# CRYOGENIC ENGINEERING

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Lecture No - 21

# Earlier Lecture

- According to Gibbs Phase Rule $F = C - P + 2$
- Temperature composition diagram is the variation of the mole fraction (**y**) with the temperature (**T**) at a constant pressure (**p**).
- When a mixture condenses or boils, there is a change in temperature (non – isothermal process).
- Repeated rectification of a mixture enriches the liquid and vapor phases with high and low boiling components respectively.

# Introduction

- In the earlier lecture, we have seen the temperature composition diagrams and an introduction to the rectification process.

- These diagrams form the basis for the rectification process.

- The molar concentrations of vapor and liquid phases of a two component two phase mixture change with temperature.

- Hence, there is a need to study various laws governing the properties of the mixtures.

# Outline of the Lecture

## Topic : Gas Separation (contd)

- Dalton’s Law of Partial Pressures
- Raoult’s Law
- Gibbs – Dalton’s Law
- Distribution Coefficient
- Tutorials

# Dalton's Law

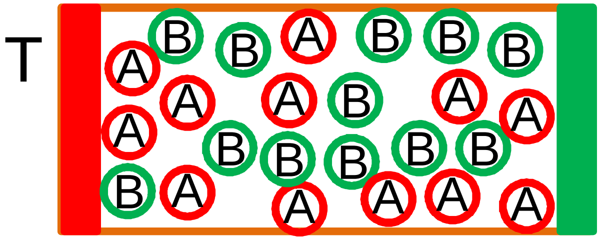
- The Dalton's Law was formulated by an English chemist, John Dalton in the year 1801 for gas mixtures.

- It relates the partial pressure of an individual component of the mixture
    - To the total pressure of the mixture.

    - To its mole fraction.

- It is applicable only to the non – reacting, ideal gas mixtures.

# Dalton's Law

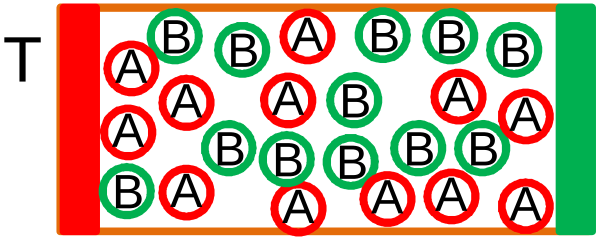


- Consider a mixture of two non – reacting, ideal gases (**Gas A** and **Gas B**) at a temperature **T** as shown.

- Let the total pressure of the mixture be $\mathbf{p_{tot}}$ and partial pressures of **Gas A** and **Gas B** be $\mathbf{p_A}$ and $\mathbf{p_B}$ respectively.

- Also, $\mathbf{y_A}$ and $\mathbf{y_B}$ are the mole fractions of **Gas A** and **Gas B** respectively.

# Dalton's Law



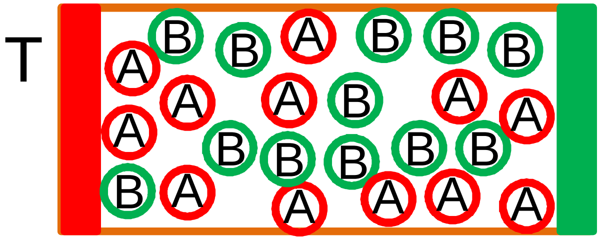
- By Dalton's law, total pressure of the mixture is equal to the sum of the partial pressures of the individual components.

- Mathematically, $p_{tot} = p_A + p_B$

- Also, the partial pressure of each component is directly proportional to its mole fraction.

$$p_A = p_{tot} y_A \qquad p_B = p_{tot} y_B$$

# Dalton's Law

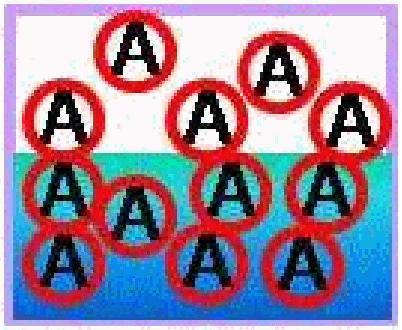


- Extending it to the mixture with **N** components, we have the following.
- Total pressure $p_{tot} = \sum_{j=1}^{N} p_j$
- Partial pressure of the **$j^{th}$** component is

$$p_j = p_{tot} y_j$$

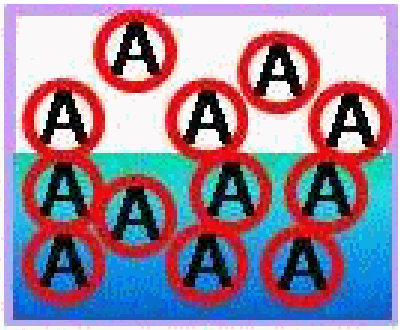
  - where **$y_j$** is the mole fraction of **$j^{th}$** component.

