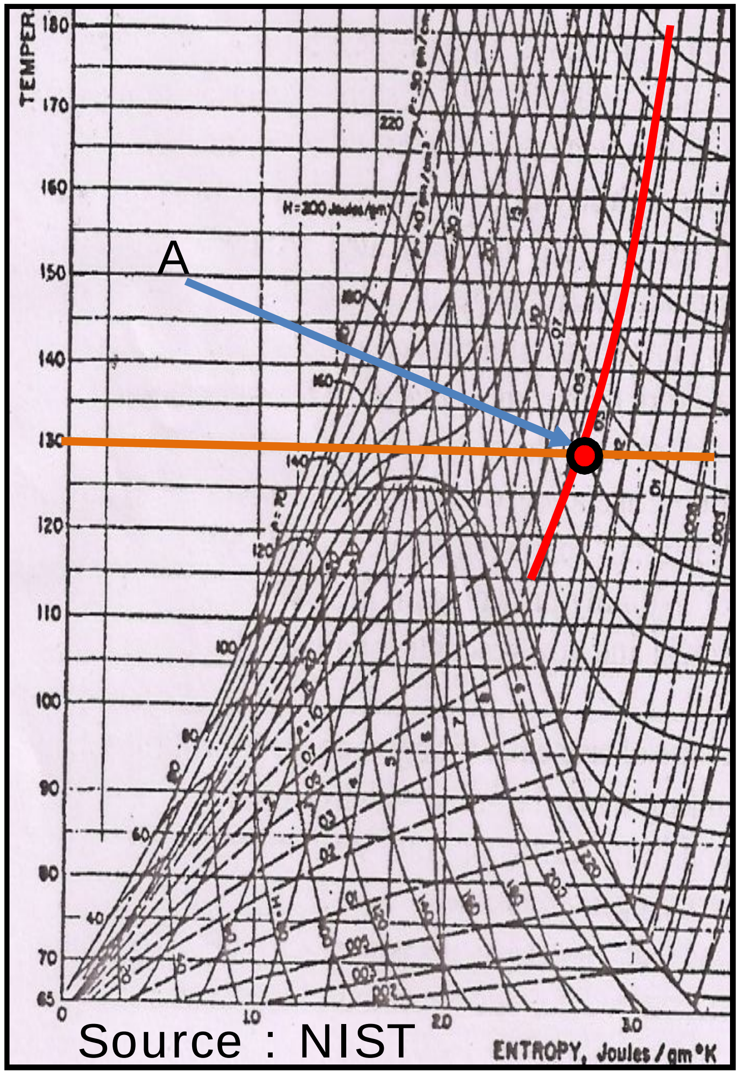
Introduction

- For any mixture, there are certain minimum number of Intensive properties required to define the complete state.
- In other words, these properties are required to locate a unique point on **T – s**, **p – T** etc. diagrams, corresponding to the unique state of the mixture.
- Gibbs Phase Rule is used in determining these properties/degrees of freedom, for a given mixture.

Gibbs Phase Rule

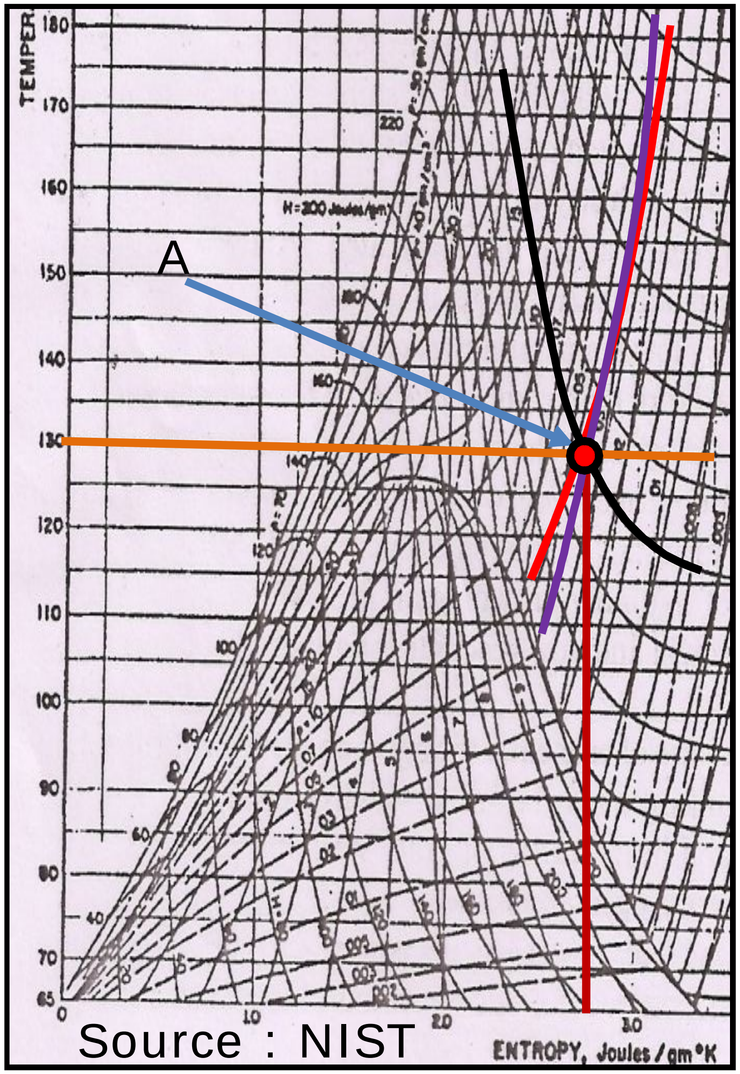
- Gibbs Phase Rule was formulated by Josiah Willard Gibbs, an American physicist, in 1878.
- If F is the degrees of freedom/minimum number of Intensive properties required to define the thermodynamic state of a system, then by Gibbs Phase Rule $F = C - P + 2$
- For example, for gaseous N_2, we have $C = 1$ and $P = 1$ Therefore, $F = 2$.
- These can be pressure and temperature or pressure and specific volume.

Gibbs Phase Rule



- The T – s diagram for $\mathbf{N_2}$ is a shown.
- Let us say that for a known **p** and **T** lines in the gaseous region, intersect at **A** as shown in the figure.
  - Pressure
  - Temperature

Gibbs Phase Rule



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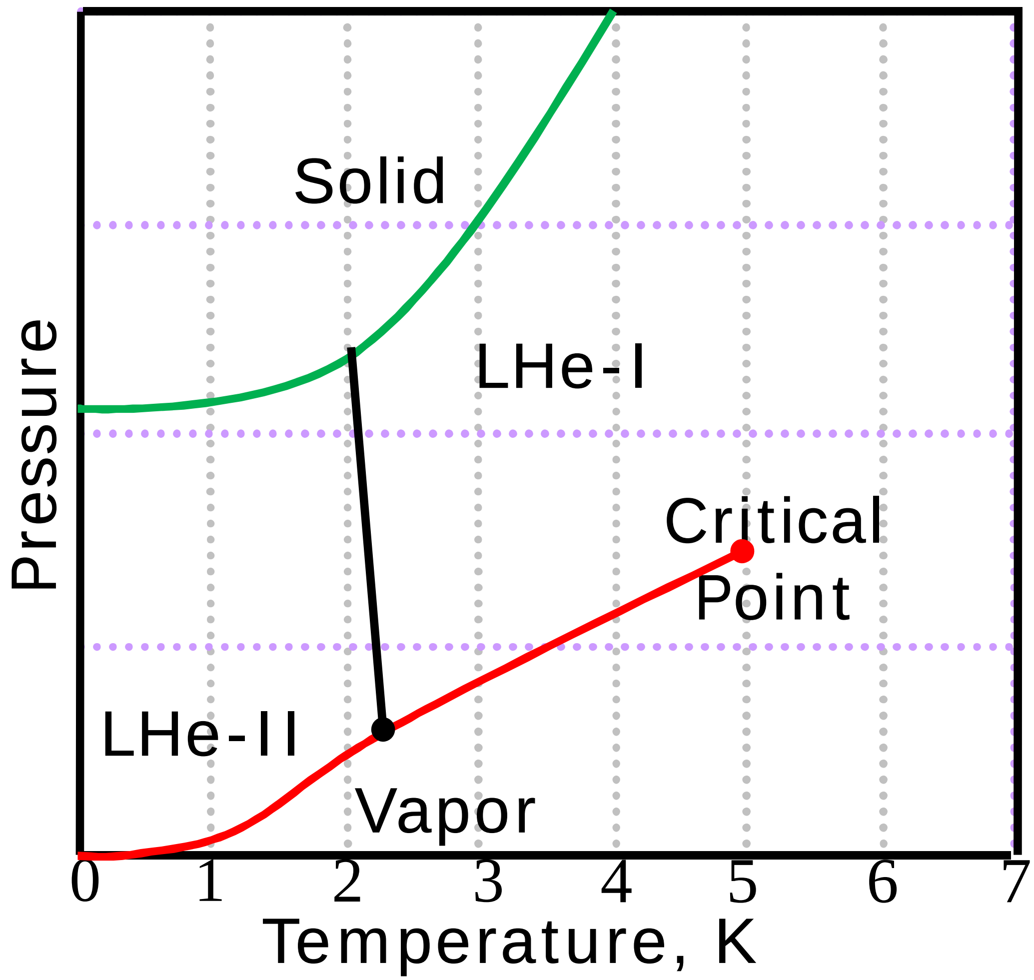
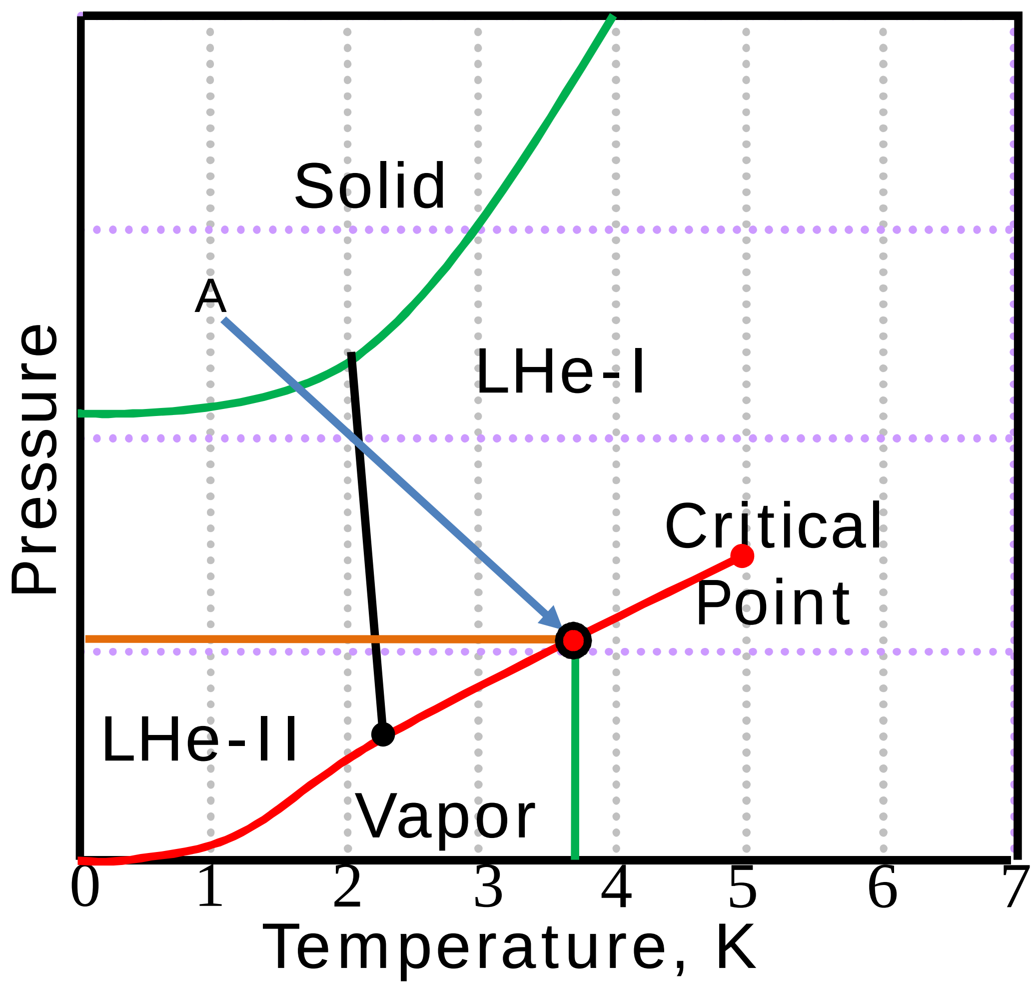
- It is clear that, all other properties can be uniquely defined.
  - Specific enthalpy
  - Specific entropy
  - Specific volume

