University of Technology
Chemical engineering department
Third year

Mass Transfer
By
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1. Introduction:

2. Mass transfer fundamentals:
   Steady state mass transfer. Diffusion in binary and multicomponent gases. 
   Diffusion in binary and multicomponent liquids. Connective mass transfer. Mass 
   transfer coefficients. Two-film theory. Penetration theory. Unsteady state mass 
   transfer methods

3. Methods of gas-liquid separation (absorption and stripping):
   Determination of interfacial mole fractions. Individual and overall mass 
   transfer coefficients. Effect of gas solubility on equilibrium curve. Single stage 
   absorption, multistage absorption. Finding number of stages graphically and through 
   use of correlations for absorption and stripping. Packed columns limits of operation. 
   Design of packed beds for dilute and concentrated solutions. Finding number of 
   transfer units. Absorption with chemical reaction.

4. Binary distillation:
   Introduction, (T-x,y) and (x,y) equilibrium curves. Flash or equilibrium 
   distillation for binary and multicomponent mixtures. Distillation with reflux using 
   Mckabe-Thiele. Sorel method to find number of stages. Fenske equation to find 
   minimum reflux ratio and minimum theoretical stages. Column efficiency. Thermal 
   method for finding number of ideal stages (Ponchoue-Savarit Method). 
   Multicomponent differential distillation.

5. Multicomponent distillation:
   Dew and bubble points calculation methods. Multicomponent equilibrium 
   relationships. Minimum reflux and minimum number of stages. Short-cut method. 
   Checking validity of reflux ratio used. Operating limits of distillation columns.

(4hrs) (25hrs) (16hrs) (25hrs) (16hrs)
Mass Transfer Operations

Introduction:
What is chemical engineering?
Chemical engineering is the field of engineering that deals with industrial processes in which raw materials are converted or separated into final useful products.

Who is the chemical Engineer?
The function of a qualified chemical engineer is to apply chemistry of a particular industrial process through the use of coordinated scientific and engineering principles. Also develop the laboratory results of chemists into economical chemical plants, he must develop, design and engineer both the complete industrial process and the equipment used in it. Then his duties can be stated as:

1- He must choose the raw material.
2- He must design and operate the plant efficiently, safely, and economically.
3- He must know that his products meet the requirements set by the customers.
4- When science does not give him a complete answer, he must use experience & judgment to combine all sources of information to reach particular solution to processing problems.

Definition of Unit Operation:-
The physical operations necessary for manufacturing chemicals deals mainly with the transfer and change of material and energy principles by physical means but also by chemical – physical means such as mass transfer, heat transfer and momentum transfer (fluid dynamics). There are two types of unit operation classifications:
The first one depends on the process type as:
1- Processes without chemical reaction, as distillation, crystallization, absorption, extraction, and filtration.
2- Processes with chemical reactions as nitrination, oxidation, and sulfonation.

While the second classification depends on the type of transfer occur within the process such as:

1- Mass transfer operations
Transfer of component from one phase to another such processes is:
Gas absorption, Distillation, Extraction, Crystallization, Drying, Evaporation, Leaching, Stripping, Mechanical separation for example (Filtration, settling, size reduction, and sedimentation).

2- Heat transfer operations
Accumulation and transfer of heat and energy such as:
Heat exchanger, Evaporation, Drying, Distillation.

3- Momentum transfer operations
Flow and transportation of fluid and solid such as:
Fluid flow, Mixing, Handling of solid, Fluid transportation.
Mass transfer is the net movement of a component in a mixture from one location to another location where the component exists at a different concentration. Often, the transfer takes place between two phases across an interface. Thus, the absorption by a liquid of a solute from a gas involves mass transfer of the solute through the gas to the gas-liquid interface, across the interface, and into the liquid. Mass transfer models are used to describe processes such as the passage of a species through a gas to the outer surface of a porous adsorbent particle and into the pores of the adsorbent, where the species is adsorbed on the porous surface. Mass transfer is also the selective permeation through a nonporous polymeric material of a component of a gas mixture. Mass transfer is not the flow of a fluid through a pipe. However, mass transfer might be superimposed on that flow. Mass transfer is not the flow of solids on a conveyor belt.

Mass transfer occurs by two basic mechanisms:

1. Molecular diffusion by random and spontaneous microscopic movement of individual molecules in a gas, liquid, or solid as a result of thermal motion; and

2. Eddy (turbulent) diffusion by random macroscopic fluid motion.

Molecular and/or eddy diffusion frequently involves the movement of different species in opposing directions. When a net flow occurs in one of these directions, the total rate of mass transfer of individual species is increased or decreased by this bulk flow or convection effect, which is a third mechanism of mass transfer. As will be shown later, molecular diffusion is extremely slow, whereas eddy diffusion, when it occurs, is orders of magnitude more rapid. Therefore, if large-scale separation processes are to be conducted in equipment of a reasonable size, fluids must be agitated, interfacial areas maximized, and distances in the direction of diffusion minimized. In a binary mixture, molecular diffusion occurs because of one or more different potentials or driving forces, including differences (gradients) of concentration (ordinary diffusion), pressure (pressure diffusion), temperature (thermal diffusion), and external force fields (forced diffusion) that act unequally on the different chemical species present. Pressure diffusion requires a large pressure gradient, which is achieved for gas mixtures with a centrifuge. Thermal diffusion columns or cascades can be employed to separate liquid and gas mixtures by establishing a temperature gradient across the mixture. More widely applied is forced diffusion in an electrical field, to cause ions of different charges to move in different directions at different speeds. In this chapter, only molecular diffusion caused by concentration gradients is considered, because this is the most common type of molecular diffusion in
Molecular diffusion occurs in solids and in fluids that are stagnant or in laminar or turbulent motion. Eddy diffusion occurs in fluids in turbulent motion. When both molecular diffusion and eddy diffusion occur, they take place in parallel and are additive. Furthermore, they take place because of the same concentration difference (gradient). When mass transfer occurs under turbulent flow conditions, but across an interface or to a solid surface, conditions may be laminar or nearly stagnant near the interface or solid surface. Thus, even though eddy diffusion may be the dominant mechanism in the bulk of the fluid, the overall rate of mass transfer is controlled by molecular diffusion because the eddy diffusion mechanism is damped or even eliminated as the interface or solid surface is approached. Mass transfer of one or more species results in a total net rate of bulk flow or flux in one direction relative to a fixed plane or stationary coordinate system. When a net flux occurs, it carries all species present. Thus, the molar flux of an individual species is the sum of all three mechanisms. If $N_i$ is the molar flux of species $i$ with mole fraction $X_i$, and $N$ is the total molar flux, with both fluxes in moles per unit time per unit area in a direction perpendicular to a stationary plane across which mass transfer occurs, then

$$N_i = X_i N + \text{molecular diffusion flux of } i + \text{eddy diffusion flux of } i \quad \ldots 1$$

Where:

$X_i N$ is the bulk-flow flux.

Each term in (1) is positive or negative depending on the direction of the flux relative to the direction selected as positive. When the molecular and eddy diffusion fluxes are in one direction and $N$ is in the opposite direction, even though a concentration difference or gradient of $i$ exists, the net mass transfer flux, $N_i$, of $i$ can be zero.

**STEADY-STATE ORDINARY MOLECULAR DIFFUSION**

Suppose a cylindrical glass vessel is partly filled with water containing a soluble red dye. Clear water is carefully added on top so that the dyed solution on the bottom is undisturbed. At first, a sharp boundary exists between the two layers, but after a time the upper layer becomes colored, while the layer below becomes less colored. The upper layer is more colored near the original interface between the two layers and less colored in the region near the top of the upper layer. During this color change, the motion of each dye molecule is random, undergoing collisions mainly with water.
molecules and sometimes with other dye molecules, moving first in one direction and then in another, with no one direction preferred. This type of motion is sometimes referred to as a random-walk process, which yields a mean-square distance of travel for a given interval of time, but not a direction of travel. Thus, at a given horizontal plane through the solution in the cylinder, it is not possible to determine whether, in a given time interval, a given molecule will cross the plane or not. However, on the average, a fraction of the molecules in the solution below the plane will cross over into the region above and the same fraction will cross over in the opposite direction. Therefore, if the concentration of dye molecules in the lower region is greater than in the upper region, a net rate of mass transfer of dye molecules will take place from the lower to the upper region. After a long period of time, the concentration of dye will be uniform throughout the solution. Based on these observations, it is clear that:

1. Mass transfer by ordinary molecular diffusion occurs because of a concentration difference or gradient; that is, a species diffuses in the direction of decreasing concentration.

2. The mass transfer rate is proportional to the area normal to the direction of mass transfer and not to the volume of the mixture. Thus, the rate can be expressed as a flux.

3. Mass transfer stops when the concentration is uniform.

**Fick's Law of Diffusion**

The above observations were quantified by Fick in 1855, who proposed an extension of Fourier's 1822 heat conduction theory. Fourier's first law of heat conduction is

\[ q_Z = -k \frac{dT}{dZ} \]  

...2

Where \( q_Z \) is the heat flux by conduction in the positive \( Z \) direction, \( k \) is the thermal conductivity of the medium, and \( (dT/dZ) \) is the temperature gradient, which is negative in the direction of heat conduction. Fick's first law of molecular diffusion is also proportionality between a flux and a gradient. For a binary mixture of A and B,

\[ J_{Az} = -D_{AB} \frac{dC_A}{dZ} \]  

...3

And

\[ J_{Bz} = -D_{BA} \frac{dC_B}{dZ} \]  

...4

Where, in (Eq. 3), \( J_A \) is the molar flux of A by ordinary molecular diffusion relative to the molar average velocity of the mixture in the positive \( z \) direction, \( D_{AB} \) is the mutual diffusion coefficient of A in B, and \( (dC_A/dz) \) is the concentration gradient of A, which
is negative in the direction of ordinary molecular diffusion. Similar definitions apply to (Eq. 4). The molar fluxes of A and B are in opposite directions. If the gas, liquid, or solid mixture through which diffusion occurs is isotropic, then values of $k$ and $D_{AB}$ are independent of direction.

Non-isotropic (anisotropic) materials include fibrous and laminated solids as well as single, Non-cubic crystals. The diffusion coefficient is also referred to as the diffusivity and the mass diffusivity (to distinguish it from thermal and momentum diffusivities). Many alternative forms of (Eq. 3) and (Eq. 4) are used, depending on the choice of driving force or potential in the gradient. For example, we can express (Eq. 3) as:

$$J_A = -C \cdot D_{AB} \frac{dX_A}{dZ} \quad \ldots 5$$

Where, for convenience, the $z$-subscript on $i$ has been dropped, $C =$ total molar concentration, and $X_i =$ mole fraction of species $i$.

### Velocities in Mass Transfer

It is also useful to formulate expressions for velocities of the various chemical species in the mixture. These velocities are based on the molar flux, $N$, and the diffusion flux, $J$. The molar average velocity of the mixture, $V_M$, relative to stationary coordinates is given for a binary mixture as:

$$V_M = \frac{N}{C} = \frac{N_A + N_B}{C} \quad \ldots 6$$

Similarly, the velocity of species $i$, defined in terms of $N_i$, is relative to stationary coordinates:

$$V_i = \frac{N_i}{C_i} \quad \ldots 7$$

Combining (Eq. 6) and (Eq. 7) with $X_i = C_i / C$ give:

$$V_M = X_A \cdot V_A + X_B \cdot V_B \quad \ldots 8$$

Alternatively, species diffusion velocities, $V_{iD}$ defined in terms of $J_i$, are relative to the molar average velocity and are defined as the difference between the species velocity and the molar average velocity for the mixture:

$$V_{iD} = \frac{J_i}{C_i} = V_i - V_M \quad \ldots 9$$

When solving mass transfer problems involving net movement of the mixture, it is not convenient to use fluxes and flow rates based on $V_M$ as the frame of reference. Rather,
it is preferred to use mass transfer fluxes referred to stationary coordinates with the observer fixed in space. Thus, from (Eq. 9), the total species velocity is:

\[ V_i = V_M + V_{id} \]  \hspace{1cm} \ldots 10

Combining (Eq. 7) and (Eq. 10),

\[ N_i = C_i \cdot V_M + C_i \cdot V_{id} \]  \hspace{1cm} \ldots 11

Combining (Eq. 11) with (Eq. 5), (Eq. 6), and (Eq. 7), then

\[ N_A = \frac{n_A}{A} = X_A \cdot N - C \cdot D_{AB} \left( \frac{dX_A}{dZ} \right) \]  \hspace{1cm} \ldots 12

Or can be written as:

\[ N_A = -C \cdot D_{AB} \left( \frac{dX_A}{dZ} \right) + X_A (N_A + N_B) \]  \hspace{1cm} \ldots 12A

And

\[ N_B = \frac{n_B}{A} = X_B \cdot N - C \cdot D_{Ba} \left( \frac{dX_B}{dZ} \right) \]  \hspace{1cm} \ldots 13

where in (Eq. 12) and (Eq. 13), \( n_i \) is the molar flow rate in moles per unit time, \( A \) is the mass transfer area, the first terms on the right-hand sides are the fluxes resulting from bulk flow, and the second terms on the right-hand sides are the ordinary molecular diffusion fluxes. Two limiting cases are important:

1. Equimolar counter diffusion (EMD)
2. Uni-molecular diffusion (UMD)

**Equimolar Counter diffusion**

In equimolar counter diffusion (EMD), the molar fluxes of \( A \) and \( B \) are equal, but opposite in direction; thus,

\[ N = N_A + N_B = 0 \]  \hspace{1cm} \ldots 14

Thus, from (Eq. 12, or 12A) and (Eq. 13), the diffusion fluxes are also equal, but opposite in direction:

\[ J_A = -J_B \]  \hspace{1cm} \ldots 15
This idealization is closely approached in distillation. From (Eq. 12) and (Eq.13), we see that in the absence of fluxes other than molecular diffusion, and

\[ N_A = J_A = -C \cdot D_{AB} \left( \frac{dX_A}{dZ} \right) \quad \text{..16} \quad \text{or} \quad N_A = -D_{AB} \left( \frac{dC_A}{dZ} \right) \quad \text{..16A} \]

And

\[ N_B = J_B = -C \cdot D_{BA} \left( \frac{dX_B}{dZ} \right) \quad \text{..17} \]

**Figure 1** Concentration profile for limiting cases of ordinary molecular diffusion in binary mixture across a stagnant film; (a) equimolar counter diffusion (EMD); (b) unimolecular diffusion (UMD)

If the total concentration, pressure, and temperature are constant and the mole fractions are maintained constant (but different) at two sides of a stagnant film between \( Z_1 \) and \( Z_2 \) then (Eq. 16) and (Eq. 17) can be integrated from \( Z_1 \) to any \( Z \) between \( Z_1 \) and \( Z_2 \) to give

\[ J_A = \frac{C \cdot D_{AB}}{Z - Z_1} (X_{A_1} - X_A) \quad \text{..18} \]

And

\[ J_B = \frac{C \cdot D_{BA}}{Z - Z_1} (X_{B_1} - X_B) \quad \text{..19} \]

Thus, in the steady state, the mole fractions are linear in distance, as shown in Fig.1a. Furthermore, because \( c \) is constant through the film, where

\[ C = C_A + C_B \quad \text{..20} \]
By differentiation,
\[ dC = 0 = dC_A + dC_B \quad \ldots 21 \]
Thus,
\[ dC_A = -dC_B \quad \ldots 22 \]
From (Eqs. 3, 4, 15, and 22),
\[ \frac{D_{AB}}{dZ} = \frac{D_{BA}}{dZ} \quad \ldots 23 \]
Therefore, \( D_{AB} = D_{BA} \).

This equality of diffusion coefficients is always true in a binary system of constant molar density.

**NOTE:**
From the ideal gas law
\[ PV = nRT \]
\[ \frac{n}{V} = \frac{P}{RT} \]
\[ C = \frac{P}{RT} \quad \text{Where C is the total mole concentration} \]
Using Dalton's law, then
\[ \frac{n_A}{V} = \frac{P_A}{RT} = C_A \]
Then
\[ J_A = -\left(\frac{D_{AB}}{RT}\right)\frac{dP_A}{dZ} \quad \text{Another formula of Fick's law for equi-molar gas diffusion} \]
And
\[ N_A = -\left(\frac{D_{AB}}{RT}\right)\left(\frac{P_{A_2} - P_{A_1}}{Z_2 - Z_1}\right) \]

Example 1
Two bulbs are connected by a straight tube, 0.001 m in diameter and 0.15 m in length. Initially the bulb at end 1 contains N\(_2\) and the bulb at end 2 contains H\(_2\). The pressure and temperature are maintained constant at 25°C and 1 atm. At a certain time after allowing diffusion to occur between the two bulbs, the nitrogen content of the gas at end 1 of the tube is 80 mol% and at end 2 is 25 mol%. If the binary diffusion coefficient is 0.784 cm\(^2\)/s, determine:
(a) The rates and directions of mass transfer of hydrogen and nitrogen in mol/s
(b) The species velocities relative to stationary coordinates, in cm/s
Solution:
(a) Because the gas system is closed and at constant pressure and temperature, mass transfer in the connecting tube is equimolar counter diffusion by molecular diffusion. The area for mass transfer through the tube, in cm$^2$, is 
\[ A = \pi \left(0.1\right)^2/4 = 7.85 \times 10^{-3} \text{ cm}^2. \]
The total gas concentration is 
\[ C = \frac{P}{R \cdot T} = \frac{1}{(82.06)(298)} = 4.09 \times 10^{-5} \text{ mol/cm}^3. \]
Take the reference plane at end 1 of the connecting tube. Applying (Eq. 18) to N$_2$ over the length of the tube,
\[ n_{N_2} = \frac{C \cdot D_{N_2H_2}}{(Z_2 - Z_1)} \left[ (X_{N_2})_1 - (X_{N_2})_2 \right] A \]
\[ n_{N_2} = \frac{(4.09 \times 10^{-5})(0.784)(0.8 - 0.25)}{15} (7.85 \times 10^{-3}) \]
\[ n_{N_2} = 9.23 \times 10^{-9} \text{ mol/s} \text{ in the positive } Z \text{ direction} \]
\[ n_{H_2} = 9.23 \times 10^{-9} \text{ mol/s} \text{ in the negative } Z \text{ direction} \]
(b) For equimolar counter diffusion, the molar average velocity of the mixture, V$_M$, is Zero.
Therefore, from (Eq. 9), species velocities are equal to species diffusion velocities. Thus,
\[ V_{N_2} = \frac{J_{N_2}}{C_{N_2}} = \frac{n_{N_2}}{A C X_{N_2}} = \frac{9.23 \times 10^{-9}}{[(7.85 \times 10^{-5})(4.09 \times 10^{-5})(X_{N_2})]} \]
\[ V_{N_2} = \frac{0.0287}{(X_{N_2})} \text{ in the positive } Z \text{ direction} \]
Similarly
\[ V_{H_2} = \frac{0.0287}{(X_{H_2})} \text{ in the negative } Z \text{ direction} \]
Thus, species velocities depend on species mole fractions, as follows:
Note that species velocities vary across the length of the connecting tube, but at any location, $Z$, $V_M = 0$. For example, at $Z = 10$ cm, from (Eq. 8)

$$V_M = (0.433)(0.0663) + (0.567)(-0.0506) = 0$$

**Unimolecular Diffusion**

In unimolecular diffusion (UMD), mass transfer of component A occurs through stagnant component B. Thus,

$$N_B = 0 \quad \ldots 24$$

And

$$N = N_A \quad \ldots 25$$

Therefore, from (Eq. 12),

$$N_A = X_A \cdot N - C \cdot D_{AB} \frac{dX_A}{dZ} \quad \ldots 26$$

This can be rearranged to a Fick's law form,

$$N_A = -\frac{CD_{AB}}{(1 - X_A)} \frac{dX_A}{dZ} \quad \ldots 27$$

The factor $(1 - X_A)$ accounts for the bulk flow effect. For a mixture dilute in A, the bulk flow effect is negligible or small. In mixtures more concentrated in A, the bulk flow effect can be appreciable. For example, in an equimolar mixture of A and B, $(1 - X_A) = 0.5$ and the molar mass transfer flux of A is twice the ordinary molecular diffusion flux.

For the stagnant component, B, (Eq. 13) becomes

$$0 = X_B N_A - C D_{AB} \frac{dX_B}{dZ} \quad \ldots 28$$

Or

$$X_B N_A = C D_{AB} \frac{dX_B}{dZ} \quad \ldots 29$$

Thus, the bulk flow flux of B is equal but opposite to its diffusion flux.

At quasi-steady-state conditions that is, with no accumulation, and with constant molar density, (Eq. 27) becomes in integral form:

$$\int_{Z_1}^{Z} dZ = -\frac{C \cdot D_{AB}}{N_A} \int_{X_{A_1}}^{X_A} \frac{dX_A}{(1 - X_A)} \quad \ldots 30$$

Which upon integration yields

$$N_A = \frac{C \cdot D_{AB}}{Z - Z_1} \ln\left(\frac{1 - X_A}{1 - X_{A_1}}\right) \quad \ldots 31$$
Rearrangement to give the mole-fraction variation as a function of $Z$ yield

$$X_A = 1 - (1 - X_{A_1}) \exp \left[ \frac{N_A(Z - Z_1)}{C.D_{AB}} \right]$$

...32

Thus, as shown in Fig. 1b, the mole fractions are nonlinear in distance.

An alternative and more useful form of (Eq. 31) can be derived from the definition of the log mean. When $Z = Z_2$, (Eq. 31) becomes

$$N_A = \frac{C.D_{AB}}{Z_2 - Z_1} \ln \left( \frac{1 - X_A}{1 - X_{A_1}} \right)$$

...33

The log mean (LM) of $(1 - X_A)$ at the two ends of the stagnant layer is

$$X_{BLM} = \frac{(1 - X_{A_2}) - (1 - X_{A_1})}{\ln \left( \frac{1 - X_{A_2}}{1 - X_{A_1}} \right)} = \frac{X_{A_1} - X_{A_2}}{\ln \left( \frac{1 - X_{A_2}}{1 - X_{A_1}} \right)}$$

...34

Combining (Eq. 33) with (Eq. 34) gives

$$N_A = \frac{C.D_{AB}}{Z_2 - Z_1} \cdot \frac{(X_{A_1} - X_{A_2})}{(1 - X_A)_{LM}} = \frac{C.D_{AB}(-\Delta X_A)}{(1 - X_A)_{LM}(\Delta Z)}$$

...35

Or

$$N_A = \frac{C.D_{AB}}{Z_2 - Z_1} \cdot \frac{(X_{A_1} - X_{A_2})}{X_{BLM}} = \frac{C.D_{AB}(-\Delta X_A)}{X_{BLM}(\Delta Z)}$$

...35 A

**Diffusion in a tube with change in path length**

Assuming steady state diffusion of component A with constant cross-sectional area and component B is non-diffusing.

Since the case is non-diffusing of B then $N_B = 0$ and $N_A$ is given as in equation 35.

$$N_A = \frac{C.D_{AB}}{Z_2 - Z_1} \cdot \frac{(X_{A_1} - X_{A_2})}{(1 - X_A)_{LM}} = \frac{C.D_{AB}(-\Delta X_A)}{(1 - X_A)_{LM}(\Delta Z)}$$

...35

$$N_A \ast A = \bar{N}_A \quad \text{mol/s}$$

$$\bar{N}_A = C_A \frac{dV}{dt} = C_A \cdot A \frac{dZ}{dt}$$

But
\( C_A = \frac{\rho_A}{Mwt_A} \)

Then:

\( N_A = \frac{\rho_A}{Mwt_A} \left( \frac{dZ}{dt} \right) \)

\[ dZ = \frac{Mwt}{\rho_A} N_A dt \]

\[ dZ = \frac{Mwt}{\rho_A} \left( \frac{C.D_{AB}(X_{A1} - X_{A2})}{(1 - X_A)LM Z} \right) dt \] ...36

Rearrange the above equation

\[ dt = \frac{\rho_A}{Mwt} \left( \frac{(1 - X_A)LM Z}{C.D_{AB}(X_{A1} - X_{A2})} \right) dZ \] ...37

But, as shown before in the equimolar condition

\[ C = \frac{P}{RT} \quad \text{and} \quad C_A = \frac{P_A}{RT} \quad \text{then} \]

\[ dt = \frac{\rho_A}{Mwt} \left( \frac{R T (P_{BLM}) Z}{P_T.D_{AB}(P_{A1} - P_{A2})} \right) dZ \] ...38

Knowing that:

\[ P_{BLM} = (1 - P_A)_{LM} = \frac{(1 - P_{A2}) - (1 - P_{A1})}{\ln\left(\frac{(1 - P_{A2})/(1 - P_{A1})}{(1 - P_{A2})/(1 - P_{A1})}\right)} = \ln\left(\frac{(1 - P_{A2})/(1 - P_{A1})}{(1 - P_{A2})/(1 - P_{A1})}\right) \]

Finally by integrating the above equation for the following boundary condition: \( t_1 = 0 \) at \( Z_1 = Z_0 \) and \( t_2 = t_f \) at \( Z_2 = Z_f \) we can determine the time required to drop the level of liquid to a certain height:

\[ t = \frac{\rho_A}{Mwt} \left( \frac{R T (P_{BLM})}{P_T.D_{AB}(P_{A1} - P_{A2})} \right) \int_{Z_0}^{Z_f} Z dZ \] ...39

**Example 2:**

As shown in Figure 2, an open beaker, 6 cm in height, is filled with liquid benzene at 25°C to within 0.5 cm of the top. A gentle breeze of dry air at 25°C and 1 atm is blown by a fan across the mouth of the beaker so that evaporated benzene is carried away by convection after it transfers through a stagnant air layer in the beaker. The vapor pressure of benzene at 25°C is 0.131 atm. The mutual diffusion coefficient for benzene in air at 25°C and 1 atm is 0.0905 cm²/s. Compute:

(a) The initial rate of evaporation of benzene as a molar flux in mol/cm².s
(b) The initial mole fraction profiles in the stagnant layer
(c) The initial fractions of the mass transfer fluxes due to molecular diffusion.
(d) The initial diffusion velocities, and the species velocities (relative to stationary coordinates) in the stagnant layer.
(e) The time in hours for the benzene level in the beaker to drop 2 cm from the initial level, if the specific gravity of liquid benzene is 0.874. Neglect the accumulation of benzene and air in the stagnant layer as it increases in height.

Figure 2 Evaporation of Benzene from a beaker

SOLUTION:

Let $A =$ benzene, $B =$ air.

\[ C = \frac{P}{R \cdot T} = \frac{1}{(82.06)(298)} = 4.09 \times 10^{-5} \text{ mol cm}^{-3} \]

(a) Take $Z_1 = 0$.

Then $Z_2 - Z_1 = \Delta Z = 0.5 \text{ cm}$.

From Dalton's law, assuming equilibrium at the liquid benzene-air interface,

\[ X_{A_1} = \frac{P_{A_1}}{P} = \frac{0.131}{1} = 0.131 \]
\[ X_{A_2} = 0 \]

Then

\[ X_{BLM} = (1 - X_A) = \frac{0.131}{\ln[(1 - 0) / (1 - 0.131)]} = 0.933 \]

From equation 35, or Equation 35A
\[ N_A = \frac{(4.09 \times 10^{-5})(0.0905)(0.131)}{0.5} = 1.04 \times 10^{-6} \text{ mol/cm}^2 \cdot s \]

(b) \[ \frac{N_A (Z - Z_l)}{C.D_{AB}} = \frac{(1.04 \times 10^{-6})(Z - 0)}{(4.09 \times 10^{-5})(0.0905)} = 0.281Z \]

From equation 32,
\[ X_A = 1 - 0.869[\exp (0.281Z)] \quad (1) \]

Using the above equation (1), the following results are obtained:

<table>
<thead>
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<th>z, cm</th>
<th>( x_A )</th>
<th>( x_B )</th>
</tr>
</thead>
<tbody>
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<td>0.0</td>
<td>0.1310</td>
<td>0.8690</td>
</tr>
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<td>0.1060</td>
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</tr>
<tr>
<td>0.5</td>
<td>0.0000</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

These profiles are only slightly curved.

(c) From (Eq. 27) and (Eq. 29), we can compute the bulk flow terms, \( X_A N_A \) and \( X_B N_A \), from which the molecular diffusion (\( J_i \)) terms are obtained.

<table>
<thead>
<tr>
<th>z, cm</th>
<th>( x_i N )</th>
<th>( J_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk Flow Flux, mol/cm^2\cdot s \times 10^6</td>
<td>Molecular Diffusion Flux, mol/cm^2\cdot s \times 10^6</td>
</tr>
<tr>
<td>0.0</td>
<td>0.1360 A, 0.9040 B</td>
<td>0.9040 A, -0.9040 B</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1100 A, 0.9300 B</td>
<td>0.9300 A, -0.9300 B</td>
</tr>
<tr>
<td>0.2</td>
<td>0.0840 A, 0.9560 B</td>
<td>0.9560 A, -0.9560 B</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0568 A, 0.9832 B</td>
<td>0.9832 A, -0.9832 B</td>
</tr>
<tr>
<td>0.4</td>
<td>0.0287 A, 1.0113 B</td>
<td>1.0113 A, -1.0113 B</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0000 A, 1.0400 B</td>
<td>1.0400 A, -1.0400 B</td>
</tr>
</tbody>
</table>

Note that the molecular diffusion fluxes are equal but opposite, and the bulk flow flux of B is equal but opposite to its molecular diffusion flux, so that its molar flux, \( N_B \), is zero.

(d) From (Eq. 6)
\[ V_M = \frac{N}{C} = \frac{N_A}{C} = \frac{1.04 \times 10^{-6}}{4.09 \times 10^{-5}} = 0.0254 \text{ cm/s} \quad (2) \]
From (Eq. 9), the diffusion velocities are given by
\[ V_{id} = \frac{J_i}{C_i} = \frac{J_i}{X_i C} \quad (3) \]

From (Eq. 10), the species velocities relative to stationary coordinates are:
\[ V_i = V_{id} + V_M \quad (4) \]

Using the above equations (2 to 4), we obtain:

<table>
<thead>
<tr>
<th>z, cm</th>
<th>$v_{id}$ Velocity, cm/s</th>
<th>$J_i$ Species Velocity, cm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>0.0</td>
<td>0.1687</td>
<td>-0.0254</td>
</tr>
<tr>
<td>0.1</td>
<td>0.2145</td>
<td>-0.0254</td>
</tr>
<tr>
<td>0.2</td>
<td>0.2893</td>
<td>-0.0254</td>
</tr>
<tr>
<td>0.3</td>
<td>0.4403</td>
<td>-0.0254</td>
</tr>
<tr>
<td>0.4</td>
<td>0.8959</td>
<td>-0.0254</td>
</tr>
<tr>
<td>0.5</td>
<td>$\infty$</td>
<td>-0.0254</td>
</tr>
</tbody>
</table>

Note that $V_B$ is zero everywhere, because its molecular diffusion velocity is negated by the molar mean velocity.

(e) The mass transfer flux for benzene evaporation can be equated to the rate of change of liquid benzene. Letting $z = \text{distance down from the mouth of the beaker and using (Eq. 35) with } \Delta Z = Z$

\[ N_A = \frac{C \cdot D_{AB} (-\Delta X_A)}{(1 - X_A)LM(Z)} = \frac{\rho_L}{M_L} \left( \frac{dZ}{dt} \right) \quad (5) \]

Separation variables and integrating,

\[ \frac{t}{\int_0^t dt} = \frac{\rho_L}{M_L \cdot C \cdot D_{AB} (-\Delta X_A)} \int_{Z_1}^{Z_2} ZdZ \quad (6) \]

$Z_1 = 0.5 \text{ cm} \text{ and } Z_2 = 2.5 \text{ cm}$

Then from equation (6) after integrating

\[ t = \frac{0.874(0.933)}{78.11(4.09 \times 10^{-5})(0.0905)(0.131)} \left( (2.5)^2 - (0.5)^2 \right) = 64590 \text{ s} = 17.94 \text{ hr} \]
Diffusion through a varying cross-sectional area

In previous cases $N_A \left( \frac{mol}{m^2.S} \right)$ was constant since the cases were at steady state and the cross-sectional area was constant too.

Now, if the cross-sectional area ($A$) varies with $Z$ (the direction of diffusion) such as evaporation of water drop or in the case of naphthalene sphere sublimation, or even in the case of diffusion in conical container, then

$$N_A = \frac{\overline{N}_A}{A} \text{ will not be constant since } A \text{ is not constant (} \overline{N}_A \text{ mole flux } \frac{mol}{S} \text{ is constant at steady state).}$$

First, we will consider the case of diffusion from a sphere material ($A$) in a large volume of gas ($B$):

Assumptions:
1- $B$ is non-diffusing material.
2- At $r = r_2$ $P_A = P_{A_2}$

Then the following equation may be applied:

$$N_A = \frac{\overline{N}_A}{A} = \frac{\overline{N}_A}{4\pi r^2} = -D_{AB} \frac{P_T}{RT} \left( \frac{dP_A}{(P_T - P_A)dr} \right) \quad \cdots 40$$

Here we substituted $dZ$ by $dr$ since the transfer occurs in the $r$ direction.

$$\frac{\overline{N}_A}{4\pi} \int_{r_1}^{r_2} \frac{dr}{r^2} = -D_{AB} \frac{P_T}{RT} \frac{P_{A_2}}{P_A} \int_{P_{A_1}}^{P_{A_2}} \frac{dP_A}{(P_T - P_A)} \quad \cdots 41$$

By integration, the final general form can be predicted:

$$\frac{\overline{N}_A}{4\pi} \left[ \frac{1}{r_1} - \frac{1}{r_2} \right] = \frac{D_{AB} P_T}{RT P_{BLM}} \left( P_{A_1} - P_{A_2} \right) \quad \cdots 42$$
If \( r_2 \gg r_1 \) then \( \frac{1}{r_2} = 0 \) and \( P_{A_2} = 0 \) (dilute solution) also \( P_{BLM} = P_T \), then

\[
\frac{N_A}{4\pi \left[ \frac{1}{r_1} \right]} = \frac{D_{AB}}{RT} \left( P_{A_1} \right)
\]...43

Dividing both sides of equation 43 by \( r_1 \), then

\[
\frac{N_A}{4\pi \left[ \frac{1}{r_1^2} \right]} = N_{A_1} = \frac{D_{AB}}{r_1 RT} \left( P_{A_1} \right)
\]...44 Only for dilute gas

\[
\frac{N_A}{4\pi \left[ \frac{1}{r_1^2} \right]} = N_{A_1} = \frac{D_{AB}}{r_1} \left( C_{A_1} \right)
\]...45 Only for dilute liquids

Another case that can be discussed as one the important cases for varying cross-sectional area; that is the diffusion through conical vessel (non–uniform cross-sectional area) as shown in below

Assumptions:-

B is non–diffusing material (i.e. \( N_B = 0 \))

Then equation 27 may be applied

\[
N_A = -\frac{CD_{AB}}{(1 - X_A)} \left( \frac{dX_A}{dZ} \right)
\]..27

And for diffusion of gases the above equation could be written as follow:
Here $N_A$ is not constant with $Z$ then by integrating the above equation we find

\[
N_A = -\frac{D_{AB} P_T}{RT(P_T - P_A)} \left( \frac{dP_A}{dZ} \right) \quad \ldots 46
\]

To overcome the above integration we must find the relationship between $A$ & $Z$, which depends on the shape. For the above shape (conical):

\[
A = \frac{\pi d^2}{4}
\]

Therefore we must find a relationship between $d$ & $Z$

\[
K = \frac{d_2 - d_1}{2}
\]

\[
\tan \theta = \frac{K}{L} = \frac{M}{L - Z}
\]

\[
M = \frac{K(L - Z)}{L}
\]

Then the diameter at height $Z$ from the top is

\[
d = d_1 + 2m = d_1 + 2M = d_1 + \frac{2K(L - Z)}{L}
\]

d, $K$, and $L$ are known. So the above equation 47 will be written as:

\[
N_A = -\frac{D_{AB} P_T}{RT(P_T - P_A)} \left[ \int_{Z_1}^{Z_2} \frac{dZ}{\pi (d_1 + \frac{2K(L - Z)}{L})} \right] = -\frac{D_{AB} P_T}{RT} \int_{P_{A1}}^{P_{A2}} \frac{dP_A}{(P_T - P_A)} \quad \ldots 47A
\]
**Diffusivity of Gases or Vapors**

Many attempts have been made to express the diffusivity in terms of other physical properties and the following empirical equation by Gilliland gives a satisfactory agreement with experimental data:

\[
D_{AB} = 4.3 \times 10^{-4} T^{1.5} \left( \frac{1}{M_{wt_A}} + \frac{1}{M_{wt_B}} \right) \sqrt{\frac{P}{V_A^{1/3} + V_B^{1/3}}}^2
\]

...48

Where:

\( D_{AB} \) = Diffusivity in \( \left( \frac{m^2}{s} \right) \), \( T \) = temperature in (K), \( P \) = absolute total pressure in (Pa)

\( M_{wt_A} \) and \( M_{wt_B} \) = molecular weight of component A & B.

\( V_A, V_B \) = molar volume of component A & B \( \left( \frac{m^3}{kmol} \right) \).

From equation (48) we can notice that:

\[
D \alpha \frac{T^{1.5}}{P}
\]

And:

\[
\frac{D_1}{D_2} = \left( \frac{T_1}{T_2} \right)^{1.5} \left( \frac{P_2}{P_1} \right)
\]

...49

Another equation is used to calculate the diffusivity coefficient, it is semi empirical equation proposed by Fuller et. al., that is:

\[
D_{AB} = \frac{0.00143 (T^{1.75})}{P_T \left( M_{AB} \right)^{1/2} \left( (\Sigma v_A)^{1/3} + (\Sigma v_B)^{1/3} \right)^2}
\]

...50

Where:

\( D_{AB} \) = Diffusivity in \( \left( \frac{cm^2}{s} \right) \), \( T \) = temperature in (K), \( P \) = absolute total pressure in (atm)

\( M_{AB} = \left( \frac{2}{\left( \frac{1}{M_{wt_A}} \right) + \left( \frac{1}{M_{wt_B}} \right)} \right) \)

...51

\( M_{wt_A}, \) and \( M_{wt_B} \) = molecular weight of component A & B.

\( \Sigma v \) = summation of the atomic and structural diffusion volumes from references such as the following table:

Atomic Diffusion Volumes
Atomic and Structural Diffusion Volume Increments

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Diffusion Volume</th>
<th>F</th>
<th>14.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>15.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>2.31</td>
<td>Cl</td>
<td>21.0</td>
</tr>
<tr>
<td>O</td>
<td>6.11</td>
<td>Br</td>
<td>21.9</td>
</tr>
<tr>
<td>N</td>
<td>4.54</td>
<td>I</td>
<td>29.8</td>
</tr>
<tr>
<td>Aromatic ring</td>
<td>-18.3</td>
<td>S</td>
<td>22.9</td>
</tr>
<tr>
<td>Heterocyclic ring</td>
<td>-18.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Diffusion Volumes of Simple Molecules

<table>
<thead>
<tr>
<th>Element</th>
<th>Diffusion Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2.67</td>
</tr>
<tr>
<td>Ne</td>
<td>5.98</td>
</tr>
<tr>
<td>Ar</td>
<td>16.2</td>
</tr>
<tr>
<td>Kr</td>
<td>24.5</td>
</tr>
<tr>
<td>Xe</td>
<td>32.7</td>
</tr>
<tr>
<td>H₂</td>
<td>6.12</td>
</tr>
<tr>
<td>D₂</td>
<td>6.84</td>
</tr>
<tr>
<td>N₂</td>
<td>18.5</td>
</tr>
<tr>
<td>O₂</td>
<td>16.3</td>
</tr>
<tr>
<td>Air</td>
<td>19.7</td>
</tr>
<tr>
<td>CO</td>
<td>18.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>26.7</td>
</tr>
<tr>
<td>N₂O</td>
<td>35.9</td>
</tr>
<tr>
<td>NH₃</td>
<td>20.7</td>
</tr>
<tr>
<td>H₂O</td>
<td>13.1</td>
</tr>
<tr>
<td>SF₆</td>
<td>71.3</td>
</tr>
<tr>
<td>Cl₂</td>
<td>38.4</td>
</tr>
<tr>
<td>Br₂</td>
<td>69.0</td>
</tr>
<tr>
<td>SO₂</td>
<td>41.8</td>
</tr>
</tbody>
</table>

From equation (50) we can notice that:

\[ D \alpha T^{1.75} \]

And:

\[ \frac{D_1}{D_2} = \left( \frac{T_1}{T_2} \right)^{1.75} \left( \frac{P_2}{P_1} \right) \]  

...52
Maxwell's Law of diffusion For Binary System

Maxwell's postulated that the pressure gradient \( dP_A \) in the direction of diffusion for a constituent of two components gaseous mixture was proportional to:

A) The relative velocity of the molecules in the direction of diffusion.

B) The product of the molar concentration of the component.

Thus;

\[
-\frac{dP_A}{dz} = F.C_A.C_B(U_A - U_B) \quad \ldots 53
\]

\( U_A \) & \( U_B \) = mean molecule of A & B respectively

\( C_A \) & \( C_B \) = molar concentration of the component A & B respectively.

