Earlier Topics

- Introduction to Cryogenic Engineering
- Properties of Cryogenic Fluids
- Properties of Materials at Cryogenic Temperature
- Gas Liquefaction and Refrigeration Systems
Current Topic

Topic: Gas Separation

- Basics of Gas Separation
- Ideal Gas Separation System
- Properties of Mixtures and the Governing Laws
- Principles of Gas Separation
- Rectification and Plate Calculations

- The current topic will be covered in 7 to 10 lectures.

- Tutorials and assignments are included at the end of each lecture.
Outline of the Lecture

Topic: Gas Separation

• Basics of Gas Separation
  • Gas Separation methods

• Ideal Gas Separation System
  • Work requirement
Introduction

- As mentioned earlier, cryogenic industry is huge owing to the various applications of the cryogens, both in liquid and gaseous states.

- For example, the use of inert gases like argon in chemical and welding industries has increased in the recent past.

- Liquid Nitrogen is used as precoolant in most of the cryogenic systems. Also, cryogens like LOX, LH₂ are used in rocket propulsion.
Introduction

• In the recent past, LH$_2$ is being considered as a fuel for an automobile.

• Production of Ammonia in RCF industry, requires separation of purge gases like Nitrogen, Argon and other inert gases at cryogenic temperatures.

• For most practical purposes, Air is considered as a mixture of 78% N$_2$ + 21% O$_2$ + 1% Ar.

• The other ingredients are Helium, Neon, Krypton etc. which occur in negligible quantities.
Introduction

• Air is the raw material for the production of most of the gases and the process of separation of any gas mixture into its individual components is called as Gas Separation.

• In other words, this topic “Gas Separation” deals with separation of various gas mixtures and their purification.
Gas Separation

- Different techniques of gas separation commonly used are
  - Synthetic membranes
  - Adsorption
  - Absorption
  - Cryogenic distillation
Gas Separation

- Synthetic membranes are the porous media which allow only a certain gas molecules to pass through.

- The membrane in the figure allows only **Gas A** to pass and hence the separation occurs.

- For example, a thin sheet of palladium allows **H\textsubscript{2}** to pass through.
Gas Separation

- Adsorption is the physical processes in which only a certain kind of gas molecules are adhered to the adsorbing surface.

- The adsorbate in the figure adheres only **Gas A** to the surface and hence the separation occurs.

- For example, finely divided Nickel adsorbs hydrogen on to its surface.
Gas Separation

• Absorption is a chemical process in which a substance in one physical state is taken into other substance at a different physical state.

• For example, liquids being absorbed by a solid or gases being absorbed by a liquid.

• When an incoming stream containing CO$_2$ is passed through a solution of Sodium hydroxide, the later absorbs the gas and hence decreases the CO$_2$ content in the outgoing stream.

• Hence, this chemical process helps in the separation of the mixture.
Gas Separation

- Distillation is a process of separation based on the differences in the volatilities (boiling points).
- If the process of distillation occurs at cryogenic temperatures, it is called as Cryogenic Distillation.
- The commercial production of gases like $O_2$, $N_2$, Argon, Neon, Krypton & Xenon is obtained by cryogenic distillation of Liquid Air.
The separation of a mixture can be done at both room temperature and cryogenic temperature.

For example in the case of Air, the following processes are possible.

- **Gas Separation**
  - Air (300K)
  - Liquefaction
    - LOX (90K)
    - LN₂ (77K)
- **Cryogenic Separation**
  - O₂ (300K)
  - N₂ (300K)
- **Room Temp. Separation**
  - LOX (90K)
  - LN₂ (77K)
Some of the advantages of Cryogenic separation over Room Temperature separation are:

- The separation at lower temperatures is most economical (explained in further slides).
- There is an increased difference in the boiling points of the ingredients (explained in further slides).
- A large quantities of the gas can be separated.
- A high purity of the gas can be obtained.
Is Gas Mixing Reversible?

- Consider a closed chamber filled with **Gas A** and **Gas B** as shown in the figure.

- Initially, the gases are separated by an impervious wall.

- If the wall is removed, the gases would mix.

- However, the replacement of wall would not result in the separation of gases.
Gas Separation

• It is clear that the mixing of two different gases is an irreversible process because unmixing or separation of the mixture requires work input.

• The system in which all the processes are reversible is called as an Ideal System.

• Although in reality such a system does not exist, a system can be conceived to serve the required purpose as explained in the next slide.
Consider a closed chamber filled with a mixture of **Gas A** and **Gas B** as shown.

