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

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

• Ideal work of separation/mole of mixture with $N$ constituents is given by

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

• where $y_j$ is mole fraction of $j^{\text{th}}$ component.
Outline of the Lecture

Topic: Gas Separation (contd)

- Gibbs Phase Rule
- Phase Equilibrium Curves
- Temperature Composition Diagrams
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 $\text{Air}$ is $\text{LOX} + \text{LN}_2 + \text{N}_2 + \text{O}_2$. 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 $N_2$ is 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

Source: NIST
Gibbs Phase Rule

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

Source: NIST
Gibbs Phase Rule

- Similarly, for a two phase mixture of Helium in thermal equilibrium, we have
  \[ P = 2 \quad C = 1 \]

- 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.
• 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.
Consider a 2 – component system (say, A and B) at some pressure \( p \) and temperature \( T \).  

Critical Pressures \( (p_c) \) of both these components are more than the pressure \( p \).  

The plot shows the variation of mole fractions of the components with temperature.
For example, consider a mixture of \( \text{N}_2 \) and \( \text{O}_2 \) 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).
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 $p_c$ less than the pressure $p$.

There is no liquid phase after a certain temperature and mole fraction.
• 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.
• 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.
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 $O_2$ and $N_2$ 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.
Temperature composition diagrams for $\text{N}_2 - \text{O}_2$ 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.
Consider a Temperature composition diagram for a mixture of $O_2$ and $N_2$ 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.
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.
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
  - $y_{\text{vap}} = 2g$
  - $y_{\text{liq}} = 2f$
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
  - \(y_{\text{vap}} = 3g\)
  - \(y_{\text{liq}} = 3f\)
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.
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

- \( y_{\text{vap}} = 4g \)
- \( y_{\text{liq}} = 4f \)
• By cooling of the mixture
• The % of low BP component in liquid 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.
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.
• Mixtures are separated by rectification and this is explained using the adjacent diagram.

• Consider a mixture of $\text{N}_2$ and $\text{O}_2$ 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.
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

- \( y_{\text{vap}} = 3g \)
- \( y_{\text{liq}} = 3f \)
Now, consider the rectification of mixture with composition at point $3f$.

Again, extending the constant temperature lines about point $3f$, we have $3f_f$ and $3f_g$ respectively.

The liquid composition of higher boiling liquid at point $3f_f$ is given by

- $y_{\text{liq}} = 3f_f$
Consider the rectification of mixture with composition at point $3g$.

Again, extending the constant temperature lines about point $3g$, we have $3gf$ and $3gg$ respectively.

The vapor composition of lower boiling component at point $3gg$ is given by

$y_{vap} = 3g_g$
• Thus, the rectification of mixture at point 3, the vapor is enriched in the lower boiling component (here, $\text{N}_2$).

• Similarly, the liquid is enriched in high boiling component (here, $\text{O}_2$).

• 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.
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 assess 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!