\( F \) = Coefficient

But

\[
U_A = \frac{N_A}{C_A} \quad \text{&} \quad U_B = \frac{N_B}{C_B}
\]

Also

\( P_A = C_A \cdot RT \)

Then

\[
-\frac{dC_A}{dz} = \frac{F}{RT}(N_A \cdot C_B - N_B \cdot C_A) \quad \ldots 54
\]

Now, applying the two cases that have been considered before, *i.e.* equimolar diffusion, and diffusion through stagnant layer, then we can reach to the final equation to calculate the rate of mass transfer as shown below:

A) For equimolar diffusion

\[
N_A = -N_B
\]

\[
-\frac{dC_A}{dz} = \frac{F}{RT}(C_B + C_A) \quad \ldots 55
\]

\[
N_A = -\frac{RT}{F.C_T} \left( \frac{dC_A}{dz} \right) \quad \ldots 56
\]

Comparing with Fick's law, we find that

\[
D_{AB} = \frac{RT}{FC_T}
\]

Or

\[
F_{AB} = \frac{RT}{D_{AB}C_T}
\]

General form \( F = \frac{RT}{DC_T} \)

B) For diffusion through stagnant layer

\( N_B = 0 \)
Then
\[-\frac{dC_A}{dz} = \frac{F}{RT} (N_A \cdot C_B)\] ...57
And
\[N_A = -\frac{RT}{F \cdot C_B} \left(\frac{dC_A}{dz}\right)\] ...58

Multiplying the right side of the equation by \(\left(\frac{C_T}{C_T}\right)\) and by comparison we find that
\[N_A = -\frac{D \cdot C_T}{C_B} \left(\frac{dC_A}{dz}\right)\] ...59

This finally will result:
\[N_A = \frac{C_T \cdot D_{AB}}{Z_2 - Z_1} \ln\left(\frac{1 - X_{A2}}{1 - X_{A1}}\right)\] ...60

**Maxwell's Law for Multi-Component Mass Transfer**

Consider the transfer of component A through a stationary gas consisting of component B, C, D … Suppose that the total partial pressure gradient can be regarded as being made up of series of terms each represent the contribution of the individual component gases, the form of the binary system equation (Eq. 54) can be written as follow:
\[-\frac{dC_A}{dz} = \frac{F_{AB} \cdot N_A \cdot C_B}{RT} + \frac{F_{AC} \cdot N_A \cdot C_C}{RT} + \frac{F_{AD} \cdot N_A \cdot C_D}{RT} + \Lambda\] ...61

As found before for F
\[F = \frac{RT}{DC_T}\]

So, for diffusion of A through multi-component B, C, and D
\[F_{AB} = \frac{RT}{D_{AB}C_T}, \quad F_{AC} = \frac{RT}{D_{AC}C_T}, \quad F_{AD} = \frac{RT}{D_{AD}C_T}\]

respectively

Therefore:
\[-\frac{dC_A}{dz} = \frac{N_A}{C_T} \left(\frac{C_B}{D_{AB}} + \frac{C_C}{D_{AC}} + \frac{C_D}{D_{AD}} + \Lambda\right)\] ...62
\[N_A = \left(\frac{C_B}{D_{AB}} + \frac{C_C}{D_{AC}} + \frac{C_D}{D_{AD}} + \Lambda\right) \frac{dC_A}{dZ}\] ...63

Multiplying the above equation by \(\left(\frac{C_T - C_A}{C_T - C_A}\right)\), then
\[ N_A = \left( \frac{1}{D_{AB}} \cdot \frac{C_B}{C_T - C_A} \right) + \left( \frac{1}{D_{AC}} \cdot \frac{C_C}{C_T - C_A} \right) + \left( \frac{1}{D_{AD}} \cdot \frac{C_D}{C_T - C_A} \right) \frac{-C_T}{C_T - C_A} \frac{dC_A}{dZ} \] ...64

Define
\[ y'_{j} = \frac{C_j}{C_T - C_i} \] then
\[ y'_{b} = \frac{C_b}{C_T - C_A}, \quad y'_{c} = \frac{C_c}{C_T - C_A} \quad \text{and} \quad y'_{d} = \frac{C_d}{C_T - C_A} \]

Therefore
\[ N_A = \frac{1}{\left( \frac{y'_{b}}{D_{AB}} \right) + \left( \frac{y'_{b}}{D_{AC}} \right) + \left( \frac{y'_{c}}{D_{AD}} \right)} \frac{-C_T}{C_T - C_A} \frac{dC_A}{dZ} \] ...65

Finally
\[ N_A = D_{AM} \frac{-C_T}{C_T - C_A} \frac{dC_A}{dZ} \] ...66

Where:
\[ D_{AM} \] is defined as the diffusivity coefficient of component A through a mixture of B, C, D, ....
And
\[ D_{AM} = \frac{1}{\left( \frac{y'_{b}}{D_{AB}} \right) + \left( \frac{y'_{c}}{D_{AC}} \right) + \left( \frac{y'_{d}}{D_{AD}} \right)} \]
Example 3:
A sphere of naphthalene having a radius of 2mm is suspended in a large volume of still air at 318 K and 101.325 kPa. The surface temperature of the naphthalene can be assumed to be at 318 K and its vapor pressure at this temperature is 0.555 mmHg. The diffusivity (D_{AB}) of naphthalene in air at 318 K & 1 atm is 6.92*10^{-6} m^2/s, calculate:
1- The rate of evaporation of naphthalene from the surface.
2- Then find the partial pressure of naphthalene at a distance 20 mm from the surface of the naphthalene sphere. Assume steady – state diffusion.

Solution:
1- To calculate the rate of evaporation of naphthalene use equation 42:
\[
\frac{N_A}{4\pi} \left[ \frac{1}{r_1} - \frac{1}{r_2} \right] = \frac{D_{AB} P_T}{RT \ P_{BLM}} \left( P_{A_1} - P_{A_2} \right)
\]

\[P_{A_1} = 0.555 \text{ mmHg} \equiv 74 \text{ Pa}\]

For large values of \(r_2\) that is \(r_2 \gg r_1\) then:
\[\frac{1}{r_1} \gg \frac{1}{r_2}\] and \(1 \approx 0\) also \(P_T = P_{BLM}\) because \(P_{A_2} = 0\) and \(P_{A_1} \ll P_T\), therefore apply equation 43:
\[
\frac{N_A}{4\pi} \left[ \frac{1}{r_1} \right] = \frac{D_{AB}}{RT} \left( P_{A_1} \right)
\]

\[\frac{N_A}{A} = \frac{4\pi . r_1 . D_{AB}}{RT} \left( P_{A_1} \right) = \frac{4\pi * 0.002 * 6.92 * 10^{-6} * 74}{8.314 * 318} = 4.8654 * 10^{-9} \text{ mol/sec}\]

The rate of evaporation from the surface is \(N_A\big|_{r_1}\)

\[\frac{N_A}{A} = \frac{4.8654 * 10^{-9}}{4\pi * (0.002)^2} = 96.8 * 10^{-5} \text{ kmol} \text{ m}^{-2} \text{ sec}^{-1}\]

2- To find the partial pressure of naphthalene at a distance 20 mm from the surface apply the following equation:
\[
\frac{N_A}{4\pi} \left[ \frac{1}{r_1} - \frac{1}{r_2} \right] = \frac{D_{AB} P_T}{RT} \ln \left( \frac{P_T - P_{A_1}}{P_T - P_{A_2}} \right)
\]

which is the original form of equation 42, for the following conditions:
\[At \ r = r_1 = 2 \text{ mm} \text{ then } P_{A_1} = 74 P_{a}\]

\[And \ r = r_2 = 22 \text{ mm} \text{ then } P_{A_2} \text{ is unkown and by applying the above equation we can find } P_{A_2}\] knowing that all other parameters in this equation is known.
Example 4:
An open tank is filled with 2ft of the top with pure methanol. The tank is tapered, as shown below. The air within the tank is stationary but circulation of air immediately above the tank is adequate to assure a negligible concentration of methanol at this point. The tank and air space are at 77°F and 1 atm and the diffusivity of methanol in air in such conditions is 0.62 ft²/s. Calculate the rate of loss of methanol from the tank at steady – state. Given that the partial pressure of methanol at 77°F is 135 mm Hg.

Solution:
Since air does not diffuse in methanol, so
\[ N_B = 0 \]
∴ the case is diffusing through stagnant layer with
variable area, apply equation 47

\[
\overline{N}_A \frac{Z_2}{Z_1} \int \frac{dZ}{A} = -\frac{D_{AB}}{RT} \frac{P_{A_2}}{P_{A_1}} \int \frac{dP_A}{(P_T - P_A)}
\]

Then we have to find the area (A) in terms of (Z)
\[
\tan \theta = \frac{1}{2} = \frac{m}{L - Z}
\]
\[
m = \frac{L - Z}{2}
\]
\[
d = 2m + 4
\]
\[
d = L - Z + 4 = 6 - Z
\]
∴ \[ A = \frac{\pi}{4} (d^2) = \frac{\pi}{4} (6 - Z)^2 \]

Then
\[
\frac{4 \cdot \overline{N}_A}{\pi} \frac{Z_2}{Z_1} \frac{dZ}{(6 - Z)^2} = -\frac{D_{AB} \cdot P_{T}}{R \cdot T} \frac{P_{A_2}}{P_{A_1}} \int \frac{dP_A}{(P_T - P_A)}
\]

For the following boundary conditions:
\[ Z_1 = 0 \quad \text{then} \quad P_{A_1} = 135 \text{ mm Hg} = 0.178 \text{ atm} \quad \text{check} \quad d = 6 \text{ft} \]
\[ Z_2 = 2 \quad \text{then} \quad P_{A_2} = 0 \text{ atm} \quad \text{check} \quad d = 4 \text{ft} \]

Now we have to calculate all the parameters in the equation, so we can find \( \overline{N}_A \). therefore:
\[ \text{P}_{B_1} = 760 - 135 = 625 \text{ mmHg} = 0.822 \text{ atm} \]
\[ \text{P}_{B_2} = 760 - 0 = 760 \text{ mm Hg} = 1 \text{ atm} \]
\[ \text{P}_{BLM} = \frac{\text{P}_{B_2} - \text{P}_{B_2}}{\ln \frac{\text{P}_{B_2}}{\text{P}_{B_1}}} = \frac{1 - 0.822}{\ln \frac{1}{0.822}} = 0.908 \text{ atm} \]

Use \( R = 0.7302 \frac{\text{atm ft}^3}{\text{lbmol} * \text{R}} \)

\[ D_{AB} = 0.62 \frac{\text{ft}^2}{\text{hr}} = 1.722 \times 10^{-4} \frac{\text{ft}^2}{\text{sec}} \]

Now by integrating the above equation, we find:
\[
\frac{4 * N_A}{\pi} \left[ \frac{1}{6 - Z_2} - \frac{1}{6 - Z_1} \right] = \frac{D_{AB} * P_T}{RT * P_{BLM}} \left[ P_{A_1} - P_{A_2} \right]
\]
\[
N_A = \frac{\pi}{4} \left[ \frac{1.722 \times 10^{-4} \times 1}{0.7302 \times 537 \times 0.908} \right] \times \left( \frac{0.178 - 0}{\frac{1}{4} - \frac{1}{6}} \right) = 8.111 \times 10^{-7} \frac{\text{lbmol}}{\text{sec}}
\]

**Example 5:**

A small diameter tube closed at one end was filled with acetone to within 18 mm of the top and maintained at 290 K and 99.75 kPa with a gentle stream of air blowing across the top. After 15 ksec, the liquid level had fallen to 27.5 mm. The vapor pressure of acetone at that temperature is 21.95 kN/m². Calculate the diffusivity of acetone in air, given the following data:

Mwt of acetone = 58

The density of acetone \( (\rho) = 790 \text{ kg/m}^3 \)

**Solution:**

Since evaporation is occurred through constant area, then apply equation 39 and by integrating this equation we find:
\[
t = \frac{\rho_A}{\text{Mwt}} \left( \frac{R T (P_{BLM})}{P_T \cdot D_{AB} (P_{A_1} - P_{A_2})} \right) \left( \frac{Z_f^2}{2} - \frac{Z_0^2}{2} \right)
\]

To apply this equation we must first calculate each parameter in the equation as:

\( P_T = 99.75 \text{ kPa} \)
\( T = 290 \text{ K} \)

\( R = 8.314 \frac{\text{kPa} \cdot \text{m}^3}{\text{kmol} \cdot \text{K}} \)
\[ P_{BLM} = \frac{P_{B2} - P_{B2}}{\ln \frac{P_{B2}}{P_{B1}}} = \frac{(99.75 - 0) - (99.75 - 21.95)}{\ln \frac{99.75}{77.8}} = 88.321 \text{kPa} \]

\[ M_{wt} = 58, \rho = 790 \text{ kg/m}^3 \]

\[ Z_0 = 18 \text{ mm} = 0.018 \text{ m} \]

\[ Z_f = 27.5 \text{ mm} = 0.0275 \text{ m} \]

\[ t = 15 \text{ ksec} = 15000 \text{ s} \]

Now solve the above equation for \( D_{AB} \) as follow to find the diffusivity:

\[ D_{AB} = \frac{\rho_A}{M_{wt}} \left( \frac{RT (P_{BLM})}{P_T \ast t \ast (P_{A1} - P_{A2})} \right) \left( \frac{Z_f^2 - Z_0^2}{2} \right) \]

\[ D_{AB} = \frac{790}{58} \left( \frac{83.14 \ast 290 \ast 88.321}{99.75 \ast 15000 \ast (21.95 - 0)} \right) \left( \frac{(0.0275)^2 - (0.018)^2}{2} \right) = 1.9 \ast 10^{-5} \text{ m}^2 / \text{s} \]

**Example 6:**

An open conical vessel is filled with water up to 10 cm from its top, as shown in the figure below. Calculate the time required to drop the level by 13 cm, given that the diffusivity of water in air at 25°C & 1 atm is 0.256 cm²/s, and the vapor pressure of water at 25°C is 0.0313 atm.

**Solution:**

To calculate the time required, we must first find the rate of diffusion using equation 47 that is

\[ N_A \int_{Z_1}^{Z_2} \frac{dZ}{A} = -D_{AB} \int_{P_{A1}}^{P_{A2}} \frac{dP_A}{RT} \frac{P_T}{P_A} \left( P_T - P_A \right) \]

Then we must find the relation between the diameter (d) & the height (Z)

From the figure:
\[
\tan \theta = \frac{1}{L} = \frac{r}{L - Z} \\
\frac{1}{\sqrt{3}} = \frac{r}{\sqrt{3} - Z} \\
\therefore r = \frac{\sqrt{3} - Z}{\sqrt{3}} \rightarrow d = \frac{2(\sqrt{3} - Z)}{\sqrt{3}}
\]

\[
A = \frac{\pi}{4} \cdot d^2 = \frac{\pi \cdot 4(\sqrt{3} - Z)^2}{4 \cdot 3} = \frac{\pi(\sqrt{3} - Z)^2}{3}
\]

Then substitute \(A\) in the above integration and solve for \(N_A\), we find that

\[
3 \cdot \frac{N_A}{\pi} \left( \frac{1}{\sqrt{3} - Z} - \frac{1}{\sqrt{3} - 0} \right)_{0.1} = \frac{D_{ab} \cdot P_T}{R \cdot T \cdot P_{BLM}} \left( p_A - p_A^o \right) \rho_{p_A}
\]

To apply this equation we must first calculate each parameter in the equation as:

\(P_T = 1\ atm\)
\(T = 298\ K\)

\[
R = 8.314\ \text{kPa} \cdot \text{m}^3 \cdot \text{kmol} \cdot \text{K}
\]

\[
P_{BLM} = \frac{P_{b_a} - P_{b_b}}{\ln \frac{P_{b_a}}{P_{b_b}}} = \frac{(1 - 0) - (1 - 0.0313)}{\ln \frac{1}{0.9687}} = 0.9843\ atm
\]

\[
PA_1 = 0.0313\ atm = 3.1685 \times 10^{-3}\ \text{Pa}
\]

So

\[
3 \cdot \frac{N_A}{\pi} \left( \frac{1}{\sqrt{3} - 0.1} - \frac{1}{\sqrt{3} - 0} \right) = \frac{2.56 \times 10^{-3} \cdot 1}{8.314 \cdot 298 \cdot 0.9843} \left( 3.1685 \times 10^{-3} - 0 \right)
\]

\[
N_A = 4.41 \times 10^{-5}\ \text{kmol}/s
\]

To find the time use the following equation:

\[
\frac{\rho}{M_{wt}} \left( \frac{dZ}{dt} \right) = \frac{N_A}{A}
\]

\[
N_A \int_0^t dt = \frac{\rho}{M_{wt}} \int_{z_0}^{z_f} AdZ
\]

\[
N_A \cdot t = \frac{\rho \cdot \pi}{3 \cdot M_{wt}} \int_{0.1}^{0.23} (\sqrt{3} - Z)^2 dZ
\]

\[
t = \frac{1000 \times \pi}{3 \times 18 \times N_A} \cdot \frac{1}{3} \left[ (\sqrt{3} - 0.23)^3 - (\sqrt{3} - 0.1)^3 \right] = \text{sec}
\]
Example 7:
Normal butanol (A) is diffusing through air (B) at 1 atm absolute pressure. Estimate the diffusivity ($D_{AB}$) for the following conditions and compare it with experimental data:

A- For 0°C & 1atm.
B- For 26°C & 1atm.
C- For 0°C & 2 atm (absolute).

Solution:
A- Fuller equation is given as (Eq. 50)

$$D_{AB} = \frac{0.00143(T^{1.75})}{P_T(M_{AB})^{1/2} \left( (\sum v_A)^{1/3} + (\sum v_B)^{1/3} \right)^2}$$

So we have to estimate the parameters of the equations:

\[ T = 0+273=273 \text{ K} \]
\[ P_T = 1 \text{ atm} \]
\[ M_{AB} \text{ Can be calculated from:} \]

\[ \frac{2}{\left( \frac{1}{M_{wt_A}} \right) + \left( \frac{1}{M_{wt_B}} \right)} = \frac{2}{\left( \frac{1}{74} + \frac{1}{29} \right)} = 41.67 \]

\[ \sum V_A = (4*15.9) + (10*2.31) + (1*6.11) = 92.81 \text{ (The values of diffusion volumes for each atom are taken from table (1).)} \]
\[ \sum V_B = 19.7 \]

Then

\[ D_{AB} = \frac{0.00143*(273)^{1.75}}{1*(41.67)^{1/2} \left( (92.81)^{1/3} + (19.7)^{1/3} \right)^2} \approx 0.077737639 \text{ cm}^2 / \text{s} \]

B- To estimate the value of the diffusivity at 26°C & 1atm use equation 52

$$\frac{D_1}{D_2} = \left( \frac{T_1}{T_2} \right)^{1.75} \left( \frac{P_2}{P_1} \right)$$

But there is no change in the pressure (both are 1 atm) then:

$$\frac{D_1}{D_2} = \left( \frac{T_1}{T_2} \right)^{1.75} \quad \text{and} \quad D_2 = \left( \frac{T_2}{T_1} \right)^{1.75} * D_1 = \left( \frac{26+273}{0+273} \right)^{1.75} * 0.077737639 = 0.091153069 \text{ cm}^2 / \text{s}$$

C- To estimate the value of the diffusivity at 0°C & 2atm also use equation 52

$$\frac{D_1}{D_2} = \left( \frac{T_1}{T_2} \right)^{1.75} \left( \frac{P_2}{P_1} \right)$$

But as we can see that the temperature is the same of part A, then:
\[
\frac{D_1}{D_2} = \left(\frac{P_2}{P_1}\right)
\]
And
\[
D_2 = \left(\frac{P_1}{P_2}\right) * D_1 = \left(\frac{1}{2}\right) * 0.077737639 = 0.03886882 \text{ cm}^2 / \text{s}
\]

**Example 8:**
Oxygen (A) is diffusing through non-diffusing gas mixture of methane (B) and hydrogen (C) in the volume ratio of 2:1. The total pressure is 101.3 kPa and the temperature is 0°C. The partial pressure of oxygen at two planes (2 mm) is 13 kN/m² and 6.5 kN/m². The diffusivity of Oxygen in Hydrogen \( D_{O_2 H_2} \) = 6.99*10⁻⁵ m²/s and the diffusivity of Oxygen in Methane \( D_{O_2 CH_4} \) = 1.86*10⁻⁵ m²/s were measured at 1 atm and 0°C. Calculate the rate of diffusion of oxygen in kmol/s through each square meter of the two planes.

**Solution:**
Apply equation 66
\[
N_A = D_{AM} \frac{C_T}{C_T - C_A} \frac{dC_A}{dZ}
\]
Rewrite the above equation for the gas phase as:
\[
N_A = -\frac{D_{AM} * P_T}{RT * (P_T - P_A)} \frac{dP_A}{dZ}
\]
And by integration the above equation we find:
\[
N_A = \frac{D_{AM} * P_T}{RT * P_{MLM}} \frac{(P_A1 - P_A2)}{(Z_2 - Z_1)}
\]
Note:
\( P_{MLM} \) means the average log mean of all partial pressures in the system accept A, that is
\[
P_{MLM} = \frac{(P_T - P_A2) - (P_T - P_A1)}{\ln \left[ \frac{P_T - P_A2}{P_T - P_A1} \right]}
\]

\( P_T = 101.3 \text{ kPa}, \ P_A1 = 13 \text{ kPa}, \) and \( P_A2 = 6.5 \text{ kPa}. \) Then:
\[
P_{MLM} = \frac{(101.3 - 6.5) - (101.3 - 13)}{\ln \left( \frac{101.3 - 6.5}{101.3 - 13} \right)} = 90.2 \text{ kPa}
\]
Now calculate \( D_{AM} \) using the following equation:
\[ D_{AM} = \frac{1}{\left( \frac{y'_B}{D_{AB}} \right) + \left( \frac{y'_C}{D_{AC}} \right) + \left( \frac{y'_D}{D_{AD}} \right)} \]

\[ y'_B = \frac{2}{3} \quad \text{and} \quad y'_C = \frac{1}{3} \] (volume ratio = mole ratio for gases)

\[ (V_T = V_A + V_B + V_C) \]

\[ (y'_B = \frac{V_B}{V_T - V_A} = \frac{V_B}{V_B + V_C}) \]

\[ D_{AM} = \frac{1}{\left( \frac{0.6667}{1.86*10^{-5}} \right) + \left( \frac{0.3333}{6.99*10^{-5}} \right)} = 2.46*10^{-5} \frac{m^2}{s} \]

\[ \therefore N_A = \frac{2.46*10^{-5} * 101.3 * (13 - 6.5)}{8.314 * 273 * 90.2 * 2*10^{-3}} = 3.91*10^{-5} \frac{kmol}{m^2* s} \]

And for 1 m² of cross-sectional area:

\[ \bar{N}_A = 3.91*10^{-5} \frac{kmol}{s} \]

**Molecular Diffusion in Liquid Phase**

Molecular diffusion in liquid phase takes place in many separation operations, such as:

1- Liquid – liquid extraction.
2- Gas absorption.
3- Distillation.
4- Oxygenation of rivers by air.
5- Diffusion of salts in blood.

Some important notes in liquid diffusion, these are:

1- Slower than in gas phase because of the density and attractive forces between molecules.
2- Diffusivities are dependent on the concentration of the diffusing component.

The rate of diffusion in liquid phase is represented by the same equation as for the gas phase, that is

\[ J_A = -D_L \frac{dC_A}{dZ} \] ...67

\[ D_L: \text{liquid phase diffusivity in} \left( \frac{m^2}{s} \right) \]

Equation 12A can be written as:
\[ N_A = -D_L \left( \frac{dC_A}{dZ} \right) + \frac{C_A}{C} (N_A + N_B) \quad \ldots \ldots \ldots 68 \]

* Then for equimolar diffusion, where \( N_A = -N_B \), then
\[ N_A = -D_L \left( \frac{C_{A_2} - C_{A_1}}{Z_2 - Z_1} \right) \quad \ldots \ldots \ldots 69 \]

Or
\[ N_A = -D_L \cdot C_{av} \left( \frac{X_{A_2} - X_{A_1}}{Z_2 - Z_1} \right) \quad \ldots \ldots \ldots 69A \]

Where
\( D_L \): diffusivity of solute A in B \( \left( \frac{m^2}{s} \right) \)
\( X_A \): mole fraction of A at any point

\[ C_{av} = \left( \frac{\rho}{Mwt} \right) = \left( \frac{\rho_1}{Mwt_1} + \frac{\rho_2}{Mwt_2} \right) \quad \ldots \ldots \ldots 70 \]

Where:
\( C_{av} \): average concentration of \((A+B)\) in \( \left( \frac{kmol}{m^3} \right) \)
\( Mwt_1 \) & \( Mwt_2 \): average molecular weight of the solution at points 1 & 2 respectively \( \left( \frac{kg}{kmol} \right) \).
\( \rho_1 \) & \( \rho_2 \): average density of the solution at points 1 & 2 in \( \left( \frac{kg}{m^3} \right) \).

The case of equimolar counter diffusion in liquid phase occurs very infrequently, while the most important case of diffusion in liquids is that where solute A is diffusing and solvent B is stagnant or non-diffusing, e.g. diffusion of propanoic acid (A) presented in propanoic acid – toluene mixture in water (B), where water does not diffuse into toluene, \( N_B = 0 \).

Therefore applying equation 54 will result:
\[ N_A = -D_L \cdot C \left( \frac{dC_A}{(C - C_A)dZ} \right) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 71 \]

After integration:
\[ N_A = -D_L \left( \frac{C_{av}}{X_{BLM}} \right) \left( \frac{X_{A_2} - X_{A_1}}{Z_2 - Z_1} \right) \quad \ldots \ldots \ldots 72 \]

Where:
\[ X_{BLM} = \frac{X_{B_2} - X_{B_1}}{\ln \left( \frac{X_{B_2}}{X_{B_1}} \right)} \] ...73

Note:
\[ X_{A_1} + X_{B_1} = X_{A_2} + X_{B_2} = 1 \]

For dilute solutions \( X_{BLM} \approx 1.0 \)

Then
\[ N_A = -D \frac{C_{A_2} - C_{A_1}}{Z_2 - Z_1} \] ...74

**Diffusivities in Liquids**

Diffusion coefficient in liquids at 293 K is given in table 10.7 in volume 1 of chemical engineering BY Coulson, J.M.; Richardson, J.F., fifth edition (page 506). In the absence of data, estimation of diffusivities can be made using Wilke & Chang equation:

\[ D_{AB} = \frac{7.4 \times 10^{-8} (\phi_B M_{wt_B})^{1/2} T}{\mu_B \nu_A^{0.6}} \] 75

**Where:**

- \( D_{AB} = \) diffusivity of solute A in very dilute solution in solvent B, (cm²/s)
- \( M_{wt_B} = \) molecular weight of solvent B.
- \( T = \) temperature (K).
- \( \mu_B = \) viscosity of solvent B, (cP or \( \frac{gm}{cm \cdot s} \))
- \( \nu_A = \) Solute molar volume at its normal boiling point (cm³/mol). For water as solute = 0.0756 m³/kmol
- \( \phi_B = \) Association factor for the solvent.
  - = 2.6 for Water as solvent.
  - = 1.9 for Methanol as solvent.
  - = 1.5 for Ethanol as solvent.
  - = 1.0 for unassociated solvents as Benzene, ethyl ether.

For diffusion of A through multi-component stagnant layer mixture, the following equation may be used:

\[ N_A = D_{\text{av}} \frac{C_T}{C_{RM}} \left( \frac{C_{A_2} - C_{A_1}}{Z_2 - Z_1} \right) \] ...76

Or

\[ N_A = D_{\text{av}} \frac{X_{\text{av}}}{X_{RM}} \left( \frac{X_{A_2} - X_{A_1}}{Z_2 - Z_1} \right) \] ...77

**Where:**

\[ D = \frac{1}{\left( \frac{X_B'}{D_{AB}} + \frac{X_C'}{D_{AC}} + \frac{X_D'}{D_{AD}} \right)} \]

\( X_{RM} = \) remaining mole fraction log mean. (Mole fraction of all components except A).
Molecular Diffusion in Solid Phase

Diffusion in solids takes place by different mechanisms depending on the diffusing atom, molecule, or ion; the nature of the solid structure, whether it be porous or nonporous, crystalline, or amorphous; and the type of solid material, whether it be metallic, ceramic, polymeric, biological, or cellular. Diffusion in solid phase can be classified as:

1- Diffusion which follows Fick's law and does not depend on the structure of solid.
2- Diffusion in which the structure of solid are important.

1- Diffusion that follows Fick's law:
That is

\[ N_A = -D_{AB} \left( \frac{dC_A}{dZ} \right) \]

Where:
\[ D_{AB} = \text{Diffusivity of fluid A in solid B in m}^2/\text{s}. \text{ It is independent of pressure, but a function of Temperature.} \]

A) For diffusion through a solid slab at steady - state:
\[ N_A = -D_{AB} \left( \frac{C_{A_2} - C_{A_1}}{Z_2 - Z_1} \right) \] ...78

B) For diffusion through a solid hollow cylinder of \( r_1 \) (inner radius) and \( r_2 \) (outer radius) with length \( L \):
\[ N_A = \frac{\bar{N}_A}{A} = \frac{\bar{N}_A}{2\pi r L} = -D_{AB} \left( \frac{dC_A}{dZ} \right) \] ...79
\[ \bar{N}_A = -D_{AB} \left( C_{A_2} - C_{A_1} \right) \frac{2\pi L}{\ln \frac{r_2}{r_1}} \] ...80

C) For diffusion through a solid hollow spherical shape of \( r_1 \) (inner radius) and \( r_2 \) (outer radius):
\[ N_A = \frac{\bar{N}_A}{A} = \frac{\bar{N}_A}{4\pi r^2} = -D_{AB} \left( \frac{dC_A}{dZ} \right) \] ...81
\[ \bar{N}_A \left( \frac{1}{r_1} - \frac{1}{r_2} \right) = D_{AB} \left( C_{A_2} - C_{A_1} \right) \] ...82

Where:
\[ C_{A_2} \ & C_{A_1} = \text{concentrations at opposite side of the sphere.} \]
In the case that gas diffuses through a solid, then the solubility of the gas in the solid is directly proportional to the partial pressure of solute. The solubility of a solute gas (A) in a solid is expressed as \( S \) in cm\(^3\) solute (at STP, e.g. 0\(^\circ\)C, and 1 atm) per cm\(^3\) solid per (atm, partial pressure of solute A), then:

\[
S = \frac{\text{cm}^3 \ (\text{STP}) \text{ of } A}{\text{cm}^3 \text{ solid} \cdot \text{atm}} \quad \ldots 83
\]

To convert the solubility \( S \) of A to concentration \( (C_A) \):

\[
C_A = S \times \frac{1}{22.414} \times P_A \quad \ldots 84
\]

Where:

\[
C_A = \frac{\text{mol } A}{\text{cm}^3}, S = \frac{\text{cm}^3 \ (\text{STP}) \text{ of } A}{\text{atm} \cdot \text{cm}^3 \text{ (solid)}}, P_A = \text{atm}, \text{ and } 22.414 = \frac{\text{cm}^3 A}{\text{mol}}
\]

In many cases the experimental data for diffusion of gases in solid are given as permeability (\( P_m \)) in cm\(^3\) of solute gas (A) at STP \{0\(^\circ\)C, and 1 atm\} per diffusing per second per cm\(^2\) cross-sectional area through of solid of 1 cm thick under a pressure difference of 1 atm.

\[
N_A = -D_{AB} \left( \frac{C_A_2 - C_A_1}{Z_2 - Z_1} \right) \quad \ldots 85
\]

Applying (Eq. 84), then

\[
C_{A_1} = \frac{S \cdot P_{A_1}}{22.414} \quad \text{&} \quad C_{A_2} = \frac{S \cdot P_{A_2}}{22.414}, \text{ then:}
\]

\[
N_A = -D_{AB} \cdot S \left( \frac{P_{A_2} - P_{A_1}}{Z_2 - Z_1} \right) = \frac{P_m (P_{A_1} - P_{A_2})}{22.414(Z_2 - Z_1)} \quad \ldots 86
\]

Where:

\[
P_m = D_{AB} \cdot S = \frac{\text{cm}^3 \ (\text{STP}) \text{ of } A}{\text{cm}^2 \cdot \text{atm}} \quad \ldots 87
\]

If series of solids are presented in series 1, 2, 3, .., etc of thickness of each \( L_1, L_2, L_3, \ldots \), etc respectively, then:

\[
N_A = \frac{(P_{A_1} - P_{A_2})}{22.414} \left( \frac{1}{L_1 + \frac{L_2}{P_{m_2}} + \frac{L_3}{P_{m_3}} + \ldots} \right) \quad \ldots 88
\]

Where:

\((P_{A_1} - P_{A_2})\) is the overall partial pressure difference.
Diffusion in which the structure of solid are important:

*Porous Solids*

When solids are porous, predictions of the diffusivity of gaseous and liquid solute species in the pores can be made. This type of diffusion is also of great importance in the analysis and design of reactors using porous solid catalysts. It is sufficient to mention here that any of the following four mass transfer mechanisms or combinations thereof may take place:

1. Ordinary molecular diffusion through pores, which present tortuous paths and hinder the movement of large molecules when their diameter is more than 10% of the pore diameter.

2. Knudsen diffusion, which involves collisions of diffusing gaseous molecules with the pore walls when the pore diameter and pressure are such that the molecular mean free path is large compared to the pore diameter.

3. Surface diffusion involving the jumping of molecules, adsorbed on the pore walls, from one adsorption site to another based on a surface concentration-driving force.

4. Bulk flow through or into the pores.

When treating diffusion of solutes in porous materials where diffusion is considered to occur only in the fluid in the pores, it is common to refer to an effective diffusivity, \( D_{\text{eff}} \), which is based on (1) the total cross-sectional area of the porous solid rather than the cross-sectional area of the pore and (2) on a straight path, rather than the pore path, which may be tortuous. If pore diffusion occurs only by ordinary molecular diffusion, the effective diffusivity can be expressed in terms of the ordinary diffusion coefficient, \( D \), by

\[
D_{\text{eff}} = \frac{D_{AB} \varepsilon}{\tau} \quad ...89
\]

And the rate of diffusion is calculated by

\[
N_A = -D_{\text{eff}} \left( \frac{C_{A_2} - C_{A_1}}{Z_2 - Z_1} \right) \quad ...90
\]

Where \( \varepsilon \) the fractional porosity (typically 0.5) of the solid and \( \tau \) is the pore-path tortuosity (typically 2 to 3), which is the ratio of the pore length to the length if the pore were straight in the direction of diffusion. The effective diffusivity is either determined experimentally without knowledge of the porosity or tortuosity or predicted from (Eq. 89) based on measurement of the porosity and tortuosity and use of the predictive methods for ordinary molecular diffusivity. As an example of the former, Boucher, Brier, and Osborn measured effective diffusivities for the leaching of processed soybean oil (viscosity = 20.1 cP at 120°F) from 1/16-in.-thick porous clay plates with liquid tetrachloroethylene solvent. The rate of extraction was controlled by
the rate of diffusion of the soybean oil from the clay plates. The measured value of $D_{\text{eff}}$ was $1.0 \times 10^{-6}$ cm$^2$/s. As might be expected from the effects of porosity and tortuosity, the effective value is about one order of magnitude less than the expected ordinary molecular diffusivity, $D$, of oil in the solvent.

**Crystalline Solids**

Diffusion through nonporous crystalline solids depends markedly on the crystal lattice structure and the diffusing entity. For the cubic lattice (simple, body-centered, and face-centered), the diffusivity is the same in all directions (isotropic). In the six other lattice structures (including hexagonal and tetragonal), the diffusivity can be different in different directions (anisotropic). Many metals, including Ag, Al, Au, Cu, Ni, Pb, and Pt, crystallize into the face-centered cubic lattice structure. Others, including Be, Mg, Ti, and Zn, form anisotropic hexagonal structures. The mechanisms of diffusion in crystalline solids include:

1. Direct exchange of lattice position by two atoms or ions, probably by a ring rotation involving three or more atoms or ions
2. Migration by small solutes through inter-lattice spaces called interstitial sites
3. Migration to a vacant site in the lattice
4. Migration along lattice imperfections (dislocations), or grain boundaries (crystal interfaces)

Diffusion coefficients associated with the first three mechanisms can vary widely and are almost always at least one order of magnitude smaller than diffusion coefficients in low-viscosity liquids. As might be expected, diffusion by the fourth mechanism can be faster than by the other three mechanisms. Typical experimental diffusivity values, taken mainly from Barrier, are given in Table 2. The diffusivities cover gaseous, ionic, and metallic solutes. The values cover an enormous 26-fold range. Temperature effects can be extremely large.

**Metals**

Important practical applications exist for diffusion of light gases through metals. To diffuse through a metal, a gas must first dissolve in the metal. As discussed by Barrier, all light gases do not dissolve in all metals. For example, hydrogen dissolves in such metals as Cu, Al, Ti, Ta, Cr, W, Fe, Ni, Pt, and Pd, but not in Au, Zn, Sb, and Rh. Nitrogen dissolves in Zr, but not in Cu, Ag, or Au. The noble gases do not dissolve in any of the common metals. When $H_2$, $N_2$, and $O_2$ dissolve in metals, they dissociate and may react to form hydrides, nitrides, and oxides, respectively. More complex molecules such as ammonia, carbon dioxide, carbon monoxide, and sulfur dioxide also dissociate. The following example illustrates how pressurized hydrogen gas can slowly leak through the wall of a small, thin pressure vessel.
Table 2 Diffusivity of Solutes in Crystalline Metals and Salts

<table>
<thead>
<tr>
<th>Metal</th>
<th>Solute</th>
<th>$T, ^\circ C$</th>
<th>$D, \text{cm}^2/\text{s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>Au</td>
<td>760</td>
<td>$3.6 \times 10^{-10}$</td>
</tr>
<tr>
<td></td>
<td>Sb</td>
<td>20</td>
<td>$3.5 \times 10^{-21}$</td>
</tr>
<tr>
<td></td>
<td>Sb</td>
<td>760</td>
<td>$1.4 \times 10^{-9}$</td>
</tr>
<tr>
<td>Al</td>
<td>Fe</td>
<td>359</td>
<td>$6.2 \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>500</td>
<td>$2 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>50</td>
<td>$1.2 \times 10^{-9}$</td>
</tr>
<tr>
<td>Cu</td>
<td>Al</td>
<td>20</td>
<td>$1.3 \times 10^{-30}$</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>850</td>
<td>$2.2 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>750</td>
<td>$2.1 \times 10^{-11}$</td>
</tr>
<tr>
<td>Fe</td>
<td>H$_2$</td>
<td>10</td>
<td>$1.66 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>H$_2$</td>
<td>100</td>
<td>$1.24 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>800</td>
<td>$1.5 \times 10^{-8}$</td>
</tr>
<tr>
<td>Ni</td>
<td>H$_2$</td>
<td>85</td>
<td>$1.16 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>H$_2$</td>
<td>165</td>
<td>$1.05 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>950</td>
<td>$4 \times 10^{-8}$</td>
</tr>
<tr>
<td>W</td>
<td>U</td>
<td>1727</td>
<td>$1.3 \times 10^{-11}$</td>
</tr>
<tr>
<td>AgCl</td>
<td>Ag$^+$</td>
<td>150</td>
<td>$2.5 \times 10^{-14}$</td>
</tr>
<tr>
<td></td>
<td>Ag$^+$</td>
<td>350</td>
<td>$7.1 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>Cl$^{-}$</td>
<td>350</td>
<td>$3.2 \times 10^{-16}$</td>
</tr>
<tr>
<td>KBr</td>
<td>H$_2$</td>
<td>600</td>
<td>$5.5 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>Br$_2$</td>
<td>600</td>
<td>$2.64 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Silica and Glass
Another area of great interest is the diffusion of light gases through various forms of silica, whose two elements, Si and O, make up about 60% of the earth's crust. Solid silica can exist in three principal crystalline forms (quartz, tridymite, and cristobalite) and in various stable amorphous forms, including vitreous silica (a non-crystalline silicate glass or fused quartz). Table 3 includes diffusivities, $D$, and solubilities as Henry's law constants, $H$, at 1 atm for helium and hydrogen in fused quartz as calculated from correlations of experimental data by Swets, Lee, and Frank and Lee, respectively. The product of the diffusivity and the solubility is called the permeability, $P_M$. Thus,

$$P_M = DH \quad \ldots 91$$
Unlike metals, where hydrogen usually diffuses as the atom; hydrogen apparently diffuses as a molecule in glass. For both hydrogen and helium, diffusivities increase rapidly with increasing temperature. At ambient temperature the diffusivities are three orders of magnitude lower than in liquids. At elevated temperatures the diffusivities approach those observed in liquids. Solubilities vary only slowly with temperature. Hydrogen is orders of magnitude less soluble in glass than helium. For hydrogen, the diffusivity is somewhat lower than in metals. Diffusivities for oxygen are also included in Table 3 from studies by Williams and Sucov. At 1000°C, the two values differ widely because, as discussed by Kingery, Bowen, and Uhlmann, in the former case, transport occurs by molecular diffusion; while in the latter case, transport is by slower network diffusion as oxygen jumps from one position in the silicate network to another. The activation energy for the latter is much larger than for the former (71,000 cal/mol versus 27,000 cal/mol). The choice of glass can be very critical in high-vacuum operations because of the wide range of diffusivity.

### Table 3 Diffusivities and solubilities of gases in amorphous silica at 1 atm

<table>
<thead>
<tr>
<th>Gas</th>
<th>Diffusivity cm²/s</th>
<th>Solubility mol/cm³-atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>$2.39 \times 10^{-8}$</td>
<td>$1.04 \times 10^{-7}$</td>
</tr>
<tr>
<td>100</td>
<td>$1.64 \times 10^{-7}$</td>
<td>$1.32 \times 10^{-7}$</td>
</tr>
<tr>
<td>300</td>
<td>$2.26 \times 10^{-6}$</td>
<td>$1.82 \times 10^{-7}$</td>
</tr>
<tr>
<td>500</td>
<td>$9.99 \times 10^{-6}$</td>
<td>$9.9 \times 10^{-8}$</td>
</tr>
<tr>
<td>1,000</td>
<td>$5.42 \times 10^{-5}$</td>
<td>$1.34 \times 10^{-7}$</td>
</tr>
<tr>
<td>H₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>$6.11 \times 10^{-8}$</td>
<td>$3.2 \times 10^{-14}$</td>
</tr>
<tr>
<td>500</td>
<td>$6.49 \times 10^{-7}$</td>
<td>$2.48 \times 10^{-13}$</td>
</tr>
<tr>
<td>1,000</td>
<td>$9.26 \times 10^{-6}$</td>
<td>$2.49 \times 10^{-12}$</td>
</tr>
<tr>
<td>O₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,000</td>
<td>$6.25 \times 10^{-9}$</td>
<td></td>
</tr>
</tbody>
</table>

**Ceramics**

Diffusion rates of light gases and elements in crystalline ceramics are very important because diffusion must precede chemical reactions and causes changes in the microstructure. Therefore, diffusion in ceramics has been the subject of numerous studies, many of which are summarized in Figure 3, taken from Kingery et al., where diffusivity is plotted as a function of the inverse of temperature in the high-temperature range. In this form, the slopes of the curves are proportional to the activation energy for diffusion, $E$, where

$$D = D_0 \exp \left(-\frac{E}{RT}\right)$$

...92
An insert at the middle-right region of Figure 3 relates the slopes of the curves to activation energy. The diffusivity curves cover a ninefold range from $10^{-6}$ to $10^{-15}$ cm$^2$/s, with the largest values corresponding to the diffusion of potassium in $\beta$-Al$_2$O$_3$ and one of the smallest values for carbon in graphite. In general, the lower the diffusivity, the higher is the activation energy. As discussed in detail by Kingery et al., diffusion in crystalline oxides depends not only on temperature but also on whether the oxide is stoichiometric or not (e.g., FeO and Fe$_{0.95}$O) and on impurities. Diffusion through vacant sites of non-stoichiometric oxides is often classified as metal-deficient or oxygen-deficient. Impurities can hinder diffusion by filling vacant lattice or interstitial sites.