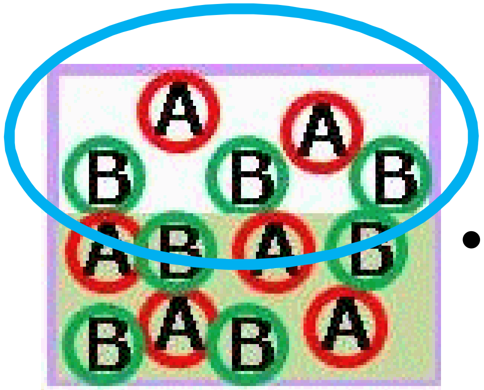
# Raoult's Law



- Consider a 1 – component, two phase system in thermodynamic equilibrium as shown in the figure.
- The vapor above the liquid phase exerts a pressure called as vapor pressure.
- It is dependent only on the temperature of the system.

# Raoult’s Law





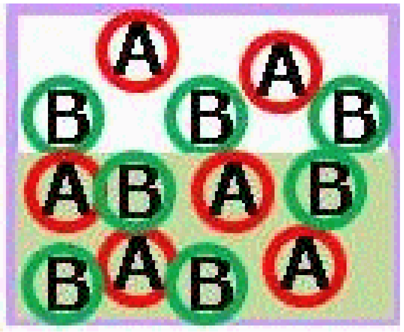
- Similarly, consider a 2 – component, two phase mixture in thermal equilibrium as shown.

- The components are assumed to be ideal (no inter – molecular forces) and chemically non – reacting.

- Such a mixture is called as a ideal mixture or a prefect mixture.

- It is clear that the vapor above the liquid has both the components.

# Raoult's Law



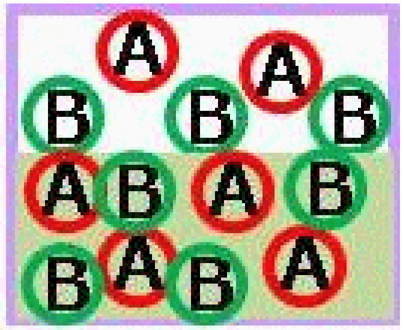
- Raoult's law was formulated by a French chemist, François-Marie Raoult in the year 1882.

- Consider a perfect mixture of **Gas A** and **Gas B** in thermodynamic equilibrium at **T**. Let **Gas A** has following parameters.

| | |
|---|---|
| $p_A$ | Partial pressure |
| $x_A$ | Mole fraction in liquid phase |
| $y_A$ | Mole fraction in vapor phase |
| $\pi_A$ | Vapor pressure at temp. **T** |

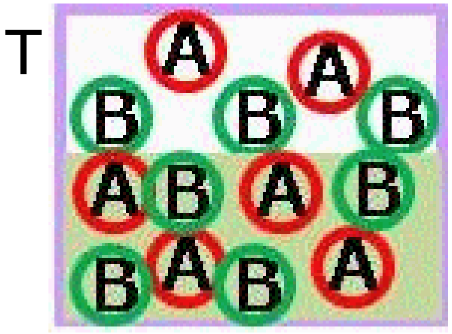
# Raoult's Law

T



- It states that the partial pressure of a component in the vapor phase is directly proportional to the mole fraction of that component in the liquid phase.
- Mathematically, $p = f\left(x\right)$
- Therefore for **Gas A**, $p_A = \pi_A x_A$
- Similarly for **Gas B**, $p_B = \pi_B x_B$

# Raoult's Law



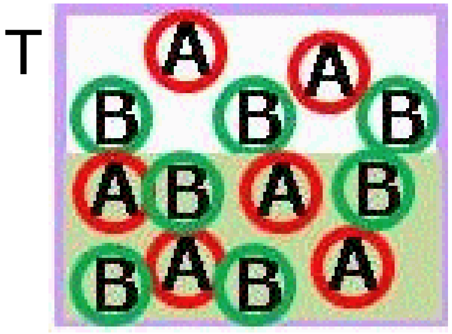
- Extending it to the mixture with **N** components, we have the following.

- Partial pressure of the **$j^{th}$** component is $p_j = \pi_j x_j$

  - where **$x_j$** is the mole fraction of **$j^{th}$** component.

  - **$\pi_j$** is the vapor pressure of **$j^{th}$** component at temperature **T**.

# Dalton's Law + Raoult's Law



- If the vapor above the liquid phase is assumed to be ideal, then combining the Dalton's and Raoult's laws, we have