Gibbs Phase Rule



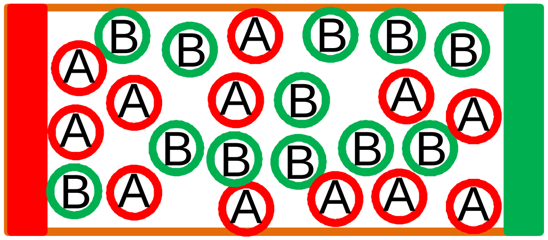
- Similarly, for a two phase mixture of Helium in thermal equilibrium, we have $P = 2$ $C = 1$
- By Gibbs Phase Rule $F = C - P + 2 = 1$
- This property can either be saturation temperature or saturation pressure.

Gibbs Phase Rule



- The p – T diagram for Helium is as shown.
- Let us say, the pressure **p** is known, it intersects the vapor line at **A**.
- The corresponding temperature can be known and vice versa.

Phase Equilibrium Curves



- Again, for a mixture of **Gas A** and **Gas B** in single phase, we have $P=1$ and $C=2$.

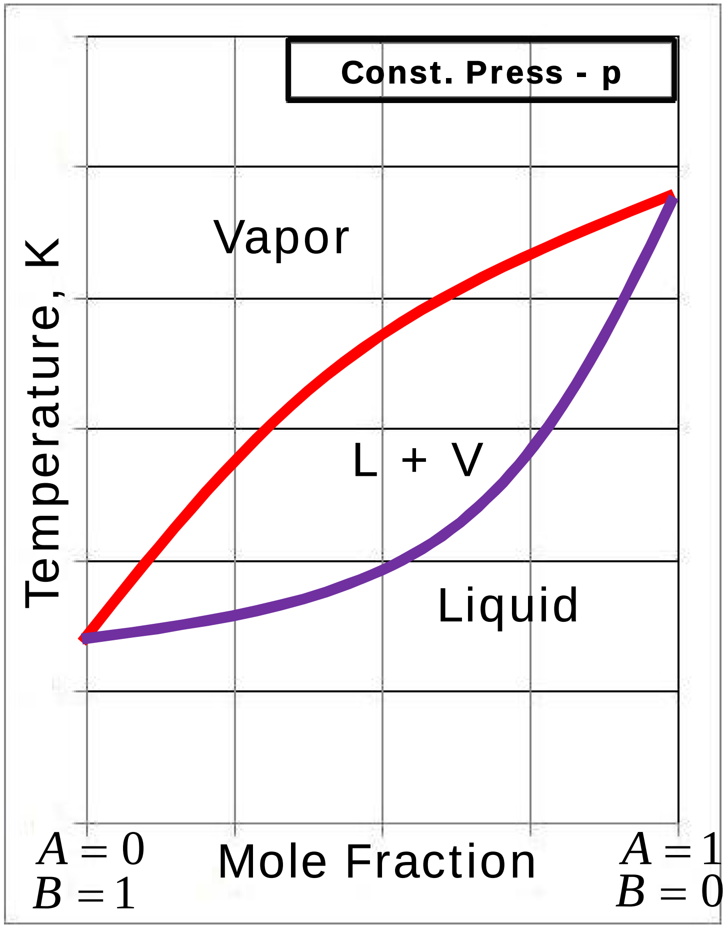
- Using the Gibbs Phase Rule, $F=3$

- These properties are pressure, temperature and mole fraction of one of the components.

Phase Equilibrium Curves

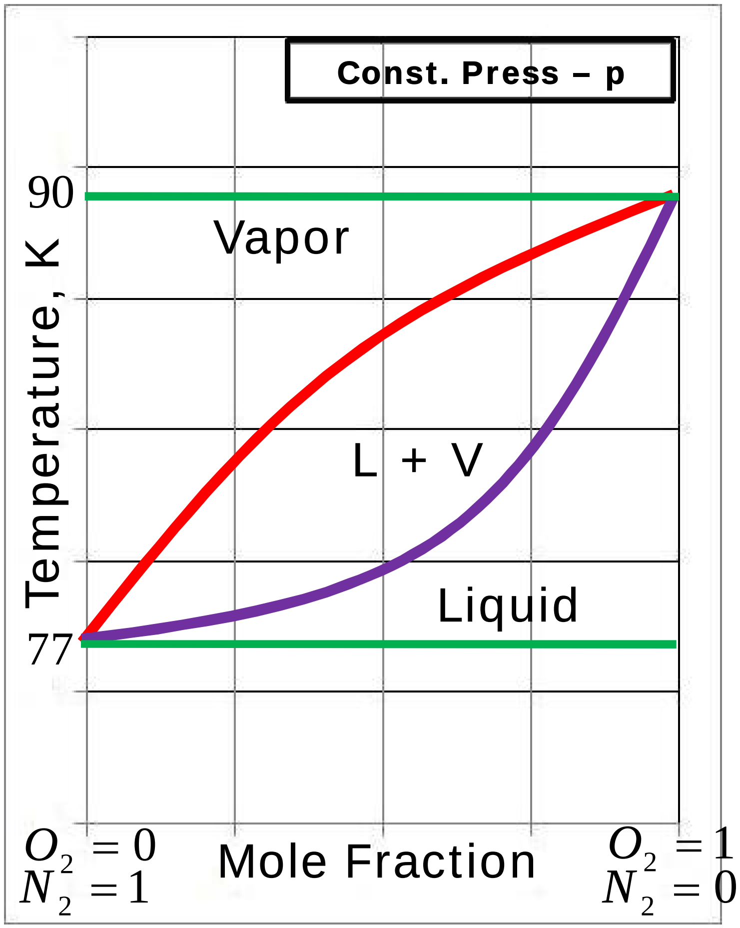
- In general, phase of a 1 – component system is governed by pressure and temperature.
- But for a 2 – component mixture at a given pressure, the mole fractions of components in vapor and liquid phases change with the temperature.
- Variation of mole fraction (**y**) with temperature (**T**) at a constant pressure (**p**) is given by **Temperature composition diagram** or **Phase – equilibrium curve**. 3 typical curves are explained in further slides.