Figure 3 Diffusion coefficient for single- and poly- crystalline ceramics
**Polymers**

Thin, dense, nonporous polymer membranes are widely used to separate gas and liquid mixtures. Diffusion of gas and liquid species through polymers is highly dependent on the type of polymer, whether it be crystalline or amorphous and, if the latter, glassy or rubbery. Commercial crystalline polymers are about 20% amorphous. It is mainly through the amorphous regions that diffusion occurs. As with the transport of gases through metals, transport of gaseous species through polymer membranes is usually characterized by the solution-diffusion mechanism of (Eq. 90). Fick's first law, in the following integrated forms, is then applied to compute the mass transfer flux

**Gas species:**

\[
N_i = \frac{H_i \cdot D_i}{Z_2 - Z_1} (P_{i1} - P_{i2}) = \frac{P_{m_i}}{Z_2 - Z_1} (P_{i1} - P_{i2})
\]

...93

Where: \(P_i\) is the partial pressure of the gas species at a polymer surface.

**Liquid species:**

\[
N_i = \frac{K_i \cdot D_i}{Z_2 - Z_1} (C_{i1} - C_{i2})
\]

...94

Where: \(K_i\), the equilibrium partition coefficient, is equal to the ratio of the concentration in the polymer to the concentration, \(C_i\), in the liquid adjacent to the polymer surface. The product \(K_i D_i\) is the liquid permeability.

Values of diffusivity for light gases in four polymers; given in Table 4, range from 1.3*10^{-9} to 1.6*10^{-6} cm²/s, which are orders of magnitude less than for diffusion of the same species in a gas. Diffusivities of liquids in rubbery polymers have been studied extensively as a means of determining visco-elastic parameters. In Table 5, diffusivities are given for different solutes in seven different rubber polymers at near-ambient conditions. The values cover a sixfold range, with the largest diffusivity being that for n-hexadecane in polydimethylsiloxane. The smallest diffusivities correspond to the case where the temperature is approaching the glass transition temperature, where the polymer becomes glassy in structure. This more rigid structure hinders diffusion. In general, as would be expected, smaller molecules have higher diffusivities. A more detailed study of the diffusivity of n-hexadecane in random styrene/butadiene copolymers at 25°C by Rhee and Ferry shows a large effect on diffusivity of fractional free volume in the polymer. Diffusion and permeability in crystalline polymers depend on the degree of crystallinity. Polymers that are 100% crystalline permit little or no diffusion of gases and liquids. For example, the diffusivity of methane at 25°C in polyoxyethylene oxyisophthaloyl decreases from 0.30*10^{-9} to 0.13*10^{-9} cm²/s when the degree of crystallinity increases from 0 (totally amorphous) to 40%. A measure of crystallinity is the polymer density. The diffusivity
of methane at 25°C in polyethylene decreases from $0.193 \times 10^{-6}$ to $0.057 \times 10^{-6}$ cm$^2$/s when the specific gravity increases from 0.914 (low density) to 0.964 (high density). A plasticizer can cause the diffusivity to increase. For example, when polyvinylchloride is plasticized with 40% tricresyl triphosphate, the diffusivity of CO at 27°C increases from $0.23 \times 10^{-8}$ to $2.9 \times 10^{-8}$ cm$^2$/s.

**Table 4 Coefficient for gas Permeation in polymers**

<table>
<thead>
<tr>
<th>Gas Species</th>
<th>H$_2$</th>
<th>O$_2$</th>
<th>N$_2$</th>
<th>CO</th>
<th>CO$_2$</th>
<th>CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low-Density Polyethylene:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D \times 10^6$</td>
<td>0.474</td>
<td>0.46</td>
<td>0.32</td>
<td>0.332</td>
<td>0.372</td>
<td>0.193</td>
</tr>
<tr>
<td>$H \times 10^6$</td>
<td>1.58</td>
<td>0.472</td>
<td>0.228</td>
<td>0.336</td>
<td>2.54</td>
<td>1.13</td>
</tr>
<tr>
<td>$P_M \times 10^{13}$</td>
<td>7.4</td>
<td>2.2</td>
<td>0.73</td>
<td>1.1</td>
<td>9.5</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>Polyethylmethacrylate:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D \times 10^6$</td>
<td>—</td>
<td>0.106</td>
<td>0.0301</td>
<td>—</td>
<td>0.0336</td>
<td>—</td>
</tr>
<tr>
<td>$H \times 10^6$</td>
<td>—</td>
<td>0.839</td>
<td>0.565</td>
<td>—</td>
<td>11.3</td>
<td>—</td>
</tr>
<tr>
<td>$P_M \times 10^{13}$</td>
<td>—</td>
<td>0.889</td>
<td>0.170</td>
<td>—</td>
<td>3.79</td>
<td>—</td>
</tr>
<tr>
<td><strong>Polyvinylchloride:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D \times 10^6$</td>
<td>0.5</td>
<td>0.012</td>
<td>0.0038</td>
<td>—</td>
<td>0.0025</td>
<td>0.0013</td>
</tr>
<tr>
<td>$H \times 10^6$</td>
<td>0.26</td>
<td>0.29</td>
<td>0.23</td>
<td>—</td>
<td>4.7</td>
<td>1.7</td>
</tr>
<tr>
<td>$P_M \times 10^{13}$</td>
<td>1.3</td>
<td>0.034</td>
<td>0.0089</td>
<td>—</td>
<td>0.12</td>
<td>0.021</td>
</tr>
<tr>
<td><strong>Butyl Rubber:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D \times 10^6$</td>
<td>1.52</td>
<td>0.081</td>
<td>0.045</td>
<td>—</td>
<td>0.0578</td>
<td>—</td>
</tr>
<tr>
<td>$H \times 10^6$</td>
<td>0.355</td>
<td>1.20</td>
<td>0.543</td>
<td>—</td>
<td>6.71</td>
<td>—</td>
</tr>
<tr>
<td>$P_M \times 10^{13}$</td>
<td>5.43</td>
<td>0.977</td>
<td>0.243</td>
<td>—</td>
<td>3.89</td>
<td>—</td>
</tr>
</tbody>
</table>

*Note. Units: $D$ in cm$^2$/s; $H$ in cm$^3$ (STP)/cm$^2$-Pa; $P_M$ in cm$^3$ (STP)-cm/cm$^2$-s-Pa.*

**Table 5 Diffusivities of solutes rubbery polymers**


Cellular Solids and Wood
Cellular solids consist of solid struts or plates that form edges and faces of cells, which are compartments or enclosed spaces. Cellular solids such as wood, cork, sponge, and coral exist in nature. Synthetic cellular structures include honeycombs, and foams (some with open cells) made from polymers, metals, ceramics, and glass. The word cellulose means "full of little cells."
A widely used cellular solid is wood, whose annual world production of the order of 1012 kg is comparable to the production of iron and steel. Chemically, wood consists of lignin, cellulose, hemi cellulose, and minor amounts of organic chemicals and elements. The latter are extractable, and the former three, which are all polymers, give wood its structure. Green wood also contains up to 25 wt% moisture in the cell walls and cell cavities. Adsorption or desorption of moisture in wood causes anisotropic swelling and shrinkage. The structure of wood, which often consists of (1) highly elongated hexagonal or rectangular cells, called tracheids in softwood (coniferous species, e.g., spruce, pine, and fir) and fibers in hardwood (deciduous or broad-leaf species, e.g., oak, birch, and walnut); (2) radial arrays of rectangular-like cells, called rays, which are narrow and short in softwoods but wide and long in hardwoods; and (3) enlarged cells with large pore spaces and thin walls, called sap channels because they conduct fluids up the tree. The sap channels are less than 3 vol. % of softwood, but as much as 55 vol. % of hardwood.
Because the structure of wood is directional, many of its properties are anisotropic. For example, stiffness and strength are 2 to 20 times greater in the axial direction of the tracheids or fibers than in the radial and tangential directions of the trunk from which

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solute</th>
<th>Temperature, K</th>
<th>Diffusivity, cm²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyisobutylene</td>
<td>n-Butane</td>
<td>298</td>
<td>1.19 × 10⁻⁹</td>
</tr>
<tr>
<td></td>
<td>i-Butane</td>
<td>298</td>
<td>5.3 × 10⁻¹⁰</td>
</tr>
<tr>
<td></td>
<td>n-Pentane</td>
<td>298</td>
<td>1.08 × 10⁻⁹</td>
</tr>
<tr>
<td></td>
<td>n-Hexadecane</td>
<td>298</td>
<td>6.08 × 10⁻¹⁰</td>
</tr>
<tr>
<td>Hevea rubber</td>
<td>n-Butane</td>
<td>303</td>
<td>2.3 × 10⁻⁷</td>
</tr>
<tr>
<td></td>
<td>i-Butane</td>
<td>303</td>
<td>1.52 × 10⁻⁷</td>
</tr>
<tr>
<td></td>
<td>n-Pentane</td>
<td>303</td>
<td>2.3 × 10⁻⁷</td>
</tr>
<tr>
<td></td>
<td>n-Hexadecane</td>
<td>298</td>
<td>7.66 × 10⁻⁸</td>
</tr>
<tr>
<td>Polymethylacrylate</td>
<td>Ethyl alcohol</td>
<td>323</td>
<td>2.18 × 10⁻¹⁰</td>
</tr>
<tr>
<td>Polyvinylacetate</td>
<td>n-Propyl alcohol</td>
<td>313</td>
<td>1.11 × 10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>n-Propyl chloride</td>
<td>313</td>
<td>1.34 × 10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>Ethyl chloride</td>
<td>343</td>
<td>2.01 × 10⁻⁹</td>
</tr>
<tr>
<td></td>
<td>Ethyl bromide</td>
<td>343</td>
<td>1.11 × 10⁻⁹</td>
</tr>
<tr>
<td>Polymethylsiloxane</td>
<td>n-Hexadecane</td>
<td>298</td>
<td>1.6 × 10⁻⁶</td>
</tr>
<tr>
<td>1,4-Polybutadiene</td>
<td>n-Hexadecane</td>
<td>298</td>
<td>2.21 × 10⁻⁷</td>
</tr>
<tr>
<td>Styrene-butadiene rubber</td>
<td>n-Hexadecane</td>
<td>298</td>
<td>2.66 × 10⁻⁸</td>
</tr>
</tbody>
</table>
the wood is cut. This anisotropy extends to permeability and diffusivity of wood penetrates, such as moisture and preservatives. According to Stamm, the permeability of wood to liquids in the axial direction can be up to 10 times greater than in the transverse direction.

Movement of liquids and gases through wood and wood products takes time during drying and treatment with preservatives, fire retardants, and other chemicals. This movement takes place by capillarity, pressure permeability, and diffusion. Nevertheless, wood is not highly permeable because the cell voids are largely discrete and lack direct interconnections. Instead, communication among cells is through circular openings spanned by thin membranes with sub micrometer-sized pores, called pits, and to a smaller extent, across the cell walls. Rays give wood some permeability in the radial direction. Sap channels do not contribute to permeability. All three mechanisms of movement of gases and liquids in wood are considered by Stamm.

The simplest form of diffusion is that of a water-soluble solute through wood saturated with water, such that no dimensional changes occur. For the diffusion of urea, glycerin, and lactic acid into hardwood, Stamm lists diffusivities in the axial direction that are about 50% of ordinary liquid diffusivities. In the radial direction, diffusivities are about 10% of the values in the axial direction. For example, at 26.7°C the diffusivity of zinc sulfate in water is $5 \times 10^{-6}$ cm$^2$/s. If loblolly pines sapwood is impregnated with zinc sulfate in the radial direction, the diffusivity is found to be $0.18 \times 10^{-6}$ cm$^2$/s.

The diffusion of water in wood is much more complex. Moisture content determines the degree of swelling or shrinkage. Water is held in the wood in different ways: it may be physically adsorbed on cell walls in monomolecular layers, condensed in preexisting or transient cell capillaries, or absorbed in cell walls to form a solid solution.

Because of the practical importance of the lumber drying rates, most diffusion coefficients are measured under drying conditions in the radial direction across the fibers. The results depend on temperature and swollen-volume specific gravity.
Example 9
Calculate the rate of diffusion of Acetic acid (A) across a film of non-diffusing water (B) solution of 1 mm thick at 17 °C. The concentrations of acid on the opposite sides of the film are 9 wt% and 3 wt% respectively. Given that the diffusivity of Acetic acid in the solution is $0.95 \times 10^{-9}$ m$^2$/s at 17 °C and the specific gravity of pure Acetic acid is 1.049. The molecular weight of Acetic acid is 60 and for water is 18.

Solution
Use equation 72

\[
N_A = -DL \left[ \frac{C_{av}}{X_{BLM}} \right] \left( \frac{X_{A2} - X_{A1}}{Z_2 - Z_1} \right)
\]

$D_L = 0.95 \times 10^{-9}$ m$^2$/s

$Z_2 - Z_1 = 1$ mm $= 0.001$ m

Now convert the wt fractions to mole fractions as:

At $Z_1$, \[X_{A1} = \frac{9/60}{9/60 + 9/18} = 0.0288\]

At $Z_2$, \[X_{A2} = \frac{3/60}{3/60 + 97/18} = 0.0092\]

And now calculate the $X_{BLM}$

\[X_{B1} = 1 - X_{A1} = 1 - 0.0288 = 0.9712\]

\[X_{B2} = 1 - X_{A2} = 1 - 0.0092 = 0.9908\]

\[X_{BLM} = \frac{X_{B2} - X_{B1}}{\ln \left( \frac{X_{B2}}{X_{B1}} \right)} = \frac{0.9908 - 0.9712}{\ln \left( \frac{0.9908}{0.9712} \right)} = 0.981\]

Finally we have to calculate $C_{av}$

\[
C_{av} = \frac{\left( \frac{\rho_1}{M_{wt1}} \right) + \left( \frac{\rho_2}{M_{wt2}} \right)}{2}
\]

$\rho_1$ = density of solution (mixture) at point 1

$M_{wt1}$ = Average molecular weight of solution (mixture) at point 1
\[ \rho_1 = X_1 \rho_{H_2O} + X_2 \rho_{Aceticacid} \]
\[ \rho_1 = (0.91*1) + (0.09*1.049) = 1.00441 \frac{gm}{cm^3} = 1004.41 \frac{kgm}{m^3} \]

Av. Mwt = mol. fraction 1 * Mwt1 + mol. fraction 2 * Mwt 2
Av. Mwt point 1 = (0.0288*60) + (0.9712*18) = 19.2
Av. Mwt point 1 = 19.2

\[ \rho_2 = X_1 \rho_{H_2O} + X_2 \rho_{Aceticacid} \]
\[ \rho_2 = (0.97*1) + (0.03*1.049) = 1.00147 \frac{gm}{cm^3} = 1001.47 \frac{kgm}{m^3} \]

Av. Mwt point 2 = (0.0092*60) + (0.9908*18) = 18.3
Av. Mwt point 1 = 18.3

\[ C_{av} = \frac{\left(\frac{1004.41}{19.2}\right) + \left(\frac{1001.47}{18.3}\right)}{2} = 53.3 \frac{kmol}{m^3} \]

\[ \therefore N_A = -0.95*10^{-9} \left( \frac{53.3}{0.981} \right) \left( \frac{0.0092 - 0.0288}{0.001} \right) = 9.318*10^{-7} \frac{kmol}{m^2 \cdot s} \]

**Example 10**

A sintered solid of silica (2mm) thick is porous with void fraction of 0.3 and tortuosity of 4. The pores are filled with water at 298 K. At one face the concentration of KCl is held at 0.1 mol / liter and fresh water flow rapidly by other face. Neglecting any other resistance but that in porous solid, calculate the diffusion of KCl at steady state. Given the diffusivity \( D_{AB} \) is equal to 1.87*10\(^{-9}\) m\(^2\)/s.

**Solution**

Since neglecting any other resistance but that in porous solid, then ordinary diffusion is occurred and then the diffusion is calculated by equation no. 90

\[ N_A = -D_{eff} \left( \frac{C_{A2} - C_{A1}}{Z_{2} - Z_{1}} \right) \]

And \( D_{eff} \) is calculated by equation 89

\[ D_{eff} = \frac{D_{AB} \varepsilon}{\tau} = \frac{1.98*10^{-9} * 0.3}{4} = 1.4025*10^{-10} \frac{m^2}{s} \]

\[ N_A = -1.4025*10^{-10} \left( \frac{0 - 0.1}{0.002} \right) = 7.01*10^{-9} \frac{kmol \ KCl}{m^2 \cdot s} \]
Unsteady – State Mass transfer

All mass transfer processes will have an initial period of time with unsteady – state conditions where the concentration at certain point varies with time until steady – state is reached.

Consider an element of dimensions dx, dy, dz;

The molar flow rate of species A by diffusion at the plane \( Z=Z \) is given by Fick's law:

\[
\overline{N}_{AZ} = - D_{AB} \left( A \left( \frac{\partial C_A}{\partial Z} \right)_Z \right) \quad \ldots 95
\]

The molar flow rate of species A by diffusion at the plane \( Z=Z+\Delta Z \) is:

\[
\overline{N}_{AZ} = - D_{AB} \left( A \left( \frac{\partial C_A}{\partial Z} \right)_{Z+\Delta Z} \right) \quad \ldots 96
\]

The accumulation of species A in the control volume is:

\[
A \frac{\partial C_A}{\partial t} \Delta Z \quad \ldots 97
\]

Since

Rate in – Rate out = accumulation

\[
- D_{AB} \left( A \left( \frac{\partial C_A}{\partial Z} \right)_Z \right) + D_{AB} \left( A \left( \frac{\partial C_A}{\partial Z} \right)_{Z+\Delta Z} \right) = A \frac{\partial C_A}{\partial t} \Delta Z \quad \ldots 98
\]

Rearranging and simplifying

\[
D_{AB} \left( \frac{\left( \frac{\partial C_A}{\partial Z} \right)_{Z+\Delta Z} - \left( \frac{\partial C_A}{\partial Z} \right)_Z}{\Delta Z} \right) = \frac{\partial C_A}{\partial t} \quad \ldots 99
\]

In the lime, as \( \Delta Z \rightarrow 0 \)

\[
\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial Z^2} \quad \ldots 100
\]

The above equation is Fick's second law for one–dimensional diffusion. The more general form, for three dimensions rectangular coordinates, is
\[
\frac{\partial C_A}{\partial t} = D_{AB} \left( \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right) \quad \ldots 101
\]

For one-dimensional diffusion in the radial direction only, for cylindrical and spherical coordinates, Fick's second law becomes, respectively,
\[
\frac{\partial C_A}{\partial t} = \frac{D_{AB}}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_A}{\partial r} \right) \quad \ldots 102
\]

And
\[
\frac{\partial C_A}{\partial t} = \frac{D_{AB}}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_A}{\partial r} \right) \quad \ldots 103
\]

Analytical solutions to these partial differential equations are available for a variety of boundary conditions. Only two of the most common useful solutions will be considered.

**Semi-infinite Medium**

The boundary conditions for this case to solve (Equ.100) are:
\[
\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial Z^2}
\]

Boundary conditions:

At \( t = 0 \) \( 0 < Z < \infty \) \( C_A = C_{A0} \)

\( t > 0 \) \( Z = 0 \) \( C_A = C_{Ai} \) \( (C_{Ai}: \text{initial concentration}) \)

\( t > 0 \) \( Z = \infty \) \( C_A = C_{A0} \)

To solve the above partial differential equation, either the method of combination of variables or the Laplace method is applicable. The result, in terms of the fractional accomplished concentration change (\( \theta \)), is
\[
\theta = \frac{C_A - C_{A0}}{C_{A_s} - C_{A0}} = \text{erfc} \left( \frac{Z}{2\sqrt{D_{AB}t}} \right) \quad \ldots 104
\]

Equation 104 is used to compute the concentration in the semi-infinite medium, as a function of time and distance from the surface, assuming no bulk flow. Thus, it applies most rigorously to diffusion in solids, and also to stagnant liquid and gases when the medium is dilute in the diffusing solute.

The instantaneous rate of mass transfer across the surface of the medium at \( Z = 0 \) can be obtained by taking the derivative of (Equ. 104) with respect to distance and substituting it into Fick's first law applied at the surface of the medium. Then
\[
n_A = -D_{AB} \frac{\partial C_A}{\partial Z} \bigg|_{Z=0} = D_{AB} A \left( \frac{C_{A_s} - C_{A0}}{\sqrt{\pi D_{AB}t}} \right) \exp \left( -\frac{Z^2}{4D_{AB}t} \right) \bigg|_{Z=0} \quad \ldots 105
\]

Thus
We can determine the total number of moles of solute, \( N_A \), transferred into the semi-infinite medium by integrating equation 106 with respect to time:

\[
N_A = \int_{0}^{t} n_A |_{z=0} \, dt = \sqrt{\frac{D_{AB}}{\pi}} \int_{0}^{t} \frac{dt}{\sqrt{t}} = 2A(C_A - C_{A_0}) \sqrt{\frac{D_{AB}t}{\pi}} \quad \cdots 107
\]

**Medium of finite Thickness with Sealed Edges**

Consider a rectangular parallelepiped medium of finite thickness 2a in the Z direction, and either infinitely long dimensions in the y and x directions or finite lengths of 2b and 2c respectively, in those directions. The boundary conditions for this case to solve (Equ.100) \( \frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial Z^2} \) are:

At \( t = 0 \quad -a < Z < a \quad C_A = C_{A_0} \)

\( t = 0 \quad Z = \pm a \quad C_A = C_{A_0} \quad (C_{A_0} > C_{A_0}) \)

\( t > 0 \quad Z = 0 \quad \frac{\partial C_A}{\partial t} = 0 \)

again by the method of separation of variables or the Laplace transform method the result in terms of the fractional unaccomplished concentration change, \( E \), is

\[
E = 1 - \theta = \frac{C_A - C_A}{C_{A_0} - C_{A_0}} = \sum_{n=0}^{\infty} \frac{(-1)^n}{\pi} \exp \left[ -D_{AB}(2n+1)^2 \frac{\pi^2 t}{4a^2} \right] \cos \left( \frac{(2n+1)\pi Z}{2a} \right) \quad \cdots 108
\]

or, in terms of complementary error function,

\[
E = 1 - \theta = \frac{C_A - C_A}{C_{A_0} - C_{A_0}} = \sum_{n=0}^{\infty} (-1)^n \left[ \text{erfc} \left( \frac{(2n+1)a - Z}{2\sqrt{D_{AB}t}} \right) + \text{erfc} \left( \frac{(2n+1)a + Z}{2\sqrt{D_{AB}t}} \right) \right] \quad \cdots 109
\]

The instantaneous rate of mass transfer across the surface of either unsealed face of the medium (i.e. at \( Z = \pm a \)), is obtained by differentiating (Eq. 108, or 109) with respect to \( Z \), evaluating the result at \( Z = a \), followed by substitution into Fick's first law to give

\[
n_A \bigg|_{Z=a} = \frac{2D_{AB}(C_A - C_{A_0}) A}{a} \sum_{n=0}^{\infty} \exp \left[ -\frac{D_{AB}(2n+1)^2 \frac{\pi^2 t}{4a^2}}{4a^2} \right] \quad \cdots 110
\]

We can also determine the total number of moles transferred across either unsealed face by integrating (Eq. 110) with respect to time. Thus

\[
N_A = \int_{0}^{t} n_A |_{Z=a} \, dt = \frac{8(C_A - C_{A_0}) Aa}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \left[ 1 - \exp \left[ -\frac{D_{AB}(2n+1)^2 \frac{\pi^2 t}{4a^2}}{4a^2} \right] \right] \quad \cdots 111
\]
Convective Mass Transfer for Binary gas Mixture

In previous sections we have considered molecular diffusion in stagnant fluid (laminar flow) where the rate of diffusion is slow. To increase the rate of mass transfer, the fluid velocity is increased until turbulent mass transfer occurs. As given before in equation (1):

\[ N_i = X_i N + \text{molecular diffusion flux of } i + \text{eddy diffusion flux of } i \]  

...1

The eddy diffusion flux term is given by:

\[ J^*_{AZ} = -E_d \frac{dC_A}{dZ} \]  

...112

Then

\[ N_A = -C^* (D_{AB} + E_D) * \frac{dX_A}{dZ} + X_A (N_A + N_B) \]  

...113

This is the general equation used to calculate the mass transfer.

1- For equi - molar mass transfer

A) For gases:

\[ N_A = \frac{-(D_{AB} + E_D)}{R*T} * \frac{dP_A}{dZ} + \frac{P_A}{P_T} * (N_A + N_B) \]  

...114

For equi – molar transfer: \((N_A = - N_B)\)

Then equation 114 will be:

\[ N_A = \frac{-(D_{AB} + E_D)}{R*T} * \frac{dP_A}{dZ} \]  

...115

By integrating equation 115 from \(P_A_1\) at \(Z_1\) to \(P_A_2\) and \(Z_2\) then:

\[ N_A = \frac{(D_{AB} + E_D) * (P_A_1 - P_A_2)}{R*T} \frac{1}{(Z_2 - Z_1)} \]  

...116

Because the film thickness can not be measured or is not known, then the value \((Z_2-Z_1)\) is not known (the distance of the path), also the amount of \(E_D\) can not be measured, then, the term (individual mass transfer coefficient) is used as shown below:

\[ N_A = K'_G (P_A_1 - P_A_2) \]  

...117

Where:

\[ K'_G = \frac{(D_{AB} + E_D)}{R*T(Z_2 - Z_1)} \]  

...118

Also for gases another form of equation 117 can be written as:

\[ N_A = K'_y (y_{A_1} - y_{A_2}) \]  

...119

A) For Liquids:

Similar to what done for gases, the rate of mass transfer is:

\[ N_A = K'_L (C_{A_1} - C_{A_2}) = K'_x (X_{A_1} - X_{A_2}) \]  

...120
The general form for the mass transfer is:
\[ N_A = K_C (C_{A_1} - C_{A_2}) \] ...121

All these individual mass transfer coefficients are related to each other.

For gases:
\[ N_A = K_C' (C_{A_1} - C_{A_2}) = K_G' (P_{A_1} - P_{A_2}) = K_y' (y_{A_1} - y_{A_2}) \] ...122

So
\[ K_C' = \frac{K_G'}{RT} = \frac{K_y'}{C_T} \]

Home work: find the relations for the liquid phase.

2- For uni - molecular mass transfer

A) For gases:
\[ N_A = \frac{-(D_{AB} + E_D)}{R \cdot T} \frac{dP_A}{dz} + \frac{P_A}{P_T} \cdot (N_A + N_B) \] ...114

For uni – molar transfer: \((N_B = 0)\)

Then equation 114 will be:
\[ N_A = \frac{-(D_{AB} + E_D)}{R \cdot T} \frac{dP_A}{dz} + \frac{P_A}{P_T} \cdot (N_A) \] ...123

By integrating equation 123 from \(P_{A_1}\) at \(Z_1\) to \(P_{A_2}\) and \(Z_2\) then
\[ N_A = \frac{(D_{ab} + E_d) \cdot P_T}{R \cdot T \cdot P_{BLM}} \cdot \frac{(P_{A_1} - P_{A_2})}{(Z_2 - Z_1)} \] ...124

Similarly as done in section 1:
\[ N_A = K_G' (P_{A_1} - P_{A_2}) = K_y' (y_{A_1} - y_{A_2}) \] ...125

B) For Liquids:

Similar to what done for gases, the rate of mass transfer is:
\[ N_A = K_L (C_{A_1} - C_{A_2}) = K_x (X_{A_1} - X_{A_2}) \] ...126

The general form for the mass transfer is:
\[ N_A = K_C (C_{A_1} - C_{A_2}) \] ...127

Home work: find the relations for the gas phase and liquid phase. Also write the units of each coefficient.
Methods to Determine the Mass transfer Coefficient

The mass transfer coefficient can be evaluated using empirical correlations involving dimensionless numbers. These empirical equations were obtained from experimental data using various types of fluids, different velocities, and different geometrics. The most important groups (dimensionless numbers) are:

1- Reynolds Number (Re No.):
Re. No indicate the degree of turbulence.

\[ Re\ No = \frac{\rho u d}{\mu} \]

Where:
\( \rho \) = density of flowing mixture fluid (solute A and solvent B).
\( \mu \) = viscosity of flowing mixture fluid (solute A and solvent B).
\( d \) = diameter of the pipe in which the fluid is flow.
\( D_p \) May be used in Reynolds number equation instead of \( d \) when flow across a sphere, also \( L \) may be used if the flow was above a flat plate.
\( U \) = mean average velocity in the pipe.
If the flow was across a packed bed, \( U \) will be substituted by:

\[ U = \frac{\bar{U}}{\varepsilon} \]

Where
\( \bar{U} \) is the superficial velocity of empty cross-section of packed bed column.
\( \varepsilon \) = void fraction.

2- Schmidt Number (Sc No.):

\[ Sc\ No = \frac{\mu}{\rho D_{AB}} \]

3- Sherwood Number (Sh No.):

\[ Sh\ No = \frac{K_C d}{D_{AB}} \]

4- Stanton Number (St No.):

\[ Sh\ No = \frac{Sh}{Re \cdot Sc} = \frac{K_C}{u} = \frac{K_C \rho}{G_m} \]

5- \( j \)-factor
In general \( j \)-factors are uniquely determined by the geometric configuration and the Reynolds number.
Now after introducing the dimensionless groups, now we will present the correlations used to calculate the mass transfer coefficient.

1- Using the analogy or similarity of momentum, heat, and mass transfer using Chilton – Colburn Analogy:

\[ j_M = j_H = j_D = \frac{f}{2} = \frac{K_C' \rho}{G_m} (Sc)^{2/3} \]  

...128

2- For flow inside pipe

For both gases and liquids, where \( Re > 2100 \)

\[ Sh \ No = \frac{K_C' d}{D_{AB}} = 0.023(Re)^{0.833} (Sc)^{0.333} \]  

...129

**Note:**

\( Sc = 0.5 – 3 \) for gases

\( Sc > 100 \) for liquids

Or

\[ j_M = j_H = j_D = 0.023(Re)^{-0.2} \]  

...130

For \( 10000 < Re < 1000000 \)

3- For flow parallel to flat plate of length \( L \)

A- for gases

\[ j_M = j_H = j_D = 0.664(Re)^{-0.5} \]  

...131

For \( Re < 15000 \) where \( Re = \frac{L \ U \ \rho}{\mu} \)

And

\[ j_M = j_H = j_D = 0.036(Re)^{-0.2} \]  

...132

For \( 15000 < Re < 300000 \) where \( Re = \frac{L \ U \ \rho}{\mu} \)

B- for liquids

\[ j_M = j_H = j_D = 0.99(Re)^{-0.5} \]  

...133

For \( 600 < Re < 50000 \) where \( Re = \frac{L \ U \ \rho}{\mu} \)

For both gases and liquids

\[ j_M = j_H = j_D = 0.037(Re)^{-0.2} \]  

...134

For \( 500000 < Re < 5*10^8 \) where \( Re = \frac{L \ U \ \rho}{\mu} \)
4- For flow normal to a long circular cylinder of diameter $D$, where the drag coefficient includes both form drag and skin friction, but only the skin friction contribution applies to the analogy:

$$ (j_M)_{\text{skin friction}} = j_H = j_D = 0.193(\text{Re})^{-0.382} \quad \ldots135 $$

For $4000 \leq \text{Re} < 40000$ where $\text{Re} = \frac{D_{\text{cylind}} U \rho}{\mu}$

$$ (j_M)_{\text{skin friction}} = j_H = j_D = 0.0266(\text{Re})^{-0.195} \quad \ldots136 $$

For $40000 \leq \text{Re} < 250000$ where $\text{Re} = \frac{D_{\text{cylind}} U \rho}{\mu}$

5- For flow past a single sphere of diameter $D_p$

$$ (j_M)_{\text{skin friction}} = j_H = j_D = 0.37*(\text{Re})^{-0.4} \quad \ldots137 $$

For $20 \leq \text{Re} < 100000$ where $\text{Re} = \frac{D_p u \rho}{\mu}$

The above equation is used for both gases and liquids. Another method is used to calculate the mass transfer coefficient.

For very low Re No. $(\text{Re} < 1)$ the Sh No. approach a value of 2, then:

$$ \text{Sh No} = \frac{K_C d}{D_{AB}} = 2 $$

$$ \therefore K_C = \text{Sh} \frac{D_{AB}}{D_p} = \frac{2 * D_{AB}}{D_p} \quad \ldots138 $$

For gases where $\text{Re} = 1 - 48000$ and $\text{Sc} = 0.6 - 2.7$, a modified equation can be used:

$$ \text{Sh No} = \frac{K_C d}{D_{AB}} = 2 + \left(0.552 \text{Re}^{0.53} * \text{Sc}^{0.333}\right) \quad \ldots139 $$

For liquids:

$$ \text{Sh No} = \frac{K_C d}{D_{AB}} = 2 + \left(0.95 \text{Re}^{0.5} * \text{Sc}^{0.333}\right) \quad \ldots140 $$

For $\text{Re} = 2 - 2000$

And also for liquids

$$ \text{Sh No} = \frac{K_C d}{D_{AB}} = 2 + \left(0.347 \text{Re}^{0.62} * \text{Sc}^{0.333}\right) \quad \ldots141 $$

For $\text{Re} = 2000 - 17000$

54
6- For flow through beds packed with spherical particles of uniform size $D_p$

$$j_H = j_D = 1.17 (Re)^{-0.415} \quad \text{...142}$$

For $10 < Re < 2500$ where $Re = \frac{D_p U \rho}{\mu}$

For other shapes of packing a correction factor can be used such as:

- $j_D$ (cylinder) = 0.79 * $j_D$ (sphere)
- $j_D$ (cube) = 0.71 * $j_D$ (sphere)

7- For fluidized beds of packed with sphere, for both gases and liquids:

$$j_D = 0.01 + \frac{0.86}{Re^{0.58} - 0.483} \quad \text{...143}$$

**Methods for Mass transfer at Fluid – Fluid Interface (Phase Boundary)**

In the previous sections, diffusion and mass transfer within solids and fluids were considered, where the interface was a smooth solid surface. Of greater interest in separation processes is mass transfer across an interface between a gas and a liquid or between two liquid phases. Such interfaces exist in absorption, distillation, extraction, and stripping. At fluid-fluid interfaces, turbulence may persist to the interface. The following theoretical models have been developed to describe mass transfer from a fluid to such an interface.

**Film Theory**

A simple theoretical model for turbulent mass transfer to or from a fluid-phase boundary was suggested in 1904 by Nernst, who postulated that the entire resistance to mass transfer in a given turbulent phase is in a thin, stagnant region of that phase at the interface, called a film. This film is similar to the laminar sub-layer that forms when a fluid flows in the turbulent regime parallel to a flat plate. This is shown schematically in Figure 4. For the case of a gas-liquid interface, where the gas is pure component A, which diffuses into nonvolatile liquid B. Thus, a process of absorption of A into liquid B takes place, without desorption of B into gaseous A. Because the gas is pure A at total pressure $P = P_A$, there is no resistance to mass transfer in the gas phase. At the gas-liquid interface, equilibrium is assumed so the concentration of A, $C_{A_i}$ is related to the partial pressure of A, $P_A$, by some form of Henry's law, for
example, \( C_{Ai} = H_A P_A \). In the thin, stagnant liquid film of thickness \( \delta \), molecular diffusion only occurs with a driving force of \((C_{Ai} - C_{AB})\). Since the film is assumed to be very thin, the entire diffusing \( A \) passes through the film and into the bulk liquid. If, in addition, bulk flow of \( A \) is neglected, the concentration gradient is linear as in Figure 4. Accordingly, Fick's first law, (Eq. 3), for the diffusion flux integrates to:

\[
J_A = \frac{D_{AB}}{\delta} (C_{Ai} - C_{Ab}) = \frac{C * D_{AB}}{\delta} (X_{Ai} - X_{Ab}) \quad \text{...144}
\]

![Figure 4 Film theory for mass transfer from a fluid – fluid interface into a liquid.](image)

If the liquid phase is dilute in \( A \), the bulk-flow effect can be neglected and (Eq. 144) applies to the total flux:

\[
N_A = \frac{D_{AB}}{\delta} (C_{Ai} - C_{Ab}) = \frac{C * D_{AB}}{\delta} (X_{Ai} - X_{Ab}) \quad \text{...145}
\]

If the bulk-flow effect is not negligible, then, from (Eq. 31),

\[
N_A = \frac{C.D_{AB}}{Z_2 - Z_1} \ln\left(\frac{1 - X_{Ab}}{1 - X_{Ai}}\right) = \frac{C.D_{AB}}{\delta(1 - X_A)_{LM}} (X_{Ai} - X_{Ab}) \quad \text{...146}
\]

Where:

\[
(1 - x_A)_{LM} = \frac{x_{Ai} - x_{Ab}}{\ln[(1 - x_{Ab})/(1 - x_{Ai})]} = (x_B)_{LM}
\]

In practice, the ratios \( D_{AB}/\delta \) in (Eq. 145) and \( D_{AB}/\delta*(1 - X_A)_{LM} \) in (Eq. 146) are replaced by mass transfer coefficients and \( K_c' \) and \( K_c \), respectively, because the film thickness, \( \delta \), which depends on the flow conditions, is not known.
The film theory, which is easy to understand and apply, is often criticized because it appears to predict that the rate of mass transfer is directly proportional to the molecular diffusivity. This dependency is at odds with experimental data, which indicate a dependency of $D^n$, where $n$ ranges from about 0.5 to 0.75. However, if $D_{AB}/\delta$ is replaced with $K'_c$, which is then estimated from the Chilton-Colburn analogy, (Eq. 128), we obtain $K'_c$ proportional to $D_{AB}^{2/3}$, which is in better agreement with experimental data. In effect, $\delta$ depends on $D_{AB}$ (Sc No.). Regardless of whether the criticism of the film theory is valid, the theory has been and continues to be widely used in the design of mass transfer separation equipment.

**Penetration Theory**

A more realistic physical model of mass transfer from a fluid-fluid interface into a bulk liquid stream is provided by the penetration theory of Higbie, shown schematically in Fig. 5. The stagnant-film concept is replaced by Boussinesq eddies that, during a cycle, (1) move from the bulk to the interface; (2) stay at the interface for a short, fixed period of time during which they remain static so that molecular diffusion takes place in a direction normal to the interface; and (3) leave the interface to mix with the bulk stream. When an eddy moves to the interface, it replaces another static eddy. Thus, the eddies are intermittently static and moving. Turbulence extends to the interface. In the penetration theory, unsteady-state diffusion takes place at the interface during the time the eddy is static. This process is governed by Fick's second law, (Eq. 100), with boundary conditions

At $t = 0$ 

- $0 \leq Z \leq \infty$  \hspace{1cm} $C_A = C_{Ab}$
- $t > 0$  \hspace{1cm} $Z = 0$  \hspace{1cm} $C_A = C_{Ai}$ \hspace{1cm} ($C_{Ai}$: initial concentration)
- $t > 0$  \hspace{1cm} $Z = \infty$  \hspace{1cm} $C_A = C_{Ab}$

![Diagram](image_url)

**Figure 5** Penetration theory for mass transfer from a fluid – fluid interface into a liquid.
Thus, the solution can be written by a rearrangement of (Eq. 104):

$$\theta = \frac{CA_i - C_A}{CA_i - C_{Ab}} = \text{erf} \left( \frac{Z}{2\sqrt{D_{AB}t_c}} \right) \quad \ldots 147$$

Where $t_c =$ "contact time" of the static eddy at the interface during one cycle. The corresponding average mass transfer flux of $A$ in the absence of bulk flow is given by the following form of (Eq. 107):

$$N_A = 2 \sqrt{\frac{D_{AB}}{\pi t_c}} (C_{Ai} - C_{Ab}) \quad \ldots 148$$

Or $$N_A = K_c (C_{Ai} - C_{Ab}) \quad \ldots 149$$

Thus, the penetration theory gives

$$K_c = 2 \sqrt{\frac{D_{AB}}{\pi t_c}} \quad \ldots 150$$

This predicts that $K_c$ is proportional to the square root of the molecular diffusivity, which is at the lower limit of experimental data. The penetration theory is most useful when mass transfer involves bubbles or droplets, or flow over random packing. For bubbles, the contact time, $t_c$, of the liquid surrounding the bubble is taken as the ratio of bubble diameter to bubble rise velocity. For example, an air bubble of 0.4 cm diameter rises through water at a velocity of about 20 cm/S. Thus, the estimated contact time, $t_c$, is $0.4/20 = 0.02$ S. For a liquid spray, where no circulation of liquid occurs inside the droplets, the contact time is the total time for the droplets to fall through the gas. For a packed tower, where the liquid flows as a film over particles of random packing, mixing can be assumed to occur each time the liquid film passes from one piece of packing to another. Resulting contact times are of the order of about 1 S. In the absence of any method of estimating the contact time, the liquid-phase mass transfer coefficient is sometimes correlated by an empirical expression consistent with the 0.5 exponent on $D_{AB}$, given by (Eq. 150) with the contact time replaced by a function of geometry and the liquid velocity, density, and viscosity.