**Dalton's Law**

$$p_{tot} = p_A + p_B$$

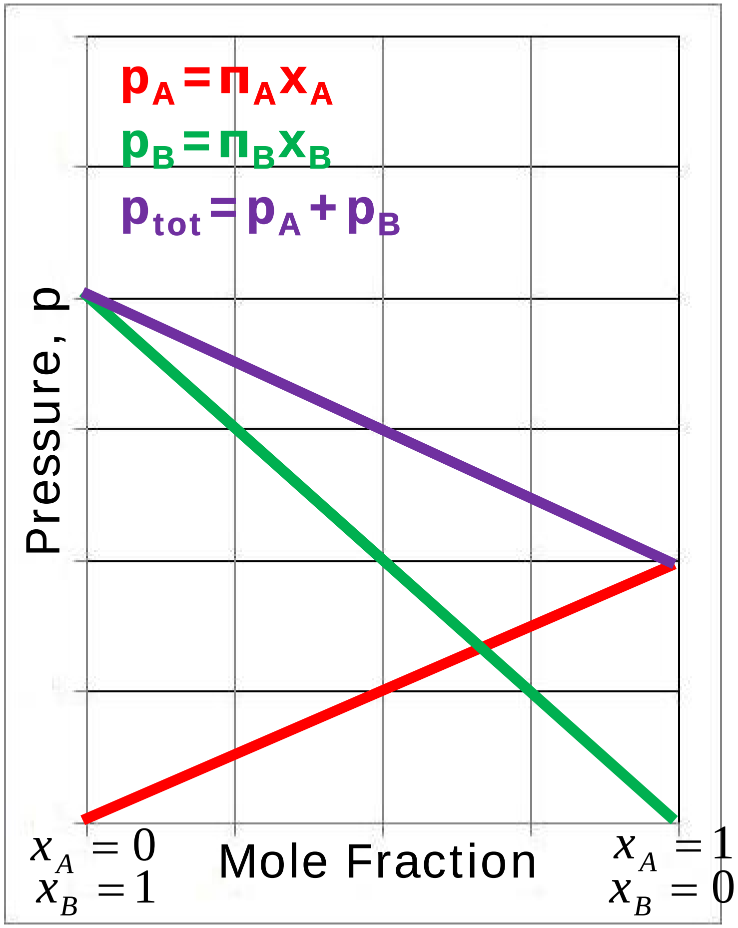
**Raoult's Law**

$$p_A = \pi_A x_A$$

$$p_B = \pi_B x_B$$

$$p_{tot} = \pi_A x_A + \pi_B x_B$$

# Raoult's Law



- Extending further for the liquid phase, the following statements hold true.

$$\boxed{x_A} + \boxed{x_B} = 1$$

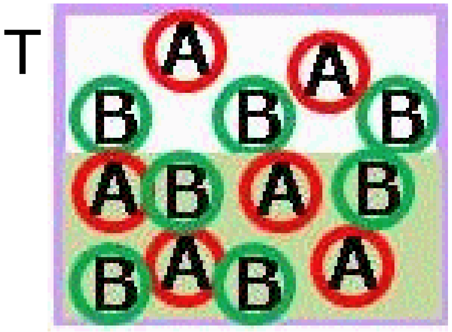
$$p_{tot} = \pi_A \boxed{x_A} + \pi_B \boxed{x_B}$$

$$p_{tot} = \pi_A x_A + \pi_B \left(1 - x_A\right)$$

$$p_{tot} = \pi_A \left(1 - x_B\right) + \pi_B x_B$$

- The variation of pressure with mole fraction is as shown.

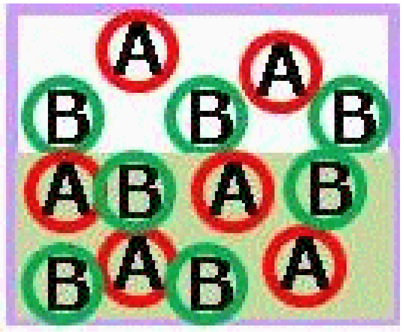
# Gibbs – Dalton’s Law



- Again, assuming the vapor above the liquid to be ideal, Gibbs – Dalton’s Law is the application of Dalton’s Law to this vapor.
- Let $\mathbf{p_A}$ and $\mathbf{p_{tot}}$ be the partial pressure of **Gas A** and total pressure of mixture respectively.
- Also, let $\mathbf{y_A}$ be the mole fraction of **Gas A** in the vapor phase only.

# Gibbs – Dalton's Law

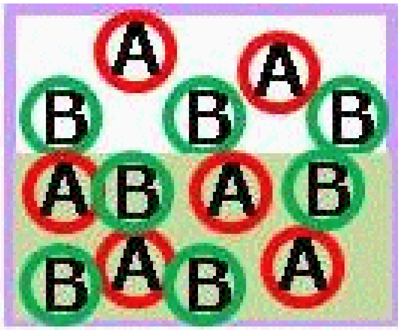
T



- Application of Dalton's Law to the vapor above the liquid, we have the following.
- For **Gas A** in vapor phase $p_A = p_{tot} y_A$
- Similarly for **Gas B** in the vapor phase can be written as $p_B = p_{tot} y_B$
- Extending for a **N** component mixture, then for **j**$^{\mathbf{th}}$ component,

$$p_j = p_{tot} y_j$$

# G – D's Law + Raoult's Law



- Combining the Gibbs – Dalton and Raoult's laws to the vapor above the liquid phase, we have

| G – D's Law | Raoult's Law |
|---|---|
| $p_A = y_A p_{tot}$ | $p_A = \pi_A x_A$ |

$$y_A = \frac{\pi_A x_A}{p_{tot}}$$

| | |
|---|---|
| $p_B = y_B p_{tot}$ | $p_B = \pi_B x_B$ |

$$y_B = \frac{\pi_B x_B}{p_{tot}}$$

# Law of Mixtures

- **Dalton's Law** : Relates partial pressures of non – reacting ideal gases.