Phase Equilibrium Curves



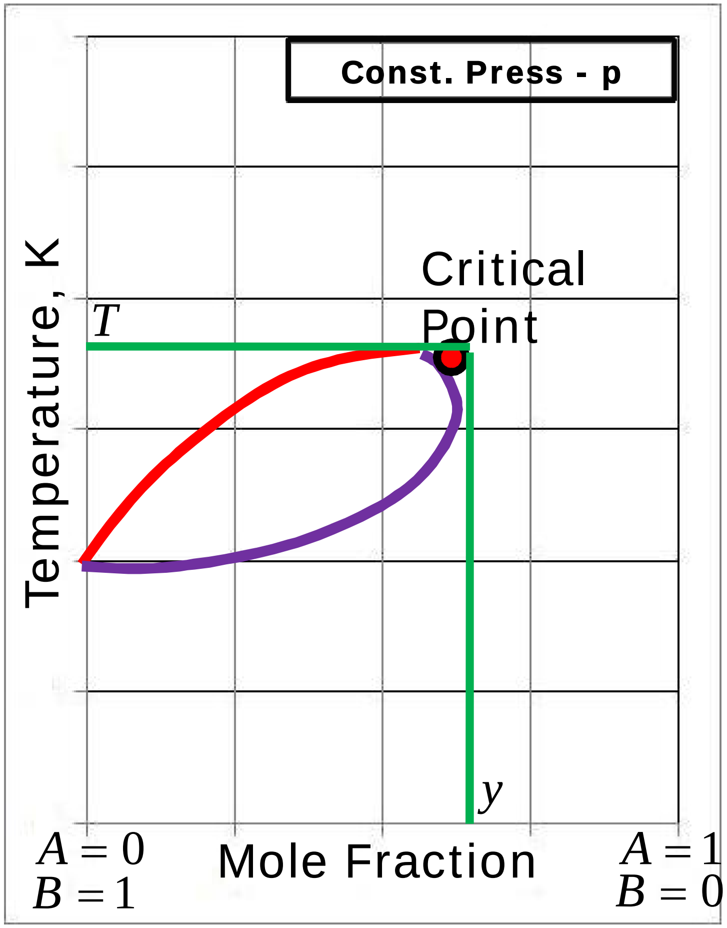
- Consider a 2 – component system (say, **A** and **B**) at some pressure **p** and temperature **T**.
- Critical Pressures ($\mathbf{p_c}$) of both these components are more than the pressure **p**.
- The plot shows the variation of mole fractions of the components with temperature.

Phase Equilibrium Curves



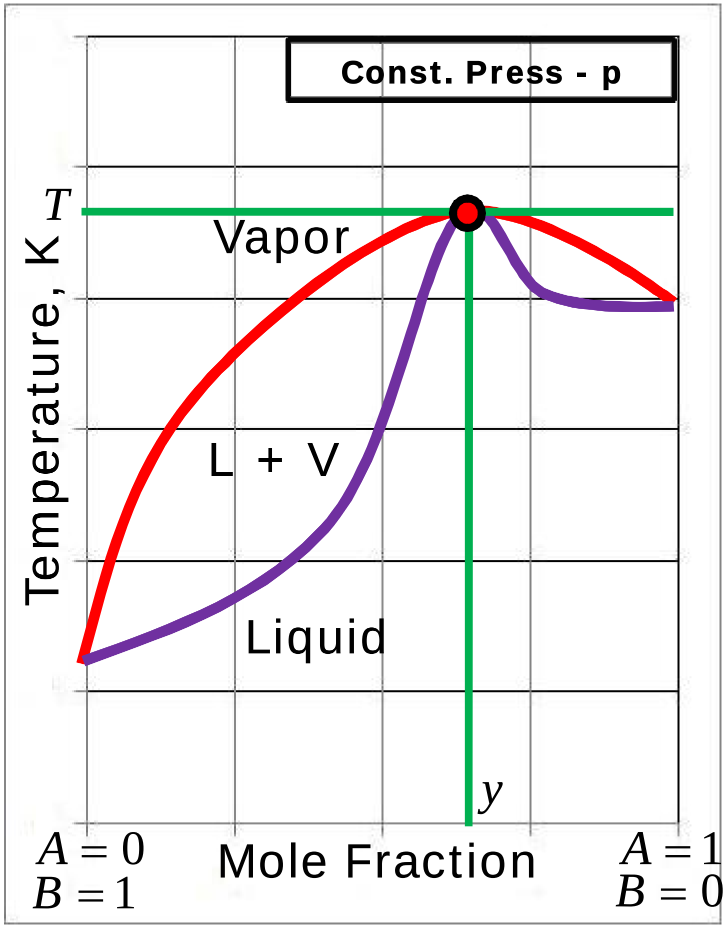
- For example, consider a mixture of $\mathbf{N_2}$ and $\mathbf{O_2}$ at 1 atm.
- It is clear that, above 90 K, the mixture is in gaseous phase and below 77 K, it is in liquid phase.
- The area formed by these curve lines indicate a two phase region (Liquid + Vapor).

Phase Equilibrium Curves



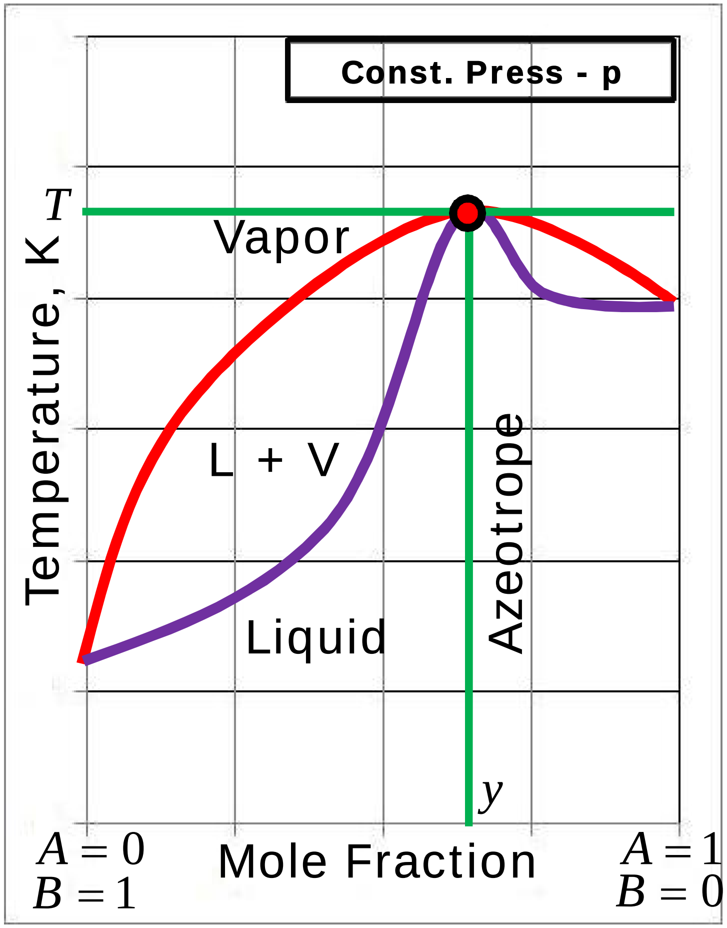
- Again consider a 2 – component system (say, **A** and **B**) at some pressure **p** and temperature **T**.
- The plot shows the case, in which one of the components has $\mathbf{p_c}$ less than the pressure **p**.
- There is no liquid phase after a certain temperature and mole fraction.

Phase Equilibrium Curves



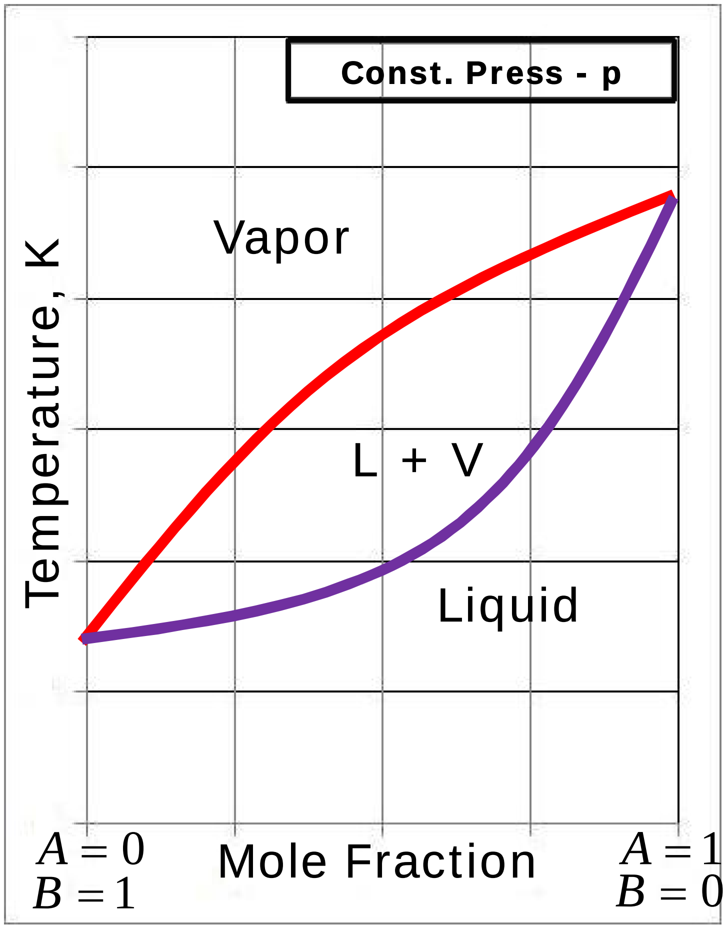
- Few substances when mixed in certain proportions, physically behave as one substance.
- For example, mixture of acetone and chloroform.
- In the figure, at **T** and mole fraction **y**, the mixture behaves as one substance.

Phase Equilibrium Curves



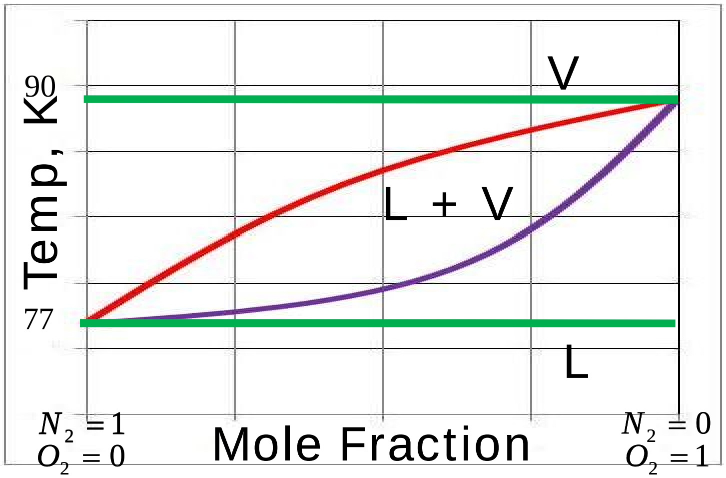
- Such mixtures are called as Azeotropic mixtures or constant boiling liquids.
- It is undesirable to separate such mixtures by rectification.
- Mixtures cannot be separated past this composition.
- Cryogens rarely exhibit such behaviors.