**Surface Renewal Theory**

The penetration theory is not satisfying because the assumption of a constant contact time for all eddies that temporarily reside at the surface is not reasonable, especially for stirred tanks, contactors with random packing, and bubble and spray columns where the bubbles and droplets cover a wide range of sizes. In 1951, Danckwerts suggested an improvement to the penetration theory that involves the replacement of the constant eddy contact time with the assumption of a residence-time distribution, wherein the probability of an eddy at the surface being replaced by a fresh eddy is independent of the age of the surface eddy.
Film – Penetration theory
Toor and Marchello, in 1958, combined features of the film, penetration, and surface renewal theories to develop a film-penetration model, which predicts a dependency of the mass transfer coefficient $K_c$ on the diffusivity, that varies from $\sqrt{D_{AB}}$ to $D_{AB}$.

Their theory assumes that the entire resistance to mass transfer resides in a film of fixed thickness $\delta$. Eddies move to and from the bulk fluid and this film. Age distributions for time spent in the film are of the Higbie or Danckwerts type.

Fick's second law, (Eq. 100), still applies, but the boundary conditions are now

At $t = 0$ \hspace{1cm} $0 \leq Z \leq \infty$ \hspace{1cm} $C_A = C_{Ab}$

$t > 0$ \hspace{1cm} $Z = 0$ \hspace{1cm} $C_A = C_{Ai}$ \hspace{1cm} ($C_{Ai}$ : initial concentration)

$t > 0$ \hspace{1cm} $Z = \delta$ \hspace{1cm} $C_A = C_{Ab}$

Infinite-series solutions are obtained by the method of Laplace transforms. The rate of mass transfer is then obtained in the usual manner by applying Fick's first law at the fluid-fluid interface.

$$N_A = -D_{AB} \frac{\partial C_A}{\partial Z} \bigg|_{Z=0} = K_c \left( C_{A_i} - C_{A_0} \right)$$

Two – Film Theory
Separation processes that involve contacting two fluid phases generally require consideration of mass transfer resistances in both phases. In 1923, Whitman suggested an extension of the film theory to two fluid films in series. Each film presents a resistance to mass transfer, but concentrations in the two fluids at the interface are in equilibrium. That is, there is no additional interfacial resistance to mass transfer. This concept has found extensive application in modeling of steady-state gas-liquid and liquid-liquid separation processes, when the fluid phases are in laminar or turbulent flow. The assumption of equilibrium at the interface is satisfactory unless mass transfer rates are very high or surfactants accumulate at the interface.

Gas- Liquid Case
Consider the steady-state mass transfer of $A$ from a gas phase, across an interface, into liquid phase. It could be postulated, as shown in Figure 6a, that a thin gas film exists on one side of the interface and a thin liquid film exists on the other side with the controlling factors being molecular diffusion through each of the films. However, this postulation is not necessary, because instead of writing the mass transfer rate as:

$$N_A = \frac{(D_{AB})_G}{\delta_G} \left( C_{A_b} - C_{A_i} \right)_G = \frac{(D_{AB})_L}{\delta_L} \left( C_{A_i} - C_{A_b} \right)_L$$

We can express the rate of mass transfer in terms of mass transfer coefficients that can be determined from any suitable theory, with the concentration gradients visualized more realistically as in Figure 6b. In addition, we can use any number of different
mass transfer coefficients, depending on the selection of the driving force for mass transfer.

Figure 6 Concentration gradients for two – resistance theory: (a) film theory; (b) more realistic gradients.

For gas phase, under dilute or equimolar counter diffusion (EMD) conditions, we write the mass transfer rate in terms of partial pressure:

\[ N_A = K_g \left( P_{A_b} - P_{A_i} \right) \]...

...152

Or for stagnant layer mass transfer (non – volatile liquid), the rate of mass transfer can be written as:

\[ N_A = K_g \left( P_{A_b} - P_{A_i} \right) \]...

...153

Where (') refers to the equimolar counter diffusion case.

The above equations can be written in terms of mole fractions as:

\[ N_A = K_g \left( y_{A_b} - y_{A_i} \right) = K_y \left( y_{A_b} - y_{A_i} \right) \]...

...154

And

\[ N_A = K_g \left( y_{A_b} - y_{A_i} \right) = K_y \left( y_{A_b} - y_{A_i} \right) \]...

...155

For the liquid phase, we might use molar concentrations:

\[ N_A = K_l \left( C_{A_i} - C_{A_b} \right) \]...

...156 for equi – molar mass transfer

\[ N_A = K_l \left( C_{A_i} - C_{A_b} \right) \]...

...157 for uni - molar mass transfer

Also can be written in terms of mole fractions:
\[ N_A = \frac{K_l}{C_T} (x_{A_i} - x_{A_b}) = K_x (x_{A_i} - x_{A_b}) \] ...158 for equi–molar mass transfer

And
\[ N_A = \frac{K_l}{C_T} (x_{A_i} - x_{A_b}) = K_x (x_{A_i} - x_{A_b}) \] ...159 for uni–molar mass transfer

At the phases interface, \( C_A \) and \( P_A \) are in equilibrium. Applying a version of Henry's law:
\[ C_A = H_A * P_A \] ...160

Equations (152), (156) and (160) are a commonly used combination for vapor-liquid mass transfer. Computations of mass transfer rates are generally made from knowledge of bulk concentrations, which in this case are \( C_{A_b} \) and \( P_{A_b} \).

The equilibrium relationship for dilute solution (Henry's law) is:
\[ P_A = H * x_A \] ...161

And for gases (Dalton's Law):
\[ P_A = P_T * y_A \] ...162

Then
\[ y_A = \frac{H}{P_T} * x_A = m * x_A \] ...163

Or
\[ y_A = m * x^* \] ...164

And for the interface
\[ y_i = m * x_i \] ...165

Equilibrium data can be presented as a curve (for concentrated solution) and straight line (for dilute solution).

The task now is how to calculate the interfacial concentration (interfacial mole fraction) because we need them in the calculation of mass transfer rate.

Depending on the two film theory, and as shown in above sections we have two cases, the EMD (for example distillation), and the UMD (absorption through non–volatile liquid).

Case 1:
For equi-molecular counter diffusion
Let
\[ y_A = y_{Ab} \]
and
\[ x_A = x_{Ab} \]
\[ N_A = K_g (y_A - y_{A_i}) = K_x (x_{A_i} - x_A) \] ...166

Then
Assume a column where a gas and a liquid are contacted. At any point (P) in the column, the gas phase has a mole fraction of A (certain composition of A) that is \( y_A \). And the liquid has a mole fraction of A (certain composition of A) that is \( x_A \). Then at that point an equilibrium between the gas phase and the liquid phase exist at \( y_A \) and \( x_A \) at point (m).

In the above figure plot the equilibrium data and also and point (p). Draw a straight line from point (P) to intersect the equilibrium curve at point (1), let it be q. The slope of this straight line (pq) is:

\[
Slop = \frac{y_A - y_A'}{x_A - x_A'} = -\frac{K'_x}{K'_y}
\]

Then, to estimate the interface composition, we must know the mass transfer coefficient for both gas phase and liquid phase also the equilibrium data must be known.

The equilibrium data are presented by a curve for concentrated solution, and by a straight line for dilute solution.
Case 2:
For uni-molecular diffusion (mass transfer of A through stagnant layer of B)
Let $y_A = y_{Ab}$
and $x_A = x_{Ab}$
$N_A = K_y (y_A - y_{A_i}) = K_x (x_{A_i} - x_A)$ ...168

Or
$N_A = \frac{K'_y}{y_{A_iLM}} (y_A - y_{A_i}) = \frac{K'_x}{x_{A_iLM}} (x_{A_i} - x_A)$ ...168A

Then
$\frac{K_x}{K_y} = \frac{(y_A - y_{A_i})}{(x_A - x_{A_i})}$ ...169

But the slope of the drawn between points (P) & (m) is
$Slop = \frac{y_A - y_{A_i}}{x_A - x_{A_i}} = -\frac{K'_x}{K'_y}$

Therefore substitute $K_y$ and $K_x$ by their equivalents as
$K_y = \frac{K'_y}{y_{A_iLM}}$

And
$K_x = \frac{K'_x}{x_{A_iLM}}$

These relations must be found from the previous section

Therefore the slope for this case is:
$Slop = -\frac{x_{A_iLM}}{K_y/y_{A_iLM}} = \frac{y_A - y_{A_i}}{x_A - x_{A_i}}$

Where
\[ x_{A_{iLM}} = \frac{(1 - x_A) - (1 - x_{A_i})}{\ln\left(\frac{1 - x_A}{1 - x_{A_i}}\right)} \]

And

\[ y_{A_{iLM}} = \frac{(1 - y_{A_i}) - (1 - y_A)}{\ln\left(\frac{1 - y_{A_i}}{1 - y_A}\right)} \]

From the slop equation we can conclude that there is a difficulty in calculating the interface composition \((y_{A_i} \text{ and } x_{A_i})\), because they are already exist in the left hand side of the slop equation. This problem will be solved by trail and error by following these steps:

1- Assume a value for \((y_{A_{iLM}} \text{ and } x_{A_{iLM}})\) and let it be equal to (1).

2- Calculate the slop.

3- Plot the line (pq).

4- From the intersection point read \(x_{Ai}\) and \(y_{Ai}\).

5- Calculate \((y_{A_{iLM}} \text{ and } x_{A_{iLM}})\), then recalculate the slop of the line (pq) and let it be \((\text{slop})_2\) if the value of the two slops are equal then the assumed values of \((y_{A_{iLM}} \text{ and } x_{A_{iLM}})\) is correct. If not, then use the value of \((\text{slop})_2\) to estimate a new values of \(x_{Ai}\) and \(y_{Ai}\) by repeating steps (3-5) until you will reach not more the 10% change in the value of the slop.

Note:
For dilute solutions \((y_{A_{iLM}} \text{ and } x_{A_{iLM}})\) are equal to (1)

Overall driving force and overall mass transfer coefficient
Because of difficulties in measuring the interface composition and the individual mass transfer coefficients in some cases, another driving force and coefficients are used, that is the overall driving force and the overall mass transfer coefficient.

Again, assume a column where a gas and a liquid are contacted. At any point (P) in the column, the gas phase has a mole fraction of A (certain composition of A) that is \(y_A\), and the liquid has a mole fraction of A (certain composition of A) that is \(x_A\). Then at that point which we will call point (1), equilibrium between the gas phase and the liquid phase exist at \(y_{A_i}\) and \(x_{A_i}\). From point P plot a vertical line to intersect the equilibrium curve at point (2), where \(y = y_A^{*}\) and \(x = x_A\). And plot a horizontal line
from point (p) to intercept the equilibrium curve at point (3) at this point $y = y_A$ and $x = x_A^*$.

$(y_A - y_A^*)$ is called the overall driving force for the gas phase, and $(x_A^* - x_A)$ is called the overall diving force for the liquid phase.

The slope of the equilibrium curve at point (1) is $m_1$:

$$m_1 = \frac{y_A - y_{A_i}}{x_A - x_{A_i}}$$

The slope of the equilibrium curve at point (2) is $m_2$:

$$m_2 = \frac{y_{A_i} - y_A^*}{x_A - x_{A_i}}$$

The slope of the equilibrium curve at point (3) is $m_3$:

$$m_3 = \frac{y_A - y_{A_i}}{x_A^* - x_{A_i}}$$

The slopes of the equilibrium curve at points 1, 2, and 3 are equivalent if the solution is a dilute solution, that is $m_1 = m_2 = m_3$.
Now, the rate of mass transfer which will be calculated based on overall driving force can be written as follow:

A) For EMD
\[ N_A = K_{oy}'(y_A - y_A^*) \]  ...170

B) For UMD
\[ N_A = K_{oy}(y_A - y_A^*) \]  ...171

Where
\[ K_{oy}' \] and \[ K_{oy} \] are the overall mass transfer coefficients with units (kmol/m^2 s mol fract), which are based on the overall driving force in the gas phase.
\[ y_A^* \] is the value of the mole fraction of A in the gas phase that would be in equilibrium with \( x_A \).

Or, and for the two cases
\[ N_A = K_{ox}'(x_A^* - x_A) \]  ...172
\[ N_A = K_{ox}(x_A^* - x_A) \]  ...173

Where
\[ K_{ox}' \] and \[ K_{ox} \] are the overall mass transfer coefficients with units (kmol/m^2 s mol fract), which are based on the overall driving force in the liquid phase.
\[ x_A^* \] is the value of the mole fraction in the liquid phase that would be in equilibrium with \( y_A \).

The relationship between the overall mass transfer coefficient and the individual mass transfer coefficient

A)Case 1 EMD
We can write the overall driving force as follow by adding and subtracting \( y_{Ai} \), that is:
\[ y_A - y_A^* = (y_A - y_{Ai}) + (y_{Ai} - y_A^*) \]

But
\[ m_2 = \frac{y_{Ai} - y_A^*}{x_A - x_{Ai}} \]

Then
\[ y_A - y_A^* = (y_A - y_{Ai}) + m_2(x_A - x_{Ai}) \]

Substitute each driving force by its equivalent in the EMD case, that is:
\[ \frac{N_A}{K_{oy}} = \frac{N_A}{K_y} + m_2 \frac{N_A}{K_x} \]

Finally
\[ \frac{1}{K_{oy}} = \frac{1}{K_y} + \frac{m_2}{K_x} \]  \(174\)

Equation 174 can be explained as follow:
The total resistance for mass transfer is equal to the summation of individual resistance for each phase (the gas phase & the liquid phase).
The same procedure could be made to find the relationship between the overall mass transfer coefficient for the liquid phase and the individual mass transfer coefficients, the relation is:
\[ \frac{1}{K_{ox}} = \frac{1}{m_3 K_y} + \frac{1}{K_x} \]  \(175\)

For the dilute solutions:
\[ m_i = m_2 = m_3 = m \]
Then:
\[ \frac{1}{K_{oy}} = \frac{1}{K_y} + \frac{m}{K_x} \]  \(176\)
\[ \frac{1}{K_{ox}} = \frac{1}{m K_y} + \frac{1}{K_x} \]  \(177\)

B) Case 1 UMD
In this case only solute A is transferred through the interface and no B is transferred. As shown in above:

\[ K_y = \frac{K_y'}{y A_{iLM}} \]

And
\[ K_x = \frac{K_x'}{x A_{iLM}} \]

Then
\[ N_A = \frac{K_y'}{y A_{iLM}} (y_A - y_{A_i}) = \frac{K_x'}{x A_{iLM}} (x_{A_i} - x_A) \]  \(168A\)

For the overall driving force, and by using the overall mass transfer coefficient, the mass transfer rate is calculated by:
\[ N_A = \frac{K'_{oy}}{y'_{A_{LM}}} \left( y_A - y_A^* \right) = \frac{K'_{ox}}{x'_{A_{LM}}} \left( x_A - x_A^* \right) \]  \( \text{...178} \)

Where:
\[ x'^*_A_{LM} = \frac{\left( 1 - x_A \right) - \left( 1 - x_A^* \right)}{\ln \left( \frac{1 - x_A}{1 - x_A^*} \right)} \]

And
\[ y'^*_A_{LM} = \frac{\left( 1 - y_A^* \right) - \left( 1 - y_A \right)}{\ln \left( \frac{1 - y_A^*}{1 - y_A} \right)} \]

Using the same procedure done in the EMD, we can find the relationship between the overall mass transfer coefficient and the individual mass transfer coefficients, as shown:

For the gas phase:
\[ \frac{y'^*_A_{LM}}{K'_{oy}} = \frac{y_{Ai_{LM}}}{K'_y} + \frac{m_2 x_{Ai_{LM}}}{K'_x} \]  \( \text{...179} \)

For the liquid phase:
\[ \frac{x'^*_A_{Lm}}{K'_{ox}} = \frac{y_{Ai_{LM}}}{m_3 K'_y} + \frac{x_{Ai_{LM}}}{K'_x} \]  \( \text{...180} \)

Again for dilute solution when:
\[ m_1 = m_2 = m_3 = m \]
Then
\[ x'^*_A_{LM} = y'^*_A_{LM} = x_{Ai_{LM}} = y_{Ai_{LM}} = 1 \]

Question:
Is there an overall mass transfer coefficient based on partial pressure for the gas phase, and another one based on concentration for the liquid phase?
Answer:
Yes, these are presented as \( K_{og} \) and \( K_{ol} \).

Question:
Find the relationships between these overall mass transfer coefficients and the individual mass transfer coefficient?
Example 11
A large volume of pure gas (B) at 2 atm absolute pressure is flowing over a surface from which pure (A) is evaporating. The liquid (A) completely wets the surface which is a blotting paper. Hence the partial pressure of (A) at the surface is the vapor pressure of (A) at 298 K which is (0.2 atm). The $K'_y$ has been estimated to be $(6.78*10^{-5}$ kmol / s.m$^2$. mol fraction). Calculate the vaporizing rate ($N_A$), and the individual mass transfer coefficient $K_g$.

Solution:
Since the case is mass transfer through a stagnant layer (non-diffusing layer of B). Then the mass transfer rate is calculated by

$$N_A = K_y (y_{A1} - y_{A2})$$

$$y_{A1} = \frac{P_{A1}}{P_T} = \frac{0.2}{2} = 0.1 \quad \& \quad y_{A2} = 0 \quad \text{(large volume of B)}$$

$$\theta K_y = \frac{K_y}{y_{BLM}}$$

$$y_{BLM} = \frac{y_{B2} - y_{B1}}{\ln(\frac{y_{B2}}{y_{B1}}) - \ln(\frac{1}{0.9})} = 0.95$$

$$K_y = \frac{K'_y}{y_{BLM}} = \frac{6.78*10^{-5}}{0.95} = 7.138*10^{-5} \frac{\text{kmol}}{m^2 \cdot \text{S} \cdot \text{mol fraction}}$$

$$N_A = K_y (y_{A1} - y_{A2}) = 7.138*10^{-5} \cdot (0.1 - 0) = 7.138*10^{-6} \frac{\text{kmol}}{m^2 \cdot \text{S}}$$

$$K'_y = K_g \cdot P_{Blm} = K_g \cdot y_{BLM} \cdot P_T$$

$$K_g = \frac{K'_y}{y_{BLM} \cdot P_T} = \frac{6.78*10^{-5}}{0.95*2} = 3.76*10^{-5} \frac{\text{kmol}}{m^2 \cdot \text{S} \cdot \text{atm}}$$
Example 12

A large volume of pure water at 26 °C is flowing parallel to a flat plate of solid benzoic acid. The length of the plate in the direction of flow is \( L = 0.244 \) m. The water velocity is 0.061 m/s. the solubility of Benzoic acid in water at that temperature = 0.0295 kmol/m\(^3\). The diffusivity of Benzoic acid in water (\( D_{AB} = 1.24\times10^{-9} \) m\(^2\)/s). Calculate the mass transfer coefficient (\( K_c \)) and the rate of mass transfer flux \( N_A \).

Assume dilute solution, given the following data:

\[
\mu = 8.71\times10^{-4} \text{ kg/m.s} \\
\rho = 996 \text{ kg/m}^3
\]

Solution

Calculate Re No.

\[
\text{Re No.} = \frac{\rho u L}{\mu} = \frac{996\times0.061\times0.244}{8.71\times10^{-4}} = 17000
\]

For liquid flow parallel a flat plate use the following equation

\[
j_M = j_H = j_D = 0.99(\text{Re})^{-0.5}
\]

For \( 600 < \text{Re} < 50000 \) where \( \text{Re} = \frac{L U \rho}{\mu} \)

\[
j_D = 0.99(\text{Re})^{-0.5} = 0.99*(17000)^{-0.5} = 0.00758
\]

Since

\[
j_D = \frac{K_C' \rho}{G_m} (Sc)^{2/3} = \frac{K_C'}{u} (Sc)^{2/3}
\]

\[
Sc = \frac{\mu}{\rho D_{AB}} = \frac{8.71\times10^{-4}}{996\times1.24\times10^{-9}} = 705
\]

\[
K_C' = \frac{j_D u}{(Sc)^{2/3}} = \frac{0.00758\times0.061}{(705)^{2/3}} = 5.83\times10^{-6} \text{ m/s}
\]

Since the benzoic acid (A) diffuses through stagnant layer of large volume of Water (B), \( N_B = 0 \)

Because we are dealing with dilute solution, therefore \( X_{BLM} = 1 \)

\[
K_C = \frac{K_C'}{X_{BLM}} = \frac{5.83\times10^{-6}}{1} = 5.83\times10^{-6}
\]

\[
N_A = K_C (C_{A_1} - C_{A_2}) = 5.83\times10^{-6}*(0.0295-0) = 1.719\times10^{-7} \text{ kmol/m}^2\text{S}
\]
Example 13
A wetted wall column of inside diameter (2 in) contains air and CO\textsubscript{2} flowing at 3 ft/s. at a certain point in the column, the CO\textsubscript{2} concentration in the air is 0.1 mol fraction, at the same point in the column, the concentration of CO\textsubscript{2} in the water at the water – air interface is 0.005 mole fraction. The column operates at 10 atm and 25 °C. Calculate the mass transfer coefficient and the mass flux at the point of consideration, given the following data:
The diffusivity of CO\textsubscript{2} in air at 25 °C and 1 atm = 0.164 cm\textsuperscript{2}/s
The density of air at STP = 0.0808 lb/ft\textsuperscript{3}
The viscosity of air at 25 °C and 10 atm = 0.018 cP
Hennery constant = 1640 atm / mol fraction

Solution
Since we are dealing with a case of fluid flow inside a pipe, then to calculate the mass transfer coefficient use the following equation:

\[
Sh \ No = \frac{K'_{C}}{D_{AB}} = 0.023(Re)^{0.833}(Sc)^{0.333}
\]

But we are dealing with mass transfer through stagnant layer (transfer of CO\textsubscript{2} from air to water only), then

\[
K_{C} = K'_{C} \frac{P_{T}}{P_{B_{LM}}}
\]

Or

\[
Sh \ No = \frac{K_{C} \cdot P_{B_{LM}} \cdot d}{P_{T} \cdot D_{AB}} = 0.023(Re)^{0.833}(Sc)^{0.333}
\]

And

\[
K_{C} = \frac{P_{T} \cdot D_{AB} \cdot 0.023(Re)^{0.833}(Sc)^{0.333}}{P_{B_{LM}} \cdot d}
\]

To calculate the dimensionless groups we must first correct the physical properties from their conditions to the operation condition (10 atm and 25 °C), also we must convert all the units of all the quantities to the SI system.
\[
u = 3 \frac{ft}{s} \cdot \frac{1m}{3.28 ft} = 0.915 \frac{m}{s}
\]
\[
d = 2\text{in} \cdot \frac{2.54 cm}{\text{in}} \cdot \frac{1m}{100 cm} = 0.0508 m
\]
\[
\mu = 0.018 \text{cP} = 0.018 \times 10^{-3} \frac{kg}{m \cdot s}
\]
\[ \rho = \frac{p \cdot m_{wt}}{R \cdot T} \]

Then

\[ \left( \frac{\rho_2}{\rho_1} \right)_{298K,10atm} = \left( \frac{P_2}{T_2} \right) = \frac{10}{298} \]

\[ \left( \frac{P_1}{T_1} \right) = \frac{1}{273} \]

\[ \rho_1 = 0.0808 \frac{lb}{ft^3} = 0.0808 \frac{lb}{ft^3} \cdot \frac{1kg}{2.2lb} \cdot \left( \frac{3.28 ft}{1m} \right)^3 = 1.296 \frac{kg}{m^3} \]

\[ \therefore \rho_2 = 1.296 \frac{kg}{m^3} \cdot \frac{10 \cdot 273}{298} = 11.973 \frac{kg}{m^3} \]

\[ \left( \frac{D_{AB}}{D_{AB}} \right)_2 = \left( \frac{P_1}{P_2} \right) \cdot \left( \frac{T_2}{T_1} \right)^{1.5} \]

\[ (D_{AB})_1 = 0.164 \frac{cm^2}{s} = 0.164 \frac{cm^2}{s} \cdot \left( \frac{1m}{100cm} \right)^2 = 1.64 \cdot 10^{-5} \frac{m^2}{s} \]

\[ (D_{AB}) = 1.64 \cdot 10^{-5} \cdot \left( \frac{1}{10} \right) \cdot \left( \frac{298}{298} \right)^{1.5} = 1.64 \cdot 10^{-6} \frac{m^2}{s} \]

\[ P_{BLm} = \frac{P_{B2} - P_{B1}}{\ln \left( \frac{P_{B2}}{P_{B1}} \right)} \]

\[ P_{A1} = y_1 \cdot P_T = 0.1 \cdot 10 = 1atm \]

\[ P_{B1} = 10 - 1 = 9atm \]

\[ P_{A2} \text{ can be estimated from Henery law} \]

\[ P_A = x_A \cdot H \]

\[ P_{A2} = 0.005 \cdot 1640 = 8.2atm \]

\[ P_{B2} = 10 - 8.2 = 1.8atm \]

\[ \therefore P_{BLM} = \frac{1.8 - 9}{\ln \left( \frac{1.8}{9} \right)} = 4.473612 \]

Now we can calculate the mass transfer coefficient
\[ K_C = \frac{P_T \cdot D_{AB}}{P_{BLM} \cdot d} \cdot 0.023(\text{Re})^{0.833}(\text{Sc})^{0.333} \]

\[ K_C = \frac{P_T \cdot D_{AB}}{P_{BLM} \cdot d} \cdot 0.023 \left( \frac{\rho \cdot u \cdot d}{\mu} \right)^{0.833} \left( \frac{\mu}{\rho \cdot D_{AB}} \right)^{0.333} \]

\[ K_C = \frac{10 \cdot 1.64 \cdot 10^{-6} \cdot 0.023}{4.473612 \cdot 0.0508} \left( \frac{11.973 \cdot 0.915 \cdot 0.0508}{0.018 \cdot 10^{-3}} \right)^{0.833} \left( \frac{0.018 \cdot 10^{-3}}{11.973 \cdot 1.64 \cdot 10^{-6}} \right)^{0.333} \]

\[ K_C = 0.008868 \frac{m}{s} \]

\[ N_A = K_g (P_{A1} - P_{A2}) \]

\[ K_g = \frac{K_C}{R \cdot T} = 0.008868 \frac{m}{s} \cdot \frac{1}{0.082 \frac{atm \cdot l}{mol \cdot K} \cdot \frac{m^3}{1000l} \cdot \frac{1000mol}{kmol} \cdot 298K} \]

\[ K_g = 3.62642 \cdot 10^{-4} \frac{kmol}{m^2 \cdot s \cdot atm} \]

\[ N_A = 3.62642 \cdot 10^{-4} \cdot (8.2 - 1) = 2.611 \cdot 10^{-3} \frac{kmol}{m^2 \cdot s} \]
Example 14
A solute (A) is being diffused from a gas mixture of A & B in a wetted wall column with a liquid flowing as a film downwards along the wall. At a certain point in the column the gas bulk contains A of \( y_A = 0.38 \) (mole fraction) and at the liquid bulk the concentration of A is \( x_A = 0.1 \) mole fraction.
The column is operated at 1 atm and 25 °C and the equilibrium data in such conditions are as follow:

<table>
<thead>
<tr>
<th>( x_A )</th>
<th>0</th>
<th>0.05</th>
<th>0.1</th>
<th>0.15</th>
<th>0.2</th>
<th>0.25</th>
<th>0.3</th>
<th>0.35</th>
</tr>
</thead>
<tbody>
<tr>
<td>( y_A )</td>
<td>0</td>
<td>0.022</td>
<td>0.052</td>
<td>0.087</td>
<td>0.131</td>
<td>0.187</td>
<td>0.265</td>
<td>0.38</td>
</tr>
</tbody>
</table>

The solute A is diffusing through stagnant layer of B and then through non-diffusing liquid. Given the individual mass transfer coefficient for equi-molar mass transfer for both gas and liquid phases as:

\[
K_y' = 1.465 \times 10^{-3} \frac{\text{kmol A}}{s * m^2 * \text{mole fraction}}
\]

\[
K_x' = 1.967 \times 10^{-3} \frac{\text{kmol A}}{s * m^2 * \text{mole fraction}}
\]

Calculate the interfacial composition and the flux \( N_A \).

Solution
Since we are dealing with a mass transfer operation through stagnant layer, therefore we can not use the slope as:

\[
slop = -\frac{K_x'}{K_y'} = \frac{y_A - y_{A_i}}{x_A - x_{A_i}}
\]

But we must use the form:

\[
Slop = -\frac{x_{A_iLM}}{y_{A_iLM}}
\]

Then:
1. Draw the equilibrium curve.
2. Plot point P (\( y_A = 0.38, x_A = 0.1 \)).
3. Assume \( y_{A_iLM} \) and \( x_{A_iLM} = 1 \).
4. Draw a line from point P with a slop of:

\[
slop = -\frac{K_x'}{K_y'} = -\frac{-1.967 \times 10^{-3}}{1.465 \times 10^{-3}} = -1.342662116
\]
5- Extent the line until it will intercept the equilibrium curve at point (m).

6- Read \((x_{Ai})_1\) and \((y_{Ai})_1\)
\((x_{Ai})_1 = 0.246\) and \((y_{Ai})_1 = 0.18\)

7- Calculate \(y_{AiLM}\) And \(x_{AiLM}\).

\[
x_{AiLM} = \frac{(1-x_A) - (1-x_{Ai})}{\ln \frac{(1-x_A)}{(1-x_{Ai})}} = \frac{(1-0.1) - (1-0.246)}{\ln \frac{(1-0.1)}{(1-0.246)}} = 0.824847594
\]

And

\[
y_{AiLM} = \frac{(1-y_A) - (1-y_{Ai})}{\ln \frac{(1-y_A)}{(1-y_{Ai})}} = \frac{(1-0.38) - (1-0.18)}{\ln \frac{(1-0.38)}{(1-0.18)}} = 0.715346711
\]

8- Recalculate the slop using the equation:

\[
Slop = -\frac{K_x'}{K_y'} \frac{x_{AiLM}}{y_{AiLM}} = -\frac{-1.967 \times 10^{-3}/0.824847594}{1.465 \times 10^{-3}/0.715346711} = -1.164419871
\]

Since \((slop)_1 \neq (slop)_2\)

1- Draw a second line of slop = -1.164419871

10- Read \((x_{Ai})_1\) and \((y_{Ai})_1\)
\((x_{Ai})_1 = 0.258\) and \((y_{Ai})_1 = 0.199\)

11- Calculate \(y_{AiLM}\) And \(x_{AiLM}\).

\[
x_{AiLM} = \frac{(1-x_A) - (1-x_{Ai})}{\ln \frac{(1-x_A)}{(1-x_{Ai})}} = \frac{(1-0.1) - (1-0.258)}{\ln \frac{(1-0.1)}{(1-0.258)}} = 0.818459811
\]

And

\[
y_{AiLM} = \frac{(1-y_A) - (1-y_{Ai})}{\ln \frac{(1-y_A)}{(1-y_{Ai})}} = \frac{(1-0.38) - (1-0.199)}{\ln \frac{(1-0.38)}{(1-0.199)}} = 0.70664075
\]

12- Recalculate the slop using the equation:
\[ Slop = -\frac{K'_x}{x_{Ai,LM}} = -\frac{-1.967 \times 10^{-3}}{0.81845811} = -1.159225845 \]
\[ Slop = -\frac{K'_y}{y_{Ai,LM}} = -\frac{1.465 \times 10^{-3}}{0.70664075} \]

Since \((slop)_2 \neq (slop)_3\)

13- Draw a second line of slope = -1.159225845

14- Read \((x_{Ai})_1\) and \((y_{Ai})_1\)

\((x_{Ai})_1 = 0.257\) and \((y_{Ai})_1 = 0.199\)

15- Calculate \(y_{Ai,LM}\) and \(x_{Ai,LM}\)

\[
x_{Ai,LM} = \frac{(1 - x_A) - (1 - x_{Ai})}{\ln \left( \frac{1 - x_A}{1 - x_{Ai}} \right)} = \frac{(1 - 0.1) - (1 - 0.257)}{\ln \left( \frac{1 - 0.1}{1 - 0.257} \right)} = 0.819
\]

And

\[
y_{Ai,LM} = \frac{(1 - y_{Ai}) - (1 - y_A)}{\ln \left( \frac{1 - y_{Ai}}{1 - y_A} \right)} = \frac{(1 - 0.38) - (1 - 0.199)}{\ln \left( \frac{1 - 0.38}{1 - 0.199} \right)} = 0.70664
\]

16- Recalculate the slope using the equation:

\[ Slop = -\frac{K'_x}{x_{Ai,LM}} = -\frac{-1.967 \times 10^{-3}}{0.819} = -1.15846 \]
\[ Slop = -\frac{K'_y}{y_{Ai,LM}} \]

Since \((slop)_3 \approx (slop)_4\)

Then we have reached the correct interface composition which is equal to:

\((x_{Ai})_1 = 0.257\) and \((y_{Ai})_1 = 0.199\)

And

\[ x_{Ai,LM} = 0.819 \]
\[ y_{Ai,LM} = 0.70664 \]

\[
N_A = K_y \left( y_A - y_{Ai} \right) = \frac{K_y}{y_{Ai,LM}} \left( y_A - y_{Ai} \right) = \frac{1.465 \times 10^{-3}}{0.70664} \left( 0.38 - 0.2 \right) = 3.7317 \times 10^{-4} \frac{kmol}{m^2 \cdot s}
\]
Example 15
Using the same data as in example 14, calculate the overall mass transfer coefficient $K_{oy}$, the flux ($N_A$) and the percent resistance in the gas and liquid films of the total resistance. Base your calculation on the case that $A$ is the only solute transferred.

Solution

$$\frac{1}{K_{oy}} = \frac{1}{K_y} + m_2$$

Knowing that

$$K_{oy} = \frac{K_y}{y_{A_{LM}}} \text{, } K_y = \frac{K_y}{y_{A_{LM}}} \text{ and } K_x = \frac{K_x}{x_{A_{LM}}}$$

So we have to calculate $m_2$, $y_{A_{LM}}$, $x_{A_{LM}}$ and $y_A^*$. Then we have to repeat the solution done in previous example to find $y_{A_{LM}}$, $x_{A_{LM}}$

We can make use of the results in example 14, then:

$x_{A_{LM}} = 0.819$

$y_{A_{LM}} = 0.70664$

From the plot we find $x_A^*$ and $y_A^*$

$x_A^* = 0.35$

$y_A^* = 0.052$

Using the following relation to calculate $m_2$

$$m_2 = \frac{y_{A_i} - y_A^*}{x_{A_i} - x_A}$$

$$m_2 = \frac{0.2 - 0.052}{0.257 - 0.1} = 0.9427$$

$$y_{A_{LM}} = \frac{1 - y_A^*}{1 - y_A} = \frac{(1 - 0.052) - (1 - 0.38)}{(1 - 0.38)} = 0.773$$

Now

$$K_y = \frac{K_y}{y_{A_{LM}}} = \frac{1.465 \times 10^{-3}}{0.70664} = 2.0732 \times 10^{-3}$$
\[ K_x = \frac{K'_x}{x_{A_{ILM}}} = \frac{1.967 \times 10^{-3}}{0.819} = 2.4017 \times 10^{-3} \]

\[ \frac{1}{K_{oy}} = \frac{1}{K'_y} + \frac{m_2}{K'_x} \]

\[ \frac{1}{K_{oy}} = \frac{1}{1.465 \times 10^{-3}} + \frac{0.9427}{1.967 \times 10^{-3}} = 1161.852 \]

\[ K_{oy} = 8.607 \times 10^{-4} \]

\[ K_{oy} = \frac{K'_{oy}}{y_{A_{ILM}}} = \frac{8.607 \times 10^{-4}}{0.773} = 1.1134 \times 10^{-3} \frac{kmol}{m^2 \cdot s \cdot mole \ fraction} \]

\[ N_A = K_{oy} \cdot (y_A - y_A^*) = 1.1134 \times 10^{-3} (0.38 - 0.052) \]

\[ N_A = 3.6521 \times 10^{-4} \frac{kmol}{m^2 \cdot s} \]

In this example the resistance of the gas film is represented by: \( \frac{1}{K_y} \), the resistance of the liquid film is represented by: \( \frac{m_2}{K_x} \) and the overall resistance is \( \frac{1}{K_{oy}} \).

\[ \frac{1}{K_y} = \frac{y_{A_{ILM}}}{K'_y} = \frac{0.70664}{1.465 \times 10^{-3}} = 482.348 \]

\[ \frac{m_2}{K_x} = \frac{m_2 \cdot x_{A_{ILM}}}{K'_x} = \frac{0.9427 \cdot 0.819}{1.967 \times 10^{-3}} = 392.512 \]

\[ \frac{1}{K_{oy}} = \frac{y_{A_{LM}}}{K'_{oy}} = \frac{0.773}{8.607 \times 10^{-4}} = 898.1062 \]

The percent gas resistance = \( \frac{\text{gas resistance}}{\text{overall resistance}} \times 100 = \frac{482.348}{898.106} \times 100 = 53.707\% \)

The percent liquid resistance = \( \frac{\text{liquid resistance}}{\text{overall resistance}} \times 100 = \frac{392.512}{898.106} \times 100 = 43.704\% \)

As you can see that the summation of percentages does not equal too 100% and that due to errors in calculating the interface compositions.
Summary

1. Mass transfer is the net movement of a component in a mixture from one region to another region of different concentration, often between two phases across an interface. Mass transfer occurs by molecular diffusion, eddy diffusion, and bulk flow. Molecular diffusion occurs because of a number of driving forces, including concentration (the most important), pressure, temperature, and external force fields.

2. Fick's first law for steady-state conditions states that the mass transfer flux by ordinary molecular diffusion is equal to the product of the diffusion coefficient (diffusivity) and the negative of the concentration gradient.

3. Two limiting cases of mass transfer are equimolar counter diffusion (EMD) and unimolecular diffusion (UMD). The former is also a good approximation for dilute conditions. The latter must include the bulk-flow effect.

4. When experimental data are not available, diffusivities in gas and liquid mixtures can be estimated. Diffusivities in solids, including porous solids, crystalline solids, metals, glass, ceramics, polymers, and cellular solids are best measured. For some solids—for example, wood-diffusivity is an anisotropic property.

5. Diffusivity values vary by orders of magnitude. Typical values are 0.10, $1 \times 10^{-5}$, and $1 \times 10^{-9}$ cm$^2$/s for ordinary molecular diffusion of a solute in a gas, liquid, and solid, respectively.

6. Fick's second law for unsteady-state diffusion is readily applied to semi-infinite and finite stagnant media, including certain anisotropic materials.

7. Molecular diffusion under laminar-flow conditions can be determined from Fick's first and second laws, provided that velocity profiles are available. Common cases include falling liquid-film flow, boundary-layer flow on a flat plate, and fully developed flow in a straight, circular tube. Results are often expressed in terms of a mass transfer coefficient embedded in a dimensionless group called the Sherwood number. The mass transfer flux is given by the product of the mass transfer coefficient and a concentration-driving force.

8. Mass transfer in turbulent flow is often predicted by analogy to heat transfer. Of particular importance, is the Chilton-Colburn analogy, which utilizes empirical j-factor correlations and the dimensionless Stanton number for mass transfer. Semi-theoretical analogies, such as extensions of the Reynolds analogy, are also sometimes useful.
9. A number of models have been developed for mass transfer across a two-fluid interface and into a liquid. These include the film theory, penetration theory, surface renewal theory, and the film-penetration theory. These theories predict mass transfer coefficients that are proportional to the diffusivity raised to an exponent that varies from 0.5 to 1.0. Most experimental data provide exponents ranging from 0.5 to 0.75.

10. The two-film theory of Whitman (more properly referred to as a two-resistance theory) is widely used to predict the mass transfer flux from one fluid phase, across an interface, and into another fluid phase, assuming equilibrium at the interface. One resistance is often controlling. The theory defines an overall mass transfer coefficient that is determined from the separate coefficients for each of the two phases and the equilibrium relationship at the interface.
Introduction:
In absorption (also called gas absorption, gas scrubbing, and gas washing), a gas mixture is contacted with a liquid (the absorbent or solvent) to selectively dissolve one or more components by mass transfer from the gas to the liquid. The components transferred to the liquid are referred to as solute or absorbate.
Absorption is used to separate gas mixture; remove impurities, contaminants, pollutants, or catalyst poisons from gas; or recovery valuable chemicals. Thus, the species of interest in the gas mixture may be all components, only the component(s) not transferred, or only the component(s) transferred.
The opposite of absorption is stripping (also called de-sorption), wherein a liquid mixture is contacted with gas to selectively remove components by mass transfer from the liquid to the gas phase.
The absorption process involves molecular and turbulent diffusion or mass transfer of solute [A] through a stagnant layer gas [B] then through non – diffusing liquid [C]. There are two types of absorption processes:
  1- Physical process (e.g. absorption of acetone from acetone – air mixture by water.
  2- Chemical process, sometimes called chemi-sorption (e.g. absorption of nitrogen oxides by water to produce nitric acid.

Equipment:
Absorption and stripping are conducted in tray towers (plate column), packed column, spray tower, bubble column, and centrifugal contactors. The first two types of these equipment will be considered in our course for this year.
1- Tray tower:
A tray tower is a vertical, cylindrical pressure vessel in which vapor and liquid, which flow counter currently, are contacted on a series of metal trays or plates. Liquid flows across any tray over an outlet weir, and into a down comer, which takes the liquid by gravity to the tray below. The gas flows upward through opening in each tray, bubbling through the liquid on the other tray. A schematic diagram for the flow patterns inside the tray column is shown below.
In Chemical Engineering vol. 2 by J. M. Coulson & J. F. Richardson a review for the types of trays used in plate towers are given in page 573.
2- **Packed tower:**
The packed column is a vertical, cylindrical pressure vessel containing one or more section of packing material over who's the liquid flows downwards by gravity as a film or as droplets between packing elements. Vapor flows upwards through the wetted packing contacting the liquid. The sections of packing are contained between a lower gas – injection support plate, which holds the packing, and an upper grid or mish hold – down plate, which prevent packing movement. A liquid distributor, placed above the hold – down plate, ensures uniform distribution of liquid as it enters the packing section.