- **Raoult's Law** : Relates the vapor pressure with the liquid mole fraction of a component.

- **Gibbs – Dalton's Law** : Application of Dalton's law to the vapor above the liquid phase.

- Raoult's Law and Gibbs – Dalton's Law together establish a relation between the vapor and liquid fractions of any component.

# Distribution Coefficient

- As derived earlier, consider the equation between $\mathbf{y_A}$ and $\mathbf{x_A}$ for the **Gas A**.

$$y_A = \frac{\pi_A x_A}{p_{tot}}$$

- Rearranging, we have

$$\frac{y_A}{x_A} = \frac{\pi_A}{p_{tot}}$$

- The ratio of $\mathbf{y_A}$ to $\mathbf{x_A}$ is called as **Distribution Coefficient** and is denoted by a constant $\mathbf{K_A}$.

- It is the ratio of mole fractions of a component (say **Gas A**), in vapor to liquid phases in a mixture at given temperature.

# Distribution Coefficient

- Extending the definition to the **j<sup>th</sup>** component of a **N** component mixture, we have

$$K_j = \frac{y_j}{x_j} = \frac{\pi_j}{p_{tot}}$$

$$y_j = K_j x_j$$

- The distribution coefficient (**K**) for an ideal or a perfect mixture is determined using the above equation.

- But for the non – ideal or real mixtures, it is determined experimentally.

# Distribution Coefficient

- For an ideal two phase mixture (**Gas A** and **Gas B**), the relation between $\mathbf{K_A}$ and $\mathbf{K_B}$, and the liquid mole fractions $\mathbf{x_A}$ and $\mathbf{x_B}$ is as given below.

$$y_A = K_A x_A \qquad y_B = K_B x_B \qquad y_A + y_B = 1$$

$$K_A \boxed{x_A} + K_B \boxed{x_B} = 1$$

$$\boxed{x_A} + \boxed{x_B} = 1$$

$$K_A x_A + K_B \left(1 - x_A\right) = 1 \qquad K_A \left(1 - x_B\right) + K_B x_B = 1$$

$$x_A = \frac{1 - K_B}{K_A - K_B} \qquad x_B = \frac{1 - K_A}{K_B - K_A}$$

# Distribution Coefficient

$$K_A = \frac{\boxed{y_A}}{\boxed{x_A}} = \frac{\pi_A}{p_{tot}}$$

- As mentioned earlier, **K** is a ratio of mole fractions of a component in vapor and liquid phases in thermodynamic equilibrium.

- It is meaningful and defined only in two phase region.

- For example, a mixture of $\mathbf{N_2}$ and $\mathbf{O_2}$ at 1 atm exists in two phase between 77 K and 90 K. hence, **K** is defined in this interval only.

# Distribution Coefficient

$$K_A = \frac{y_A}{x_A} = \frac{\pi_A}{p_{tot}}$$

- The values of **K** are determined experimentally at some reference pressure (**$p_0$**). Usually this pressure (**$p_0$**) is 1 atm.
- In the literature, the values for $\ln\left(\frac{Kp_{mix}}{p_0}\right)$ are given, from which the **K** values are calculated.
- Data for **$N_2$**, **$O_2$** and **Ar** are given in the next slide. A tutorial has been solved on this concept.

# Distribution Coefficient

- The values for $\ln\left(Kp_{mix} / p_0\right)$ **$O_2$** and **$N_2$** are as given below.

| | Nitrogen ($P_0$=1 atm) | | | Oxygen ($P_0$=1 atm) | | |
|---|---|---|---|---|---|---|
| **T** | **1 atm** | **2 atm** | **5 atm** | **1 atm** | **2 atm** | **5 atm** |
| 78 | 0.080 | ... | ... | -1.337 | ... | ... |
| 80 | 0.304 | ... | ... | -1.116 | ... | ... |
| 82 | 0.528 | ... | ... | -0.896 | ... | ... |
| 84 | 0.758 | 0.704 | ... | -0.675 | -0.457 | ... |
| 86 | 0.977 | 0.903 | ... | -0.455 | -0.302 | ... |
| 88 | 1.201 | 1.101 | ... | -0.235 | -0.146 | ... |
| 90 | 1.425 | 1.299 | ... | -0.014 | +0.009 | ... |
| 92 | ... | 1.497 | ... | ... | 0.165 | ... |

# Distribution Coefficient

- The values for $\ln\left(Kp_{mix}/p_0\right)$ **$O_2$** and **$N_2$** are as given below.