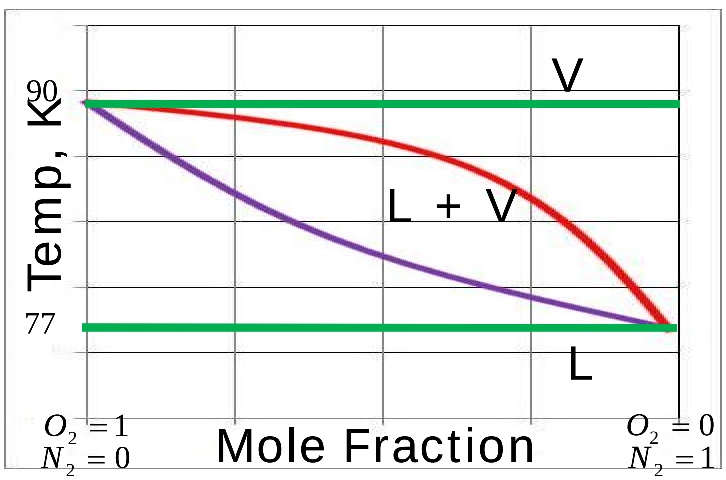
Temp. Composition Diagrams



- In **Gas Separation**, the first type of diagram is of great importance.
- The process of rectification is best understood with these curves.
- Hence, it is important to study the **Temperature Composition Diagram** to estimate the composition of vapor and liquid phases.

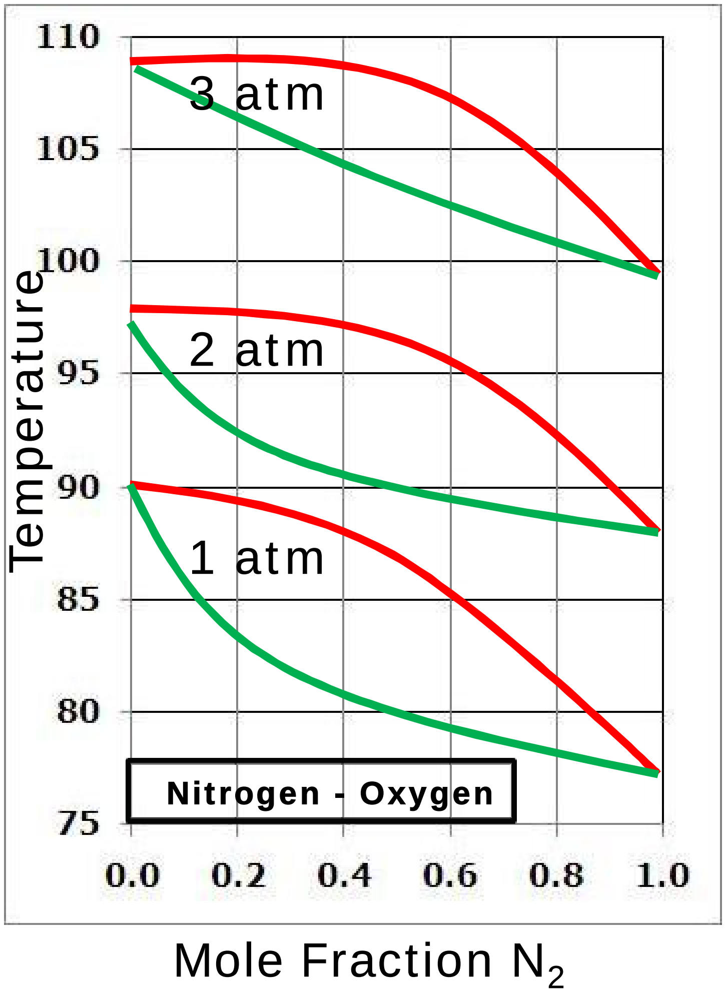
Temp. Composition Diagrams





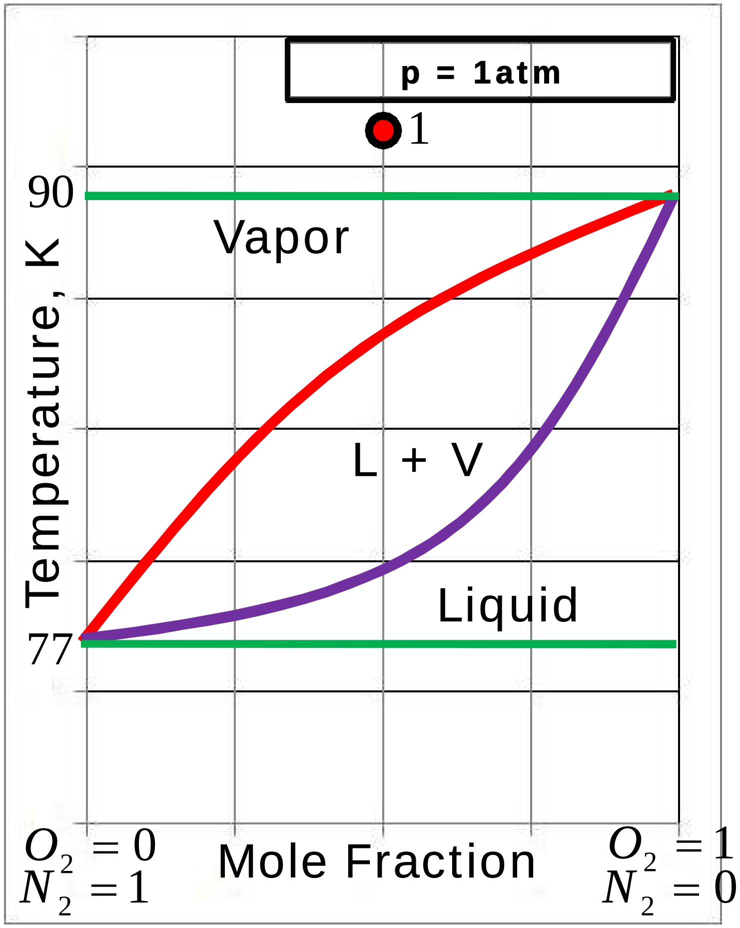
- Consider a mixture of $\mathbf{O_2}$ and $\mathbf{N_2}$ at a given constant pressure.
- If the components on the **x – axis** are interchanged, the diagram is as shown.
- It is important to note that, these two plots are one and the same. Either of the plots are commonly used in the literature.

Temp. Composition Diagrams



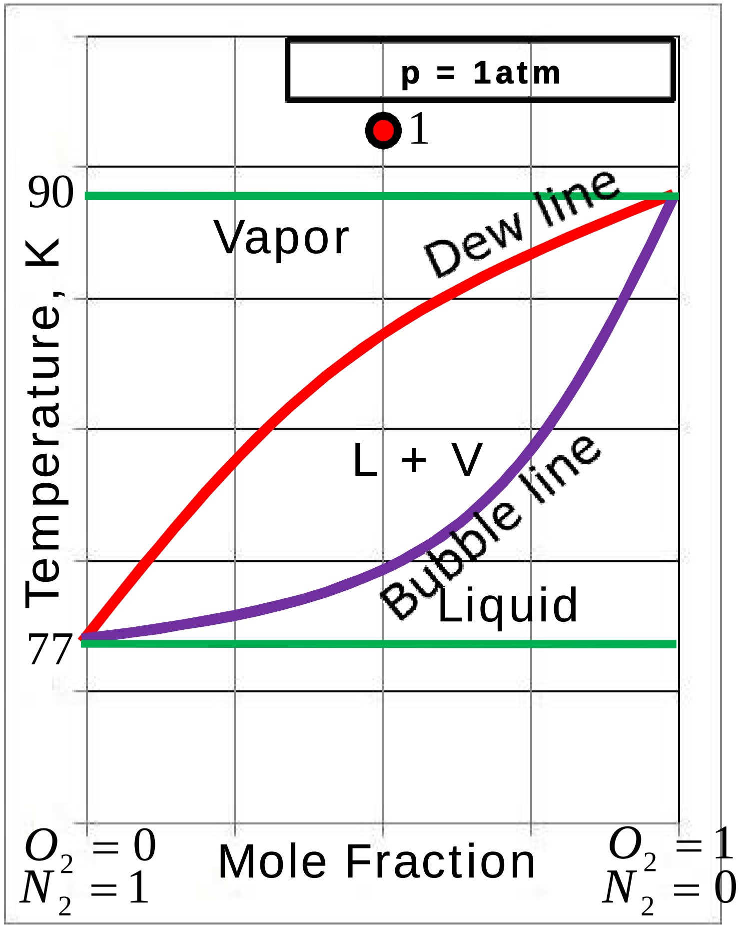
- Temperature composition diagrams for $\mathbf{N_2 – O_2}$ mixture for different pressures are as shown.
- These plots are obtained experimentally and are a strong function of inter – molecular forces.
- However, theoretical plots can be drawn based on some assumptions.