**General Design Consideration**
Design or analysis of an absorber (or stripper) requires consideration of a number of factors, including:
1- Entering gas (liquid) flow rate, composition, temperature, and pressure.
2- Design degree of recovery (R) of one or more solutes.
3- Choice absorbent (stripping) agent.
4- Operating pressure and temperature and allowable pressure drop.
5- Minimum absorbent (stripping) agent flow rate and actual absorbent (stripping) agent flow rate as a multiple of the minimum rate needed to make the separation.
6- Number of equilibrium stages.
7- Heat effects and need for cooling (heating).
8- Type of absorber (stripper) equipment.
9- Height of absorber (stripper) column.
10- Diameter of absorber (stripper) column.

**The ideal absorbent should have**
- High solubility for the solute(s) to minimize the need for absorbent.
- A low volatility to reduce the loss of absorbent and facilitate separation of absorbent from solute(s).
c- Be stable to maximize absorbent life and reduce absorbent makeup requirement.
d- Be non-corrosive to permit use of common material of construction.
e- Have a low viscosity to provide low pressure drop and high mass and heat transfer rates.
f- Be non-foaming when contacted with gas so as to make it unnecessary.
g- Be non-toxic and non-flammable to facilitate its safe use.
h- Be available, if possible.

The most widely absorbent used are water, hydrocarbon oils, and aqueous solutions of acids and bases. While the most common stripping agents used are water vapor, air, inert gases, and hydrocarbon gases.

**Equilibrium Relations Between Phases**
The equilibrium relationship in gas – liquid system is given in terms of Henry's law constants such as:

A- for dilute solutions:

\[ P_A = H \times x_A \]

Or

\[ y_A = H^{'} \times x_A \]

Where:

H: is the Henry's law constant in \( \frac{\text{atm-mole fraction}}{} \)

H^{'}: is the modified Henry's law constant in \( \frac{\text{mole fraction of solute in gas}}{\text{mole fraction of solute in liquid}} \), that means

\[ H^{'} = \frac{H}{P_T} \]

B- for concentrated solutions:
The \((y_A-x_A)\) data, may give the equilibrium relationship, which is obtained from K-value.

**In the following section, the physical process** type of absorption will be considered.

**1- Tray column**
The absorption process can be carried out in countercurrent flow process, which may be carried out in a single stage unit or multistage unit.

**A- Single stage:**
Consider the countercurrent flow process that operates under isobaric, isothermal, continuous steady-state flow condition. The liquid phase enters from the top while the gas enters from the bottom, with known amounts and composition for both.

Phase equilibrium is assumed to be achieved, that is the two-exit streams (liquid & gas) leave in equilibrium with each other. Consider the following figure:
Where:
L: moles of liquid phase/ unit time
G: moles of gas phase/ unit time

We will denote the streams in the top of the equipment by (T), and those in the bottom of the equipment by (B).

Then, the overall material balance equation for the above consideration can be written as:

\[ L_T + G_B = L_B + G_T \]

(Mole balance can be used because there is no chemical reaction)

[A] M.B.

\[ L_T \times x_T + G_B \times y_B = L_B \times x_B + G_T \times y_T \]

Where:
x: is the mole fraction of solute A in the liquid phase.
y: is the mole fraction of solute A in the gas phase.

Since only component A is redistributed between the two phases then, a balance component for A can be written as follow:

\[ L \left( \frac{x_T}{1 - x_T} \right) + G \left( \frac{y_B}{1 - y_B} \right) = L \left( \frac{x_B}{1 - x_B} \right) + G \left( \frac{y_T}{1 - y_T} \right) \]

The above equation is called the operating equation where:
L : Moles of inert liquid (solute–free absorbent) / unit time
G : Mole of inert gas {solute–free gas (or career gas)} / unit time

The operating equation can also be written as:

\[ L \times X_T + G \times Y_B = L \times X_B + G \times Y_T \]

Where:

\[ X = \frac{x}{1 - x} = \frac{\text{moles of solute A in the liquid phase}}{\text{moles non - A components (inerts) in the liquid phase}} \]
That is, $X$ is the mole ratio of \( A \) in the liquid phase to the moles of inert liquid phase, and $Y$ is the mole ratio of \( A \) in the gas phase to the moles of inert gas phase. Both $L$ and $G$ are constants and usually known and $x_B$, $y_T$ are in equilibrium. So the use of Henry's law for dilute solution will solve the operating equation.

**Note:**

If $y_B > 0.1$ or $x_T > 0.1$ then the solution is considered as concentrated solution.

If $y_B < 0.1$ & $x_T < 0.1$ then the solution is considered as dilute solution.

**Example 1:**

In a single stage absorption process, a gas mixture at 1 atm pressure containing air and H\(_2\)S is contacted with pure water at 30\(^o\)C. The exit gas and liquid streams reach equilibrium. The inlet gas flow rate is (200 kmole / hr), with 0.2 mole fraction of H\(_2\)S, while the liquid flow rate entering is 600 kmole/hr. Calculate the amount and composition of the two outlet phases. Assume water does not vaporize to the gas phase. Given:

$H = 0.0609 \times 10^4$ atm/mole fraction (at 1 atm and 30\(^o\)C).

**Solution:**

Since the inlet liquid is pure water, thus

\[ x_T = 0 \]

And,

\[ L' = L_T = 600 \text{ kmole/hr} \]

\[ G' = G_B (1-y_B) = 200 \times (1-0.2) = 160 \text{ kmole/hr} \]

Applying the operating equation of the single stage absorption

\[
L' \left( \frac{x_T}{1-x_T} \right) + G' \left( \frac{y_B}{1-y_B} \right) = L' \left( \frac{x_B}{1-x_B} \right) + G' \left( \frac{y_T}{1-y_T} \right)
\]

\[
600 \times \frac{0}{1-0} + 160 \times \frac{0.2}{1-0.2} = 600 \times \frac{x_B}{1-x_B} + 160 \times \frac{y_T}{1-y_T}
\]

\[
40 = 600 \times \frac{x_B}{1-x_B} + 160 \times \frac{y_T}{1-y_T}
\]

Since $x_B$ is in equilibrium with $y_T$ and Henry's constant is given, then

\[
y_T = \frac{H}{P_{total}} x_B = 609 \times x_B
\]

Substitute in the above equation then

\[
40 = 600 \times \frac{x_B}{1-x_B} + 160 \times \frac{609 \times x_B}{1-609 \times x_B}
\]
Solve the equation for \( x_B \)
\( x_B = 0.000327116 \) and then, \( y_T = 0.199213892 \)
To calculate the total flow rates:
\[
L_B = \frac{L}{1-x_B} = \frac{600}{1-0.000327117} = 600.1963341 \text{ kmole/hr}
\]
\[
G_T = \frac{G}{1-y_T} = \frac{160}{1-0.199213892} = 199.8036659 \text{ kmole/hr}
\]

**B- Multiple – contact stages (plate tower):**

**1- Graphical equilibrium – stage method for tray towers**
Consider the countercurrent flow, tray tower for absorption (or stripping) operating under isobaric, isothermal, continuous, steady state flow conditions as shown in the figure below. Phase equilibrium is assumed to be achieved at each tray between the vapor and liquid streams leaving the tray. That is, each tray is treated as equilibrium stage. Assume that the only component transferred from one phase to the other is solute A

For application to an absorber, make an overall material balance for the section denoted:

**O.M.B.**
\[
L_T + G_{n+1} = L_n + G_T
\]

**Solute (A) M.B.**
\[
L_T \cdot x_T + G_{n+1} \cdot y_{n+1} = L_n \cdot x_n + G_T \cdot y_T
\]
Then
\[
G_{n+1} \cdot y_{n+1} = L_n \cdot x_n + G_T \cdot y_T - L_T \cdot x_T
\]
Where:

\( y_{n+1} \): The composition of solute A in the gas phase that leaves the plate (n+1)

\( x_n \): The composition of solute A in the liquid phase that enters the plate (n+1)

Since the solute A is the only component that transferred between the two phases, then the above equation can be written as:

\[
G \left( \frac{y_{n+1}}{1-y_{n+1}} \right) = L \left( \frac{x_n}{1-x_n} \right) + G \left( \frac{y_T}{1-y_T} \right) - L \left( \frac{x_T}{1-x_T} \right)
\]

And

\[
\left( \frac{y_{n+1}}{1-y_{n+1}} \right) = \left( \frac{x_n}{1-x_n} \right) + \left( \frac{y_T}{1-y_T} \right) - \left( \frac{x_T}{1-x_T} \right) \tag{1}
\]

Or

\[
Y_{n+1} = \frac{L}{G} X_n + \left( Y_T - \frac{L}{G} X_T \right) \tag{2}
\]

This is the equation of straight line, with a slope of \( \frac{L}{G} \) and \( Y_T - \frac{L}{G} X_T \) is its intercept with Y-axis. It is called the operating line equation.

When using the normal axis (y, x) the operating line equation will appear as a curve and not as a straight line unless we are dealing with dilute solutions, otherwise we have to convert the equilibrium data to (Y, X) and use the axis as (Y, X) axis to draw the operating line and the equilibrium data.

When dealing with dilute solutions, we can use the ordinary axis and the operating line equation will appear as a straight line also the equilibrium data as

\[
\frac{y_{n+1}}{1-y_{n+1}} \quad \text{and} \quad \frac{x_n}{1-x_n}
\]

will nearly equal to \( y_{n+1} \) and \( x_n \) respectively.

**How to calculate the number of plates in a plate tower using the graphical method:**

1- Complete the material balance to calculate all the unknowns (all compositions and flow rates of the inlet and the outlet streams must be known).
2- Draw the equilibrium line (or curve) either from given data or from the equilibrium equation: \( y = m \times x \).
3- Draw the operating line equation using either equation (1) or equation (2) according to the condition of the process.
4- Draw a vertical line from point 1 which represents the point \((y_B, x_B)\) {as shown in the figure} to point 2 which will intersect the equilibrium line (Curve). Then draw a horizontal line from point 2 to point 3, intersecting the operating line. The triangular formed will represent the plate number one.
5- Continue drawing the vertical lines and horizontal lines as in step 4 (shown in the fig.).

6- Count the triangles constructed, this number represents the number of theoretical plates.

7- To calculate the actual number of plates, use the following equation:

\[
\text{The actual number of plates} = \frac{\text{Theoretical number of plates}}{\eta}
\]

Where:

\( \eta \) = the efficiency of the plate

**Note:**

\( Y_T = (1-R) \times Y_B \)
**Minimum absorbent flow rate:**
In the design of absorbers \( G_T, G_B, y_B, y_T, \) and \( x_T \) are set by process requirements, but the quantity of entering liquid \( L_T \) is subjected to choice in which finally \( x_B \) depend on.

In the following figure, there are four operating lines for different flow rates, where each operating line passes through the terminal point, \( P (y_T, x_T) \), at the top of the column and corresponding to a different slope \( \frac{L}{G} \).

Consider the following:
1- \( P \) is fixed, since \( y_T, x_T \) are fixed in the process and the line \( PS \) is the operating line with slop \( \frac{L}{G} \).

2- Also, since \( G' \) is fixed, then by reducing the absorbent (liquid) flow rate will lead to reduce the slop of the operating line causing an increase in \( x_B \) (line 2, \( PN \)). This reduction will cause also a more contact time which mean requirement of increasing the height of the tower. In other point of view, the decrease in slop will cause a decrease in the driving force, which means the absorption process is more difficult.

3- Keeping the reduction in liquid flow rate once more as in point \( O \) (line \( PO \)) reaching to pint \( M \) the operating line will intersect the equilibrium curve, which will give a value of Zero of the driving force, i.e. no absorption is carried on and equilibrium is reached. The slop of line \( 4 \) (line \( PM \)) called the minimum slop of the operating line, which means the minimum liquid flow rate. And below this value no absorption is done.

\[
\left( \frac{L}{G} \right)_{\text{min}} \text{ means } (L')_{\text{min}} \text{ since } G' \text{ is fixed.}
\]

From literatures

\[
\left( \frac{L}{G} \right)_{\text{operating}} = 1.5 * \left( \frac{L}{G} \right)_{\text{min}}
\]

Then to find \( x_B \) (which is normally will not be known), we must follow these steps:
1- Draw the equilibrium data.
2- Set the point \( P (y_T, x_T) \) on the figure.
3- Find \( \left( \frac{L}{G} \right)_{\text{min}} \) from the figure.
4- Find the slope of line 4 (PM) $x_B$ either from the figure or using the following equation:

$$\left(\frac{L}{G}\right)_{\text{min}} = \frac{y_B - y_T}{x_B^* - x_T}$$

Where $x_B^* = \frac{y_B}{m}$ or $y_B = m*x_B$

Or this value can be withdrawn from the figure.

5- Calculate $(\frac{L}{G})_{\text{operating}}$ by using suitable factor $(1.1 - 1.5)$ or as defined in the problem. Then calculate the actual value (operating) of $L_T$.

6- Substitute the operating line slope in the equation of the operating line to find $x_B$.

$$\left(\frac{y_B}{1-y_B}\right) = \frac{L}{G} \left(\frac{x_B}{1-x_B}\right) + \left(\frac{y_T}{1-y_T}\right) - \frac{L}{G} \left(\frac{x_T}{1-x_T}\right)$$

7- Continue to find the number of theoretical plates.
For stripping:
The process can be shown in the figure:

O.M.B. on the denoted block for solute (A):
\[ L_{n+1}x_{n+1} + G_B y_B = L_B x_B + G_n y_n \]

And
\[ G \left( \frac{y_B}{1-y_B} \right) + L \left( \frac{x_{n+1}}{1-x_{n+1}} \right) = L \left( \frac{x_B}{1-x_B} \right) + G \left( \frac{y_n}{1-y_n} \right) \]

Solve for \( y_n \), then
\[ \frac{y_n}{1-y_n} = \frac{L}{G} \left( \frac{x_{n+1}}{1-x_{n+1}} \right) + \left\{ \left( \frac{y_B}{1-y_B} \right) - \frac{L}{G} \left( \frac{x_B}{1-x_B} \right) \right\} \]
**Algebraic method for determining the number of equilibrium stages:**

Graphical methods for determining equilibrium stages have great educational value because of fairly complex multistage problem can be readily followed and understood. Furthermore, one can quickly gain visual insight into the phenomena involved. However, the application of graphical method can become very tedious when (1) the problem speciation fixes the number of stages rather than the percent recovery of solute, (2) when more than one solute is being absorbed or stripped, (3) when the best operating conditions of temperature and pressure are to be determined so that the location of the equilibrium curve is unknown, and/or (4) if very low or very high concentrations force the graphical construction to the corners of the diagram so that multiple \( y - x \) diagrams of varying sizes and dimensions are needed. Then the application of an algebraic method may be preferred.

When the flow rate of \( L \) and \( G \) are constant and the process is countercurrent and the equilibrium line is a straight line and can be presented by the relation \( y = m \times x \), also if the operating line is a straight line (i.e. dilute solution), a simplified analytical equation found by Kremser et al. can be used to find the number of theoretical plates as follow:

1- For absorption:

\[
\frac{y_B - y_T}{y_B - y_T^*} = \frac{A^{N+1} - A}{A^{N+1} - 1}
\]

Then

\[
N = \frac{\log \left[ \frac{y_B - m \times x_T}{y_T - m \times x_T} (1 - \frac{1}{A}) + \frac{1}{A} \right]}{\log A}
\]

Where

\( N \): Theoretical number of plates.

\( y_T^* = m \times x_T \) (Equilibrium relation for dilute solution)

\( A \): absorption factor which is the ratio of slope of operating line \( (L/G) \) to the slope of equilibrium line \( (m) \), then:

\[
A = \frac{L}{m \times G}
\]

For high degree of absorption (high % recovery):

1- Use large number of plates.

2- Use high absorption factor \( A \), since \( m \) is constant by the system, then to get high value of \( A \) means \( (L/G) \) must be larger than \( m \).

The most economic value of \( A \) is about (1.3) \{suggested by Calburn\}.  

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2- For stripping:

\[
\frac{x_T - x_B}{x_T - \left(\frac{y_B}{m}\right)} = \left(\frac{1}{A}\right)^{N+1} - \left(\frac{1}{A}\right)
\]

And

\[
N = \frac{\log \left[\frac{x_T - \left(\frac{y_B}{m}\right)}{x_B - \left(\frac{y_B}{m}\right)}\right]}{\log \left(\frac{1}{A}\right)}
\]

Where:

\[
\frac{y_B}{m} = x^*_B
\]

Example 2:

When molasses is fermented to produce a liquor containing ethyl alcohol, a CO\textsubscript{2}- rich vapor containing a small amount of ethyl alcohol is evolved. The alcohol can be recovered by absorption with water in a sieve-tray tower. For the following conditions, determine the number of equilibrium stages required for countercurrent flow of liquid and gas, assuming isothermal, isobaric conditions in the tower and neglecting mass transfer of all components except ethyl alcohol.

Entering gas:
180 kmole/hr; 98 mol% CO\textsubscript{2}, 2 mol% ethyl alcohol; 30 °C, 110 kPa

Entering liquid absorbent:
100 % water; 30 °C, 110 kPa

Required recovery (absorption) of ethyl alcohol (R): 97%

Equilibrium relationship: \( y = 0.57x \)

Solution:

\[
Y_T = (1 - R) \cdot Y_B
\]

\[
y_B = \frac{y_B}{1 - y_B} = \frac{0.02}{1 - 0.02} = 0.02041
\]

\[
y_T = 0.03 \cdot 0.02041 = 0.00061 \text{ (mole fraction of ethyl alcohol in the top)}
\]

\[
x_B^* = \frac{y_B}{m} = 0.02/0.57 = 0.03509
\]
\[
\left( \frac{L}{G} \right)_{\text{min}} = \frac{y_B - y_T}{x_B - x_T} \\
\left( \frac{L}{G} \right)_{\text{min}} = \frac{0.02 - 0.00061}{0.03509 - 0} = 0.5529
\]

Take the operating factor 1.5

Then:

\[
\left( \frac{L}{G} \right)_{\text{operating}} = 1.5 \times 0.5529 = 0.8293
\]

\[
\left( \frac{L}{G} \right)_{\text{operating}} = \frac{y_B - y_T}{x_B - x_T}
\]

\[
\left( \frac{L}{G} \right)_{\text{operating}} = \frac{0.02 - 0.00061}{x_B - 0} = \frac{0.0194}{x_B}
\]

So \( x_B = 0.0194 / 0.8293 \)

\( x_B = 0.0234 \) (the mole fraction of the liquid exits from the bottom)

Now

Draw the equilibrium data using the given equation (the result curve is a straight line)

Draw the operating line using the two points \((y_B, x_B)\) and \((y_T, x_T)\) \{ because we are dealing with dilute solution \( y_B < 0.1 \) \}

From the figure calculate the number of plates = 7
2- Packed column:
Absorption and stripping are frequently conducted in packed columns, particularly when:
(1) the required column diameter is less than 2 ft.
(2) the pressure drop must be low, as for a vacuum service.
(3) corrosion consideration favor the use of ceramic or polymeric material.
(4) low liquid holdup is desirable.
Structured packing is often favored over random packing for revamps to overcome capacity limitation of trayed towers.
The countercurrent packed towers operates in a different manner from plated towers. In packed towers the fluids are in contact continuously in their path through the tower, while in plated towers the fluids are contacted occasionally. So, packed columns are continuous differential contacting devices that do not have the physically distinguishable stages found in tray towers. Thus, packed columns are best analyzed by mass transfer considerations rather than by the equilibrium – stage concept. Nevertheless, in practice packed – towers performance is often analyzed on the basis of equivalent equilibrium stages using a packed height equivalent to a theoretical (equilibrium) plates (stage), called the HETP or HETS and defined by the equation:

\[
\text{HETP} = \frac{\text{packed height}}{\text{number of equivalent equilibrium stages}} = \frac{I_T}{N_t}
\]

The most important reason to use packed towers in absorption is to provide a large contact area as possible as can. There are many types of packing such as, Rasching rings, Lessing rings, Bert Saddles, Pall ring, and many others, most of these types of packing are made of cheap inert materials such as glass, ceramic, graphite or, plastic, but some times it may be made of stainless –steel.
A schematic diagram of the packed tower is shown in below.
Calculations of the height of packing:
A- for dilute mixtures
Consider the following figure, then
\[ L + (G + dG) = (L + dL) + G \]
\[ \therefore dG = dL \]

\[ [A] \ M. \ B. : \]
\[ d (G* y) = d (L*x) \]

\[ \Theta d (G * y) = \overline{N}_A \]
And
\[ \Theta \overline{N}_A = k_y (y - y_1) dA \]
\[ \text{or} \]
\[ \overline{N}_A = k_{o_y} (y - y^*) dA \]
Then
\[ d(Gy) = k_y (y - y_1) dA \]
\[ \text{or} \]
\[ d(Gy) = k_{o_y} (y - y^*) dA \]

Where:
\( dA \): is the interfacial area associated with differential tower length, it is very difficult to measure in packed towers so, for packed towers
\( dA = a*s*dZ \)

Where:
\( a \): Specific interfacial area per unit volume of packing (m\(^2\)/m\(^3\))
\( s \): empty tower cross-sectional area (m\(^2\))
\( dZ \): differential height in (m)
Then:
\[ d(Gy) = k_y a (y - y_1) sdz = k_{o_y} a(y - y^*) sdz \]

So
\[ \int_0^y dZ = \int_{y_1}^y \frac{d(Gy)}{k_y a (y - y_1) s} = \int_{y_1}^y \frac{d(Gy)}{k_{o_y} a(y - y^*) s} \]

In absorption of dilute solution the flow rate does not effected by the small change in concentration, so
\[ G = G_m = \frac{G_T + G_B}{2} \] (i.e. constant through out the column)
The equation is based on gas phase and is used in calculating the height of the packing (Z) are applied only for dilute or weak solution which leads to the assumption that \( L_m \) & \( G_m \) are constant throughout the solution. Don't forget that the solutions can be considered dilute if the mole fraction of the solute in the inlet streams (gas & liquid) are less than 0.1 (i.e. \( \leq 10\% \)). So the operating line can be considered as a straight line and also the equilibrium curve.

Therefore the integration terms:

\[
\int_{y_i}^{y_T} \frac{dy}{y-y_i} = \frac{y_T - y_i}{(y - y_i)_m}
\]

Where:

\[(y - y_i)_m = \frac{(y_T - y_i) - (y_T - y_i^*)}{\ln \left( \frac{y_T - y_i^*}{y_i - y_i^*} \right)}\]

Also

\[
\int_{y_i}^{y_T} \frac{dy}{y-y_i} = \frac{y_T - y_i}{(y - y_i)_m}
\]

Where:

\[(y - y_i)_m = \frac{(y_T - y_i) - (y_T - y_i^*)}{\ln \left( \frac{y_T - y_i^*}{y_i - y_i^*} \right)}\]

Now let us name the following terms

1- \( \frac{G_m}{k_{y,as}} \) is called the height of transfer unit based on gas film (HTU)_y with the units of (m)

2- \( \frac{G_m}{k_{oy,as}} \) is called the height of transfer unit based on overall gas phase (HTU)_oy with the units of (m)

3- \( \int_{y_i}^{y_T} \frac{dy}{y-y_i} \) is called the number of transfer units based on gas film (NTU)_y (without units).

4- \( \int_{y_i}^{y_T} \frac{dy}{y-y_i} \) is called the number of transfer units based on overall gas phase (NTU)_oy (without units).

Then the height of packing is calculated as follow:

\[ Z = (\text{NTU})_y \times (\text{HTU})_y = \frac{G_m}{k_{y,as}} \int_{y_i}^{y_T} \frac{dy}{y-y_i} \]

Or
\[ Z = (NTU)_{oy} \times (HTU)_{oy} = \frac{G_m}{k_{oy,as}} \int_{y_r}^{y} dy \]

All the above derivations can be done on the basis of liquid phase which will lead to:

\[ z = \frac{L_m}{k_{as}} \int_{x_i}^{x} dx = \frac{L_m}{k_{as}} \int_{x}^{x_i} dx \]

Where:
1. \( \frac{L_m}{k_{as}} \) is called the height of transfer unit based on liquid film (HTU)_x with the units of (m)
2. \( \frac{L_m}{k_{as}} \) is called the height of transfer unit based on overall liquid phase (HTU)_{ox} with the units of (m)
3. \( \int_{x_i}^{x} \frac{dx}{x - x_i} \) is called the number of transfer units based on liquid film (NTU)_x (without units).
4. \( \int_{x}^{x_i} \frac{dx}{x - x_i} \) is called the number of transfer units based on overall liquid phase (NTU)_{ox}

That is:
\[ Z = (NTU)_{ox} \times (HTU)_{ox} = (NTU)_x \times (HTU)_x \]

The terms \( k_{ya}, k_{xa} \) are called the volumetric film coefficient and their units are:
\[ \frac{kmole}{Sec \times molefraction \times m^3 \text{ packing}} \]

Where \( k_{Oya}, k_{Oxa} \) are called the volumetric overall mass transfer coefficient and their units:
\[ \frac{kmole}{Sec \times molefraction \times m^3 \text{ packing}} \]

Therefore, depending on the liquid film (overall mass transfer coefficient) the derivation will be as:
\[ d(lx) = k_{a}(x - x_i)sdz = k_{oa}(x - x^*)sdz \]

So
\[ \int_{0}^{z} dZ = \int_{x_i}^{x} \frac{d(lx)}{k_{a}(x - x_i)s} = \int_{x}^{x_i} \frac{d(lx)}{k_{oa}(x - x^*)s} \]

In absorption of dilute solution the flow rate does not effected by the small change in concentration, so
\[ L = L_m = \frac{L_B + L_T}{2} \text{ (i.e. constant through out the column)} \]

\[ z = \frac{L_m}{k_{as}} \int_{x_i}^{x} dx = \frac{L_m}{k_{as}} \int_{x}^{x_i} dx \]

This is finally can be written as:
\[ Z = (NTU)_x \times (HTU)_x = (NTU)_{ox} \times (HTU)_{ox} \]
All the above (number of transfer units and height of transfer units) were based on mole fraction, and also they can be written as:

\[ Z = (\text{NTU})_{OL} \times (\text{HTU})_{OL} = (\text{NTU})_L \times (\text{HTU})_L \]

Or

\[ Z = (\text{NTU})_{OG} \times (\text{HTU})_{OG} = (\text{NTU})_G \times (\text{HTU})_G \]

Where:

1- \( \frac{G_m}{k_G as} \) is called the height of transfer unit based on gas film (HTU)_G with the units of (m)

2- \( \frac{G_m}{k_{OG} as} \) is called the height of transfer unit based on overall gas phase (HTU)_OG with the units of (m)

3- \( \int_{p_{iG}}^{p_{G}} \frac{dp_A}{P_{A} - P_{Ai}} \) is called the number of transfer units based on gas film.

4- \( \int_{c_{iG}}^{c_G} \frac{dc_A}{c_{Ai} - c_A} \) is called the number of transfer units based on overall gas phase (NTU)_OG (without units).

Also

1- \( \frac{L_m}{k_L as} \) is called the height of transfer unit based on liquid film (HTU)_L with the units of (m)

2- \( \frac{L_m}{k_{OL} as} \) is called the height of transfer unit based on overall liquid phase (HTU)_OL with the units of (m)

3- \( \int_{c_{iL}}^{c_L} \frac{dc_A}{c_{Ai} - c_A} \) is called the number of transfer units based on liquid film (NTU)_L (without units).

4- \( \int_{c_{iL}}^{c_L} \frac{dc_A}{c_{Ai} - c_A} \) is called the number of transfer units based on overall liquid phase (NTU)_OL

**Home work:**

1- What are the units of \( k_G \), \( k_{OG} \), \( k_L \), and \( k_{OL} \)?

2- Solve the integration to find the number of transfer unit?

The following terms, (HTU)_G, (HTU)_L, and (HTU)_x, are called the individual height of transfer units. While the terms (HTU)_OG, (HTU)_oy, (HTU)_OL, and (HTU)_ox are the overall height of transfer units.
**The relation between the individual and overall height of transfer units:**

1- For gas film

From previous lectures

\[
\frac{1}{k_{oy}} = \frac{1}{k_y} + \frac{m_1}{k_x}
\]

By multiplying both sides by \( \frac{G_{m_{as}}}{G_{m}} \), then we will get

\[
\frac{G_{m_{as}}}{k_{oy} \cdot as} = \frac{G_{m}}{k_y \cdot as} + \frac{m_1 \cdot G_{m}}{k_x \cdot as}
\]

Also from previous lectures, \( m_1 = m_2 = m \), then the above equation can be written as follow:

\[
(HTU)_{oy} = (HTU)_{y} + \left( \frac{m_1 \cdot G_{m}}{k_x \cdot as} \right) \frac{L_m}{L_m}
\]

Rearrange

\[
(HTU)_{oy} = (HTU)_{y} + \left( \frac{L_m}{k_x \cdot as} \right) m_1 \cdot G_{m} \frac{L_m}{L_m}
\]

But we have \( A = \frac{L_m}{m \cdot G_{m}} \)

Then finally

\[(HTU)_{oy} = (HTU)_{y} + \left( \frac{1}{A} \right) (HTU)_{x}\]

2- For liquid phase

From previous lectures

\[
\frac{1}{k_{ox}} = \frac{1}{m_2 \cdot k_y} + \frac{1}{k_x}
\]

By multiplying both sides by \( \frac{L_m}{as} \), then we will get

\[
\frac{L_m}{k_{ox} \cdot as} = \frac{L_m}{m_2 \cdot k_y \cdot as} + \frac{L_m}{k_x \cdot as}
\]

Also from previous lectures, \( m_1 = m_2 = m \), then the above equation can be written as follow:

\[
(HTU)_{ox} = \left( \frac{L_m}{m \cdot k_y \cdot as} \right) \frac{G_{m}}{G_{m}} + (HTU)_{x}
\]

Rearrange

\[
(HTU)_{ox} = \left( \frac{G_{m}}{k_y \cdot as} \right) \frac{L_m}{m \cdot G_{m}} + (HTU)_{x}
\]

But we have \( A = \frac{L_m}{m \cdot G_{m}} \)
Then finally

\[(HTU)_{ox} = A \cdot (HTU)_{y} + (HTU)_{x}\]

**Home work:** find the relation between the individual height of transfer units based on \((k_G, k_L)\) and the overall height of transfer units which are based on the \((k_{OG}, k_{OL})\).

**Influence of solubility of gas on equilibrium curve & mass transfer coefficient:**

In absorption, the equation which relates the individual mass transfer coefficient to the overall mass transfer coefficient, as given in the above, is:

\[
\frac{1}{k_{oy}} = \frac{1}{k_y} + \frac{m_1}{k_x} \quad \text{(For gas phase)}
\]

\[
\frac{1}{k_{ox}} = \frac{1}{m_2 \cdot k_y} + \frac{1}{k_x} \quad \text{(For liquid phase)}
\]

Or

\[
\frac{1}{k_{OG}} = \frac{1}{k_G} + \frac{m_1}{k_L} \quad \text{(For gas phase)}
\]

\[
\frac{1}{k_{OL}} = \frac{1}{m_2 \cdot k_G} + \frac{1}{k_L} \quad \text{(For liquid phase)}
\]

And as mentioned before, that for dilute solutions: \(m=m_1=m_2\)

We have to two cases:

A) Very soluble gas

If \(m\) is very small, the equilibrium line is almost horizontal, that is a small change in the value of \(y_A\) in the gas phase will result a large change in the value of \(x_A\) in the liquid phase. So the solute is then called very soluble in liquid, then the term \(\frac{m}{k_x} \rightarrow 0\) (because \(m\) is very small, or we can say that the resistance in the liquid phase is negligible). Then:

\[
\frac{1}{k_{oy}} \approx \frac{1}{k_y}
\]

Also in such case, it is called (gas controlling process)

Then, the point \(m\) will move down very close to point E, that means:

\[y - y^* \approx y - y_i\]

B) Very insoluble gas

If \(m\) is very large, the equilibrium line is almost vertical, that is a large change in the value of \(y_A\) in the gas phase will result a small change in the value of \(x_A\) in the liquid phase. So the solute is then called very insoluble in liquid, then the term \(\frac{1}{m \cdot k_y} \rightarrow 0\)
(because \( m \) is very large, or we can say that the resistance in the gas phase is negligible). Then:
\[
\frac{1}{k_{\text{ox}}} \approx \frac{1}{k_{\text{x}}}
\]
Also in such case, it is called (liquid controlling process)

Then, the point \( m \) will move up very close to point \( D \), that means:
\[
x^* - x \approx x_1 - x
\]

**How to calculate the height of packing**

Follow the following steps to calculate the height of packing:

1. Plot the equilibrium data.
2. From the given data \((y_T, x_T, G_B, \text{ and } y_B)\) make use of \((\frac{L}{G})_{\text{min}}\) to find \( x_B \).
3. Plot the operating line (since we are dealing with dilute solution) with slope \((\frac{L}{G})_m\).
4. From point \( P_1 \) \((x_B, y_B)\) draw a line of slope \(-\frac{k_Xa}{k_Ya}\) {and if the data is given as \((a_x, a_y)\) then the slope = \(-\frac{k_Xa/(1-x_B)}{k_Ya/(1-y_B)}\)} to intersect the equilibrium line at \( m_1 \).

Read \((y_iB, x_iB)\) as shown in the figure.
5. From point \( P_2 \) \((x_T, y_T)\) draw a line of slope \(-\frac{k_Xa}{k_Ya}\) {and if the data is given as \((a_x, a_y)\) then the slope = \(-\frac{k_Xa/(1-x_B)}{k_Ya/(1-y_B)}\)} to intersect the equilibrium line at \( m_2 \).

Read \((y_iT, x_iT)\) as shown in the figure.

Note:
If the overall mass transfer coefficient is being used then \( y^*_B, y^*_T, x^*_B, \text{ and } x^*_T \) must be determined as shown in the figure instead of steps 4 \\& 5.

6. Calculate \((y-y_i)_m\) and \((x-x_i)_m\) or \((y-y^*_i)_m\) and \((x-x^*_i)_m\) depending on the given data using the equations given in previous sections.
7. Calculate \((HTU)\), \((NTU)\) depending on the given data, finally calculate \( Z \).
Example 3:
When molasses is fermented to produce a liquor containing ethyl alcohol, a CO_2- rich vapor containing a small amount of ethyl alcohol is evolved. The alcohol can be recovered by absorption with water in a tower packed with 1.5-in metal Pall rings. For the following conditions, determine the height of packing required for countercurrent flow of liquid and gas, assuming isothermal, isobaric conditions in the tower and neglecting mass transfer of all components except ethyl alcohol. Given that (HTU)_{oy}=2.0 \text{ ft.}

Entering gas:
180 kmole/hr; 98 mol% CO_2, 2 mol% ethyl alcohol; 30 °C, 110 kPa

Entering liquid absorbent:
100 % water; 30 °C, 110 kPa

Required recovery (absorption) of ethyl alcohol (R): 97%

Equilibrium relationship: \( y = 0.57 \times x \)

Solution:

\[
Y_T = (1 - R) \times Y_B
\]

\[
Y_B = \frac{y_B}{1 - y_B} = \frac{0.02}{1 - 0.02} = 0.02041
\]

\[
y_T = 0.03 \times 0.02041 = 0.00061 \text{ (mole fraction of ethyl alcohol in the top)}
\]

\[
x_B^* = \frac{y_B}{m} = \frac{0.02}{0.57} = 0.03509
\]

\[
\left(\frac{L}{G}\right)_{\text{min}} = \frac{Y_B - y_T}{x_B^* - x_T}
\]

\[
\left(\frac{L}{G}\right)_{\text{min}} = \frac{0.02 - 0.00061}{0.03509 - 0} = 0.5529
\]

Take the operating factor 1.5

Then:

\[
\left(\frac{L}{G}\right)_{\text{operating}} = 1.5 \times 0.5529 = 0.8293
\]

\[
\left(\frac{L}{G}\right)_{\text{operating}} = \frac{y_B - y_T}{x_B - x_T}
\]

\[
\left(\frac{L}{G}\right)_{\text{operating}} = \frac{0.02 - 0.00061}{x_B} = 0.0194
\]

So \( x_B = 0.0194/0.8293 \)

\( x_B = 0.0234 \) (the mole fraction of the liquid exits from the bottom)

Now:

\[
(NTU)_{oy} = \int_{y_2}^{y_1} \frac{dy}{y - y_i} = \frac{y_B - y_T}{(y - y_i)_m}
\]
\[(y - y^*)_{m} = (y_{n} - y_{n}^*) - (y_{T} - y_{T}^*) = \frac{(0.02 - 0.57*0.0234)-(0.00061 - 0.57*0)}{0.02 - 0.57*0.0234} = 0.002531459 \]

\[\ln\left(\frac{y_{n} - y_{n}^*}{y_{T} - y_{T}^*}\right) = \ln\left(\frac{0.02 - 0.57*0.0234}{0.00061 - 0.57*0}\right) = 0.0000321459 \]

\[\therefore (NTU)_{oy} = \frac{0.02 - 0.00061}{0.002531459} = 7.66 \]

\[Z = (HTU)_{oy} * (NTU)_{oy} = 2 * 7.66 = 15.32 \text{ ft} \]

**Example 4:**
Experimental data have been obtained for air containing 1.6 vol% SO\(_2\) being scrubbed with pure water in a packed column of 1.5 m\(^2\) in cross-sectional area and 3.5 m in packed height. Entering gas and liquid flow rates are 0.062 and 2.2 kmole/sec, respectively. If the outlet mole fraction of SO\(_2\) in the gas is 0.004 and column temperature is near ambient, calculate from the data:

(a) The \((NTU)_{oy}\) for absorption of SO\(_2\)
(b) The \((HTU)_{oy}\) in meters
(c) The volumetric overall mass transfer coefficient, \(k_{oy}a\) for SO\(_2\) in (kmole/m\(^3\) s mole fraction)

**Solution**
(a) First we must find \(x_B\)

\([\text{SO}_2]\) O.M. B.

\[L_T * x_T + G_B * y_B = L_B * x_B + G_T * y_T \]

And finally

\[L' * x_T + G * y_B = L' * x_B + G * y_T \]

\[L' = L_T \text{ (because } x_T = 0)\]

\[L' = 2.2 \text{ kmole/s}\]

\[G' = G_B *(1- y_B) = 0.062 * (1- 0.016) = 0.061008 \text{ kmole/s}\]

Then

\[x_B = \frac{(L_T * 0) + [0.061008 * \left(\frac{0.016}{1-0.016}\right)] - [0.061008 * \left(\frac{0.004}{1-0.004}\right)]}{2.2} = 0 + 0.000992 - 0.000245012 X_B \]

\[= 0.00034 \]

Then

\[x_B = 0.00034 \text{ (dilute solution } X_B = x_B)\]

\[(NTU)_{oy} = \int_{y_B}^{y_T} \frac{dy}{y-y^*} = \frac{y_B - y_T}{(y - y^*)_{m}} \]

\[(y-y^*)_{m} = \frac{(y_{n} - y_{n}^*) - (y_{T} - y_{T}^*)}{(y - y^*)_{m}} = \frac{(0.016 - 40*0.00034) - (0.004 - 40*0)}{0.016 - 40*0.00034} = 0.003132184 \]

\[\ln\left(\frac{y_{n} - y_{n}^*}{y_{T} - y_{T}^*}\right) = \ln\left(\frac{0.016 - 40*0.00034}{0.004 - 40*0}\right) = 0.0000321459 \]

\[\therefore (NTU)_{oy} = \frac{0.016 - 0.004}{0.003132184} = 3.8312 \]

(b) \[Z = (HTU)_{oy} * (NTU)_{oy} \]
\[(HTU)_{oy} = \frac{Z}{(NTU)_{oy}} = 3.5/3.8312 = 0.9136 \text{ m}\]

(c) \( (HTU)_{oy} = \frac{G_m}{k_{oyas}} \)

\[\therefore k_{oy} a = \frac{G_m}{(HTU)_{oy} s} = \frac{0.062}{0.9136 \times 1.5} = 0.045245 \text{ kmole} \text{ m}^3 \text{ Sec mole fraction} \]

**Example 5:**

Acetone is being absorbed by water in a packed tower having a cross-sectional area of 0.186 m² at 293 k and 101.3 kPa. The inlet air contains 2.6 mol% acetone and the outlet 0.5 mol%. The gas flow rate is 13.65 kmole air inlet/ hr. The pure water inlet flow rate is 45.36 kmole/ hr. The film coefficients for the given conditions in the tower are:

\[k_{y} a = 3.78 \times 10^{-2} \frac{\text{kmole}}{\text{Sec.m}^3 \text{packing.mole fraction}}\]

\[k_{x} a = 6.16 \times 10^{-2} \frac{\text{kmole}}{\text{Sec.m}^3 \text{packing.mole fraction}}\]

The equilibrium data is given by the equation: \((y = 1.186 x)\)

Calculate the height of packing using:

(a) \(k_{y} a\)

(b) \(k_{x} a\)

Also calculate \((k_{oy} a)\) and the height of packing based on this coefficient.

**Solution:**

(a) \(Z = (HTU)_{y} \times (NTU)_{y}\)

Where:

\[(NTU)_{y} = \int_{y_i}^{y_f} \frac{dy}{y - y_i} = \frac{y_B - y_T}{(y - y_i)_m}\]

And \((y - y_i)_m = \frac{(y_B - y_B) - (y_T - y_T)}{\ln \left( \frac{y_B - y_B}{y_T - y_T} \right)}\)

Also \((HTU)_{y} = \frac{G_m}{k_{y} a}\)

Then we have to find \(x_B\) so then we can find each of \(x_iB, y_iB, x_iT,\) and \(y_iT\)

**[A] M. B.**

\[L' \times x_T + G' \times y_B = L' \times x_B + G' \times y_T \text{ (Dilute solution)}\]

\[L' = L_T = 45.31 \text{ kmole/hr} \ (x_T = 0)\]

\[G' = 13.65 \text{ kmole/hr} \ (\text{given in data})\]

Then:

\[x_B = \frac{(0 \times 45.36) + (0.026 \times 13.65) - (0.005 \times 13.65)}{45.36} = 0.00632\]
Now to find the interface composition:

1- Plot the equilibrium data and the operating line as shown in the figure.