| | Nitrogen ($P_0$=1 atm) | | | Oxygen ($P_0$=1 atm) | | |
|---|---|---|---|---|---|---|
| **T** | **1 atm** | **2 atm** | **5 atm** | **1 atm** | **2 atm** | **5 atm** |
| 94 | ... | 1.696 | 1.550 | ... | 0.321 | 0.661 |
| 96 | ... | 1.894 | 1.702 | ... | 0.477 | 0.788 |
| 98 | ... | ... | 1.853 | ... | ... | 0.915 |
| 100 | ... | ... | 2.004 | ... | ... | 1.042 |
| 102 | ... | ... | 2.156 | ... | ... | 1.169 |
| 104 | ... | ... | 2.307 | ... | ... | 1.296 |
| 106 | ... | ... | 2.459 | ... | ... | 1.423 |
| 108 | ... | ... | 2.610 | ... | ... | 1.551 |

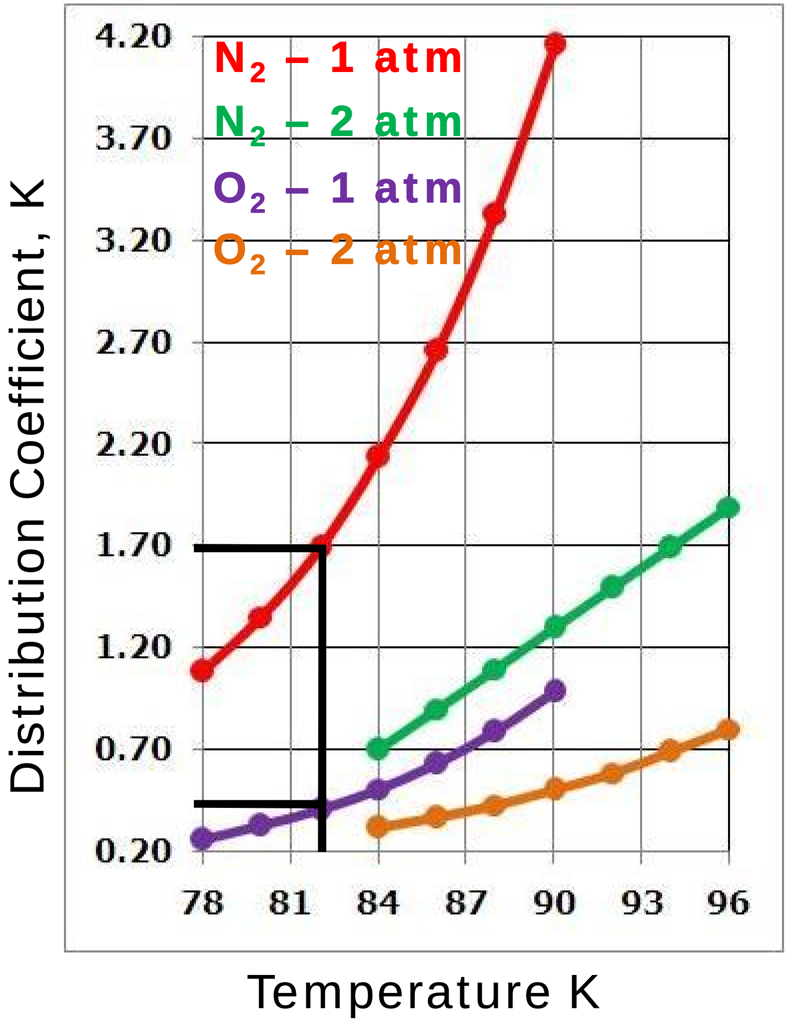
# Distribution Coefficient

- The values for $\ln\left(Kp_{mix} / p_0\right)$ **Ar** are as given below.

| | Argon ($P_0$=1 atm) | | |
|---|---|---|---|
| **T** | **1 atm** | **2 atm** | **5** |
| 78 | -0.907 | … | … |
| 80 | -0.716 | … | … |
| 82 | -0.524 | … | … |
| 84 | -0.332 | -0.252 | … |
| 86 | -0.140 | -0.072 | … |
| 88 | -0.052 | +0.108 | … |
| 90 | +0.140 | 0.288 | … |
| 92 | … | 0.468 | … |