- The temperature and mixture pressure are $T_m$ and $p_m$ respectively.
- The partial pressures of **Gas A** and **Gas B** are given by $p_{1a}$ and $p_{1b}$ respectively.
Ideal Separation System

• The chamber has two frictionless opposing pistons made of semi-permeable membranes as shown in the figure.

• As seen earlier, a semi-permeable membrane is a film which allows only one kind of gas to pass through but not the other.
Ideal Separation System

- The left piston (red) allows only the Gas A to pass through, but not the Gas B.

- Similarly, the right piston (green) allows only the Gas B to pass through, but not the Gas A.

- When both pistons are moved inward, the mixture is separated.
Since the processes are reversible, the system interacts with the surroundings to maintain a constant temperature.

The work of separation is the work required to compress each gas from $p_{1a}$ or $p_{1b} \rightarrow p_m$ at a constant temperature $T_m$. 
Ideal Separation System

Since the left piston is permeable to **Gas A**, the **Gas A** exerts no pressure on the left piston.

Similarly, the **gas B** exerts no pressure on the right piston.

When both the pistons are moved inward, the mixture is separated at constant $T_m$. 
Ideal Separation System

- The entire processes are assumed to be reversible.

- The process is reversed due to the difference in the concentrations of **Gas A** and **Gas B**.

- Hence, the mixing of the gases would move the pistons away and produce work.
Ideal Separation System

The Work produced in this mixing process is same as the Work done to separate at constant $T_m$. The final condition is a system with a mixture of Gas A and B at $p_m$ and $T_m$. Also, the partial pressures of Gas A and B are $p_{1a}$ and $p_{1b}$. 

$T_m, p_m$

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• In other words, thermodynamically each gas is compressed **reversibly** and **isothermally** from its partial pressure to the mixture pressure.
In order to understand the process of compression, say for a Gas A, from \( p_{1a} \) to \( p_m \), the following analysis is done.
Let the mol. wt. of **Gas A** and **Gas B** be **molw\textsubscript{a}** and **molw\textsubscript{b}** respectively.

- Number of moles of **Gas A** is given by \( n_a = \frac{m_a}{molw_a} \)

- Similarly, number of moles of **Gas B** is \( n_b = \frac{m_b}{molw_b} \)

- Then total number of moles in the mixture \( n_m \) is \( n_m = n_a + n_b \)

- Then the ratios \( y_a = \frac{n_a}{n_m} \) and \( y_b = \frac{n_b}{n_m} \) are the mole fractions of **Gas A** and **Gas B** respectively.
Ideal Separation System

- The volume occupied by each of the gas is directly proportional to its number of moles.
Ideal Separation System

• From the earlier lectures, the work requirement for a unit mass of gas compressed isothermally is given by

\[
\frac{-W_i}{m} = T_m \left( s_1 - s_2 \right) - \left( h_1 - h_2 \right)
\]

• The net ideal work requirement of the separation process is the sum of the ideal work requirement by Gas A and Gas B.

• Mathematically,

\[
-W_i = (-W_{i,a}) + (-W_{i,b})
\]

• Dividing the above equation by the mass of the mixture \( m_m \), we get

\[
\frac{-W_i}{m_m} = \frac{-W_{i,a}}{m_m} + \frac{-W_{i,b}}{m_m}
\]
The total mass of mixture $m_m$ is the sum of mass of Gas A and Gas B.

Mathematically, we have

$$m_m = m_a + m_b$$

Rearranging the terms, we can write the above equation as

$$-\frac{W_i}{m_m} = -\frac{W_{i,a}}{m_a} \left( \frac{m_a}{m_m} \right) + -\frac{W_{i,b}}{m_b} \left( \frac{m_b}{m_m} \right)$$

Here, $m_a$ and $m_b$ are the mass of the Gas A and Gas B respectively.
The work requirement for each of the individual gas is given by the following equations.

\[
\frac{-W_i}{m_m} = \left( \frac{-W_{i,a}}{m_a} \right) \left( \frac{m_a}{m_m} \right) + \left( \frac{-W_{i,b}}{m_b} \right) \left( \frac{m_b}{m_m} \right)
\]

Substituting and rearranging, we get

\[
\frac{-W_{i,a}}{m_a} = T_m \left( s_{1a} - s_{2a} \right) - \left( h_{1a} - h_{2a} \right)
\]

\[
\frac{-W_{i,b}}{m_b} = T_m \left( s_{1b} - s_{2b} \right) - \left( h_{1b} - h_{2b} \right)
\]
• It is clear that the work requirement decreases with the decrease in the temperature.