2- Find the slope of line $P_1M_1$

$$\text{slop} = \frac{-k_xa}{k_ya} \frac{(1-x_B)}{(1-y_B)} = \frac{-6.16 \times 10^{-2}}{3.78 \times 10^{-2}} \frac{(1-0.00632)}{(1-0.026)} = -1.5974$$

3- Draw the line $P_1M_1$ of slope -1.5974, then read $x_{iB}$, $y_{iB}$

$x_{iB} = 0.013$  ,  $y_{iB} = 0.0154$

4- Find the slope of line $P_2M_2$

$$\text{slop} = \frac{-k_xa}{k_ya} \frac{(1-x_T)}{(1-y_T)} = \frac{-6.16 \times 10^{-2}}{3.78 \times 10^{-2}} \frac{(1-0)}{(1-0.005)} = -1.6215$$

5- Draw the line $P_1M_1$ of slope -1.6215, then read $x_{iT}$, $y_{iT}$

$x_{iT} = 0.00186$  ,  $y_{iT} = 0.002$

6- Calculate $(NTU)_y$

$$(NTU)_y = \int_{y_i}^{y_f} \frac{dy}{y-y_i} = \frac{y_f-y_i}{(y-y_i)_m}$$
\[(y - y_i)_m = \frac{(y_B - y_B_i) - (y_T - y_T_i)}{\ln \left(\frac{y_B - y_B_i}{y_T - y_T_i}\right)} = \frac{(0.026 - 0.0154) - (0.005 - 0.002)}{0.026 - 0.0154} = 0.0068\]

\[(NTU)_y = \frac{y_B - y_T}{(y - y_i)_m} = \frac{0.026 - 0.005}{0.0068} = 3.08\]

7- Calculate \((HTU)_y\)

\[(HTU)_y = \frac{G_m}{k_yas}\]

\[G_m = \frac{G_T + G_B}{2}\]

\[G_B = \frac{G}{1 - y_B} = \frac{13.65}{1 - 0.026} = 14.0144\text{ kmole/hr}\]

\[G_T = \frac{G}{1 - y_T} = \frac{13.65}{1 - 0.005} = 13.72\text{ kmole/hr}\]

\[G_m = \frac{14.0144 + 13.72}{2} = 13.866\text{ kmole/hr} = 0.00385\text{ kmole/Sec}\]

\[\therefore (HTU)_y = \frac{0.00385}{3.78 \times 10^{-2} \times 0.186} = 0.5476\text{ m}\]

Then

\[Z = 3.08 \times 0.5476 = 1.686\text{ m}\]

(b) \(Z = (HTU)_x \times (NTU)_x\)

Repeat the same steps in (a) from step 1 to step 5, then

6- \((NTU)_x = \int_{x_T}^{x_i} \frac{x_B - x_T}{x_T - x_i - x} \, dx = \frac{x_B - x_T}{(x_i - x)_m}\]

\[x_B - x_T = \frac{(x_iB - x_B) - (x_iT - x_T)}{ln((x_iB - x_B)/(x_iT - x_T))} = \frac{(0.013 - 0.00632) - (0.00186 - 0)}{ln((0.013 - 0.00632)/(0.00186 - 0))} = 0.00377\]

\[(NTU)_x = \frac{(0.00632 - 0)}{0.00377} = 1.6764\]

\[(HTU)_x = \frac{L_m}{k_xas}\]

\[L_m = \frac{L_B + L_T}{2}\]

\[L_T = L' \cdot (1 - x_T) \rightarrow L' = L_T = 45.36\text{ kmole/hr} (x_T = 0,\ pure\ water)\]

\[L_B = \frac{L}{1 - x_B} = \frac{45.36}{1 - 0.00632} = 45.38864\text{ kmole/hr}\]

\[\therefore L_m = \frac{45.36 + 45.38864}{2} = 45.37432\text{ kmole/hr} = 0.012604\text{ kmole/Sec}\]
\[(HTU)_x = \frac{0.012604}{6.16 \times 10^{-2} \times 0.186} = 1.1 \text{ m}\]
\[Z = 1.1 \times 1.6764 = 1.844 \text{ m}\]

B- for concentrated mixtures

For absorption of concentrated solutions (that is the mole % of the gas feed and/or liquid exceed 10%), which means that the operating line will be curved, therefore will be called operating curve, also the equilibrium data will be presented as curve, because the film coefficient of mass transfer will vary with flow and concentration. Therefore, the height of column will be calculated as follow:

As done before for the dilute solution, M.B. for the interval height of (dZ):
\[d(G_y) = (d(L_x) = N_A \cdot A = \frac{N_A}{A}\]

Then
\[d(G_y) = k_y a (y - y_i) s \text{ d}Z\]
Or
\[= k_{oy} a (y - y^*) s \text{ d}Z\]

Since (G) varies with concentration throughout the column, so we substitute G by \(\frac{G^*}{1-y}\)
where \((G^*)\) is constant, therefore
\[d(G_y) = G^* d(\frac{dy}{1-y}) = G^* \frac{dy}{(1-y)^2} = k_y a (y - y_i) s \text{ d}Z\]

\[dZ = \frac{G^* dy}{s * k_y a (1-y)^2 (y - y_i)}\]

Ω \(k_y a = \frac{k_{oy} a}{y_{im}} \) (\(y_{im} \neq 1\) concentrated system)

Then
\[Z = \frac{G^*}{s} \int_{y_T}^{y_B} \frac{dy}{k_y a (1-y)^2 (y - y_i)}\]

As done above the following can be driven:
\[ Z = \frac{G^y B}{s} \int \frac{k_{oy} a}{y_m (1 - y)^2 (y - y^*)} \, dy \]

Or

\[ Z = \frac{L^x B}{s} \int \frac{k_{ox} a}{x_m (1 - x)^2 (x - x^*)} \, dx \]

All the above design equations cannot be solved analytically and must be solved by graphical integration as the following steps:

1- Draw the operating curve by using the following equation:

\[
\left( \frac{y_{n+1}}{1 - y_{n+1}} \right) = \frac{L}{G} \left( \frac{x_n}{1 - x_n} \right) + \left( \frac{y_T}{1 - y_T} \right) - \frac{L}{G} \left( \frac{x_T}{1 - x_T} \right)
\]

By assuming \( x_n \) and then find \( y_{n+1} \), plot \( (y_{n+1} \text{ vs. } x_n) \).

2- Draw the equilibrium data (given).

3- The values of \( (k_{x} a) \) & \( (k_{y} a) \) are obtained from empirical equations (will be given to you), where the film coefficient are functions of \( (G^n_y) \) \( \frac{Kgm \text{ total gas}}{m^2 * \text{Sec}} \) & \( (L^n_x) \) \( \frac{Kgm \text{ total liquid}}{m^2 * \text{Sec}} \) where \( (n & m) \) in the range of \( (0.2 – 0.8) \).

\( G_y, L_x \) will be calculated for different values of \( y \) & \( x \) using that were found by the operating equation. So, for different values of \( y, x \) in the tower convert the value of \( G \) & \( L \) to \( G_y, L_x \) as follow:

\[
G_y = G^* \text{Mwt of inert gas (carrier)} + G^* \text{Mwt absorbed gas (mass flow rate of carrier gas) + mass flow rate of absorbed gas at any section in the column}
\]
\[ \text{mass flow rate of carrier liquid} + \text{mass flow rate of absorbed gas at any section in the column} \]

Then the value of \((k_x a)\) & \((k_y a)\) are calculated as mentioned before using the empirical equation for each value of \(G_y\) & \(L_x\) which means calculate \((k_x a)\) & \((k_y a)\) for each \(y\) & \(x\).

4- Starting with tower bottom composition \(P_1 (y_B, x_B)\), the interface composition \((y_iB, x_iB)\) is determined by plotting line \(P_1M_1\) with a slope calculated by:

\[
\text{Slop} = \frac{k_x a}{k_y a} \times \frac{\text{im}}{\text{im}}
\]

Where:

\[ x_{im} = \frac{(1-x_B)-(1-x_{iB})}{\ln \left(\frac{1-x_B}{1-x_{iB}}\right)} \]

\[ y_{im} = \frac{(1-y_B)-(1-y_{iB})}{\ln \left(\frac{1-y_B}{1-y_{iB}}\right)} \]

Starting with \(x_{im} = 1 - x_B\) & \(y_{im} = 1 - y_B\) then, the slope of the line \(P_1M_1\) is calculated by trial and error.

5- The second point taken is \(P_2 (y_T, x_T)\) and determine the slope of line \(P_2M_2\) using the same procedure done in step 4 by using \(x_{im} = 1 - x_T\) & \(y_{im} = 1 - y_T\) as the starting point. Repeating this technique for several intermediate points in the tower to find the interface composition for each point.

6- Set up the following table from the collected data:

<table>
<thead>
<tr>
<th>(x)</th>
<th>(y)</th>
<th>(G_y)</th>
<th>(L_x)</th>
<th>(k_x a)</th>
<th>(k_y a)</th>
<th>(x_i)</th>
<th>(y_i)</th>
<th>(x_{im})</th>
<th>(y_{im})</th>
<th>((1-y)^2)</th>
<th>((y-y_i))</th>
<th>(F(y))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x_B)</td>
<td>(y_B)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(x_1)</td>
<td>(y_1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(x_2)</td>
<td>(y_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(x_3)</td>
<td>(y_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(x_T)</td>
<td>(y_T)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Where:
\[ f(y) = \frac{1}{k_y a \left(1-y \right)^2 (y - y_1)} \]

7-
8- Plot \( f(y) \) vs. \( (y) \) and then calculate the area under the curve starting from \( y_B \) to \( y_T \).

To calculate the area under the curve. There are two methods:
(a) By counting the squares formed and multiply the number of squares by the area of each square as shown below.

(b) Using Simpson's rule:
\[
\text{Area} = \frac{h}{3} \left[ f(y_0) + f(y_n) + 4(f(y_1) + f(y_3) + f(y_5) + \ldots + f(y_{2n+1})) + 2(f(y_2) + f(y_4) + f(y_6) + \ldots + f(y_{2n})) \right]
\]

As shown below.
Absorption with chemical reaction (chemisorption)

Some processes involve chemical reaction of gas (A) with one component in the liquid phase (B). Absorption with chemical reaction enlarges the liquid capacity and increase the absorption rate. In the following some absorption processes involve chemical reaction:

<table>
<thead>
<tr>
<th>Solute gas (A)</th>
<th>Liquid (B) reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>Carbonates, hydroxides, Ethanol amines</td>
</tr>
<tr>
<td>NO₂</td>
<td>H₂O</td>
</tr>
<tr>
<td>CO</td>
<td>Cuprous, ammonium chloride</td>
</tr>
<tr>
<td>SO₂</td>
<td>Ca(OH)₂, KOH</td>
</tr>
<tr>
<td>Cl₂</td>
<td>H₂O, FeCl₂</td>
</tr>
<tr>
<td>H₂S</td>
<td>Ethanol amines, Fe(OH)₂</td>
</tr>
<tr>
<td>SO₃</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>NO</td>
<td>FeSO₄, Ca(OH)=, H₂SO₄</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>KOH</td>
</tr>
</tbody>
</table>

**Mechanism of chemical absorption:**
The condition in the gas phase is the same as for physical absorption, but in the liquid phase there is liquid film followed by reaction zone. To understand the mechanism of chemisorption, there are some assumptions to be considered:

1- Irreversible, fast reaction (preferred first order reaction).
2- Ideal film model.
3- Gas (A) only absorbed by component (B) in liquid phase (stagnant).

Assume the reaction is:

\[ nA + mB \rightarrow AB \]

Where: AB is non-volatile liquid. See the below figure
Based on this model, Van Krevelen & Hoftijzer derived the chemical acceleration factor or (Enhancement factor E):

$$E = \frac{H_a[1-(E-1)Z]^{0.5}}{\tanh[H_a\{1-(E-1)Z\}^{0.5}]}$$

Where:

$$H_a: \text{Hatta number} = \left(\frac{2}{n+1}\right)K_{AB}C_B^{m}C_{Ai}^{n-1}D_A\frac{1}{k_L}$$

$$Z = \frac{m}{n}D_A^{C_B}\frac{A_i}{D_B^{C_B}}$$

(Z is a parameter)

Where:

$$\frac{m}{n}: \text{Stochiometric constant ratio, (m) moles of B react with (n) moles of A.}$$

$$K_{AB}: \text{Chemical reaction rate constant (m}^3/\text{s} \times \text{kmole)}$$

$$C_B: \text{Concentration of B in the liquid bulk (kmole/m}^3)$$

$$C_{Ai}: \text{Concentration of A at the interface (kmole/m}^3)$$

$$D_A: \text{Diffusivity of A in liquid (m}^2/\text{s)}$$

$$D_B: \text{Diffusivity of B in liquid (m}^2/\text{s)}$$

$$k_L: \text{Liquid phase mass transfer coefficient by physical absorption (m/s)}$$

This relationship is shown in Log-Log plotting presented in vol. 2 of Chemical engineering by J. M. Coulson & J. F. Richardson (fig. 12.12) page 549.
Let us consider the reaction model equation of the form:
\[ \frac{dC_A}{dt} = K_{AB} C^n_A C^m_B \]

For first order reaction \( n = m = 1 \), then:
\[ H_A = \frac{(K_{AB} C BD_A)^{0.5}}{K_c} \]

Same procedure as for physical absorption in the gas phase, but in the liquid phase \( E \) has the effect of reaction, then

Slop of \( PM = \tan \alpha = \frac{y_i - y}{x - x_i} = \frac{k_x}{k_y} \left( \frac{E}{y_{im}} \right) \)

And
\[ \frac{1}{k_{oy}} = \frac{1}{k_y} + \frac{m}{Ek_x} \]

Or
\[ \frac{1}{k_{ox}} = \frac{1}{m'' k_y} + \frac{1}{E' k_x} \]

Or
\[ \frac{1}{k_{ox}''} = \frac{1}{m''' k_y''} + \frac{1}{E'' k_x''} \]

In the packed tower, shown below, the gas stream containing component A with mole flow rate of \( G \) kmole/hr & liquid stream flow rate \( L \) kmole/hr of concentration \( x_{B0} \):

**Component M. B.**

\[ G \frac{y}{1-y} L x_B = L x_B + G \frac{y_1}{1-y_1} \]

\[ \frac{y}{1-y} = \frac{L x_B}{G} + \frac{y_1}{1-y_1} - \frac{L x_B}{G} \]

(Equation of operating line assuming \( L \) is constant because when comparing the moles of the reactant component to the total moles we will found that it is small (the moles of B is large), beside that the liquid phase will gain the moles of the product which will replace the losses in A.

The height of packing is calculated by the equation:
\[ Z = \frac{G y_n}{k_y as} \int_{y_1}^{y_{im}} \frac{y_{im} dy}{(1-y)^2 (y-y_i)} \]
Note:
The equilibrium curve is \( y = f(x_A) \)
While the operating curve is \( y = g(x_B) \)

**Example 6:**
A tower packed with 25.4 mm (1") ceramic Rasching rings is to be designed to absorb SO\(_2\) from air using pure water at 293 K and 101.3 kPa absolute pressure. The entering gas contains 20 mol% SO\(_2\) and that leaving 2 mol%. The inert air flow at 6.53x10\(^{-4}\) kmole/air/s and the inert water flow is 0.042 kmole water/s. The tower cross-sectional area is 0.0929 m\(^2\). For dilute SO\(_2\), the film mass transfer coefficients at 293 K are given by the following equations:

\[
k_y a = 0.0594 \times G_y^{0.7} \times L_x^{0.25} \text{ kmole/s m}^3 \text{ mole fraction}
\]

\[
k_x a = 0.152 \times L_x^{0.82} \text{ kmole/s m}^3 \text{ mole fraction}
\]

Where:
\(G_y\) is: kg total gas flow rate /m\(^2\) s
\(L_x\) is: kg total liquid flow rate /m\(^2\) s

Calculate the tower height, given the equilibrium data for SO\(_2\)/air-water system at 293 K and 101.3 kPa as follow:

<table>
<thead>
<tr>
<th>(x_A) mole fraction SO(_2) in liquid</th>
<th>(Y_A^*) mole fraction SO(_2) in gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000562</td>
<td>0.000658</td>
</tr>
<tr>
<td>0.0001403</td>
<td>0.000158</td>
</tr>
<tr>
<td>0.0002800</td>
<td>0.004210</td>
</tr>
<tr>
<td>0.0004220</td>
<td>0.007630</td>
</tr>
<tr>
<td>0.0005640</td>
<td>0.011200</td>
</tr>
<tr>
<td>0.0008420</td>
<td>0.018550</td>
</tr>
<tr>
<td>0.0019650</td>
<td>0.051300</td>
</tr>
<tr>
<td>0.004200</td>
<td>0.12100</td>
</tr>
<tr>
<td>0.006980</td>
<td>0.21200</td>
</tr>
</tbody>
</table>

**Solution:**

\[Z = \frac{G \int_s^y \frac{k_y a}{y_y} (1-y)^2 (y-y_i) \ dy}{s}
\]

**Step one:**
From the given data, plot the equilibrium data.
\(G' = 6.53 \times 10^{-4}\) kmole/s
\(L' = 0.0042\) kmole/s
\(y_B = 0.2\)
\[ y_T = 0.02 \]
\[ x_T = 0 \]

Make material balance to calculate \( x_B \)

\[
\frac{y_B}{1-y_B} = \frac{L}{G} \left( \frac{x_B}{1-x_B} - \frac{x_T}{1-x_T} \right) + \frac{y_T}{1-y_T} \]

\[
\frac{0.2}{1-0.2} = 0.042 \left( \frac{x_B}{1-x_B} - \frac{0}{1-0} \right) + \frac{0.02}{1-0.02} \]

Then: \( x_B = 0.00355 \)

**Step two:**

Now the operating equation can be written as:

\[
\frac{y_{n+1}}{1-y_{n+1}} = 0.042 \left( \frac{x_n}{1-x_n} - \frac{0}{1-0} \right) + \frac{0.02}{1-0.02} \]

Now plot the operating line by assuming \( y_{n+1} \) to find \( x_n \) starting from \( y_T \) to \( y_B \), the following data are obtained:

<table>
<thead>
<tr>
<th>( X_n )</th>
<th>( Y_{n+1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.02</td>
</tr>
<tr>
<td>0.000332</td>
<td>0.04</td>
</tr>
<tr>
<td>0.000855</td>
<td>0.07</td>
</tr>
<tr>
<td>0.00207</td>
<td>0.13</td>
</tr>
<tr>
<td>0.002631</td>
<td>0.16</td>
</tr>
<tr>
<td>0.00356</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Step three:**

By using the equations of mass flow calculate \( G_y, L_x \) for each \( y, x \) as shown

\[ G_y = G \frac{29}{1-y} \]

For example, use \( y = 0.2 \), whereas \( x = 0.00356 \)

Therefore:

\[ G_y = [(0.000653 \times 29) + 0.000653 \times \frac{0.2}{1-0.2}] / 0.0929 = 0.3164 \text{ kg/m}^2\text{ sec} \]

\[ L_x = L \frac{x}{1-x} \]

\[ L_x = (0.042 \times 18) + 0.042 \times \frac{0.00356}{1-0.00356} \times 64 / 0.0929 = 8.241 \text{ kg/m}^2\text{ sec} \]

**Step four:**

Now we have to calculate \( k_{y}a \) and \( k_{x}a \) for each value of \( G_y, L_x \) estimated in above using the following equations:

\[ k_{y}a = 0.0594 \times G_y^{0.7} \times L_x^{0.25} \text{ kmole/s m}^3 \text{ mole fraction} \]

\[ k_{y}a = 0.0594 \times (0.3164)^{0.7} \times (8.241)^{0.25} = 0.04496 \text{ kmole/s m}^3 \text{ mole fraction} \]
\[ k_x \alpha = 0.152 \times L_x^{0.82} \text{ kmole/s m}^3 \text{ mole fraction} \]
\[ k_x \alpha = 0.152 \times (8.241)^{0.82} = 0.857 \text{ kmole/s m}^3 \text{ mole fraction} \]

Next we have to calculate the interfacial composition \( y_i, x_i \) for each \( y, x \) estimated above using the technique explained in the first chapter using trial and error.

The first point to be considered is \( y_T = 0.02, x_T = 0 \):

The first trial

Assume \( x_{im} = 1 - x_T = 1 - 0.00355 = 0.99645 \)

And \( y_{im} = 1 - y_B = 1 - 0.2 = 0.8 \)

\[
\text{Slop} = -\frac{k_x \alpha}{y_{im}} = -\frac{0.857/0.99645}{0.04496/0.8} = -15.3
\]

Plotting this on \( y - x \) diagram we get \( y_i = 0.1688, x_i = 0.00566 \)

Now, calculate the new \( y_{im}, x_{im} \) which will equal to 0.816, 0.996 respectively, calculate the value of the new slop:

\[
\text{Slop} = -\frac{k_x \alpha}{y_{im}} = -\frac{0.857/0.995}{0.04496/0.816} = -15.6
\]

As you can see the new value of the slop is different from the first one, so, repeat the trials until you find a better results of \( y_i, x_i \).

Repeat steps (3 to 5) for each value of \((y, x)\) found from the operating curve equation.

**Step six:**

Calculate the height of the tower:

\[
Z = \int_{y_B}^{y_T} \frac{G \, y_B}{y_T \, k_y \alpha \, (1 - y)^2 (y - y_i)} \, dy
\]

All the results of calculations are represented in the following table, and by using graphical integration between \( y = 0.2, y = 0.02 \) to get height of the tower required, and that was equal to 1.588.
<table>
<thead>
<tr>
<th>y</th>
<th>X</th>
<th>G_y</th>
<th>L_x</th>
<th>k_xa</th>
<th>k_ya</th>
<th>y_i</th>
<th>x_i</th>
<th>(1-y)^2</th>
<th>y_im</th>
<th>y-y_i</th>
<th>( \frac{G^-}{k_{asy}} )</th>
<th>( \frac{y_{ym}}{(1-y)^2(y-y_i)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0</td>
<td>0.213</td>
<td>8.138</td>
<td>0.848</td>
<td>0.03398</td>
<td>0.009</td>
<td>0.00046</td>
<td>0.96</td>
<td>0.985</td>
<td>0.011</td>
<td></td>
<td>19.295</td>
</tr>
<tr>
<td>0.04</td>
<td>0.000335</td>
<td>0.2226</td>
<td>8.147</td>
<td>0.849</td>
<td>0.03504</td>
<td>0.0235</td>
<td>0.00103</td>
<td>0.9216</td>
<td>0.968</td>
<td>0.0165</td>
<td></td>
<td>12.77</td>
</tr>
<tr>
<td>0.07</td>
<td>0.000855</td>
<td>0.2378</td>
<td>8.162</td>
<td>0.85</td>
<td>0.03674</td>
<td>0.0476</td>
<td>0.00185</td>
<td>0.8649</td>
<td>0.941</td>
<td>0.0224</td>
<td></td>
<td>9.292</td>
</tr>
<tr>
<td>0.13</td>
<td>0.00201</td>
<td>0.2712</td>
<td>8.196</td>
<td>0.853</td>
<td>0.04032</td>
<td>0.1015</td>
<td>0.00355</td>
<td>0.7569</td>
<td>0.885</td>
<td>0.0285</td>
<td></td>
<td>7.131</td>
</tr>
<tr>
<td>0.16</td>
<td>0.002631</td>
<td>0.2895</td>
<td>8.214</td>
<td>0.855</td>
<td>0.04224</td>
<td>0.13</td>
<td>0.0045</td>
<td>0.7056</td>
<td>0.855</td>
<td>0.03</td>
<td></td>
<td>6.718</td>
</tr>
<tr>
<td>0.2</td>
<td>0.00355</td>
<td>0.3164</td>
<td>8.241</td>
<td>0.857</td>
<td>0.04496</td>
<td>0.1685</td>
<td>0.00565</td>
<td>0.64</td>
<td>0.816</td>
<td>0.0315</td>
<td></td>
<td>6.327</td>
</tr>
</tbody>
</table>
Example 7:
A tower packed with 25.4 mm (1") ceramic Rasching rings is to be designed to absorb SO\textsubscript{2} from air using pure water at 293 K and 101.3 kPa absolute pressure. The entering gas contains 20 mol\% SO\textsubscript{2} and that leaving 2 mol\%. The inert air flow at 6.53\times10^{-4}\text{ kmole/air/s} and the inert water flow is 0.042 kmole water/s. The tower cross-sectional area is 0.0929 m\textsuperscript{2} for dilute SO\textsubscript{2} the overall mass transfer coefficient: 
k_{OG}a =16 \text{k mole/hr m}^3\text{packing 10}^5\text{pa}
Calculate the tower height on the basis of the overall driving force that is [(NTU)\textsubscript{oy}, (HTU)\textsubscript{oy}], given the equilibrium data for SO\textsubscript{2}/air-water system at 293 K and 101.3 kPa as follow:

| x\textsubscript{A} mole fraction SO\textsubscript{2} in liquid | Y\textsubscript{*A} mole fraction SO\textsubscript{2} in gas |
|---------------------------------------------------------------|
| 0.0000562 | 0.000658 |
| 0.0001403 | 0.000158 |
| 0.0002800 | 0.004210 |
| 0.0004220 | 0.007630 |
| 0.0005640 | 0.011200 |
| 0.0008420 | 0.018550 |
| 0.0019650 | 0.051300 |
| 0.0042000 | 0.121000 |
| 0.0069800 | 0.212000 |

Solution

\[
Z = \frac{G}{k_{oy}s} \int_{y_B}^{y_T} \frac{y_md y}{(1-y)^2(y-y^*)}
\]

**Step one:** From the given data, plot the equilibrium data.
G' =6.53\times10^{-4}\text{ kmole/s} = 2.3508 \text{k mole/hr}
L' = 0.0042 kmole/s
y\textsubscript{B} = 0.2
y\textsubscript{T} = 0.02
x\textsubscript{T} = 0
Make material balance to calculate x\textsubscript{B}

\[
\frac{y_B}{1-y_B} = \frac{L}{G}(\frac{x_B}{1-x_B} - \frac{x_T}{1-x_T}) + \frac{y_T}{1-y_T}
\]

\[
0.2 = \frac{0.042}{0.000653}(\frac{x_B}{1-x_B} - \frac{0}{1-0}) + \frac{0.02}{1-0.02}
\]

Then: \(x_B = 0.00355\)

**Step two:**
Assume $x_n$, and find $y_n^*$ for each one assumed using the equilibrium curve (you use the equilibrium data given instead of assuming).

**Step three:** for each $x_n$ assumed calculate $y$ using the operating equation curve:

$$\frac{y}{1-y} = 0.042 \left( \frac{x_n}{1-x_n} - \frac{0.02}{1-0.02} \right)$$

**Step four:**

Now, calculate: $(1-y)^2, (y - y^*), y_m^*$ and then establish the following table:

<table>
<thead>
<tr>
<th>x</th>
<th>Y*</th>
<th>y</th>
<th>$(1-y)^2$</th>
<th>$Y_m^*$</th>
<th>y-y*</th>
<th>$f(y) = \frac{G \cdot y_m^<em>}{k \cdot (1-y)^2 \cdot (y^</em> - y)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000562</td>
<td>0.000658</td>
<td>0.023459</td>
<td>0.953631</td>
<td>0.987897</td>
<td>0.952973</td>
<td>1.71921642</td>
</tr>
<tr>
<td>0.0001403</td>
<td>0.000158</td>
<td>0.028592</td>
<td>0.943634</td>
<td>0.985557</td>
<td>0.943476</td>
<td>1.75076248</td>
</tr>
<tr>
<td>0.0002800</td>
<td>0.004210</td>
<td>0.037001</td>
<td>0.927368</td>
<td>0.979303</td>
<td>0.923158</td>
<td>1.80912837</td>
</tr>
<tr>
<td>0.0004220</td>
<td>0.007630</td>
<td>0.045403</td>
<td>0.911256</td>
<td>0.973362</td>
<td>0.903626</td>
<td>1.86949741</td>
</tr>
<tr>
<td>0.0005640</td>
<td>0.011200</td>
<td>0.053661</td>
<td>0.895557</td>
<td>0.967414</td>
<td>0.884357</td>
<td>1.93184301</td>
</tr>
<tr>
<td>0.0008420</td>
<td>0.018550</td>
<td>0.06943</td>
<td>0.865961</td>
<td>0.955784</td>
<td>0.847411</td>
<td>2.05990726</td>
</tr>
<tr>
<td>0.0019650</td>
<td>0.051300</td>
<td>0.128193</td>
<td>0.760047</td>
<td>0.909712</td>
<td>0.708747</td>
<td>2.67086378</td>
</tr>
<tr>
<td>0.0042000</td>
<td>0.121000</td>
<td>0.225818</td>
<td>0.599358</td>
<td>0.825482</td>
<td>0.478358</td>
<td>4.55352709</td>
</tr>
<tr>
<td>0.0069800</td>
<td>0.212000</td>
<td>0.320886</td>
<td>0.461196</td>
<td>0.732208</td>
<td>0.249196</td>
<td>10.0760174</td>
</tr>
</tbody>
</table>

**Step four:**

Plot $f(y)$ vs. $y$ and then calculate the area under the curve.

$Z = \text{Area under the curve} = m$
SUMMARY
1. A liquid can be used to selectively absorb one or more components from a gas mixture. A gas can be used to selectively desorb or strip one or more components from a liquid mixture.
2. The fraction of a component that can be absorbed or stripped in a countercurrent depends on the number of equilibrium stages and the absorption factor.
3. Absorption and stripping are most commonly conducted in trayed towers equipped with sieve or valve trays, or in towers packed with random or structured packing.
4. Absorbers are most effectively operated at high pressure and low temperature. The reverse is true for stripping. However, high costs of gas compression, refrigeration. and vacuum often preclude operation at the most thermodynamically favorable conditions.
5. For a given gas flow rate and composition, a desired degree of absorption of one or more components, a choice of absorbent, and an operating temperature and pressure, there is a minimum absorbent flow rate, that corresponds to the use of an infinite number of equilibrium stages. For the use of a finite and reasonable number of stages, an absorbent rate of 1.5 times the minimum is typical. A similar criterion, holds for a stripper.
6. The number of equilibrium stages required for a selected absorbent or stripping agent flow rate for the absorption or stripping of a dilute solution can be determined from the equilibrium line, and an operating line, using graphical, algebraic, or numerical methods. Graphical methods, offer considerable visual insight into stage-by-stage changes in compositions of the gas and liquid streams.
7. Packed column height can be estimated using the HTU/NTU concepts, with the latter having a more fundamental theoretical basis in the two-film theory of mass transfer.
8. One significant advantage of a packed column is its relatively low pressure drop per unit of packed height, as compared to a trayed tow
Chapter Four
Distillation

In distillation (fractionation), a feed mixture of two or more component is separated into two or more products, including, and often limited to an overhead distillate and a bottoms, whose compositions differ from that of the feed. Most often, the feed is a liquid or vapor – liquid mixture. The bottoms products is almost always a liquid, but the distillate may be a liquid or a vapor or both. The separation requires that (1) a second phase be formed so that both liquid and vapor phases are present and can contact each other on each stage within a separation column, (2) the components have different volatilities so that they will partition between the two phases to different extents, and (3) the two phases can be separated by gravity or other mechanical means. Distillation differs from absorption and stripping in that the second phase is created by thermal means (vaporization and condensation) rather than by the introduction of a second phase that usually contains an additional component or component not present in the feed mixture. The word distillation is derived from Latin word destillare, which means dripping or trickling down. By at least the sixteenth century, it was known that the extent of separation could be improved by providing multiple vapor-liquid contacts (stages) in a so-called Rectificatorium. The term rectification is derived from the Latin words recte facere, meaning to improve. Modern distillation derives its ability to produce almost pure products from the use of multistage contacting.

A- Distillation of binary mixtures

Binary Mixture: mixture contains only two components differ in boiling point.

Equipment and Design Consideration

Industrial distillation operations are most commonly conducted in trayed towers, but packed columns are finding increasing use. Occasionally, distillation columns contain both trays and packing. Types of trays and packing are identical to those used for absorption and stripping.

A schematic diagram for the distillation column for binary mixture is presented below.
Factors that influence the design or analysis of a binary distillation operation include:

1. Feed flow rate, composition, temperature, pressure, and phase condition.
2. Desired degree of separation between two components.
3. Operating pressure (which must be below the critical pressure of the mixture).
4. Vapor pressure drop, particularly for vacuum operation.
5. Minimum reflux ratio and actual reflux ratio.
6. Minimum number of equilibrium stages and actual number of equilibrium stages (stage efficiency).
7. Type of condenser (total, partial, or mixed).
8. Degree of sub-cooling, if any, of the liquid reflux.
9. Type of re-boiler (partial or total).
10. Type of contacting (trays or packing or both).
11. Height of the column.
12. Feed entry stage.
13. Diameter of the column.
14. Column internals.

**Equilibrium Relationships**

Experimental data have been published for several thousand binary and many multi-component systems. The book by Chu *et al* (1956) and Hala *et al* (1968, 1973) cover most of the published experimental data.

Otherwise the equilibrium relationship between $y_A$ and $x_A$ can be obtained by two methods either in terms of the relative volatility ($\alpha_{AB}$), or using the vapor pressure.

A- The volatility ($\alpha$) of any component can be defined as the ratio of the partial pressure to the mole fraction in the liquid phase of that component, so

$$\alpha_A = \frac{P_A}{x_A} \quad \text{and} \quad \alpha_B = \frac{P_B}{x_B}$$

Where:

$$\alpha_{AB} = \frac{\alpha_A}{\alpha_B} = \frac{P^0_A}{P^0_B}$$

Two methods for estimating the relative volatility ($\alpha_{AB}$):

1- Using $K$- value method:

$K_i$: is the equilibrium constant which is also called k-value and it is a function of temperature and pressure for certain component. Some of these values are reported in fig. 11.38 in the chemical engineering vol. 2 page 459 or fig. 8.3 in chemical engineering vol. 6 figs. 8.3a & 8.3b page 268 & 269. Where:

$$y_A = K^* x_A \quad \text{, also} \quad k_A = \frac{P^0_A}{p}$$

Then
\[ a_{AB} = \frac{K_A}{K_B} = \frac{\left( \frac{y_A}{x_A} \right)}{\left( \frac{y_B}{x_B} \right)} = \frac{\left( \frac{y_A}{x_A} \right)}{\left( \frac{1-y_A}{1-x_A} \right)} = \frac{p_A^0}{p_B^0} \]

2- Another method to estimate the relative volatility is by making use of Dalton's law, Raoult's law, as shown below:

\[ P_T = \sum P_i \] and then \[ P_A = y_A * P_T \]  (Dalton's law)

\[ P_A = p_A^0 * x_A \]  (Raoult's law)

\[ y_A = \frac{p_A^0 * x_A}{P_T} \] and \[ y_B = \frac{P_B^0 * x_B}{P_T} \]

\[ \alpha_{AB} = \frac{p_A^0}{P_B^0} = \frac{\left( \frac{y_A}{x_A} \right)}{\left( \frac{y_B}{x_B} \right)} = \frac{\left( \frac{y_A}{x_A} \right)}{\left( \frac{1-y_A}{1-x_A} \right)} \]

Now to make use of the relative volatility \((a_{AB})\) value estimated by both methods:

\[ \Theta a_{AB} = \frac{\alpha_A}{\alpha_B} = \frac{\frac{p_A}{x_A}}{\frac{p_B}{x_B}} = \frac{p_A^0}{p_B^0} \]

Using Dalton's law to substitute \(P_i (y_i * P_T)\), then

\[ \alpha_{AB} = \frac{y_A * x_B}{y_B * x_A} = \frac{y_A (1-x_A)}{x_A (1-y_A)} \]

Rewrite the above equation either in terms of \(y_A\)

\[ y_A = \frac{\alpha_{AB} * x_A}{1+(\alpha_{AB} - 1)x_A} \] ...1

\[ x_A = \frac{y_A}{\alpha_{AB} - y_A (\alpha_{AB} - 1)} \] ...2

Equations (1) & (2) are used also to calculate the equilibrium composition of a binary system from the vapor pressure or volatility.

B- Using the vapor pressure, where by making use of Dalton's law and Raoult's law as follow:

\[ \Theta y_A = \frac{p_A^0 * x_A}{P_T} \] and \[ y_B = \frac{P_B^0 * x_B}{P_T} \]

And \[ \Theta y_A + y_B = 1 \]

Then
\[
\frac{p_A^0 \cdot x_A}{p_T} + \frac{p_B^0 \cdot x_B}{p_T} = 1
\]

\[
\therefore x_A = \frac{p_T - p_A^0}{p_A^0 - p_B^0} \quad \ldots 3
\]

So, from equation (3) we can calculate the composition of A in liquid phase if the vapor pressure of components A, B are known. Also the composition of A & B in vapor phase could be calculated from the following equation:

\[
y_A = \frac{p_A^0 \cdot x_A}{p_T} \quad \ldots 4
\]

**Note:** the vapor pressure can be estimated using Antoine equation:

\[
\ln p^o = A - \frac{B}{C+T}
\]

where (A,B and C are constants which can be found from references).

If \( \alpha_{AB} = 1 \) then the separation can not be achieved by distillation.

And if \( \alpha_{AB} \neq 1 \) then separation can be achieved by distillation for the two cases:

1. \( \alpha_{AB} > 1 \) that means component A is the more volatile component.
2. \( \alpha_{AB} < 1 \) that means component A is the less volatile component.

Let us first define some important terms which will be considered in this section:

**More volatile component (M. V. C.):** components of lower boiling point and it concentrate in vapor phase.

**Less volatile component (L. V. C.):** components of higher boiling point and it concentrate in liquid phase.

**Boiling point curve:**

For binary mixture the equilibrium data can be presented in T-x-y diagram as shown in below:
1- If we start we start with a mixture (A+B), where A is the more volatile component (M. V. C.) & component B is the L. V. C. and the composition of the mixture is $x_A$.

2- At a point R the mixture is all liquid at temperature $T_1$, $x_A$ mole fraction at fixed pressure.

3- Start heating the mixture, and when $T_2$ is reached, the mixture will start boiling at point N; where the composition of the first bubble $y_A$ is in equilibrium with the liquid composition $x_A$. So we will call $T_2$ the bubble point of the mixture.

4- As we continue heating, the composition of the liquid $x_A$ will move to the left of the figure, since A is redistributed between the two phase (the vapor will be rich with A).

5- At temperature $T_3$, all the mixture is vaporized and reaches the saturation condition (saturated vapor), therefore we will call $T_3$ the dew point of the mixture.

6- At temperature $T_4$, the mixture will be superheated vapor.

At each temperature from $T_2$ to $T_3$, we have a saturated vapor in which the mole fraction of component A in the liquid phase is in equilibrium with its mole fraction in the vapor phase, and then an equilibrium relation could be established as y-x diagram.

**y-x equilibrium diagram:**

In distillation it is more convenient to plot $y$ vs. $x$ as follow:

1- Draw a 45° line on the y-x plot.

2- From the boiling point diagram, or volatility relationship find $y_A$ for each value of $x_A$, the graph will be established as shown below:

---

**Example 1:**

Vapor pressures of Benzene – Toluene mixture are given in the table below. Assuming that this mixture follow Raualt's law, calculate and plot the boiling point diagram and the equilibrium composition curve. Note the total pressure is 1 atm.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$P^0_{Ben}$ (mmHg)</th>
<th>$P^0_{Tol}$ (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80.1</td>
<td>760</td>
<td>0</td>
</tr>
<tr>
<td>85</td>
<td>877</td>
<td>345</td>
</tr>
<tr>
<td>90</td>
<td>1016</td>
<td>405</td>
</tr>
<tr>
<td>100</td>
<td>1344</td>
<td>557</td>
</tr>
<tr>
<td>110</td>
<td>1748</td>
<td>743</td>
</tr>
<tr>
<td>110.6</td>
<td>1800</td>
<td>760</td>
</tr>
</tbody>
</table>
Solution:
To plot the T-y-x diagram find y, x at each temperature for component (Benzene), because it is the more volatile component since its boiling point at 1 atm (80.1 °C) is lower that of Toluene at the same pressure (110.6 °C), therefore apply equations 1, 2 to calculate \( y_A, x_A \)

\[
\begin{align*}
\therefore x_A &= \frac{p_T - p^0_B}{p^0_A - p^0_B} \\
y_A &= \frac{p^0_A * x_A}{p_T}
\end{align*}
\]

At \( T = 85 \) °C
\[
\therefore x_A = \frac{760 - 345}{877 - 345} = 0.78 \\
y_A = \frac{877 * 0.78}{760} = 0.9
\]

Repeat for all the given temperatures establish the following table:

<table>
<thead>
<tr>
<th>T °C</th>
<th>80.1</th>
<th>85</th>
<th>90</th>
<th>100</th>
<th>110</th>
<th>110.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x_A )</td>
<td>1</td>
<td>0.78</td>
<td>0.581</td>
<td>0.258</td>
<td>0.017</td>
<td>0</td>
</tr>
<tr>
<td>( y_A )</td>
<td>1</td>
<td>0.9</td>
<td>0.777</td>
<td>0.456</td>
<td>0.039</td>
<td>0</td>
</tr>
</tbody>
</table>

The following diagram is plotted according to the above data:

**How to calculate the bubble point temperature, or dew point temperature of mixture:**
For bubble point temperature calculation at fixed pressure, assume a temperature and then from literatures find \( k_i \) for each component at that temperature and pressure. Calculate \( y_i \) using the following equation:
\[ k_i = \frac{y_i}{x_i} \]

If \( \sum y_i = 1 \), then the assumption is correct.

If \( \sum y_i > 1 \) that means that the assumed temperature is larger than the bubble point, and then assumes smaller temperature for second trail.

If \( \sum y_i < 1 \) that means that the assumed temperature is lower than the bubble point, and then assumes larger temperature for second trail.

For dew point temperature calculation at fixed pressure, assume a temperature and then from literatures find \( k_i \) for each component at that temperature and pressure.

Calculate \( x_i \) using the following equation:

\[ k_i = \frac{y_i}{x_i} \]

If \( \sum x_i = 1 \), then the assumption is correct.

If \( \sum x_i > 1 \) that means that the assumed temperature is larger than the dew point, and then assumes smaller temperature for second trail.