Temp. Composition Diagrams



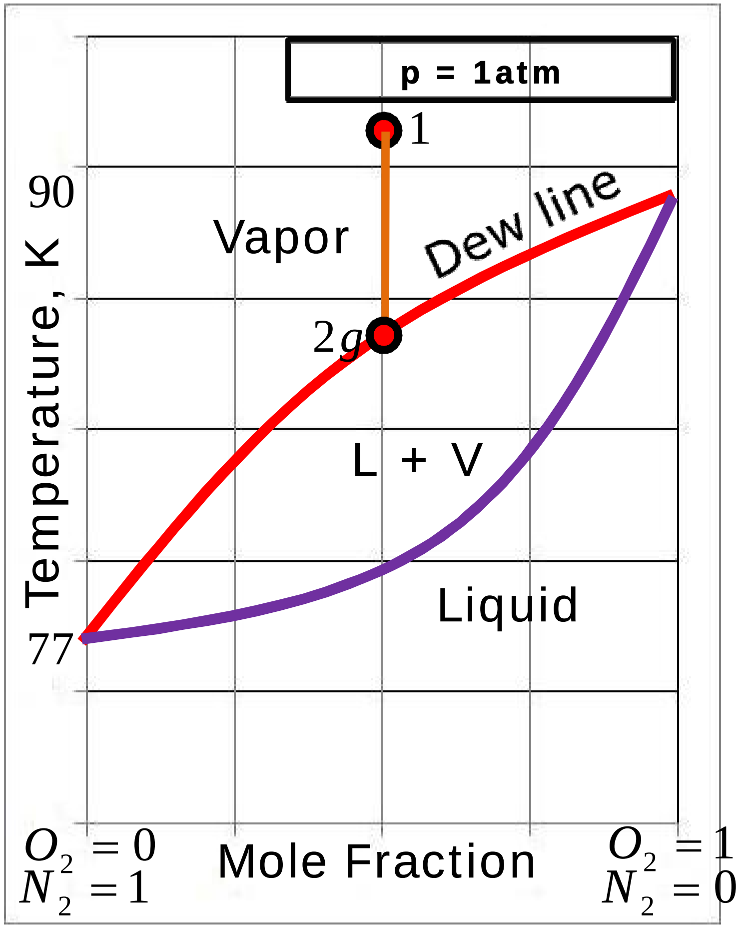
- Consider a Temperature composition diagram for a mixture of $\mathbf{O_2}$ and $\mathbf{N_2}$ at a pressure of 1 atm.
- Let the initial state of the mixture be at point **1** as shown in the figure.
- Since the temperature at point **1** is more than 90 K, the mixture exists in complete gaseous phase.

Temp. Composition Diagrams



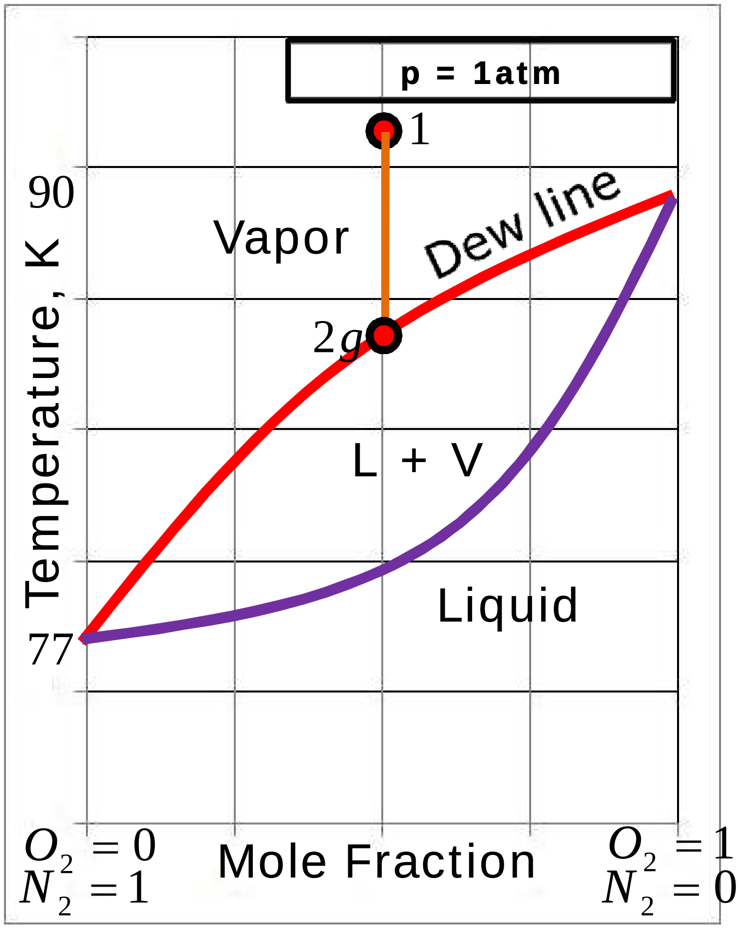
- The upper curve (Red) is called as the **Dew line**.
- Similarly, the lower curve (violet) is called as the **Bubble line**.
- The area formed by these curve lines indicate a two phase region.
- It means that, it has both Liquid and Vapor phases.

Temp. Composition Diagrams



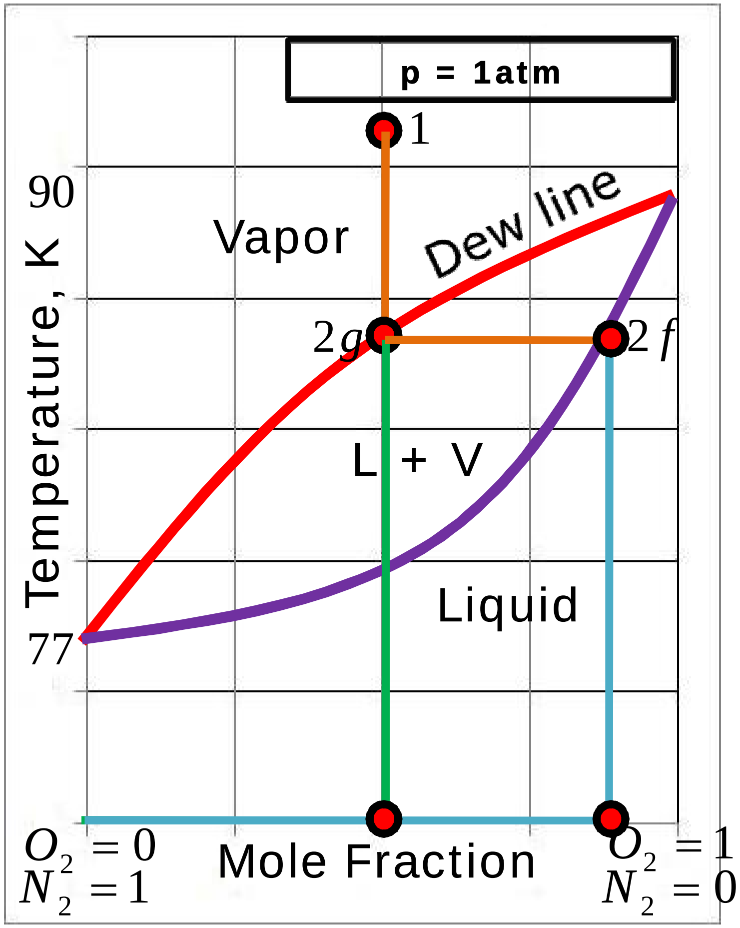
- Let the mixture be cooled at constant pressure.
- When the temperature of the mixture reaches point **2g**, the mixture starts condensing.
- The point **2g** lies on the dew line and the first drop or the dew appears in the mixture.

Temp. Composition Diagrams



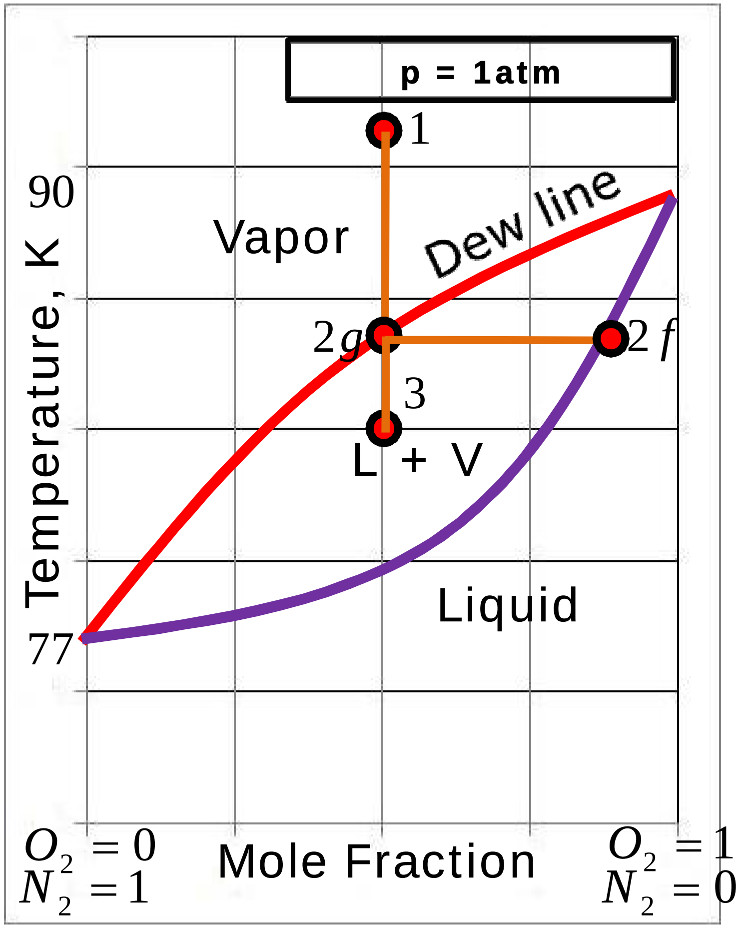
- Therefore, the mixture at point **2g** is a two – phase mixture with liquid – vapor phases in equilibrium.
- Condensate liquid has mole fractions of both high boiling and low boiling liquids.
- Liquid content is obtained by a constant temperature line about the point **2g**.