• Hence, the separation of mixtures at the cryogenic temperatures is most economical.

• The subscripts $1$ and $2$ denote the initial and the final conditions respectively.
It means that for each gas, \( s_1 \) and \( h_1 \) are at the partial pressure before the separation. And \( s_2 \) and \( h_2 \) are at mixture pressure after the separation of the mixture.

For the sake of understanding, let us first evaluate only \textbf{entropy} and \textbf{enthalpy} terms for each of the gases.
For an ideal gas, the specific entropy $s$ and specific enthalpy $h$ can be expressed as

\[ s = c_p \ln T - R \ln p + s_r \]

\[ h = c_p T + h_r \]

where, $s_r$ and $h_r$ are some reference values.

Hence, $s$ and $h$ for Gas A are given by

\[ s_{1a} = c_{pa} \ln T_m - R_a \ln p_{1a} + s_{ra} \]

\[ h_{1a} = c_{pa} T_m + h_{ra} \]

\[ s_{2a} = c_{pa} \ln T_m - R_a \ln p_{1a} + s_{ra} \]

\[ h_{2a} = c_{pa} T_m + h_{ra} \]
The entropy and enthalpy term for **Gas A** is as given below.

\[(s_{1a} - s_{2a}) - (h_{1a} - h_{2a})\]

Substituting, we get

\[
\left( c_{pa} \ln T_m - R_a \ln p_{1a} + \frac{s_{ra}}{R_a} - c_{pa} \ln T_m + R_a \ln p_m - \frac{s_{ra}}{R_a} \right)

- \left( c_{pa} T_m + h_{ra} - c_{pa} T_m - h_{ra} \right)

\]

\[
((s_{1a} - s_{2a}) - (h_{1a} - h_{2a})) = R_a \ln \left( \frac{p_m}{p_{1a}} \right)
\]

Also, for **Gas B**

\[
((s_{1b} - s_{2b}) - (h_{1b} - h_{2b})) = R_b \ln \left( \frac{p_m}{p_{1b}} \right)
\]
Substituting, we get the ideal work requirement as

$$\left( s_{1a} - s_{2a} \right) - \left( h_{1a} - h_{2a} \right) = R_a \ln \left( \frac{p_m}{p_{1a}} \right)$$

$$\left( s_{1b} - s_{2b} \right) - \left( h_{1b} - h_{2b} \right) = R_b \ln \left( \frac{p_m}{p_{1b}} \right)$$

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

$$-\frac{W_i}{m_m} = T_m \left( \left( \frac{m_a}{m_m} \right) R_a \ln \left( \frac{p_m}{p_{1a}} \right) + \left( \frac{m_b}{m_m} \right) R_b \ln \left( \frac{p_m}{p_{1b}} \right) \right)$$
Since the process occurs at constant volume $V_m$, using an ideal gas equation we can write

$$p_m V_m = n_m RT_m$$
$$p_{1a} V_m = n_a RT_m$$
$$p_{1b} V_m = n_b RT_m$$

Dividing one over the other, we have

$$\frac{p_m V_m}{p_{1a} V_m} = \frac{n_m RT_m}{n_a RT_m}$$
$$\frac{p_m V_m}{p_{1b} V_m} = \frac{n_m RT_m}{n_b RT_m}$$

$$\frac{p_m}{p_{1a}} = \frac{n_m}{n_a} = \frac{1}{y_a}$$
$$\frac{p_m}{p_{1b}} = \frac{n_m}{n_b} = \frac{1}{y_b}$$

Where $y_a$ and $y_b$ are the mole fractions of Gas A and Gas B respectively.
The ideal gas equation can also be expressed in terms of the mass of the gas as shown below.

\[ p_m V_m = n_m \overline{R} T_m \]
\[ p_{1a} V_m = n_a \overline{R} T_m \]
\[ p_{1b} V_m = n_b \overline{R} T_m \]

\[ p_m V_m = \frac{m_m}{molw_m} \overline{R} T_m \]
\[ p_{1a} V_m = \frac{m_a}{molw_a} \overline{R} T_m \]
\[ p_{1b} V_m = \frac{m_b}{molw_b} \overline{R} T_m \]

\[ p_m V_m = m_m R_m T_m \]
\[ p_{1a} V_m = m_a R_a T_m \]
\[ p_{1b} V_m = m_b R_b T_m \]