If \( \sum x_i < 1 \) that means that the assumed temperature is lower than the bubble point, and then assumes larger temperature for second trail.
For the binary system we consider the following types of distillation:

1- Batch distillation.
2- Flash distillation.
3- Multi-stage distillation.

1- Batch Distillation

In batch separation operations, a feed mixture is charged to the equipment and one or more products are withdrawn. A familiar example is laboratory distillation, shown in Figure 1, where a liquid mixture is charged to a still pot, retort, or flask and heated to boiling. The vapor formed is continuously removed and condensed to produce a distillate.

The composition of both the initial charge and distillate change with time; there is no steady state. The still temperature increases and the relative amount of lower-boiling components in the charge decreases as distillation proceeds.

Batch operations can be used to advantage under the following circumstances:
1. The capacity of a facility is too small to permit continuous operation at a practical rate.
2. It is necessary, because of seasonal demands, to distill with one unit different feed stocks to produce different products.
3. It is desired to produce several new products with one distillation unit for evaluation by potential buyers.
4. Upstream process operations are batch wise and the composition of feed stocks for distillation vary with time or from batch to batch.
5. The feed contains solids or materials that form solids, tars, or resin that plug or foul a continuous distillation column.

A- Differential Distillation

The simplest case of batch distillation, as discussed by Lord Rayleigh, is differential distillation, which involves use of the apparatus shown in Figure 1. There is no reflux; at any instant, vapor leaving the still pot with composition $y_D$ is assumed to be in equilibrium with perfectly mixed liquid in the still. For total condensation, $y_D=x_D$.

Thus, there is only a single equilibrium stage, the still pot. This apparatus is useful for separating wide boiling mixtures. The following nomenclature is used for variables that vary with time, $t$, assuming that all compositions refer to a particular species in the multi-component mixture.

- $D =$ instantaneous distillate rate, mol/h
- $y = Y_D = X_D =$ instantaneous distillate composition, mole fraction
- $W =$ moles of liquid left in still
- $x = X_w =$ composition of liquid left in still, mole fraction
- $o =$ subscript referring to $t = 0$
For any component in the mixture:
Instantaneous rate of output = $D y_D$

Instantaneous rate of depletion in the still:

$$-\frac{d}{dt} (w^* x_w) = -w \frac{dx_w}{dt} - x_w \frac{dw}{dt}$$

The distillate rate and, therefore, the rate of depletion of the liquid in the still depend on the rate of heat input to the still. By material balance at any instant:

$$\frac{d}{dt} (w^* x_w) = w \frac{dx_w}{dt} + x_w \frac{dw}{dt} = -D y_D \quad \ldots 5$$

Multiplying by $dt$:

$$w dx_w + x_w dw = y_D (-D dt) = y_D dw \quad \ldots 6$$

Since by total balance ($-D dt = dW$) Separating variables and integrating from the initial charge condition:

$$\int_{x_{W_0}}^{x_W} \frac{dx_w}{y_D - x_w} = \int_{W_0}^{W} \frac{dw}{w} = \ln \left( \frac{W}{W_0} \right) \quad \ldots 7$$

This is the well-known Rayleigh equation, which was first applied to the separation of wide-boiling mixtures such as HCl-H$_2$O, H$_2$SO$_4$-H$_2$O, and NH$_3$-H$_2$O. Without reflux, $y_D$ and $x_w$ are in equilibrium and (equation 7) simplifies to:

$$\int_{x_0}^{x} \frac{dx}{y - x} = \ln \left( \frac{W}{W_0} \right) \quad \ldots 8$$

Equation (8) is easily integrated only when pressure is constant, temperature change in the still pot is relatively small (close-boiling mixture), and K-values are composition independent. Then $y = K x$, where K is approximately constant, and (equation 8) becomes

$$\ln \left( \frac{W}{W_0} \right) = \frac{1}{K - 1} \ln \left( \frac{x}{x_0} \right) \quad \ldots 9$$

For a binary mixture, if the relative volatility $a$ is assumed constant, substitution of (equation 1) into (equation 8), followed by integration and simplification, gives
\[
\ln \left( \frac{W_0}{W} \right) = \frac{1}{\alpha_{AB} - 1} \left[ \ln \left( \frac{x_0}{x} \right) + \alpha_{AB} \ln \left( \frac{1 - x_0}{1 - x} \right) \right] \tag{10}
\]

If the equilibrium relationship \( y = f(x) \) is in graphical or tabular form, integration of (equation 8) can be performed graphically or numerically. The final liquid remaining in the still pot is often referred to as the \textit{residue}.

The average composition of the distillate can be calculated from the following equation:
\[
\left( x_D \right)_{\text{avg}} = \left( y_D \right)_{\text{avg}} = \frac{W_0 * x_0 - W * x}{W_0 - W} \tag{11}
\]

The Rayleigh equation (equation 7) can be applied to any two components, A and B of a multi – component mixture. Thus for a binary mixture if we let
\[
M_A = W * x_{wA} \tag{12}
\]

Where: \( M_A \) is the moles of A in the still at any time.

Then
\[
\frac{dM_A}{dM_B} = \frac{y_{DA}}{y_{DB}} \tag{13}
\]

For constant \( \alpha_{AB} \)
\[
\alpha_{AB} = \frac{y_D A * x_{wB}}{y_D B * x_{wA}} \tag{14}
\]

Then equation 13 becomes
\[
\frac{dM_A}{dM_B} = \alpha_{AB} \left( \frac{x_{wA}}{x_{wB}} \right) \tag{15}
\]

Substituting equation 12 for both A and B into equation 15 gives
\[
\frac{dM_A}{dM_B} = \alpha_{AB} \left( \frac{dM_B}{dM_A} \right) \tag{16}
\]

Integration from the initial – charge condition gives
\[
\ln \left( \frac{M_A}{M_{A_0}} \right) = \alpha_{AB} * \ln \left( \frac{M_B}{M_{B_0}} \right) \tag{17}
\]

This equation is useful for determining the effect of relative volatility on the degree of separation that can be achieved by Rayleigh distillation.
Example 2
A batch still is loaded with 100 kmol of a liquid containing a binary mixture of 50 mol% benzene in toluene. As a function of time, make plots of
(a) Still temperature,
(b) Instantaneous vapor composition,
(c) Still-pot composition,
(d) Average total distillate composition.
Assume a constant boil-up rate of 10 kmol/h and a constant relative volatility of 2.41 at a pressure of 101.3 kPa (1 atm).

Equilibrium data is given as follow at 101.3 kPa:

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>105.3</th>
<th>101.5</th>
<th>98.0</th>
<th>95.1</th>
<th>92.3</th>
<th>89.7</th>
<th>87.3</th>
<th>85.0</th>
<th>82.7</th>
<th>81.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>x_{Ben}</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.7</td>
<td>0.8</td>
<td>0.9</td>
<td>0.95</td>
</tr>
<tr>
<td>y_{Ben}</td>
<td>0.208</td>
<td>0.372</td>
<td>0.507</td>
<td>0.612</td>
<td>0.713</td>
<td>0.791</td>
<td>0.857</td>
<td>0.912</td>
<td>0.959</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Solution:
Initially, W_0 = 100 kmol, x_0 = 0.5.
Solving (equation 10) for W at values of x from 0.5 in increments of 0.05, and determining corresponding values of time from t = (W_0 - W)/10, the following table is generated:

<table>
<thead>
<tr>
<th>T, hr</th>
<th>2.12</th>
<th>3.75</th>
<th>5.04</th>
<th>6.08</th>
<th>6.94</th>
<th>7.66</th>
<th>8.28</th>
<th>8.83</th>
<th>9.35</th>
</tr>
</thead>
<tbody>
<tr>
<td>W, kmole</td>
<td>78.85</td>
<td>62.51</td>
<td>49.59</td>
<td>39.16</td>
<td>30.59</td>
<td>23.38</td>
<td>17.19</td>
<td>11.69</td>
<td>6.52</td>
</tr>
<tr>
<td>x = x_W</td>
<td>0.45</td>
<td>0.4</td>
<td>0.35</td>
<td>0.3</td>
<td>0.25</td>
<td>0.2</td>
<td>0.15</td>
<td>0.1</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The instantaneous vapor composition, y, is obtained from (equation 1), which is

\[ y_A = \frac{\alpha_{AB} * x_A}{1 + (\alpha_{AB} - 1)x_A} \]  \text{...1}

For constant \( \alpha_{AB} \), Then:

\[ y_A = \frac{2.41 * x_A}{1 + 1.41 * x_A} \]

The average value of \( y_D \) or \( x_D \) over the time interval 0 to t is related to \( x \) and \( W \) at time \( t \) by combining overall component and total material balances as given in equation 11

\[ (x_D)_{avg} = (y_D)_{avg} = \frac{W_0 * x_0 - W * x}{W_0 - W} \]  \text{...11}

To obtain the temperature in the still, it is necessary to use experimental T-X-Y data for benzene - toluene at 101.3 kPa as given. The temperature and compositions as a function of time are shown in the figure below.
Example 3:
Repeat Example 2, except instead of using a constant value of 2.41 for the relative volatility use the vapor-liquid equilibrium data for benzene-toluene at 101.3 kPa, given in the data, to solve the problem graphically or numerically with (equation 8) rather than (equation 11).

Equation (8) can be solved by plotting \( \frac{1}{y - x} \) versus \( x \) with a lower limit of \( x_0 = 0.5 \).

Using the equilibrium data given for \( y \) as a function of \( x \), points for the plot in terms of benzene are as follows:

<table>
<thead>
<tr>
<th>( x )</th>
<th>0.5</th>
<th>0.4</th>
<th>0.3</th>
<th>0.2</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{y - x} )</td>
<td>4.695</td>
<td>4.717</td>
<td>4.831</td>
<td>5.814</td>
<td>9.259</td>
</tr>
</tbody>
</table>

The area under the plotted curve from \( x_0 = 0.5 \) to a given value of \( x \) is equated to \( \ln \left( \frac{W}{W_0} \right) \) and \( W \) is computed for \( W_0 = 100 \) kmol. In the region from \( x = 0.5 \) to 0.3, the value of \( 1/(y - x) \) changes only slightly. Therefore, a numerical integration by the trapezoidal rule is readily made:

For \( x = 0.4 \):

\[
\ln \left( \frac{W}{W_0} \right) = \int_{0.5}^{0.4} \frac{dx}{y - x} \approx \Delta x \left[ \frac{1}{y - x} \right] \approx (0.4 - 0.5) \left[ \frac{4.695 + 4.717}{2} \right] = -0.4706
\]

\( W/W_0 = 0.625, W = 0.625(100) = 62.5 \) kmol
For \( x = 0.3 \)

\[
\ln \left( \frac{W}{W_0} \right) = 0.3 \int_{0.5}^{y} \frac{dx}{y-x} \approx \Delta x \left[ \frac{1}{y-x} \right]_{\text{avg}} = (0.3 - 0.5) \left[ \frac{4.695 + 4.717 + 4.717 + 4.831}{4} \right] = -0.948
\]

\( W/W_0 = 0.388, \ W = 0.388(100) = 38.8 \text{kmol} \)

These two values are in good agreement with those in Example 2. A graphical integration from \( x_0 = 0.4 \) to \( x = 0.1 \) gives \( W = 10.7 \), which is approximately 10% less than the result in example 2, which uses a constant value of the relative volatility.

**Example 4:**
The charge to a simple batch still consists of an equimolar binary mixture of A and B. For values of \( \alpha_{AB} \) of 2, 5, 10, 100, and 1,000, and 50% vaporization of A, determine the percent vaporization of B and the mole fraction of B in the total distillate.

**Solution:**
For \( \alpha_{AB} = 2 \) and

\[
\left( \frac{M_A}{M_{A_0}} \right) = \left( \frac{1-0.5}{1} \right) = 0.5, \text{ (equation 17) gives}
\]

\[
\left( \frac{M_B}{M_{B_0}} \right) = \left( \frac{M_A}{M_{A_0}} \right)^{1/\alpha_{AB}} = (0.5)^{0.5} = 0.7071
\]

Percent vaporization of B = \( (1 - 0.7071) \times (100) = 29.29% \).
For 200 moles of charge, the amounts of components in the distillate are:
\[ D_A = (0.5) \times (0.5) \times (200) = 50 \text{ mol} \]
And
\[ D_B = (0.2929) \times (0.5) \times (200) = 29.29 \text{ mol} \]

Mole fraction of B in the total distillate = \( \frac{29.29}{29.29 + 50} = 0.3694 \)

Similar calculations for other values of \( \alpha_{AB} \) give the following results:

<table>
<thead>
<tr>
<th>( \alpha_{AB} )</th>
<th>% vaporization of B</th>
<th>Mole fraction B in the distillate</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>29.29</td>
<td>0.3694</td>
</tr>
<tr>
<td>5</td>
<td>12.94</td>
<td>0.2057</td>
</tr>
<tr>
<td>10</td>
<td>6.70</td>
<td>0.1182</td>
</tr>
<tr>
<td>100</td>
<td>0.69</td>
<td>0.0136</td>
</tr>
<tr>
<td>1000</td>
<td>0.07</td>
<td>0.0014</td>
</tr>
</tbody>
</table>

These results show that a sharp separation between A and B for 50% vaporization of A is only achieved if \( \alpha_{AB} = 100 \).
Furthermore, the purity achieved depends on the percent vaporization of A.
For \( \alpha_{AB} = 100 \), if 90% of A is vaporized, the mole fraction of B in the total distillate increases from 0.0136 to 0.0247. For this reason, it is common to conduct a binary
batch distillation separation of M.V.C. (only for binary light key, LK) and L.V.C. (only for binary heavy key, HK) in the following manner:
1. Produce a distillate LK cut until the limit of impurity of HK in the total distillate is reached.
2. Continue the batch distillation to produce an intermediate cut of impure LK until the limit of impurity of LK in the liquid in the still is reached.
3. Empty the HK-rich cut from the still.
4. Recycle the intermediate cut to the next still charge.
For desired purities of the LK cut and the HK cut, the fraction of intermediate cut increases as the LK-HK relative volatility decreases.

B- BINARY BATCH RECTIFICATION WITH CONSTANT REFLUX AND VARIABLE DISTILLATE COMPOSITION
To achieve a sharp separation and/or reduce the intermediate-cut fraction, a trayed or packed column, located above the still, and a means of sending reflux to the column, is provided as shown for the batch rectifier of Figure 2. For a column of a given diameter, the molar vapor boil-up rate is usually fixed at a value safely below the column flooding point. If the reflux ratio $R$ is fixed, distillate and still bottoms compositions vary with time.

The reflux ratio $R = \frac{\text{The mole flow rate of liquid recycled}}{\text{The mole of liquid withdrawn as product}} = \frac{L}{D}$

For a total condenser, negligible holdup of vapor and liquid in the column, phase equilibrium at each stage, and constant molar overflow, equation 7 still apply with $y_D = x_D$.

When the column is operated at a constant reflux ratio $R$, the concentration of the M.V.C. in the top product will continuously fall. Over a small interval of time (dt), the top product composition will fall from $x_D$ to $(x_D - dx_D)$. If in this time the amount of product is $dD$, then the material balance for the M.V.C. will be as follow:
\[ D_A = dD \left[ x_D - \frac{dx_D}{2} \right] \]

\[ D_A = x_D * dD \]

\[ X_D * dD = - d(Wx_w) \]

But

\[ dD = - dW \]

Then

\[ - x_d * dW = - (W * dx_w) - (x_w * dW) \]

\[ Wdx_w = (x_d - x_w) * dW \]

\[ \int_{w_1}^{w_2} \frac{dx}{W} = \int_{w_1}^{w_2} \frac{dx_w}{x_d - x_w} \]

\[ \ln \frac{W_1}{W_2} = \int_{x_w_{w_1}}^{x_w_{w_2}} \frac{dx_w}{x_d - x_w} \]

Or

\[ \ln \frac{W_1}{W_2} = \int_{x_w_{w_1}}^{x_w_{w_2}} \frac{dx_w}{y_d - x_w} \quad (y_D=x_D) \]

The right-hand side of this equation can be integrated by plotting \( \frac{1}{y_d - x_w} \) vs. \( x_w \). This will enable the ratio of the initial to final quantity in the still to be found for any desired change in \( x_w \), and hence the amount of distillate \( D \).

The heat to be supplied to provide the reflux will now be:

\[ Q_R = \lambda * R * D \]

**C - BINARY BATCH RECTIFICATION WITH CONSTANT DISTILLATE COMPOSITION AND VARIABLE REFLUX**

Suppose a column with \( N \) ideal plates be used to separate a binary mixture of A & B. Initially there are in the still \( S_1 \) moles of liquid with \( x_{S1} \) mole fraction of the more volatile component A. The top product is to contain a mole fraction \( x_d \) and this necessitate a reflux ration \( R_1 \). Suppose the distillation to be continued till there are \( S_2 \) moles in the still, of mole fraction \( x_{S2} \). Then, for the same number of plates the reflux ration will have been increased to \( R_2 \) in order to keep the composition of the product constant. If the amount of product obtained is \( D_b \) moles, by a material balance:

\[ S_1 * x_{S1} - S_2 * x_{S2} = D_b * x_d \]

\[ S_1 - S_2 = D_b \]

\[ \therefore S_1 * x_{S1} - (S_1 - D_b) * x_{S2} = D_b * x_d \]

\[ S_1 * x_{S1} - S_1 * x_{S2} = D_b * x_d - D_b * x_{S2} \]
\[
D_b = S_1 \left[ \frac{x_{s1} - x_{s2}}{x_d - x_{s2}} \right] = \frac{a}{b} * S_1
\]

\[
y_{n+1} = \frac{R}{R+1} * x_n + \frac{x_D}{R+1}
\]

If \( \phi \) is the intercept on the y-axis of any operating line in U.O.L. equation:
Then:
\[
\frac{x_D}{R+1} = \phi
\]
Or
\[
R = \frac{x_D}{\phi} - 1
\]

The above equations enable the final reflux ratio to be found for any desired end concentration in the still, and also give the total quantity of distillate obtained.
When comparing the operation at constant reflux ratio with that at constant product composition, we find that there is a difference in the total amount of steam used in the distillation, for a given quantity \( D_b \) of product that is the most important point to be considered.
If the reflux ratio \( R \) is assumed to be adjusted continuously to keep the top product at constant quality, then at any moment the reflux ratio is given by
\[
R = \frac{dL_b}{dD_p}
\]
Then
\[
L_p \int_{0}^{R_2} dL_p = \int_{R_1}^{R_2} RdD_p
\]
To provide reflux \( dL_b \) requires the removal of heat \( \lambda dL_b \) in the condenser; (\( \lambda \) is latent heat per mole). Thus, the heat to be supplied in the re-boiler \( Q_R \) to provide this reflux during the total distillation is given by:
\[
Q_R = \lambda * \int_{0}^{L_p} dL_p = \lambda * \int_{R_1}^{R_2} RdD_p
\]
Equations 1 and 2 can be integrated graphically if the relation between \( R \) and \( D_b \) is found.
Example 5:
A mixture of ethyl alcohol and water with 0.55 mole fraction of alcohol is distilled in batch column
to give a top product of 0.75 mole fraction of alcohol. The column has four ideal plates. The
distillation is stopped when the reflux ratio has to be increased beyond 4.
Find the amount of distillate obtained and the heat required per kmole of product, given the
following data:

<table>
<thead>
<tr>
<th>x</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>y</td>
<td>0</td>
<td>0.42</td>
<td>0.52</td>
<td>0.58</td>
<td>0.61</td>
<td>0.65</td>
<td>0.7</td>
<td>0.75</td>
<td>0.82</td>
<td>0.9</td>
<td>1.0</td>
</tr>
</tbody>
</table>

\(\lambda_{\text{aver.}} = 4000 \text{ J/kmol}\)

**Solution:**

1- Find \(\frac{x_D}{R + 1}\) for \(R = 4\)

\[\phi = \frac{0.75}{5} = 0.15\]

2- Plot operating line for the points

Point 1: \(y = x = x_D = 0.75\)
Point 2: \(y = \phi = 0.15, x = 0\)

3- Draw 4 plates starting from:
\(y = x = 0.75\), then read \(x_{s2}\)

\(x_{s2} = 0.05\)

4- Find \(D_p\) from

\[D_b = S_1 \left[ \frac{x_{s1} - x_{s2}}{x_s - x_{s2}} \right] \]

For \(S_1 = 100 \text{ kmole}\)

\[D_b = 100 \left[ \frac{0.55 - 0.05}{0.75 - 0.05} \right] = 71.4\]

To find the heat required we must solve the equation:

\[Q = \lambda \int_{R_1}^{R_2} R dD_p\]

Then we have to construct a table shows the effect of \(R\) on \(D_p\) as follow from:

\(R_1 = 0.5\) (chosen) to \(R_2 = 4\) (given)

<table>
<thead>
<tr>
<th>(R)</th>
<th>(\phi)</th>
<th>(x_{s2})</th>
<th>(D_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>0.56</td>
<td>-5.26316</td>
</tr>
<tr>
<td>0.85</td>
<td>0.405405</td>
<td>0.55</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.375</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>1.5</td>
<td>0.3</td>
<td>0.37</td>
<td>47.36842</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>0.2</td>
<td>63.63636</td>
</tr>
<tr>
<td>3</td>
<td>0.1875</td>
<td>0.075</td>
<td>70.37037</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>0.05</td>
<td>71.42857</td>
</tr>
</tbody>
</table>

**Note:** you can start from \(R = 4\) and then start to reduce its value until reaching \(x = x_{s2}\)
Now plot $D_p$ vs. $R$ and calculate the area under the curve obtained, where:

\[
\text{Area} = \int_{R_1}^{R_2} R dD_p = 96 \text{ kmole}
\]

\[
Q_R = \lambda \int_{R_1}^{R_2} R dD_p
\]

\[
Q_R = 96 \times 4000 = 384000 \text{ kJ}
\]

For producing 71.4 kmole

\[
Q_R = \frac{384000}{71.4} = 5.32 \text{ MJ}
\]
2- FLASH OR EQUILIBRIUM DISTILLATION

The simplest separation process is one in which two phases in contact are brought to physical equilibrium, followed by phase separation. If the separation factor between two species in the two phases is very large, a single contacting stage may be sufficient to achieve a desired separation between them; if not, multiple stages are required. For example, if a vapor phase is in equilibrium with a liquid phase, the separation factor is the relative volatility, $\alpha$, of a volatile component called the light key, LK, with respect to a less-volatile component called the heavy key, HK, where, $\alpha_{LK, HK} = \frac{K_{LK}}{K_{HK}}$. If the separation factor is 10000, an almost perfect separation is achieved in a single stage. If the separation factor is only 1.1, an almost perfect separation requires hundreds of stages.

For single stage, a liquid mixture is partially vaporized, then pressure is reduced. The vapor and liquid in contact reach equilibrium, then separation into vapor phase from top and liquid phase from the bottom as shown in below:

\[ F = V + S \]
\[ F*x_f = V*y + S*x \]
\[ F*x_f = V*y + (F-V)*x \]
\[ \frac{V}{F}*y = x_f - x*(1 - \frac{V}{F}) \]

Let $f_v = \frac{V}{F}$ (the molar fraction of the feed that is vaporized and withdrawn continuously)

So, $(1 - f_v)$ is the molar fraction of the feed that leaves continuously as liquid.

Then:
\[ y = \frac{x_f}{f_v} - \left(\frac{1-f_v}{f_v}\right)*x \]

This is a straight line equation of slope $-\frac{1-f_v}{f_v}$, and intersects the y-axis at $\frac{x_f}{f_v}$.

To solve the above equation for $y$, we have two unknowns, namely $x$, $f_v$, so we need another relationship to solve it. This relation is the equilibrium data, such as $(y-x)$ diagram, $(T, y-x)$ diagrams, or others like $k_i$, or $\alpha$.

We have two cases:
Case 1:
Known product composition and known feed composition
Draw the operating line between the following two points:
Point 1 is at $x = x_f$ which lies on the 45° line, while the second point is the product composition $(y, x)$ which lies on the equilibrium curve.

Calculate the slope of the operating line, which equals to $(-\frac{1-f_v}{f_v})$ and then calculate $f_v$.

Case 2:
Known product amount and known feed composition
Draw the operating line from point $(y = x = x_f)$ with a slope of $(-\frac{1-f_v}{f_v})$, then from the intersect point of the operating line with the equilibrium curve; calculate the composition of the product.
Example 6:
100 kmole/hr of a liquid mixture containing 60 mol% n-butane and 40 mol% n-hexane is subjected to an equilibrium flash distillation giving products at 250°F. 80 % of the hexane is to recovered in the liquid. Calculate the vapor flow rate and the composition of the liquid and vapor, and the required pressure.

Solution:

\[ F = 100 \text{ kmole/hr} \]

\[ x_{fb} = 0.6 \]

\[ x_{fh} = 0.4 \]

Basis: 1 hr

Hexane in feed = 0.4 * 100 = 40 kmole

Hexane in liquid = 0.8 * Hexane in feed

Hexane in liquid = 0.8 * 40 = 32 kmole

So, Hexane in vapor = 40 – 32 = 8 kmole

O.M. B.

\[ F = V + S \]

Hexane M. B.

\[ F * x_{fh} = V * y_{h} + S * x_{h} \]

\[ \Theta k_i = \frac{y_i}{x_i} \]

Then

\[ F_h = V_h + S * \frac{y_h}{k_h} * \left( \frac{V}{V} \right) \]

\[ \therefore F_h = V_h + S * \left( \frac{y_h}{k_h} * \frac{V}{V} \right) \]

\[ \therefore F_h = V_h + V_h * \left( \frac{S}{k_h * V} \right) \]

\[ V_h = \frac{F_h}{1 + \frac{S}{k_h * V}} \]

Or \[ \frac{S}{k_h * V} = \frac{F_h}{V_h} - 1 \quad \ldots 1 \]

Benzene M. B.

Repeat the same steps as above to derive the following equation:

\[ \frac{S}{k_h * V} = \frac{F_h}{V_h} - 1 \quad \ldots 2 \]

Dived equation 2 by equation one, then

\[ \frac{k_h}{k_b} = \left( \frac{F_h}{V_h} \right) - 1 \left( \frac{F_b}{V_b} \right) - 1 \quad \ldots 3 \]

Where:
$F_i = \text{molar flow rate of component (i) in feed}$

$V_i = F_i = \text{molar flow rate of component (i) in vapor}$

In equation 3, $F_h = 40$, $V_h = 8$, and $F_b = 60$

But because the pressure of the process is unknown, then we have three variables, namely ($k_h$, $k_b$, and $V_b$) in that equation, which can not be solved directly.

Then, this equation is solved by trial and error, by assuming a pressure, to find the k-values, which must be done as in the bubble point temperature calculation ($\Sigma y_i = \Sigma (k_i \times x_i) = 1$), then evaluating the correct values of $k_i$, $V_b$ can be calculated.

Assume $P_T = 10$ atm, then from k-value charts for $P_T = 10$ atm, and $T = 250^\circ$F:

$k_h = 0.48 \quad \text{and} \quad k_b = 1.87$

Solving equation (3) for $V_b$, then:

$V_b = 29.603 \text{ kmole/hr}$

$V = V_h + V_b = 8 + 29.603 = 37.603 \text{ kmole/hr}$

**Remember**

$\Sigma y_i = \Sigma (k_i \times x_i) = 1$

Then we must test find $x_h$, and $x_b$

$x_h = \frac{\text{Hexane in S}}{\text{Total S}} \quad \text{and} \quad x_b = \frac{\text{Benzene in S}}{\text{Total S}}$

$S = F - V = 100 - 37.603 = 62.397 \text{ kmole/hr}$

$x_h = \frac{32}{62.397} = 0.5128$

$x_b = 1 - 0.5128 = 0.4872$

$\Sigma y_i = (0.48 \times 0.5128) + (1.87 \times 0.4872) = 1.1572$

Which means that the assumption was not correct; we have to assume another pressure higher than the first one and let it be 11.6 atm.

At $P_T = 11.6$ atm and $T = 250^\circ$F

$k_h = 0.415 \quad \text{and} \quad k_b = 1.615$

Repeat the same calculation as in the first step, you will find that:

$V_b = 29.6 \text{ kmole/hr}, V = 37.6 \text{ kmole/hr}, S = 62.4 \text{ kmole /hr}, x_h = 0.5128205, \text{and } x_b = 0.4871795$

Then:

$\Sigma y_i = (0.415 \times 0.5128205) + (1.615 \times 0.487195) = 1$

So, the assumption was correct.

The final results are:

$S = 62.4 \text{ kmole/hr}$

$V = 37.6 \text{ kmole/hr}$

$x_b = 0.4872 \quad \text{and} \quad y_b = 1.615 \times 0.487195 = 0.787$

$x_h = 0.5128 \quad \text{and} \quad y_b = 0.415 \times 0.512805 = 0.213$
C- RECTIFICATION WITH REFLUX

It is also called fractionation (distillation) or multiple stages with reflux. On each stage there are liquid and vapor flow counter-currently, mixed and equilibrated on each stage. Therefore, the liquid and vapor leave the stage are in equilibrium.

The final vapor comes from overhead contains high concentration of the M. V. C., is condensed and portion of it removed as top product, while the remaining liquid is returned to the top tray of the column as reflux liquid.

The liquid leaving the bottom, which is less in the M. V. C. or in other words rich of the L. V. C., is withdrawn as bottom product, portion of this product is evaporated in the re-boiler and sent back to the bottom stage (or tray).

The methods of calculation of the number of stages are:

1- McCabe – Thiele Method

In 1925, McCabe and Thiele published an approximate graphical method for combining the equilibrium with the operating – line curves to estimate, for a given binary feed mixture and column operating pressure, the number of equilibrium stages and the amount of reflux required for a desired degree of separation of the feed.

The McCabe – Thiele method determine not only N, the number of equilibrium stages, but also N_{min}, R_{min}, and the optimal stage for feed entry. Following the application of the McCabe – Thiele method, energy balances are applied to estimate condenser and re-boiler heat duties.

Besides the equilibrium curve, the McCabe – Thiele method involve a 45° reference line, separate operating lines for the upper rectifying (enriching) section of the column and the lower stripping (exhausting) section of the column, and a fifth line (the q-line or feed line) for the phase or thermal condition of the feed. The most important assumptions made to apply this method are:

1- The two components have equal and constant molar enthalpies of vaporization (latent heat).
2- Component sensible enthalpy changes (C_p ∆T) and heat of mixing are negligible compared to latent heat changes.
3- The column is well insulated so that heat loss is negligible.
4- The pressure is uniform throughout the column (no pressure drop).

These assumptions are referred to as the McCabe – Thiele assumptions leading to the condition of constant molar flow rate in both sections of the column (rectifying & stripping) or we can say constant molar flow rate in the tower.

Establishing the operating line equation

Consider the following section in the distillation column

O. M. B. on a certain stage (n):

\[ V_{n+1} + L_{n-1} = V_n + L_n \]

(A) M. B. on stage (n):

\[ V_{n+1} \times y_{n+1} + L_{n-1} \times x_{n-1} = V_n \times y_n + L_n \times x_n \]

Where:

- \( V_{n+1} \): molar vapor flow rate from stage n+1, mol/hr
- \( L_n \): molar liquid flow rate from stage n, mol/hr
- \( y_{n+1} \): mole fraction of (A) in stream \( V_{n+1} \)
- \( x_n \): mole fraction of (A) in stream \( L_n \)

\( y_n \) & \( x_n \) are in equilibrium on tray n with a temperature of \( T_n \).
A- Equations for rectification (enriching) section:

**O. M. B. for the entire column:**
\[ F = D + W \]

**[A] M. B. for the entire column:**
\[ F \times x_f = D \times x_D + W \times x_w \]

**O. M. B. around the selected section:**
\[ V_{n+1} = L_n + D \]

**[A] M. B. for the selected section:**
\[ V_{n+1} \times y_{n+1} = L_n \times x_n + D \times x_D \]

Solving for \( y_{n+1} \)
\[ y_{n+1} = \frac{L_n}{V_{n+1}} \times x_n + \frac{D}{V_{n+1}} \times x_D \]

Since \( R = \text{reflux ratio} = \frac{L_n}{D} = \text{constant} \)
\[ V_{n+1} = L_n + D = D \times (R + 1) \]

Then
\[ y_{n+1} = \frac{R}{R + 1} \times x_n + \frac{x_D}{R + 1} \]

...1

The above equation (equation 1) is a straight line equation of slope \( \frac{R}{R + 1} \) & y-intercept \( \frac{x_D}{R + 1} \) at \( x=0 \).

It is called the upper operating line equation (U. O. L.). It intersects the 45° line at \( y = x = x_D \).

The theoretical number of stages is determined by starting from \( x_D \) and stepping off the first plate at \( x_1 \) and so on.

Slop of the operating line
\[ \text{Line} = \frac{R}{R + 1} \]
B- Equations for stripping section:

**O. M. B. around the selected section (stripping section):**

\[ V_{m+1} = L_m - W \]

**[A] M. B. for the selected section:**

\[ V_{m+1} \times y_{m+1} = L_m \times x_m - W \times x_w \]

Solving for \( y_{m+1} \)

\[ y_{m+1} = \frac{L_m}{V_{m+1}} \times x_m - \frac{W}{V_{m+1}} \times x_w \] \( \ldots 2 \)

The above equation (equation 2) represents the lower operating line equation (L. O. L.) of slop \( \frac{L_m}{V_{m+1}} \) and it intersects the 45° line (that is \( y = x \)) at \( x = x_w \). And at \( x = 0 \) it intersects the y-axis at \( y = \frac{-W \times x_w}{V_{m+1}} \)

![Graph](image)

C- Effect of feed condition:

The condition of feed \( F \) entering the tower determines the relation between \( V_m \) and \( V_n \) also \( L_m \) and \( L_n \), such as partially vaporized feed. So we represent the condition of feed by \( q \) where:

\[ q = \frac{\text{Heat needed to vaporize one mole of feed at entering condition}}{\text{Molal latent heat of vaporization of feed}} \]

So we can define \( q \) as the fraction of feed that is entered as liquid.

\[ q = \frac{H_v - H_f}{H_v - H_l} \]

Where:

\( H_v \): enthalpy of feed at the dew point (saturated vapor enthalpy).

\( H_l \): enthalpy of feed at the bubble point (saturated liquid enthalpy).

\( H_f \): enthalpy of feed at its entering temperature (entrance conditions).

Therefore;

If the feed enters as saturated vapor, then \( q = 0 \)
If the feed enters as saturated liquid, then q = 1
If the feed enters as partially vaporized (mixture of vapor and liquid, then 0 < q < 1
If the feed enters as supper heated vapor, then q < 0
If the feed enters as sub-cooled liquid, then q > 1
The effect of feed entering condition is presented by a line called the (q-line), so to find the equation of the q-line:

**M. B. around feed plate**

\[ L_m = L_n + q \cdot F \]
\[ V_n = V_m + (1-q) \cdot F \]

The point of intersection of the upper operating line can be derived as follow:
Rewrite the equations of (U. O. L.) & (L. O. L.) without tray subscripts, as:
\[ V_n \cdot y = (L_n \cdot x) + (D \cdot x_D) \quad \text{...(U. O. L.)} \]
\[ V_m \cdot y = (L_m \cdot x) - (W \cdot x_w) \quad \text{...(L. O. L.)} \]
Where x & y is the point of intersection of the two operating lines, Subtract the above two equations from each other:
\[ (V_m - V_n) \cdot y = (L_m - L_n) \cdot x - (D \cdot x_D + W \cdot x_w) \]

**O. M. B. on feed plate**

\[ F + V_m + L_n = V_n + L_m \]
Rewrite
\[ V_m - V_n = L_m - L_n - F \]
And since:
\[ L_m - L_n = q \cdot F \text{ and } V_m - V_n = (q - 1) \cdot F \]
Then:
\[ (q - 1) \cdot F \cdot y = q \cdot F \cdot x - (D \cdot x_D + W \cdot x_w) \]
And since
\[ F \cdot x_f = D \cdot x_D + W \cdot x_w \quad \text{(from material balance equation)} \]
Then:
\[ (q - 1) \cdot F \cdot y = q \cdot F \cdot x - F \cdot x_f \]
So the above equation can be written for y as:
\[ y = \frac{q}{q - 1} \cdot x - \frac{x_f}{q - 1} \quad \text{....3} \]

The above equation (equation 3) is the equation of the q-line of slope \( \frac{q}{q - 1} \) & y-intercept \( \frac{-x_f}{q - 1} \)
At \( x = x_f \) y = \( x = x_f \) so this point is plotted on 45° line.
For different states of feed given above, that is if:
If the feed enters as saturated vapor, then q = 0, the slop is 0, the q-line is plotted parallel to x-axis from point y = x = \( x_f \).
If the feed enters as saturated liquid, then q = 1, the slop is \( \infty \), the q-line is plotted parallel to y-axis from point y = x = \( x_f \).
If the feed enters as partially vaporized (mixture of vapor and liquid, then 0 < q < 1, the slop is - the q-line is plotted in the second quarter of the axis.
If the feed enters as supper heated vapor, then q < 0, the slop is + the q-line is plotted in the third quarter of the axis.
If the feed enters as sub-cooled liquid, then q > 1, the slop is + the q-line is plotted in the first quarter of the axis.
Location of feed tray and the number of theoretical trays (or stages):  
Using the equilibrium data, and the equations (1, 2, and 3), the number of theoretical plates and the feed tray can be determined as follow:

1- Complete the material balance so the values of all streams and their composition are known.
2- Plot the equilibrium data.
3- Locate $x_D$, $x_F$, $x_w$ on the 45° line.
4- Plot the U. O. L. between $x_D$ on the 45° line & the point $(y = \frac{x_D}{R+1}, x = 0)$.
5- Plot the q-line from the point of $x_F$ on the 45° line with slope of $\frac{q}{q-1}$.
6- From the point of intersection of q-line with the U. O. L. draw a line between this point and the point $y=x=x_w$ on the 45° line (L. O. L.).
7- Either from $x_D$, or from $x_w$ step off the number of theoretical stages.
8- Locate the feed plate from the figure.

NOTE:
Theoretical number of stages = the number of stages from the curve – 1
Total and minimum reflux for McCabe – Thiele Method

A reflux ratio must be established before any quantitative fractionation design calculation can be made. It was pointed out that a distillation column can only produce the desired products between the limits of minimum reflux and total reflux.

A- Total reflux (minimum number of plates)

In this case, that means no top product (i.e. D = 0), so

\[ R = \frac{L_n}{D} = \infty \]

From the U. O. L. equation

\[ y_{n+1} = \frac{L_n}{V_{n+1}} x_n + \frac{D}{V_{n+1}} x_D \]

Where

\[ V_{n+1} = L_n + D \]

Then

\[ y_{n+1} = \frac{L_n}{L_n + D} x_n + \frac{D}{L_n + D} x_D \]

For D = 0, then the U. O. L. equation will be

\[ y_{n+1} = x_n \]

This is a straight line equation of slope = 1 and coincide with the 45° line.

This gives the minimum number of plates that can possibly used to obtain the desired separation. This requires infinite size of condenser, re-boiler, and tower diameter for a given feed rate.

B- Minimum reflux:

From figures before, if the efflux ratio reduced, the slope of the U. O. L. is decreased and the intersection of the U. O. L. with the q-line and with L. O. L. move far from the 45° line and closer to the equilibrium curve so the number of stages (required to achieve the desired products mole fraction \( x_D, x_w \)) increases.
When the two operating lines touch the equilibrium curve, a (Pinch point) at \( y', \) and \( x' \) occurs. Where the number of stages required becomes infinite, so the slop of the U. O. L. is as follow:

\[
\frac{R_{\min}}{R_{\min} + 1} = \frac{x_D - y}{x_D - x'}
\]

For vertical q-line (\( y', \) and \( x' \)) are substituted by (\( y_f, \) and \( x_f \)) as shown in the figure and then the above equation can be written as

\[
R_{\min} = \frac{x_D - y_f}{y_f - x_f}
\]

And for horizontal q-line \( y', \) and \( x' \) are substituted by (\( y_f, \) and \( x_c \)) as shown in the figure and then the above equation can be written as

\[
R_{\min} = \frac{x_D - x_f}{x_f - x_c}
\]

Or can be determined graphically as shown:

**NOTE:**

At minimum reflux, it requires minimum size of condenser & re-boiler.

The number of plates and minimum reflux ratio can be found analytically using Underwood & Fenske equations:

\[
N + 1 = \frac{\log(\frac{x_A}{x_D})}{\frac{x_B}{x_A}}
\]

For small variation in \( \alpha \)

\[
\alpha_{\text{aver.}} = (\alpha_D \times \alpha_w)^{\frac{1}{2}}
\]

\( \alpha_D : \) Relative volatility of the overhead product

\( \alpha_w : \) Relative volatility of the bottom product

While the minimum reflux ratio equation is:

\[
R_{\min} = \frac{1}{\frac{x_D}{x_f} - \frac{\alpha(1 - x_D)}{1 - x_f}}
\]
So if the number of plates is plotted vs. reflux ratio, the resulting curve is shown as below:

Selection of economic and operating reflux ratio:

It has been shown for many cases that:
\[ R_{\text{op.}} = (1.2 - 1.5) \, R_{\text{min.}} \]

**Heating and cooling requirements:**
Radiation from a column is small and the column itself is essentially adiabatic. So the heat effects of the entire plant are confined to the condenser & re-boiler.
Assume \( \lambda \) is constant, so is saturated steam is used at the heating media in the re-boiler, the steam required is
\[ W_S = \frac{V \cdot \lambda}{\lambda_S} \]

*W<sub>S</sub>*: mass of steam required in kg/hr.
*V*: vapor mole flow rate from re-boiler in kmole/hr.
*\( \lambda \)*: latent heat of vaporization of the mixture at the bottom of the column in kJ/kmole.
*\( \lambda_S \)*: latent heat of vaporization of the steam at P & T in kJ/kmole.
Whereas for the condenser:

\[ W_C = \frac{-V_n \lambda}{C_p (t_2 - t_1)} \]

- \( W_C \): mass flow rate of cold water required in kg/hr.
- \( V_n \): vapor mole flow rate of overhead in kmole/hr.
- \( \lambda \): latent heat of vaporization of the condensate at the top of the column in kJ/kmole.
- \( C_p \): heat capacity of water in (kJ/kg, °C).
- \( (t_2 - t_1) \): the temperature difference of outlet and inlet of cooling water (°C).