Temp. Composition Diagrams



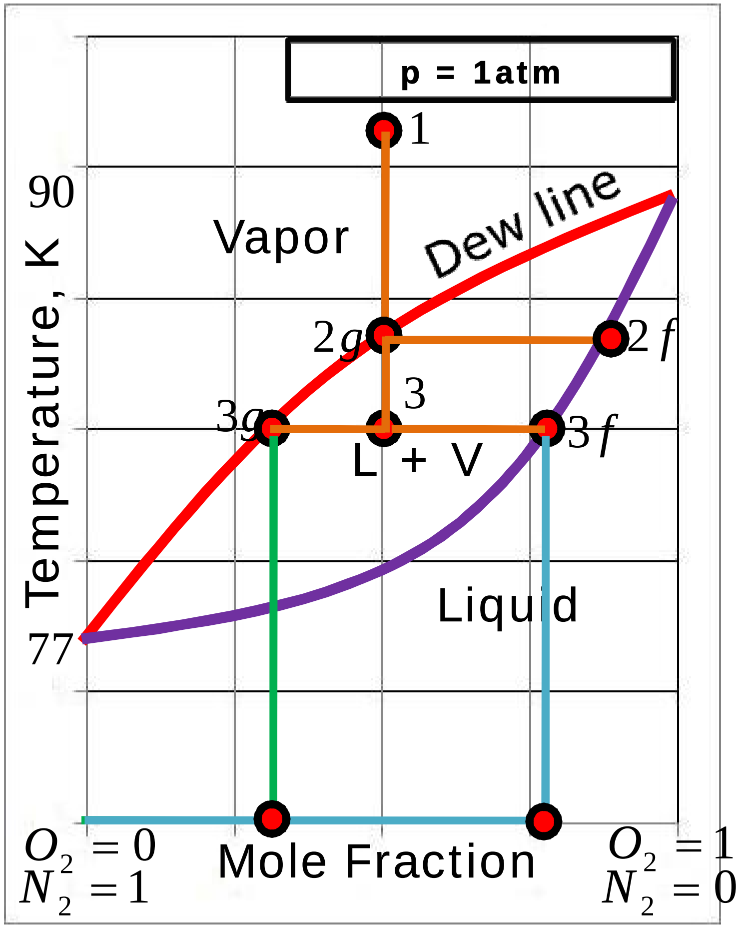
- Extending a constant temperature line about **2g**, it intersects the bubble line at point **2f**.
- **2g** and **2f** denote the mole fractions of higher BP liquid (**O_2**) in gaseous and liquid phases respectively.
- The compositions are
  - y_{vap} = **2g**
  - y_{liq} = **2f**

Temp. Composition Diagrams



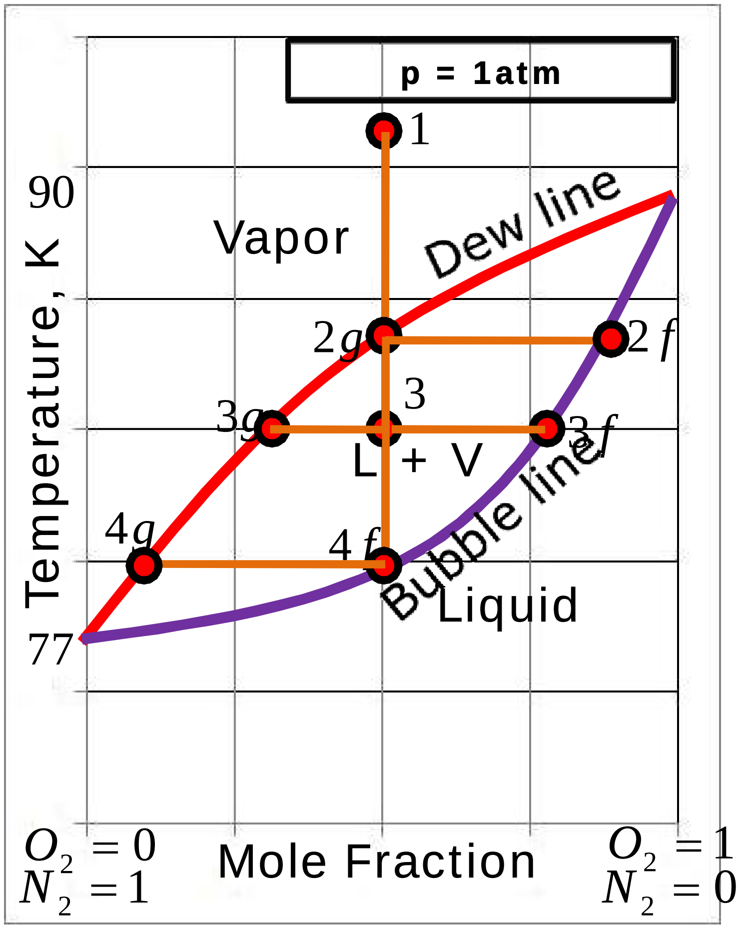
- The mixture is now cooled to a point **3** as shown in the figure.
- Again, extending a constant temperature line to the left and the right about the point **3**, we have the following.

Temp. Composition Diagrams



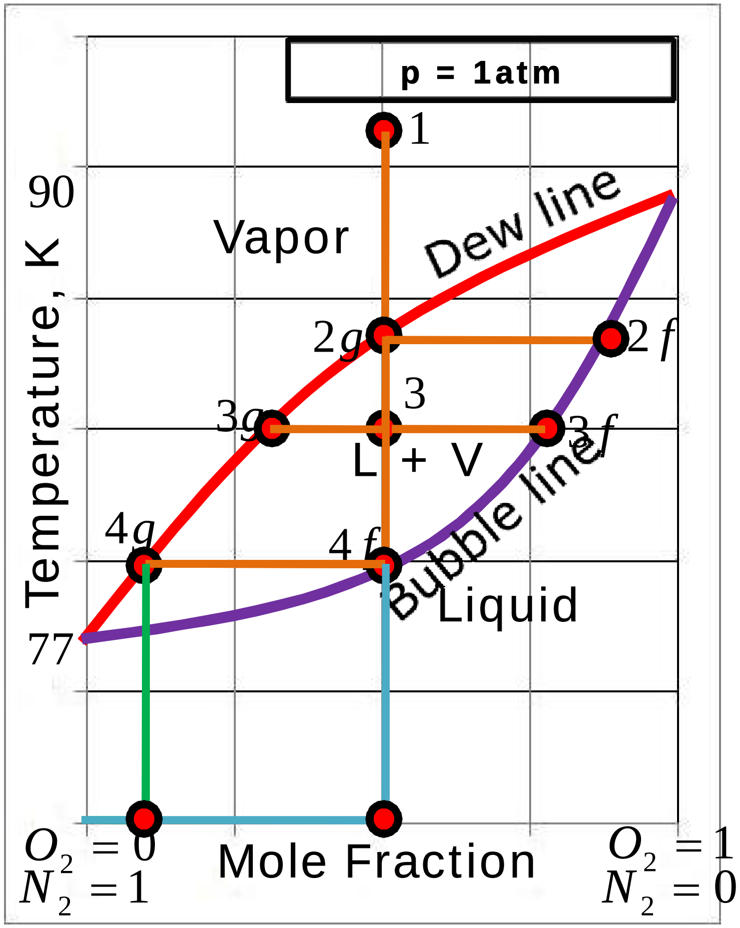
- The line extended to the left side intersects the Dew line at the point **3g**.
- And, the line extended to the right side intersects the bubble line at the point **3f**.
- The compositions of the higher boiling component at point **3** are given by
  - y_{vap} = **3g**
  - y_{liq} = **3f**

Temp. Composition Diagrams



- On further cooling of the mixture, the temperature reaches a point **4f** as shown in the figure.
- At this point, most of the high boiling component of the vapor is condensed.
- Extending a constant temperature line about the point **4f** to left, we have **4g**.

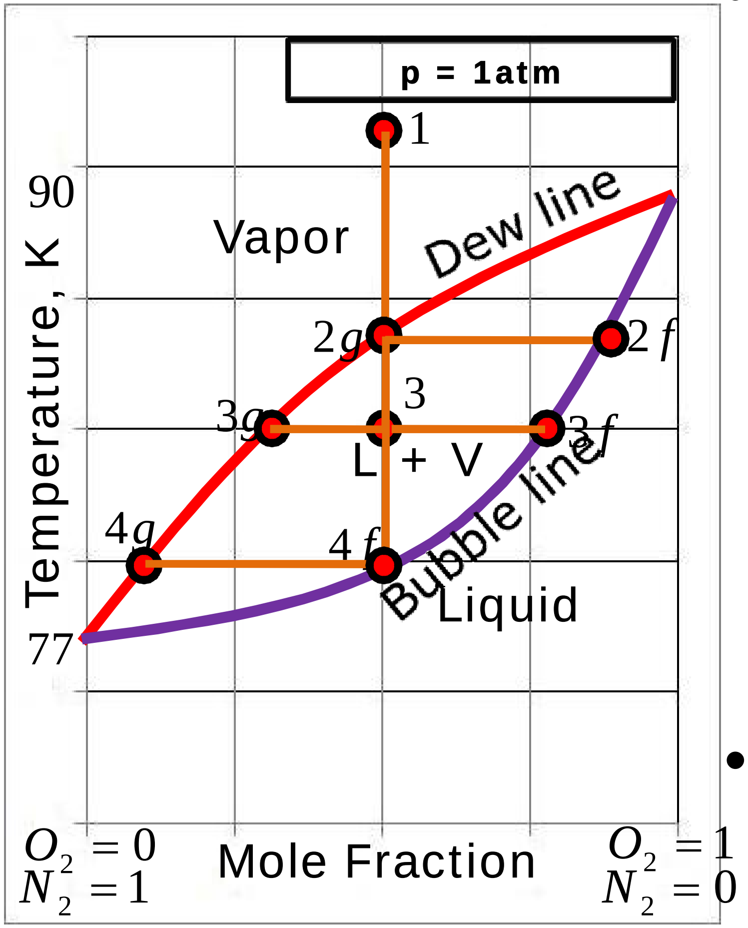
Temp. Composition Diagrams



- As mentioned earlier, this curve is called as **Bubble line** because when the liquid mixture is heated, the first bubble or vapor appears on this line.