In general, \[ \overline{R} \] and \[ R \] are the Universal Gas Constant and Specific Gas Constant respectively.

\[ R_a = \frac{\overline{R}}{molw_a} \]
\[ \overline{R} = 8.314 \text{ } J/\text{mol} - K \]
Ideal Separation System

- From the earlier slide, using the ideal gas equation in terms of the gas mass, we have

\[
p_m V_m = m_m R_m T_m \quad \frac{p_m V_m}{p_{1a} V_m} = \frac{m_m R_m T_m}{m_a R_a T_a} \quad \frac{p_m V_m}{p_{1b} V_m} = \frac{m_m R_m T_m}{m_b R_b T_b}
\]

- Dividing one over the other, we have

\[
\frac{p_m}{p_{1a}} = \frac{m_m R_m}{m_a R_a} = \frac{1}{y_a} \quad \frac{p_m}{p_{1b}} = \frac{m_m R_m}{m_b R_b} = \frac{1}{y_b}
\]

\[
\frac{m_a R_a}{m_m} = R_m y_a \quad \frac{m_b R_b}{m_m} = R_m y_b
\]
Ideal Separation System

Substituting, we have

- \( \frac{p_m}{p_{\lambda a}} = \frac{1}{y_a} \)
- \( \frac{p_m}{p_{\lambda b}} = \frac{1}{y_b} \)
- \( \frac{m_a R_a}{m_m} = R_m y_a \)
- \( \frac{m_b R_b}{m_m} = R_m y_b \)

- \( \frac{-W_i}{m_m} = T_m \left( \frac{m_a}{m_m} R_a \ln \left( \frac{p_m}{p_{\lambda a}} \right) + \frac{m_b}{m_m} R_b \ln \left( \frac{p_m}{p_{\lambda b}} \right) \right) \)

- \( p_m V_m = m_m R_m T_m = n_m \Re T_m \)

- \( \frac{-W_i}{n_m} = \Re T_m \left( y_a \ln \left( \frac{1}{y_a} \right) + y_b \ln \left( \frac{1}{y_b} \right) \right) \)
Ideal Separation System

- The ideal work of separation per mole of mixture (Gas A and Gas B) is given by

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

- On the similar lines, if the mixture is composed of three different gases, say Gas A, Gas B and Gas C, the ideal work of separation per mole of mixture is given by

\[
-\frac{W_i}{n_m} = R T_m \left( y_a \ln \left( \frac{1}{y_a} \right) + y_b \ln \left( \frac{1}{y_b} \right) + y_c \ln \left( \frac{1}{y_c} \right) \right)
\]
Ideal Separation System

- Generalizing the above equation for a mixture of \( N \) constituents, we have

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

- where \( y_j \) is the mole fraction of \( j^{th} \) component.

- Similar to the Liquefaction systems, the Figure of Merit (FOM) is defined as given below.

\[
FOM = \frac{-W_i}{n_m} = \frac{-W_i}{m_m} = \frac{-W}{n_m} = \frac{-W}{m_m}
\]
Summary

• Different techniques employed are Synthetic membranes, Adsorption, Absorption and distillation.

• The separation can be done at both room temperature and cryogenic temperature.

• In an Ideal system all the processes are reversible and the work requirement in an ideal gas separation is called as an Ideal Work.
Summary

- Ideal work requirement per mole of mixture to separate a mixture with $N$ constituents is given by

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

- where $y_j$ is the mole fraction of $j^{th}$ component.
• A self assessment exercise is given after this slide.

• Kindly asses yourself for this lecture.
Self Assessment

1. Air is considered as a mixture of __________.
2. Thin sheet of palladium allows only __ to pass through.
3. __________ is the processes in which only a certain kind of gas molecules are adhered.
4. ___ is a chemical process for gas separation.
5. ______ separation is most economical.
6. In an ideal system, each gas is compressed from its _____ to the _______.

7. In an ideal system, \( ((s_{1a} - s_{2a}) - (h_{1a} - h_{2a})) \) is _______.

8. The Specific Gas constant for a Gas A \( (R_a) \) is _______.
1. 78% N₂ + 21% O₂ + 1% Ar
2. Hydrogen
3. Adsorption
4. Absorption
5. Cryogenic
6. partial pressure, mixture pressure
7. \((s_{1a} - s_{2a}) - (h_{1a} - h_{2a}) = R_a \ln \left( \frac{p_m}{p_{1a}} \right)\)
8. \(R_a = \mathcal{R} / \text{mol}_a\)
Thank You!