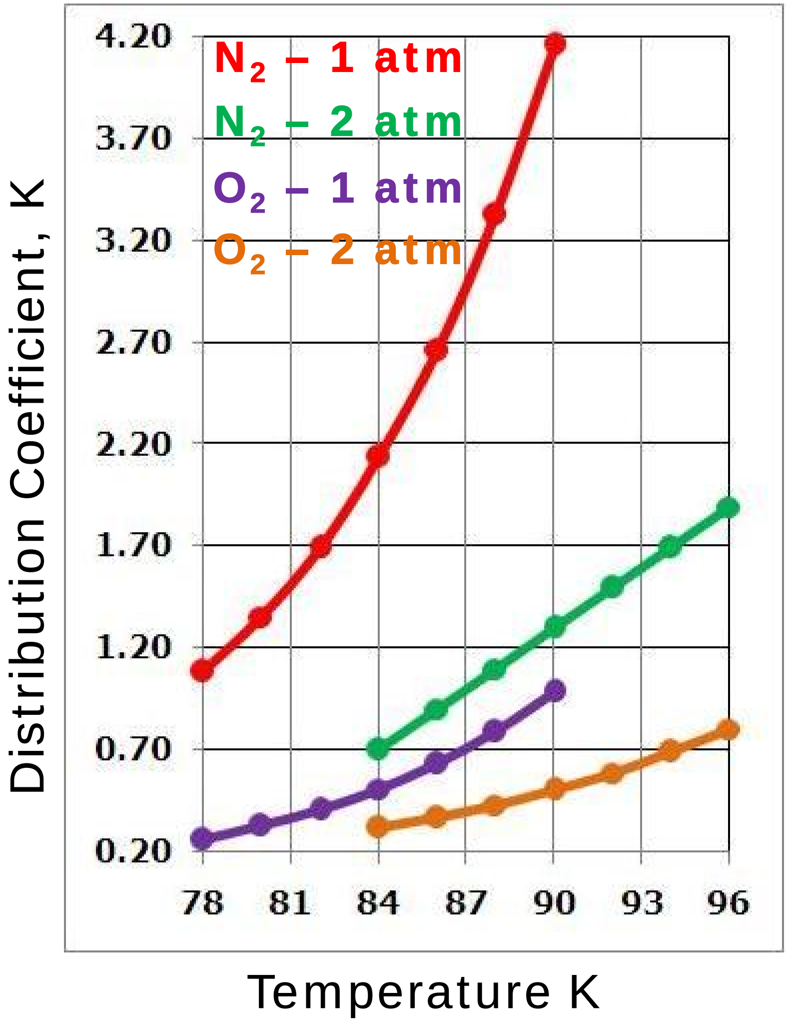
| | Argon ($P_0$=1 atm) | | |
|---|---|---|---|
| **T** | **1** | **2 atm** | **5 atm** |
| 94 | … | 0.648 | 0.552 |
| 96 | … | 0.828 | 0.732 |
| 98 | … | … | 0.863 |
| 100 | … | … | 1.043 |
| 102 | … | … | 1.224 |
| 104 | … | … | 1.405 |
| 106 | … | … | 1.585 |
| 108 | … | … | 1.766 |

# Distribution Coefficient



- The variation of **K** with **T**, for $\mathbf{N_2}$ – $\mathbf{O_2}$ mixture at 1 and 2 atm is as shown.
- The **K** decreases with the decrease in the temperature for any given pressure.
- The component with lower boiling point (here, $\mathbf{N_2}$) has higher **K** at any given **T** and **p**.

# Distribution Coefficient



- For any component, the value of **K** approaches to 1 at its boiling point.
- Also, the value of **K** is less than 1 when the temperature is below the boiling point of the component.
- When **K** is less than 1, the **Ln(K)** is negative.

# Tutorial – 1

- Consider a mixture of $\mathbf{N_2}$ and $\mathbf{O_2}$ at 5 atm and temperature of 100 K.

- Calculate the distribution coefficients for $\mathbf{N_2}$ and $\mathbf{O_2}$. Also, calculate the vapor and liquid compositions using the obtained **K** values.

- Use the data from the tables given in the earlier slides.

# Tutorial – 1

| Given |
|---|
| Working Pressure : 5 atm |
| Temperature : 100 K |
| Mixture : $N_2$ + $O_2$ |

| For above mixture, Calculate | |
|---|---|
| $K_{N2}$ | Distribution coefficient of $N_2$ |
| $K_{O2}$ | Distribution coefficient of $O_2$ |
| $x_{N2}$ | Mole fraction of $N_2$ in liquid phase |
| $x_{O2}$ | Mole fraction of $O_2$ in liquid phase |
| $y_{N2}$ | Mole fraction of $N_2$ in vapor phase |
| $y_{O2}$ | Mole fraction of $O_2$ in vapor phase |

# Tutorial – 1

- $K_{N2}$

$$\ln\left(\frac{Kp_{mix}}{p_0}\right)\bigg|_{N2} = 2.004$$

$$K_{N2} = \frac{p_0}{p_{mix}} e^{2.004}$$

**Data**

$p_{mix}$ = 5 atm

T = 100 K

$p_0$ = 1 atm

$$K_{N2} = \left(\frac{1}{5}\right) e^{2.004} = 1.483$$

| | $N_2$ |
|---|---|
| **T** | **5 atm** |
| 94 | 1.550 |
| 96 | 1.702 |
| 98 | 1.853 |
| 100 | 2.004 |
| 102 | 2.156 |
| 104 | 2.307 |
| 106 | 2.459 |
| 108 | 2.610 |

# Tutorial – 1

- $K_{O2}$

$$\ln\left(\frac{Kp_{mix}}{p_0}\right)\Bigg|_{O2} = 1.042$$

$$K_{O2} = \frac{p_0}{p_{mix}} e^{1.042}$$

| Data |
|---|
| $p_{mix}$ = 5 atm |
| T = 100 K |
| $p_0$ = 1 atm |

$$K_{O2} = \left(\frac{1}{5}\right) e^{1.042} = 0.567$$

|  | $O_2$ |
|---|---|
| **T** | **5 atm** |
| 94 | 0.661 |
| 96 | 0.788 |
| 98 | 0.915 |
| 100 | 1.042 |
| 102 | 1.169 |
| 104 | 1.296 |
| 106 | 1.423 |
| 108 | 1.551 |