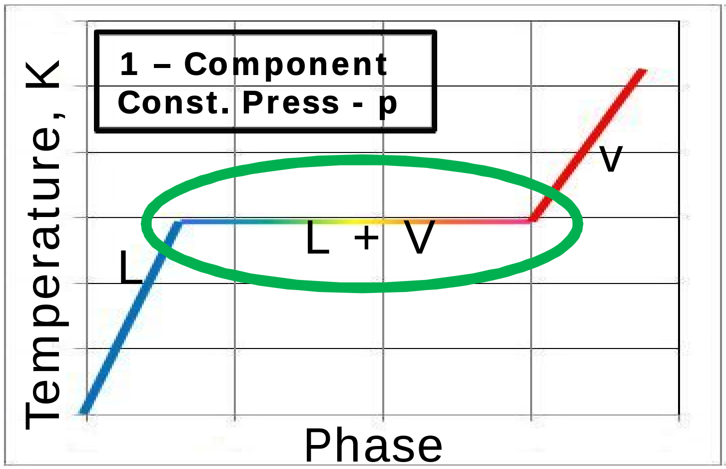
- The compositions of the higher boiling liquid are given by
  - y_{vap} = **4g**
  - y_{liq} = **4f**

Temp. Composition Diagrams



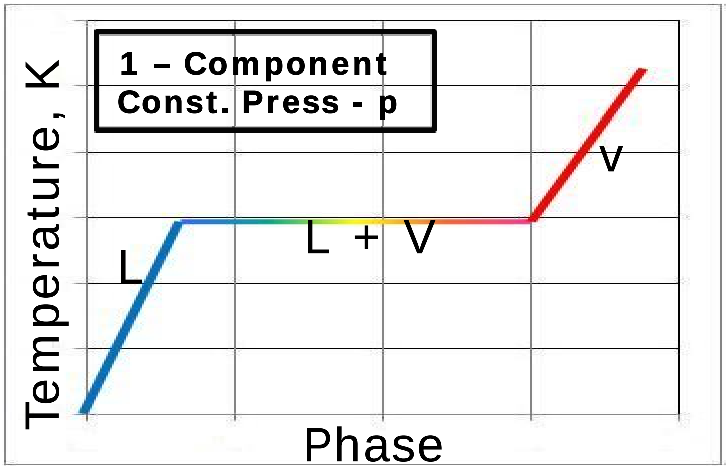
- By cooling of the mixture
  - The **%** of low BP component has increased
  - The **%** of high BP component has decreased in vapor and liquid phases.
- The mole fraction of mixture is unchanged, but the mole fractions in vapor and liquid phases have changed.

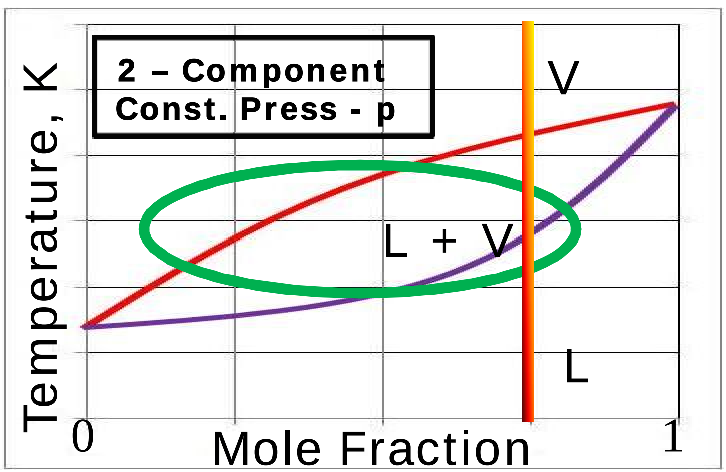
Temp. Composition Diagrams



- The temperature – phase diagram for a 1 – component system is as shown.
- It is clear that, during the phase change the temperature remains constant.
- It is an isothermal process.

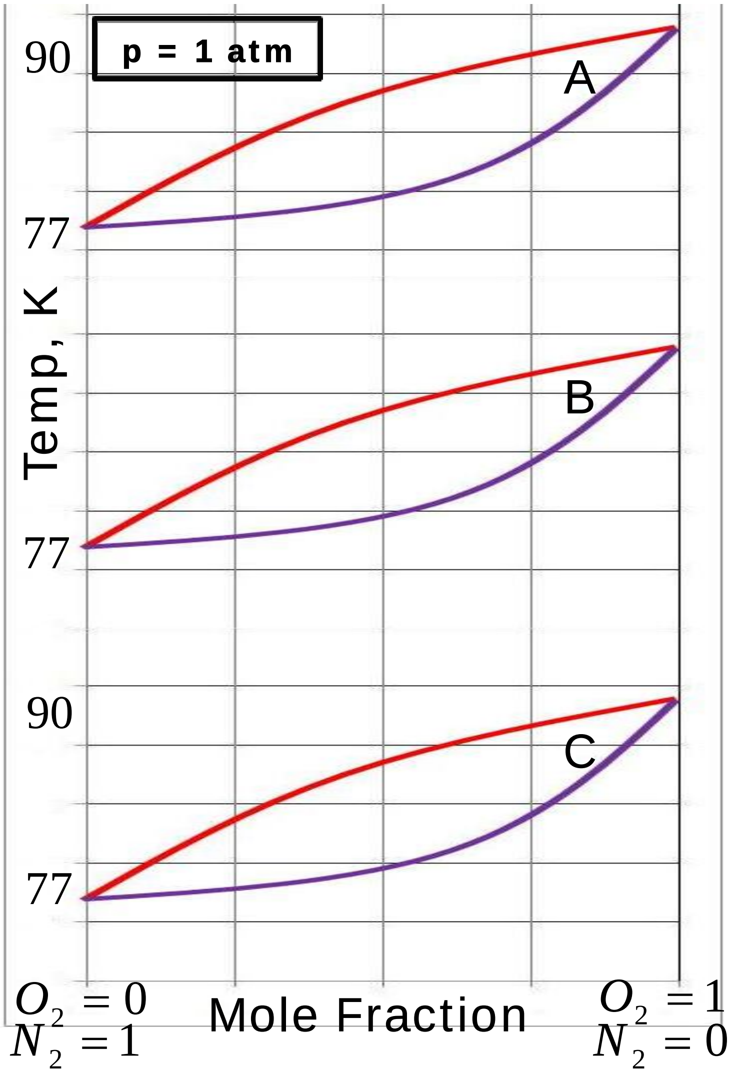
Temp. Composition Diagrams





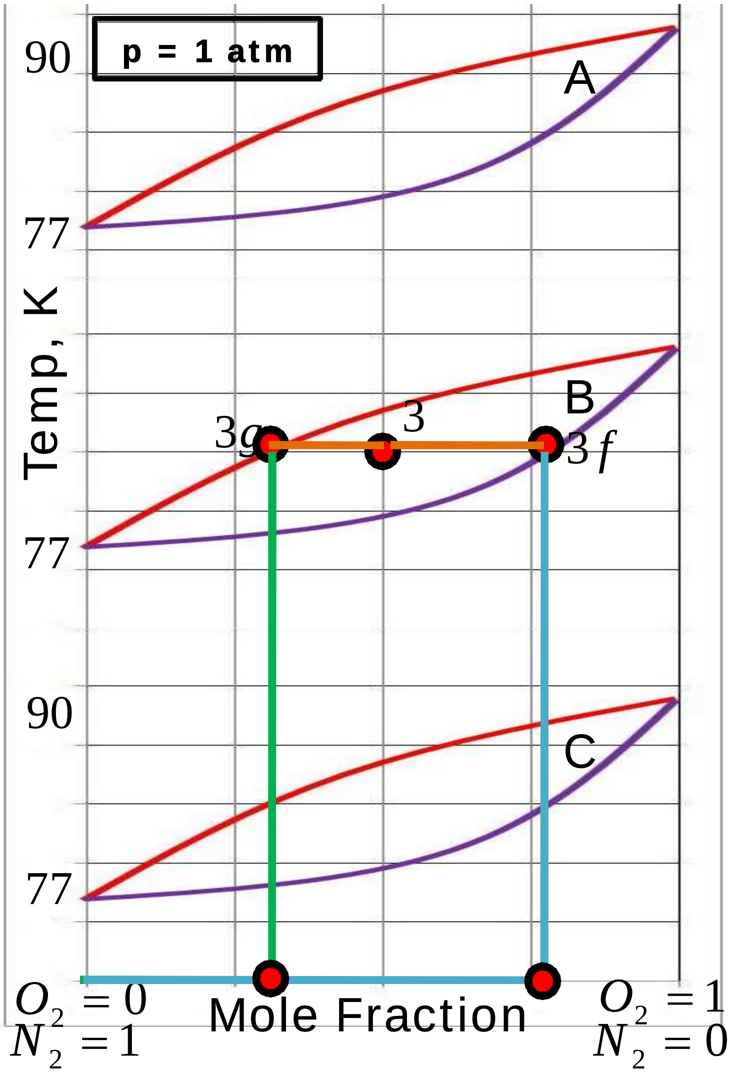
- Similarly, the temperature composition diagram for a 2 – component mixture is as shown.
- There is a change in the temperature when the mixture condenses or boils.
- Therefore, the phase change is an non – isothermal process for mixtures.

