THERMODYNAMICS OF SEPARATION OPERATIONS

- Thermodynamic properties and equations play a major role in separation operations, particularly with respect to energy requirements, phase equilibria, and sizing equipment.

- Consider the continuous, steady-state, flow system for a general separation process in the following figure. One or more feed streams flowing into the system are separated into two or more product streams that flow out of the system.

\[ n = \text{molar flow rates.} \]
\[ z_i = \text{component mole fractions.} \]
\[ T = \text{temperature.} \]
\[ P = \text{pressure.} \]
\[ h = \text{molar enthalpies.} \]
\[ S = \text{molar entropies.} \]
\[ b = \text{molar availabilities.} \]
ENERGY, ENTROPY, AND AVAILABILITY BALANCES

Energy balance:

\[ \sum_{\text{out of system}} (nh + Q + W_s) - \sum_{\text{in to system}} (nh + Q + W_s) = 0 \]

Entropy balance:

\[ \sum_{\text{out of system}} \left( nS + \frac{Q}{T_s} \right) - \sum_{\text{in to system}} \left( nS + \frac{Q}{T_s} \right) = \Delta S_{\text{irr}} \]

Availability balance:

\[ \sum_{\text{in to system}} \left[ nb + Q \left( 1 - \frac{T_0}{T_s} \right) + W_s \right] - \sum_{\text{out of system}} \left[ nb + Q \left( 1 - \frac{T_0}{T_s} \right) + W_s \right] = LW \]

where \( b = h - T_0s \) = availability function
Minimum work of separation:

\[ W_{\text{min}} = \sum_{\text{out of system}} nb - \sum_{\text{in to system}} nb \]

Second-law efficiency:

\[ \eta = \frac{W_{\text{min}}}{LW + W_{\text{min}}} \]

Where \( LW = T_0 S_{\text{irr}} \) = lost work
The criterion of equilibrium is that all potentials for change are in balance: there are no changes in the equilibrium state and no tendency to leave that state.

For three phases (vapor (V), Liquid (L), and solid (S), the temperatures and pressures must be equal at equilibrium:

\[ T^V = T^L = T^S \]  
thermal equilibrium

\[ P^V = P^L = P^S \]  
mechanical equilibrium
Vapor-liquid equilibrium data can be measured by placing a mixture of the two components in a vessel held at either constant temperature or constant pressure.

Equilibrium between the liquid and vapor phases will be approached slowly, but may be promoted by agitating the vessel or by circulating the vapor phase so that it bubbles through the liquid.
After equilibrium, the pressure and temperature are measured and samples are taken to determine the vapor and liquid compositions.

There are several different types of plots for binary system:

1. $P_{xy}$ diagram: $x$ and $y$ as functions of pressure at constant temperature.
2. $T_{xy}$ diagram: $x$ and $y$ as functions of temperature at constant pressure.
3. $xy$ diagram: $x$ versus $y$ at constant pressure (temperature is a parameter along the curve).

Since most applications require data at constant pressure, $T_{xy}$ and $xy$ diagrams are the most commonly used.
1. $P_{xy}$ Diagrams

- $P_{xy}$ diagram for a binary mixture at constant temperature. In this diagram, compositions are given as mole fraction of the light component.

- The upper curve gives the liquid composition $x$ versus pressure $P$. The lower curve gives the vapor composition $y$ versus pressure.

$P_H =$ vapor pressure of pure heavy component at the temperature at which the data were collected ($x=0$).

$P_L =$ vapor pressure of pure light component at the temperature at which the data were collected ($x=1.0$).
The liquid and vapor compositions \( x_1 \) and \( y_1 \) are obtained from the intersection of the phase envelope with the \( P_1 \) constant pressure line.
For composition \( z \). If the pressure is increased at constant temperature to \( P_{DP} \) a liquid phase will begin to form.

\( P_{DP} \) is called the *dew point* pressure, because the first drops of liquid form as "dew."

The liquid droplets that form will be much leaner in the light component. The composition of the first drop of liquid formed at \( P_{DP} \) is \( x_{DP} \).
As the pressure is increased further, more liquid forms. At a pressure $P_1$ there is almost as much liquid of composition $x_1$ as vapor of composition $y_1$.

As the pressure is further increased, $P_{BP}$ is reached. Here the last bit of the vapor phase exists as bubbles, so this pressure is known as the *bubble point* pressure of the mixture with composition $z$ at the specified temperature.
The boiling point temperature of the pure light component $T_L$ at the pressure specified in the diagram is the temperature at the point $x = y = 1$. $T_H$ is the boiling temperature of the heavy component at the system pressure.
The mixture is all liquid until it reaches the bubble point temperature $T_{BP}$, where the first bubble of vapor forms and has a composition $y_{BP}$.

Increasing the temperature further to the dew point temperature $T_{DP}$ yields a mixture that is all vapor. The last drops of liquid have a composition $x_{DP}$. 
Effect of pressure on Txy diagram

If Txy diagrams for the same system at different total pressures, then:

1. $P_2 > P_1$

2. The vapor-liquid equilibrium temperatures are higher at $P_2$ than at $P_1$

2. The phase equilibrium lines at the higher pressure are usually closer together.
xy Diagrams

- xy diagram for a binary system, relates the compositions of the liquid and vapor phases in equilibrium with each other.

- These diagrams can be generated from either constant-P or constant-T data. However, they are most commonly drawn for constant pressure, since most applications are essentially isobaric.
If the diagram is plotted for a constant pressure, temperature is a parameter along the curve.

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Example:

In a 2-component (binary) mixture, an equilibrium condition can exist between the vapour and the liquid phase. The Figure shows a typical equilibrium condition attained under a certain pressure $P$ and temperature $T$. The 2 components that made up the mixture distribute themselves unequally in both the vapour and liquid phases.

The substance with the lower boiling point is known as the more volatile component (MVC) and correspondingly the substance with the higher boiling point is known as the less volatile component (LVC).

If we let $A = \text{MVC}$ and $B = \text{LVC}$, we can use mole fractions as a measure of concentrations of the components in the 2 phases:

$$y_A = \text{mole fraction of component-A in the vapour phase.}$$

$$x_A = \text{mole fraction of component-A in the liquid phase}$$
At a different temperature and/or pressure, the 2-components will distribute differently. For example, the Figure shows equilibrium at pressure $P$ and temperature $T_1$. The mole fraction of A in the vapour and liquid are $y_{A1}$ and $x_{A1}$ respectively.
At another higher temperature $T_2$ but at the same pressure $P$, another equilibrium is attained, with different mole fractions than at temperature $T_1$. As shown in the Figure, the mole fractions of A in the vapour and liquid are $y_{A2}$ and $x_{A2}$ respectively.

VLE - Temperature $T_2$ :
Vapour $y_{A2} = 28 \div (28 + 24) = 0.538$
Liquid $x_{A2} = 12 \div (12 + 36) = 0.250$
NONIDEALITY IN VAPOR-LIQUID EQUILIBRIUM

At low and moderate pressures, nonideal vapor-liquid equilibrium can be described by modified Raoult's law:

\[ P_{yj} = P_j^s x_j \gamma_j \]

This equation assumes that most of the nonideal behavior is caused by liquid phase effects.

In the liquid phase, molecules are much more closely spaced than in the vapor phase. Therefore, attraction and repulsion among molecules have larger effects.
It is useful for graphical design in determining the number of theoretical stages required for a distillation column.