# Tutorial – 1

- $x_{N2}$

$$x_{N2} = \frac{1 - K_{O2}}{K_{N2} - K_{O2}}$$

$K_{N2} = 1.483$

$K_{O2} = 0.567$

$$x_{N2} = \frac{1 - 0.567}{1.483 - 0.567} = 0.472$$

# Tutorial – 1

- $x_{O2}$

$$x_{N2} + x_{O2} = 1$$

$$x_{O2} = 1 - x_{N2}$$

$$x_{N2} = 0.472$$

$$x_{O2} = 1 - 0.472 = 0.528$$

# Tutorial – 1

- $y_{N2}$

$$y_{N2} = K_{N2} x_{N2}$$

$$K_{N2} = 1.483$$

$$x_{N2} = 0.472$$

$$y_{N2} = (1.483)(0.472) = 0.699$$

# Tutorial – 1

- $y_{O2}$

$$y_{N2} + y_{O2} = 1$$

$$y_{O2} = 1 - y_{N2}$$

$$y_{N2} = 0.699$$

$$y_{O2} = 1 - 0.699 \quad = 0.301$$

# Tutorial – 2

- Consider a two phase mixture of $\mathbf{N_2}$ and $\mathbf{O_2}$ at a pressure of 2 atm. Use the T – s diagrams for the vapor pressures of $\mathbf{N_2}$ and $\mathbf{O_2}$ at 86 K.

- Determine the liquid and vapor composition of the mixture if the temperature of the mixture is 86 K.

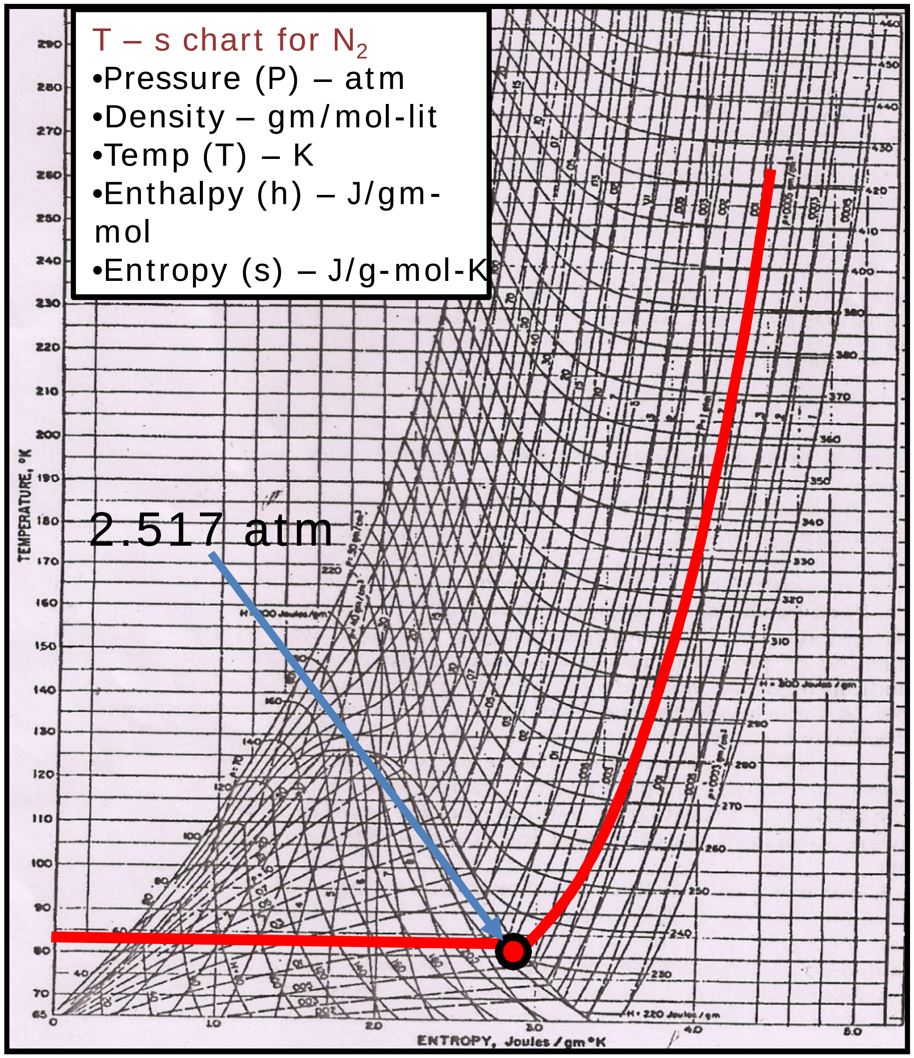
- Also, calculate $\mathbf{K_{N2}}$ and $\mathbf{K_{O2}}$ and compare them with the experimental data.