Temp. Composition Diagrams



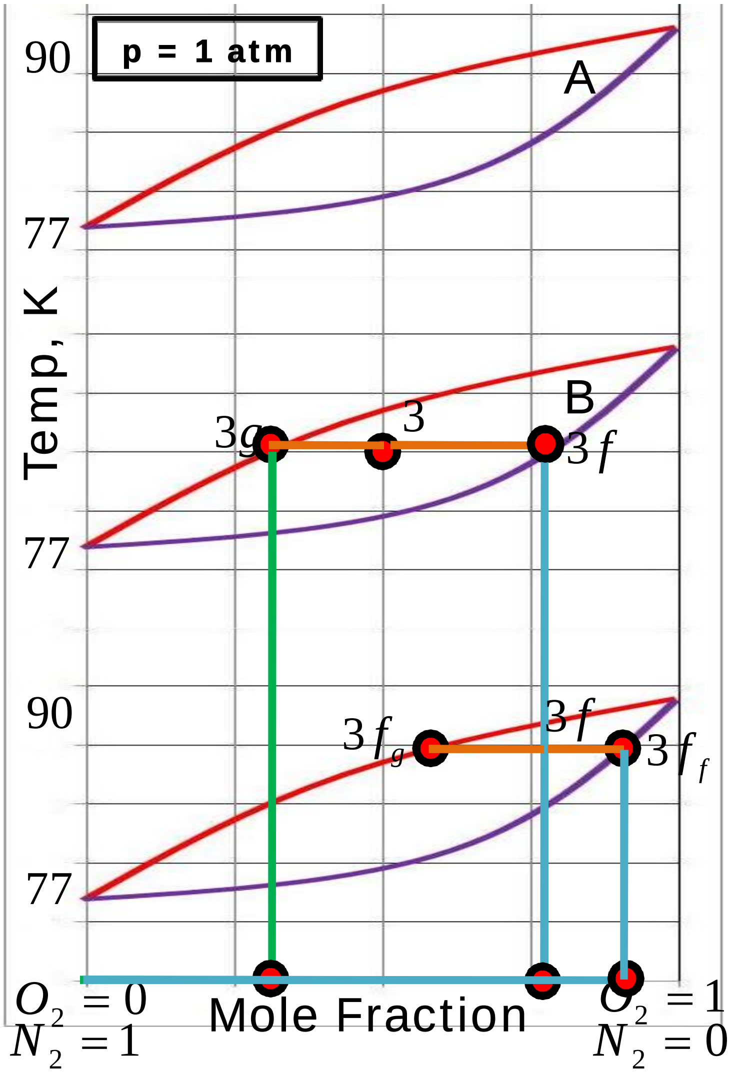
- Mixtures are separated by rectification and this is explained using the adjacent diagram.
- Consider a mixture of $\mathbf{N_2}$ and $\mathbf{O_2}$ at 1 atm.
- The figure has three diagrams **A**, **B** and **C**. They all are same but are placed one over the other for the ease of understanding.

Temp. Composition Diagrams



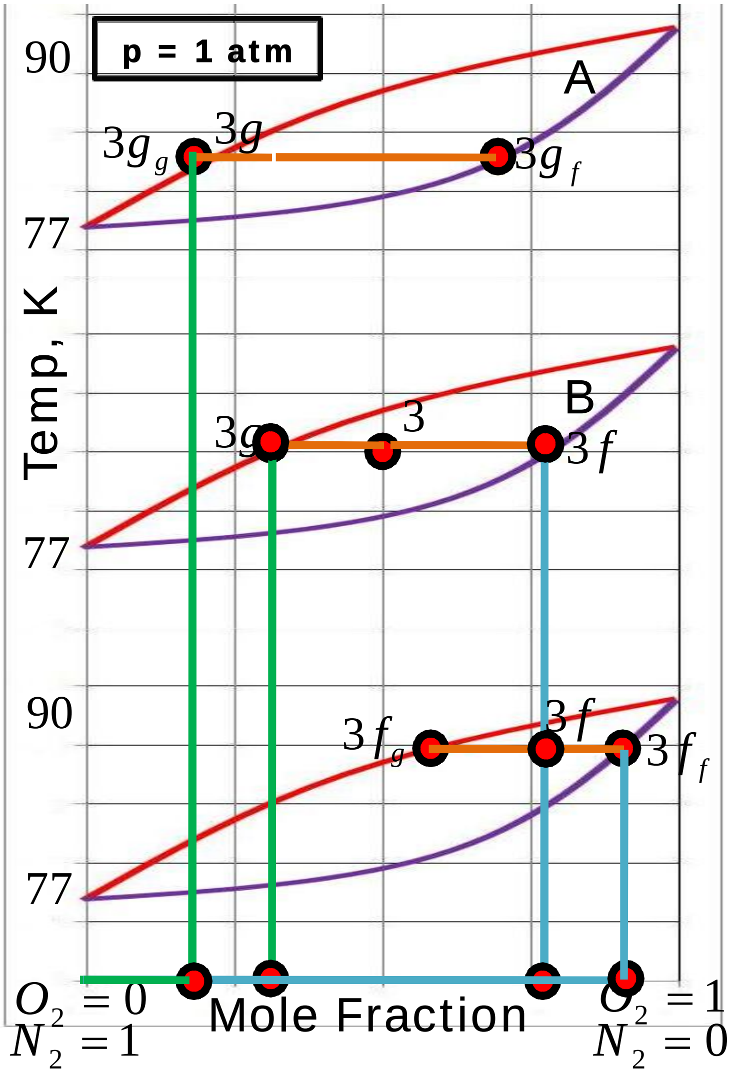
- Let the initial condition of the mixture be at point **3** as shown in the figure.
- The compositions of the higher boiling liquid at point **3** are given by
  - y_{vap} = **3g**
  - y_{liq} = **3f**

Temp. Composition Diagrams



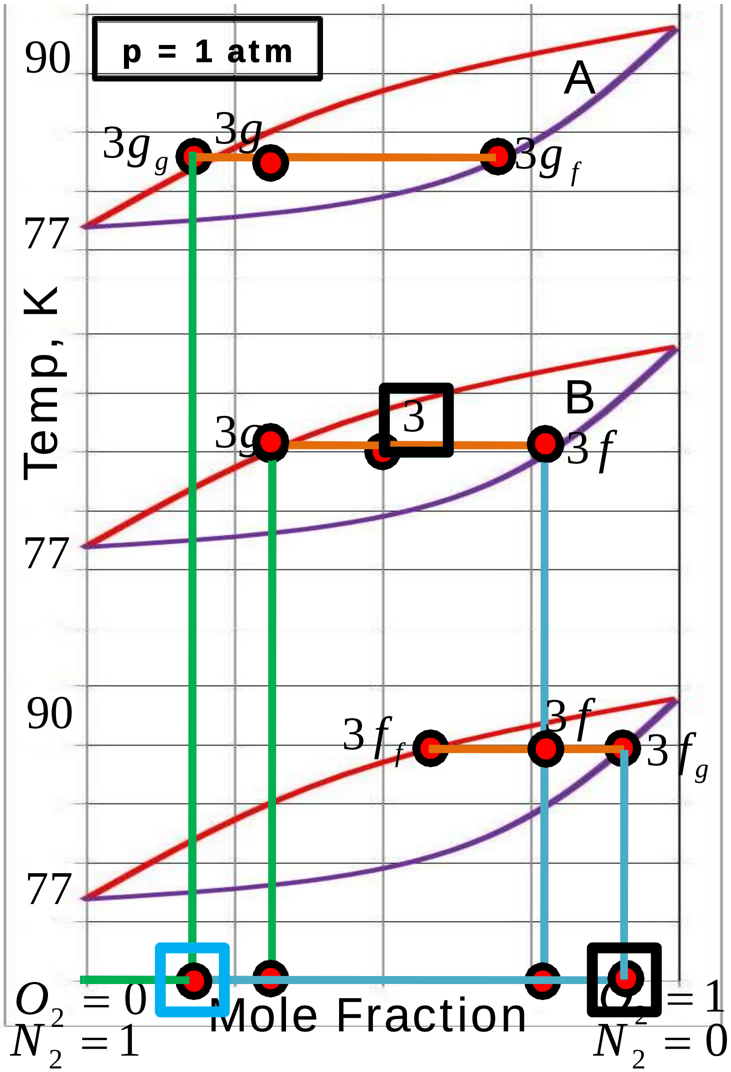
- Now, consider the rectification of mixture with composition at point **3f**.
- Again, extending the constant temperature lines about point **3f**, we have $\mathbf{3f_f}$ and $\mathbf{3f_g}$ respectively.
- The liquid composition of higher boiling liquid at point $\mathbf{3f_f}$ is given by
  - $y_{liq} = \mathbf{3f_f}$

Temp. Composition Diagrams



- Consider the rectification of mixture with composition at point **3g**.
- Again, extending the constant temperature lines about point **3g**, we have $\mathbf{3g_f}$ and $\mathbf{3g_g}$ respectively.
- The vapor composition of lower boiling component at point $\mathbf{3g_g}$ is given by
  - $y_{vap} = \mathbf{3g_g}$

Temp. Composition Diagrams



- Thus, the rectification of mixture at point **3**, the vapor is enriched in the lower boiling component (here, $\mathbf{N_2}$).

- Similarly, the liquid is enriched in high boiling component (here, $\mathbf{O_2}$).

- This process forms the fundamental step for the rectification column.

Summary

- If number of components, number of phases and degrees of freedom for a mixture in thermal equilibrium are denoted by C , P and F respectively, then the Gibbs Phase Rule

$$F = C - P + 2$$

- The variation of mole fraction (**y**) with temperature (**T**) at a constant pressure (**p**) is given by **Temperature composition diagram** or **Phase – equilibrium curve**.

- Condensation or boiling of a mixture is a non – isothermal process.

Summary

- Repeated rectification of a mixture enriches the liquid and vapor phases with high and low boiling components respectively.

- A self assessment exercise is given after this slide.

- Kindly asses yourself for this lecture.

Self Assessment

1. According to Gibbs Phase Rule _________.
2. For a two phase mixture of argon, $F =$ __.
3. Mixtures which behave as one substance at certain **T** and **y** are __________.
4. Temperature composition diagrams are a strong function of ____________ forces.
5. Area enclosed by dew and bubble lines is a ______ region.
6. Condensation or boiling of mixture is __ process.

Answers

1. $F = C - P + 2$
2. $F = 1$
3. Azeotropic mixtures.
4. Inter - molecular
5. Two – phase
6. Non – isothermal

Thank You!