# Tutorial – 2

| Given |
|---|
| Working Pressure : 2 atm |
| Temperature : 86 K |
| Mixture : $N_2$ + $O_2$ |

| For above mixture, Calculate | |
|---|---|
| $x_{N2}$ | Mole fraction of $N_2$ in liquid phase |
| $x_{O2}$ | Mole fraction of $O_2$ in liquid phase |
| $y_{N2}$ | Mole fraction of $N_2$ in vapor phase |
| $y_{O2}$ | Mole fraction of $O_2$ in vapor phase |
| $K_{N2}$ | Distribution coefficient of $N_2$ |
| $K_{O2}$ | Distribution coefficient of $O_2$ |

# Tutorial – 2



T – s chart for $N_2$
- Pressure (P) – atm
- Density – gm/mol-lit
- Temp (T) – K
- Enthalpy (h) – J/gm-mol
- Entropy (s) – J/g-mol-K

2.517 atm

- Vapor pressures of $\mathbf{N_2}$ is taken from the T – s diagram.

- Following the similar procedure for $\mathbf{O_2}$, we have the vapor pressures as

| Vapor Pr. |
|---|
| $\pi_{N2}$ = 2.517 atm |
| $\pi_{O2}$ = 0.640 atm |

# Tutorial – 2

- **$x_{N2}$**

$$p_{tot} = \pi_{N2} x_{N2} + \pi_{O2}\left(1 - x_{N2}\right)$$

$$x_{N2} = \frac{p_{tot} - \pi_{O2}}{\pi_{N2} - \pi_{O2}}$$

| Data |
|---|
| $p_{tot}$ = 2 atm |
| $\pi_{N2}$ = 2.517 atm at 86 K |
| $\pi_{O2}$ = 0.640 atm at 86 K |

$$x_{N2} = \frac{2 - 0.980}{3.550 - 0.980} = 0.724$$

# Tutorial – 2

- $x_{O2}$

$$x_{N2} + x_{O2} = 1$$

$$x_{O2} = 1 - x_{N2}$$

$$x_{N2} = 0.724$$

$$x_{O2} = 1 - 0.724 \quad = 0.276$$

# Tutorial – 2

- $y_{N2}$

$$y_{N2} = \frac{\pi_{N2} x_{N2}}{p_{tot}}$$

| Data |
|---|
| $p_{tot}$ = 2 atm |
| $\pi_{N2}$ = 2.517 atm at 86 K |
| $\pi_{O2}$ = 0.640 atm at 86 K |

$$x_{N2} = 0.724$$

$$y_{N2} = \frac{(2.517)(0.724)}{(2)} = 0.911$$

# Tutorial – 2

- $y_{O2}$

$$y_{N2} + y_{O2} = 1$$

$$y_{O2} = 1 - y_{N2}$$

$$y_{N2} = 0.911$$

$$y_{O2} = 1 - 0.911 = 0.089$$

# Tutorial – 2

- $K_{N2}$

$$K_{N2} = \frac{y_{N2}}{x_{N2}}$$

$$x_{N2} = 0.724$$

$$y_{N2} = 0.911$$

$$K_{N2} = \frac{0.911}{0.724} = 1.2583$$

# Tutorial – 2

- **$K_{O2}$**

$$K_{O2} = \frac{y_{O2}}{x_{O2}}$$

$$x_{O2} = 0.276 \qquad y_{O2} = 0.089$$

$$K_{O2} = \frac{0.089}{0.276} = 0.3224$$

# Tutorial – 2

- The calculated and experimental **K** values are as tabulated below.

| **Calculated** | |
|---|---|
| $K_{N2}$ | 1.2583 |
| $K_{O2}$ | 0.3224 |

| **Experimental** | |
|---|---|
| $K_{N2}$ | 1.2335 |
| $K_{O2}$ | 0.3697 |

- The ideal (calculated) values differed from the experimental values by small amount.
- This is because, the effect of inter – molecular forces is neglected in the ideal mixtures.

# Summary

- Dalton's Law relates partial pressures of non – reacting ideal gases.
- Raoult's Law relates the vapor pressure with the liquid mole fraction of a component in a mixture.
- Gibbs – Dalton's Law is an application of Dalton's law to the vapor above the liquid phase.
- Distribution Coefficient (**K**) is the ratio of mole fractions of a component in vapor to liquid phases. It is meaningful and defined only in two phase region of a mixture.

# Assignment

- Consider a two phase mixture of **$N_2$** and **$O_2$** at a pressure of 1 atm. Determine the liquid and vapor composition of the mixture if the temperature of the mixture is 80 K.

- The vapor pressures of **$N_2$** and **$O_2$** at 80 K are as given below.

| Data |
|---|
| $\pi_{N2}$ = 1.349 atm |
| $\pi_{O2}$ = 0.297 atm |

# Answers

| 1 atm | 80 K |
|---|---|
| $x_{N2}$ | 0.654 |
| $x_{O2}$ | 0.346 |
| $y_{N2}$ | 0.887 |
| $y_{O2}$ | 0.113 |

# Thank You!