**Special cases for rectification using McCabe – Thiele Method:**

**1- Stripping column distillation:**
The feed is liquid and usually saturated liquid (at bubble point). It is introduced at the top of the column (similar to the stripping column). The overhead product \( V_D \) goes to a condenser with no reflux. This process is used when the feed is rich with the M.V.C.

**M. B. on the bottom of the column**

\[ L_m = V_{m+1} + W \]
\[ L_m = F \quad \text{If the feed enters at its bubble point} \]
\[ \text{And } L_m = F \cdot q \quad \text{If the feed enters as sub-cooled liquid} \]

The operating line equation is:

\[ y_{m+1} = \frac{L_m}{V_{m+1}} \cdot x_m - \frac{W \cdot x_w}{V_{m+1}} \]

This is a straight line equation (operating line equation) with slope \( \left( \frac{L_m}{V_{m+1}} \right) \). It intersects the 45° line at \( x = X_w \). The \( q \)-line is plotted from the point \( x = x_f \) on the 45° line either with slope = \( \infty \) if the feed is saturated liquid, or with slope > 1 if the feed is sub-cooled.

![Diagram of McCabe-Thiele Method](image-url)
2- Enriching tower:
This process is used for mixtures lean in M. V. C.
Feed is introduced from the bottom of the column as saturated vapor or superheated vapor, where no re-boiler is used. The composition of bottom product is comparable to feed composition (slightly less than $x_f$).

**O. M. B. on the top of the column**

\[ V_{n+1} = L_n + D \]

**[A] M. B. on the bottom of the column**

\[ y_{n+1} \cdot V_{n+1} = x_n \cdot L_n + x_D \cdot D \]

The operating line equation is:

\[ y_{n+1} = \frac{L_n \cdot x_n}{V_{n+1}} + \frac{D \cdot x_D}{V_{n+1}} \]

$V_n = F$ if the feed is saturated vapor
And $V_n = (1-q) \cdot F$ if the feed is superheated vapor

3- Rectification with direct steam injection:
In this type of processes the heat is supplied to the bottom of the tower by direct steam injection, where the re-boiler is not needed.

**O. M. B. on the column**

\[ F + S = D + W \]

**[A] M. B.**

\[ F \cdot x_f = D \cdot x_D + W \cdot x_W \]

The enriching section is not affected, because no change done but for the stripping section, the material balance will be:

**O. M. B.**

\[ L_m + S = V_{m+1} + W \]

**[A] M. B.**

\[ L_m \cdot x_m = V_{m+1} \cdot y_{m+1} + W \cdot x_W \]
If the steam was saturated steam, then \( S = V_{m+1} \) and \( L_{m+1} = W \)
That will cause to write the L. O. L. as

\[
y_{m+1} = \frac{L_m}{V_{m+1}} x_m - \frac{W x_w}{V_{m+1}}
\]

This is an equation of straight line with slop of \((W/S)\), to draw this equation, use the following two points:
The first one is at
Y = 0 then \( x = x_w \),
And the second one is
At \( y = x_m \), then \( x_m = \frac{W x_w}{W - S} \)

Using direct steam is the simplest heater construction and it is used when one component of the feed mixture is water.

4- Rectification with side stream:
Sometime, intermediate product or side streams are removed sections of the tower between the distillate and the bottom. These streams may be vapor or liquid. To solve such problem we will consider the case that the side stream is withdrawn above the feed and it will be saturated liquid, as shown below:
The upper operating line equation is derived as before and will be as

\[
y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1}
\]

M. B. for the loop donated:
\( V_{s+1} = L_s + Z + D \)
Where \( Z = \) mole/hr side stream assumed saturated liquid
\( L_n = L_s + Z \)
\( L_s = L_n - Z \)
Remember:
Vs+1 = Vn+1 = Ln + D
Vn+1 = Ln + D

[A] M. B.
y_{s+1} * V_{s+1} = x_s * L_s + x_D * D + x_Z * Z
Rewrite for y and substitute V_{s+1} by V_{n+1}, so
\[ y_{s+1} = \frac{L_s * x_s}{V_{n+1}} + \frac{D * x_D + Z * x_Z}{V_{n+1}} \]

\[ y_{s+1} = \frac{L_n - Z}{L_n + D} * x_s + \frac{D * x_D + Z * x_Z}{L_n + D} \]

\[ \Theta R = \frac{L_n}{D} \]
\[ \therefore y_{s+1} = \frac{R - Z}{R + 1} * x_s + \frac{x_D + Z}{R + 1} \]

The above equation is the operating line equation for the side stream of slop \( \frac{R - Z}{R + 1} \) (\( \frac{L_n}{V_{n+1}} \)) and intersect the y-axis at \( y = \frac{x_D + Z}{R + 1} \) (\( \frac{D * x_D + Z * x_Z}{V_{n+1}} \)). So to calculate the number of plates using the McCabe-Thiele method, follow the steps:

1- Complete the M. B., so the mole fraction of all streams must be known.
2- Plot the equilibrium data and locate \( x_D, x_Z, x_f, x_w \) on the 45° line.
3- Plot the U. O. L. using the points, \((y = x = x_D), (y = \frac{x_D}{R + 1}, x = 0)\).
4- Plot the side stream q-line which has a slop = \( \infty \) (saturated liquid), from the point \( y = x = x_Z \).
5- Plot the side stream operating line between the points; the intersection of the U.O.L. & the side stream q-line and the \((y = \frac{x_D + Z}{R + 1} * x_Z, x = 0)\), with slop \( \frac{R - Z}{R + 1} \).
6- Plot the q-line of the feed from the point \( y = x = x_f \) as before (depending on the feed condition).
7- From the point of intersection of the side stream operating line and the q-line of the feed draw the L.O.L. to intersect the 45° line at \( y = x = x_w \).
8- Step off the stages as before.
Then the theoretical number of plates = \( N - 1 \)
As shown in below
5- Rectification with two feeds:
There are occasions when two or more feeds composed of the same substances but different concentrations require giving the same distillate and residue products. A single fractionating column will then sufficient for that.

**O. M. B.:**
\[ F_1 + F_2 = D + W \]

**M.V.C. M. B.:**
\[ x_{F_1} * F_1 + x_{F_2} * F_2 = x_D * D + x_W * W \]
The upper operating line equation is derived as before and will be as

\[ y_{n+1} = \frac{R}{R+1} * x_n + \frac{x_D}{R+1} \]

The equation of the operating line between the two feeds is derived as follow:

**M. B. for the loop donated:**
\[ V_{r+1} + F = D + L_r \]

**M.V.C. M. B.:**
\[ V_{r+1} + x_{F_1} * F_1 = x_D * D + x_r * L_r \]
Solve for \( y_{r+1} \)
\[ y_{r+1} = \frac{D * x_D - F_1 * x_{F_1}}{V_{r+1}} + \frac{L_r * x_r}{V_{r+1}} \]

Remember:
\[ V_{r+1} = V_{n+1} = L_n + D \]
\[ L_r = L_n + F \]

\[ \therefore y_{r+1} = \frac{D * x_D - F_1 * x_{F_1}}{L_n + D} + \frac{(L_n + F) * x_r}{L_n + D} \]
\[ R = \frac{L}{D} \]

\[ \therefore y_{r+1} = \frac{R + F}{R + 1} \frac{1}{x_r} + \frac{x_D - F \cdot x_{f1}}{R + 1} \frac{1}{D} \]

This is the operating line equation with slope of \( \frac{R + F}{R + 1} \) and intersects the y-axis at

\[ \frac{x_D - F \cdot x_{f1}}{R + 1} \frac{1}{D} \]

The lower operating line is the same as before, that is:

\[ y_{m+1} = \frac{L}{V} \frac{m}{m+1} \cdot x_m - \frac{W}{V} \frac{m}{m+1} \cdot x_W \]

With slope \( \frac{L}{V} \frac{m}{m+1} \) and it intersects the 45° line (that is \( y = x \)) at \( x = x_w \). And at \( x = 0 \) it intersects the y-axis at

\[ \frac{W \cdot x_w}{V} \frac{m}{m+1} \]

So to calculate the number of plates using the McCabe-Thiele method, follow the steps:

1- Complete the M. B., so the mole fraction of all streams must be known.

2- Plot the equilibrium data and locate \( x_D, x_Z, x_{f1}, x_W \) on the 45° line.

3- Plot the U. O. L. using the points, \( y = x = x_D \), \( y = \frac{x_D}{R + 1} \), \( x = 0 \).

4- Plot the first feed q-line (depending on its entering conditions), from the point \( y = x = x_{f1} \).

5- Plot the second feed operating line between the points; the intersection of the U.O.L. & the first feed q-line and the \( y = \frac{x_D - F \cdot x_{f1}}{R + 1} \frac{1}{D} \), \( x = 0 \), with slope \( \frac{R + F}{R + 1} \).

6- Plot the q-line of the second feed from the point \( y = x = x_{f2} \) as before (depending on the feed condition).

7- From the point of intersection of the side stream operating line and the q-line of the second feed draw the L.O.L. to intersect the 45° line at \( y = x = x_w \).

8- Step –off the stages as before.

Then the theoretical number of plates = \( N - 1 \)

As shown in below
2- Sorel & lewis Method (Stage by stage calculation)

Assumptions were made for this method that there is equilibrium over-flow (approximately the same assumption in MaCabe-Thiele method), that is:

\[ V_n = V_{n+1} = V_1 = V_2 = \ldots \]
\[ L_n = L_{n+1} = L_1 = L_2 = \ldots \]

Both the upper operating line equation and the lower operating line equation (derived in previous section) can be applied for this method also.

\[
y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1} \quad \ldots 1
\]
\[
y_{m+1} = \frac{L_m}{V_{m+1}} x_m - \frac{W}{V_{m+1}} x_W \quad \ldots 2
\]

To calculate the number of theoretical stages required using this method follow these steps:

1- Find all streams F, D, W and their compositions.
2- Find R, either graphically or analytically.
3- Draw the equilibrium data.
4- Start from the first plate at the top of the column, where \( y_1 = x_D \) (from the U.O.L. for \( x_n = x_D \)). Then from the equilibrium curve find \( x_1 \) (which will in equilibrium with \( y_1 \)). Substitute \( x_1 \) in the U.O.L. equation so to find \( y_2 \), and then find \( x_2 \) from the equilibrium curve. Keep on as in the above procedure until you reach the feed plate (\( x_f \)).
5- From the value of \( y \) that exceed \( y_F \) find \( x \) from the equilibrium curve, apply this value of \( x \) in the lower operating line equation to find \( y_m \) and then from the equilibrium curve find \( x_m \). Reuse the L.O.L. to find \( y_{m+1} \) and so on until you reach \( x_W \), which will be the last plate.
6- The theoretical number of plates = \( N-1 \)

**H.W.**

Solve example 11.2 in vol. 2 page 426-428
Stage efficiency

Graphical and algebraic methods for determining stage requirements for distillation assume equilibrium with respect to both heat and mass transfer at each stage. Thus, the number of equilibrium stages (theoretical stages, ideal stages, or ideal plates) is determined or specified when using those methods. The McCabe-Thiele method assumes that the two phases leaving each stage are in thermodynamic equilibrium. In industrial countercurrent, multistage equipment, it is not always practical to provide the combination of residence time and intimacy of contact required to approach equilibrium closely. Hence, concentration changes for a given stage are usually less than predicted by equilibrium.

The simplest approach for staged columns is to apply an overall stage (or column) efficiency, defined by Lewis as:

$$E_0 = \frac{N_t}{N_a}$$

Where $E_0$ is the fractional overall stage efficiency, usually less than 1.0 (may vary from 0.3 to 1.0); $N_t$ is the calculated number of equilibrium (theoretical) stages; $N_a$ is the actual number of contacting trays (stages, plates), usually greater than $N_t$ required. Based on the results of extensive research conducted over a period more than 60 years, the overall stage efficiency has been found to be a complex function of the:

1. Geometry and design of the contacting trays.
2. Flow rates and flow paths of vapor and liquid streams.
3. Compositions and properties of vapor and liquid streams.

There are several empirical correlations for estimating the overall stage efficiency.

Another method used to describe the performance of the distillation column is the stage efficiency, which is frequently used to describe individual tray performance for individual components; one of these methods is Murphree plate efficiency. This efficiency can be defined on the basis of either phase and, or for a given component, is equal to the change in actual composition in the phase, divided by the change predicted by equilibrium. This definition applied to the vapor phase can be expressed as:

$$E_{MV} = \frac{y_n - y_{n+1}}{y_\text{*} - y_{n+1}}$$

Where:

- $y_n$: average actual composition of vapor leaving tray $n$.
- $y_{n+1}$: average actual composition of vapor leaving tray $n$ (leaving tray $n+1$).
- $y_\text{*}$: Concentration of vapor in equilibrium with liquid composition $x_n$ leaving the tray to the downcomer.

This equation gives the efficiency in vapor terms, but if the concentrations in the streams are used then the plate efficiency is given as:

$$E_{ML} = \frac{x_{n+1} - x_n}{x_\text{*} - x_n}$$

Where:

- $x_n$: average actual composition of liquid leaving tray $n$.
- $x_{n+1}$: average actual composition of liquid leaving tray $n+1$ (entering tray $n$).
- $x_\text{*}$: Composition of liquid in equilibrium with vapor composition $y_n$ leaving the tray to the downcomer.
The ratio $E_{MV}$ is shown graphically in below.

There are many empirical expressions for efficiency such as Drickamer & Bardford, and Chu in which physical properties of feed and relative flow rates of liquid and vapor inside the column, (see vol. 2 pages 507-511 for more details).

**Binary Mixture non-equimolal flow conditions**

In the previous methods the case of constant molar latent heat has been considered with no heat of mixing, and hence constant molar rate of reflux in the column. These simplifying assumptions are extremely useful in that they enable a simple geometrical method to be used for finding the change in concentration on the plate and, whilst they are rarely entirely true in industrial conditions, they often provide convenient start for design purposes.

For non-ideal system where the molar latent heat is no longer constant and there is a substantial heat of mixing, the calculations become much more tedious. For binary mixture of this kind a graphical model has been developed by Ruhemann, Ponchon, and Savarit, based on the use of an enthalpy – composition chart.

A typical enthalpy – composition or (H-y-x chart) is indicated in the following diagram:
This diagram is based on the following geometrical properties, as illustrate in the following figure:

A quantity of mixture in any physical state is known as "phase" and it is denoted by mass composition and enthalpy. The phase is indicated upon the diagram by a point which shows enthalpy and composition, but which does not show the mass. If m is the mass, x the composition and H is the enthalpy of the phase, then the addition of two phases A and B to give phase C is governed by:

\[ m_A + m_B = m_C \]
\[ m_A \cdot x_A + m_B \cdot x_B = m_C \cdot x_C \]
\[ m_A \cdot H_A + m_B \cdot H_B = m_C \cdot H_C \]

Similarly, if an amount \( Q \) of heat is added to mass \( m_A \) of a phase, the increase in enthalpy from \( H_A \) to \( H_C \) will be given by

\[ H_A + (Q/m_A) = H_C \]

Thus, the addition of two phases A and B is shown on the diagram by point C on the straight line joining the two phases, whilst the difference A-B is found by a point C on the extension of the line AB.

In figure (1), a phase represented by C in the region between the dew-point and boiling-point curves is considered, then this phase will be divided into two phases A and B at the ends of a tie line through the point C, so that:

\[ \frac{MA}{MB} = \frac{CB}{CA} \]

The H-y-x chart, therefore, enables the effect of adding two phases with or without the addition of heat to be determined geometrically. The diagram may be drawn for unit mass or for one mole of material, though as a constant molar reflux does not now apply, it is more convenient to use unit mass as the basis. Thus, working with unit mass of product, the mass of the individual streams as proportions of the product will be calculated.

**Equilibrium Data:**
It takes into account the latent heat of vaporization, sensible heat and heat of solution or mixing. So, the saturated liquid line in H-y-x diagram is:

\[ h_L = H_A + H_B + \Delta H_{sol} \]
\[ h_L = x_A \cdot C_{pA} \cdot (T - T_{ref}) + (1 - x_A) \cdot C_{pB} \cdot (T - T_{ref}) + \Delta H_{sol} \]
\[ H_V = h_L \cdot \lambda_{mix} \]

Where:
\[ \lambda_{mix} = x_A \cdot \lambda_A + (1 - x_A) \cdot \lambda_B \]

**Properties and uses of enthalpy – concentration chart**

**Lever – arm rule:-**

Let the streams \( S_1 \) and \( S_2 \) of composition \( Z_1 \) & \( Z_2 \) respectively mixed adiabatically to give another mixture \( S_3 \) of composition \( Z_3 \), so the material balance and energy balances will be:

**O. M. B.**
\[ S_1 + S_2 = S_3 \]

**[M.V.C.] M. B.**
\[ S_1 \cdot Z_1 + S_2 \cdot Z_2 = S_3 \cdot Z_3 \]

**[M.V.C.] E. B.**
\[ S_1 \cdot H_1 + S_2 \cdot H_2 = S_3 \cdot H_3 \]

From equations (1, 2)
\[ \frac{S_1}{S_2} = \frac{Z_2 - Z_3}{Z_3 - Z_1} \]

And from equations (1, 3)
\[ \frac{S_1}{S_2} = \frac{H_3 - H_1}{h_3 - h_1} \]
\[ \frac{S_1}{S_2} = \frac{CB}{CA} \]

\[ h_L \text{ & } H_V \]

\[ x_A \text{ & } y_A \]

\[ (kJ/kg) \]

\[ (kJ/kmole) \]

h

\[ Z \]

y_A

The tie (ab) represents the enthalpy

For non – adiabatic mixing which is similar to that for adiabatic but with addition of \( Q \) (\( Q \) is heat of mixing or heat losses or the net), so
\[ S_1 \cdot H_1 + S_2 \cdot H_2 = S_3 \cdot H_3 + Q \]
Example 7

Two pure liquids A & B are to be mixed adiabatically with each other and then mixed with another mixture of A & B. The pure A & pure B streams are in the ratio of 4:1 (mass ratio). Initially pure A has an enthalpy of 4 units/kgm while pure B has initially 2 units/kgm. Mixture 2 has a mass fraction of B (0.75) with an enthalpy of 7 units/kgm. Determine the composition of mixture 3 if its enthalpy is 5 units/kgm. What mass of mixture 2 is required with respect to 1 kgm of pure A used in the mixture 1.

Solution

Basis 1 kgm of A

ө Mixture 1 composed of 4 kgm A and 1 kgm of B

That means that mass fraction of B = 0.2

So total mass of mixture 1 (S₁) = 1.25 kgm

Enthalpy of mixture 1 (h₁) = xₐ * hₐ + (1 - xₐ) * hₐ

h₁ = (0.8 * 4) + (1 - 0.8) * 2 = 3.6 units/kgm

ө \( \frac{S₁}{S₂} = \frac{Z₂ - Z₃}{Z₃ - Z₁} \)

From the figure:

Z₃ = 0.42

\[ \frac{1.25}{S₂} = \frac{0.75 - 0.42}{0.42 - 0.2} \]

\[ S₂ = 0.833 \]

Operating Data:

As done before we will divide the operating data into five parts, the first part is the equilibrium data, the second part is similar to the 45° line, the third part is above the feed the forth part is below the feed and finally the fifth part which concern the feed entrance.

Part one:

The equilibrium data is given as \( (h_L \text{ vs. } x) \), and \( (h_V \text{ vs. } y) \) which must be plot on the same diagram. Some times the enthalpies of liquid and vapor must be calculated as mentioned in above. Part Two:
Overall column M.B.

F = D + W ...1

[M.V.C.] M. B.

F * x_f = D * x_D + W * x_w ...2

[M.V.C.] E. B.

F * h_f + q_r = q_c + D * h_D + W * h_w ...3

Then:

F * h_f = D * (h_D + \frac{q_c}{D}) + W * (h_W - \frac{q_r}{W})

Let Q_c = \frac{q_c}{D} (heat lost by condenser per kgm of distillate)

And Q_r = \frac{q_r}{W} (heat gained by re-boiler per kgm of residue)

Then:

F * h_f = D * h_D' + W * h_W'

...4

Where:

h_D' = h_D + Q_c

h_W' = h_W - Q_r

Substitute equation 1 into 2 and 4, then

(D + W) * x_f = D * x_D + W * x_w

D * (x_D - x_f) = W * (x_w - x_f) ...5

(D + W) * h_f = D * h_D' + W * h_W'

D * (h_D' - h_f) = W * (h_W' - h_f) ...6

Dived equation 5 by 6

\frac{x_D - x_f}{h_D' - h_f} = \frac{x_f - x_w}{h_f - h_W'}

This equation states that h_D, h_f and h_W is on a straight line at the points D', f, and W'

Where:

D': is the pole point of all operating lines above feed.
W': is the pole point of all operating lines below feed.
f: is the feed point.
Part three:  
Operating lines above the feed:  

**Total M. B.**  
\[ V_n = L_{n+1} + D \quad \ldots 1 \]

**[M.V.C.] M. B.**  
\[ V_n \times y_n = L_{n+1} \times x_{n+1} + D \times x_D \quad \ldots 2 \]

**Enthalpy M. B.**  
\[ V_n \times h_n = L_{n+1} \times h_{n+1} + D \times (h_D + Q_c) \]

Or  
\[ V_n \times h_n = L_{n+1} \times h_{n+1} + D \times \left( h_D \right) \quad \ldots 3 \]

Substitute equation (1) into (2) and (3)  
\[ (D + L_{n+1}) \times y_n = L_{n+1} \times x_{n+1} + D \times x_D \quad \ldots 4 \]

\[ (D + L_{n+1}) \times h_n = L_{n+1} \times h_{n+1} + D \times h_D \quad \ldots 5 \]

Dived equation 4 by 5  
\[ \frac{h_D - h_n}{h_D} = \frac{y_n - x_{n+1}}{x_D} \]

Which is also as before an equation of straight line, which states that \( D', y_n, \) and \( x_{n+1} \) are points of the line.

---

Part Four  
Operating lines below the feed:  

**Total M. B.**  
\[ L_{k+1} = V_k + W \]

\[ V_k = L_{k+1} - W \quad \ldots 1 \]

**[M.V.C.] M. B.**  
\[ V_k \times y_k = L_{k+1} \times x_{k+1} - W \times x_W \quad \ldots 2 \]

**Enthalpy M. B.**  
\[ V_k \times h_k = L_{k+1} \times h_{k+1} - W \times (h_W - Q_c) \]

Or  
\[ V_k \times h_k = L_{k+1} \times h_{k+1} - W \times \left( h_W \right) \quad \ldots 3 \]

Substitute equation (1) into (2) and (3), and by using the same procedure as done in before, then:
And the same conclusion is obtained as before, that is $W', y_k$, and $x_{k+1}$ are points of the line. Where $y_k$ is with equilibrium with $x_k$.

Now, part five which concerns the effect of the feed conditions, this is not similar to that in McCabe-Thiele method; i.e. there is no q-line. The effect of feed conditions is directly presented on the diagram by locating the feed enthalpy and its composition. The feed enthalpy is calculated depending on its condition either if it is sub-cooled liquid, or saturated liquid, or two phase mixture, or saturated vapor, or superheated vapor.

1- For sub-cooled liquid:
$$h_f = h_L - \Delta h_L$$
$$\Delta h_L = x_A * C_{pA} * (T_{bubble} - T_{entry}) + (1 - x_A) * C_{pB} (T_{bubble} - T_{entry})$$

Where:
$$h_L = x_A * C_{pA} * (T - T_{ref}) + (1 - x_A) * C_{pB} * (T - T_{ref}) + \Delta H_{sol}$$

This point is located at $x = x_f$ below the bubble curve by a value of $\Delta h_L$.

2- for saturated liquid:
This point is located directly on the bubble curve at $x = x_f$.

3- For two phase mixture:
$$h_f = (1 - X) * h_L + X * h_V$$

Where: $X$ is the quality of the feed.

4- For saturated vapor:
This point is located directly on the dew curve at $x = x_f$.

5- For superheated vapor:
$$h_f = h_V + C_{pmixv} * (T_{entry} - T_{dew})$$

Where:
$$h_V = h_L * \lambda_{mix}$$
$$\lambda_{mix} = x_A * \lambda_A + (1-x_A) * \lambda_B$$

**Reflux Ratio**

The reflux $R = \frac{L_r}{D}$ can be determined as follow:

$$V_n = L_r + D$$
$$q_C = V_n * (H_D - h_D)$$

Where: $H_D$ is the enthalpy of saturated vapor whose composition is $y = x_D$
\[ h'_D = h_D + \frac{q_c}{D} \]
\[ \frac{q_c}{D} = h'_D - h_D \]
\[ V_n * (H_D - h_D) \]
\[ \therefore \quad \frac{V_n * (H_D - h_D)}{D} = h'_D - h_D \]

Substitute \( V_n \) by \( \frac{L_r}{D} \) and rearrange the above equation then:

\[ \frac{(L_r + D)}{D} = \frac{(h'_D - h_D)}{(H_D - h_D)} \]

\[ R + 1 = \frac{(h'_D - h_D)}{(H_D - h_D)} \]

\[ R = \frac{(h'_D - h_D)}{(H_D - h_D)} - 1 \]

\[ R = \frac{h'_D - h_D - H_D + h_D}{(H_D - h_D)} \]

Now to calculate the number of theoretical plates required, follow the steps:

1. Complete the material balance and energy balance, so all the streams and their composition are known in addition to that calculated the heat required in the re-boiler (not very necessary) and the heat rejected in the condenser (also not necessary).
2. Plot the equilibrium data.
3. Draw vertical lines from \( x_D \), \( X_f \), and \( x_W \).
4. Locate \( D' \), \( f \), and then plot the line joining these two points and then extent to intersect the vertical line drawn from \( x_W \) (then point \( w' \) is located). Point \( D' \) is located at \( x = x_D \) and \( h_D' \) which is calculated from the equation of the reflux ratio, while \( f \) is located at \( x = x_f \) and depending on the feed condition.
5. From the equilibrium data find \( x_n^* \), and draw the tie line.
6. Join the point \( D' \) with \( x_n^* \) it will intersect the dew curve. The intersection point is \( y_1 \).
7. Repeat steps 5 & 6 until you accede \( x_f \).
8. From point \( W' \) plot a line to join \( W' \) with \( x_{n+1} \) and extent to intersect the dew point curve.
9. Read \( y_k \), and from the equilibrium data find \( x_k^* \) (draw the tie line).
10. Join the point \( W' \) with \( x_k^* \) and extent to intersect the dew curve. The intersection point is \( y_{k+1} \).
11. Repeat steps 9 & 10 until you accede \( x_W \). Step-off the number of plates (N) from the figure.

Then:

The theoretical number of plates = N - 1.

Check the figure below (for saturated feed case)
**Total reflux (minimum number of plates) & Minimum reflux ratio:**

**A- Total reflux**

As $R = \frac{L_f}{D}$ is increased, the operating point $D'$ must be located at higher position since

$$h'_D = h_D + \frac{q_c}{D}$$

increased (decreasing $D$) $R = \infty$ when $D \rightarrow 0$

At the same time the point $W'$ become in lower position, since $D'$, $f$, $W'$ lie on the same line. This behavior was also noticed before on the y-x diagram when the operating lines become closer to the 45° line which yield the minimum number of plates, so 

On the enthalpy diagram as $R \rightarrow \infty$ the point $D'$ & $W'$ goes to $\infty$, then all the operating lines will become vertical and parallel. So to find the minimum number of plates, no product (i.e. $R \rightarrow \infty$ ) draw a vertical line from the point $(h_D, x_D)$ on the bubble curve until it intersects the dew curve, then from equilibrium data draw the tie line between $y_D$ and $x_1$ then draw a vertical line from the bubble curve to intersect the dew curve and carry on repeating this procedure until you reach $x_W$ the number of triangular form represent the minimum theoretical plates needed, as shown in the figure.
B- Minimum reflux ratio (infinite number of plates)
As done before when using minimum reflux ratio the number of plates required to achieve the required separation will approach to infinity. To calculate the minimum reflux ratio follow the following steps:
1- Locate \( x_D \) and draw a vertical line.
2- Locate \( x_F \) and find \( y_F \) from \((y-x\) diagram) which is in equilibrium with \( x_F \) and locate \( y_F \) on the dew curve.
3- Draw a line connecting \((y_F, x_F)\) and extend it until intersects the vertical line drawn from \( x_D \).
4- The point of intersection of the above two lines will called \( H_m' \), and this value will be used to calculate the value of the minimum reflux ratio \( (R_{\text{min}}) \) as shown in below:

\[
R_{\text{min}} = \frac{H_m' - H_D}{H_D - h_D}
\]

To find the condenser duty
\[
q_C = (h_{D'} - h_D) * D
\]
And for re-boiler duty:
\[
q_r = (h_W - h_{W'}) * W
\]
Multi-component Distillation

A multi-component distillation problem contains many variables. The conditions of equilibrium are more complex, thus $y_A$ depend not only on $x_A$ but also on the relative proportion of the other components.

The simplest relationship can be used for equilibrium is:

$$y_A = k_A * x_A$$

K-values varies with temperature and pressure, some of it are presented in figure 11.38 in (chemical engineering vol. 2) and also in any thermodynamic text book.

Other methods used for many systems which are chemically similar where the relative volatilities remain constant over a wide range of temperature and composition.

**Light key and heavy key**

Suppose four components namely (A, B, C, and D) are to be distilled where A is the M.V.C. and D is the L.V.C., the final products are shown in below:

<table>
<thead>
<tr>
<th>Feed</th>
<th>Top product</th>
<th>Bottom product</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>A</td>
<td>--</td>
</tr>
<tr>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>D</td>
<td>--</td>
<td>D</td>
</tr>
</tbody>
</table>

Component B is the highest component appearing in the bottom product so it is called the "**light key component**"; where the component C is the heaviest component appearing in the top product, component C is the "**heavy key component**".

The mean purpose of fractionation is the separation B from C.

**Equilibrium Data:**

Let the four components (A, B, C, and D) are to be distilled where B is the heavy key component (HK) then:

$$y_A + y_B + y_C + y_D = 1$$

And

$$\frac{y_A}{y_B} + \frac{y_C}{y_B} + \frac{y_D}{y_B} + \frac{y_B}{y_B} = 1$$

...1

Then

$$\frac{y_A}{y_B} = \frac{P_A}{P_B} / \frac{x_A}{x_B}$$

But $P_A = y_A * P_T$

Then

$$\frac{y_A}{y_B} = \frac{y_A}{y_B} / \frac{x_A}{x_B}$$

...2

Or

$$y_A = \frac{\alpha_{AB} * x_A}{y_B}$$
Also \( \alpha_{AB} = \frac{k_A}{k_B} \)

Hence:

\[
\frac{y_A}{y_B} = \alpha_{AB} \cdot \frac{x_A}{x_B}
\]

The same is done for each component, then substitute in equation 2 to get:

\[
\alpha_{AB} \cdot \frac{x_A}{x_B} + \alpha_{BB} \cdot \frac{x_B}{x_B} + \alpha_{CB} \cdot \frac{x_C}{x_B} + \alpha_{DB} \cdot \frac{x_D}{x_B} = \frac{1}{y_B}
\]

Or

\[
\sum_{n=1}^{n=i} \alpha \cdot x \cdot \frac{x_B}{y_B} = 1
\]

Or

\[
\frac{x_B}{y_B} = \sum_{n=1}^{n=i} \alpha \cdot x
\]

Substitute in equation 2, then:

\[
y_A = \frac{\alpha_{AB} \cdot x_A}{\sum_{n=1}^{n=i} \alpha \cdot x} \quad \ldots 3
\]

\[
y_C = \frac{\alpha_{CB} \cdot x_C}{\sum_{n=1}^{n=i} \alpha \cdot x} \quad \ldots 4
\]

\[
y_D = \frac{\alpha_{DB} \cdot x_D}{\sum_{n=1}^{n=i} \alpha \cdot x} \quad \ldots 5
\]

Equations 3, 4, and 5 are the equilibrium equations.

**Calculations of bubble point and dew point**

Vapor pressure of a liquid at certain temperature and total pressure can be found from Henry's law.

\[
P_A = P_0 \cdot x_A
\]

Also \( P_A = y_A \cdot P_T \)

And \( P_A = \overline{H} \cdot x_A \) where: \( \overline{H} \) is Henry's constant

\[
y = \frac{P_A}{P_T} = \frac{\overline{H} \cdot x_A}{P_T} = k_A \cdot x_A
\]

So the partial pressure for component A is given as:

\[
P_A = P_T \cdot k_A \cdot x_A
\]

Then at bubble point the total vapor pressure = \( P \cdot (\Sigma k \cdot x) = P_T \)

If any inert gas present, then:

\[
P_{\text{inert}} = P_T \cdot [1 - (\Sigma k \cdot x)]
\]
To calculate the bubble point of multi-component mixture (boiling point of a mixture):

At bubble point:

1- Total vapor pressure of the mixture = ambient pressure \((P_T)\).

2- \(\Sigma k \times x = 1\)

So by trial and error the bubble point can be predicted following the steps:

A- Assume a probable value of bubble point, \((P_T)\) is known.

B- At this temperature read \(k\) values from figures (monogram fig.) for each component.

C- Find \(\Sigma (k \times x)\).

If the \(\Sigma (k \times x) = 1\) then the assumption is correct.

If the \(\Sigma (k \times x) > 1\) then the assumed temperature is too high.

If the \(\Sigma (k \times x) < 1\) then the assumed temperature is less than the bubble point.

For the calculation of dew point, follow the same steps as in above but for \(\Sigma \frac{y}{k}\) = 1.

**Example 8**

Determine the vapor pressure and the bubble point of the liquid mixture with the following composition under total pressure of 2 bar and a temperature of 25°C:

<table>
<thead>
<tr>
<th>Component</th>
<th>n-C4H10</th>
<th>n-C5H12</th>
<th>n-C6H14</th>
<th>n-C7H16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol%</td>
<td>20</td>
<td>40</td>
<td>30</td>
<td>10</td>
</tr>
</tbody>
</table>

**Solution**

From monogram vol. 6 figure 8.3 read \(k\)-value for each component at 2 bar and 25°C as shown in the table below:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
<th>k-value</th>
<th>(X_i \times k_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C4</td>
<td>0.2</td>
<td>1.25</td>
<td>0.25</td>
</tr>
<tr>
<td>n-C5</td>
<td>0.4</td>
<td>0.35</td>
<td>0.14</td>
</tr>
<tr>
<td>n-C6</td>
<td>0.3</td>
<td>0.109</td>
<td>0.0327</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.1</td>
<td>0.031</td>
<td>0.0031</td>
</tr>
</tbody>
</table>

\(\Sigma X_i \times k_i = 0.426 \neq 1\)

Therefore there is an inert in the vapor phase.

So, the inert gas pressure = \(P_T(1 - \Sigma X_i \times k_i) = 2 \times (1 - 0.426) = 1.148\) bar

The vapor pressure mixture = 0.852 bar

Since at 25°C the vapor pressure of the liquid is less than the total pressure; therefore the bubble point of the mixture at 2 bar is larger than 25°C. Assume it is equal to 50°C, then

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
<th>k-value</th>
<th>(X_i \times k_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C4</td>
<td>0.2</td>
<td>2.3</td>
<td>0.46</td>
</tr>
<tr>
<td>n-C5</td>
<td>0.4</td>
<td>0.8</td>
<td>0.32</td>
</tr>
<tr>
<td>n-C6</td>
<td>0.3</td>
<td>0.29</td>
<td>0.087</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.1</td>
<td>0.09</td>
<td>0.009</td>
</tr>
</tbody>
</table>

\(\Sigma X_i \times k_i = 0.876 < 1\)

Assume \(T = 60°C\)

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
<th>k-value</th>
<th>(X_i \times k_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C4</td>
<td>0.2</td>
<td>2.8</td>
<td>0.56</td>
</tr>
<tr>
<td>n-C5</td>
<td>0.4</td>
<td>1.0</td>
<td>0.4</td>
</tr>
<tr>
<td>n-C6</td>
<td>0.3</td>
<td>0.38</td>
<td>0.114</td>
</tr>
<tr>
<td>n-C7</td>
<td>0.1</td>
<td>0.14</td>
<td>0.014</td>
</tr>
</tbody>
</table>

\(\Sigma X_i \times k_i = 1.088 > 1\)
Let $T = 56^\circ\text{C}$

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
<th>k-value</th>
<th>$X_i \times k_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C$_4$</td>
<td>0.2</td>
<td>2.59</td>
<td>0.518</td>
</tr>
<tr>
<td>n-C$_5$</td>
<td>0.4</td>
<td>0.92</td>
<td>0.368</td>
</tr>
<tr>
<td>n-C$_6$</td>
<td>0.3</td>
<td>0.34</td>
<td>0.102</td>
</tr>
<tr>
<td>n-C$_7$</td>
<td>0.1</td>
<td>0.21</td>
<td>0.012</td>
</tr>
</tbody>
</table>

$\sum x_i \times k_i = 1.0$

So the bubble point of the mixture = $56^\circ\text{C}$

The vapor pressure of each component are roughly estimated by

$P_A = P_t \times (k_A \times x_A)$, then

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
<th>k-value</th>
<th>$X_i \times k_i$</th>
<th>$P_A$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C$_4$</td>
<td>0.2</td>
<td>2.59</td>
<td>0.518</td>
<td>1.036</td>
</tr>
<tr>
<td>n-C$_5$</td>
<td>0.4</td>
<td>0.92</td>
<td>0.368</td>
<td>0.736</td>
</tr>
<tr>
<td>n-C$_6$</td>
<td>0.3</td>
<td>0.34</td>
<td>0.102</td>
<td>0.204</td>
</tr>
<tr>
<td>n-C$_7$</td>
<td>0.1</td>
<td>0.21</td>
<td>0.012</td>
<td>0.024</td>
</tr>
</tbody>
</table>

**A- Flash distillation**

For multi-component system the equilibrium relation will $y = k \times x$ as shown in above, so for component $i$

$y_i = k_i \times x_i$

As derived before in binary system, the operating equation for multi-component mixture is written as:

$$y_i = \frac{x_i}{f_v} \times \left(\frac{1 - f_v}{f_v}\right) \times \frac{y_i}{k_i}$$

Or

$$y_i = \frac{k_i \times x_i}{f_v \times (k_i - 1) + 1}$$

For multi-component calculation to find $y_i$ (mole fraction of vapor leaving the flash drum):

1- Assume $f_v$ (always $< 1$), then calculate $y_i$ for each component.

2- Find $\Sigma y_i$

If the $(\Sigma y_i) = 1$ then the assumption is correct.

If the $(\Sigma y_i) \neq 1$ then assume another $f_v$.

To calculate the heat duty done to heat the feed. Make energy balance as:

$F \times H_f + q = S \times H_s + V \times H_v$

**Example 9:**

The following mixture is to be subjected to equilibrium flash vaporization at $150^\circ\text{C}$ and $1930$ kN/m$^2$. Determine the bubble point and the dew point of this mixture and then find the amount and composition of the liquid and vapor phases resulting from this separation process, for feed rate of 100 kmole/hr with the following composition:

<table>
<thead>
<tr>
<th>Feed components</th>
<th>C$_3$</th>
<th>n-C$_4$</th>
<th>n-C$_5$</th>
<th>n-C$_6$</th>
<th>n-C$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole fraction</td>
<td>0.28</td>
<td>0.24</td>
<td>0.24</td>
<td>0.08</td>
<td>0.16</td>
</tr>
</tbody>
</table>

**Solution:**
1- Calculation of the bubble point temperature
At $P_T = 1930 \text{ kN/m}^2$, assume a temperature say 116°C, find the $k$-value for each component:

<table>
<thead>
<tr>
<th>component</th>
<th>$K_i$</th>
<th>$x_i$</th>
<th>$K_i \times x_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$</td>
<td>2.2</td>
<td>0.28</td>
<td>0.616</td>
</tr>
<tr>
<td>n-C$_4$</td>
<td>0.95</td>
<td>0.24</td>
<td>0.228</td>
</tr>
<tr>
<td>n-C$_5$</td>
<td>0.49</td>
<td>0.24</td>
<td>0.1176</td>
</tr>
<tr>
<td>n-C$_6$</td>
<td>0.245</td>
<td>0.08</td>
<td>0.0196</td>
</tr>
<tr>
<td>n-C$_8$</td>
<td>0.077</td>
<td>0.16</td>
<td>0.01152</td>
</tr>
</tbody>
</table>

$\sum K_i \times x_i = 0.9927 < 1$

Assume another temperature, $T = 120$ °C

<table>
<thead>
<tr>
<th>component</th>
<th>$K_i$</th>
<th>$x_i$</th>
<th>$K_i \times x_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$</td>
<td>2.3</td>
<td>0.28</td>
<td>0.672</td>
</tr>
<tr>
<td>n-C$_4$</td>
<td>1</td>
<td>0.24</td>
<td>0.24</td>
</tr>
<tr>
<td>n-C$_5$</td>
<td>0.52</td>
<td>0.24</td>
<td>0.1248</td>
</tr>
<tr>
<td>n-C$_6$</td>
<td>0.28</td>
<td>0.08</td>
<td>0.0224</td>
</tr>
<tr>
<td>n-C$_8$</td>
<td>0.08</td>
<td>0.16</td>
<td>0.0128</td>
</tr>
</tbody>
</table>

$\sum K_i \times x_i = 1.072 > 1$

Assume another temperature, $T = 119.8$ °C

<table>
<thead>
<tr>
<th>component</th>
<th>$K_i$</th>
<th>$x_i$</th>
<th>$K_i \times x_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$</td>
<td>2.22</td>
<td>0.28</td>
<td>0.6216</td>
</tr>
<tr>
<td>n-C$_4$</td>
<td>0.956</td>
<td>0.24</td>
<td>0.22944</td>
</tr>
<tr>
<td>n-C$_5$</td>
<td>0.492</td>
<td>0.24</td>
<td>0.11808</td>
</tr>
<tr>
<td>n-C$_6$</td>
<td>0.24</td>
<td>0.08</td>
<td>0.0192</td>
</tr>
<tr>
<td>n-C$_8$</td>
<td>0.078</td>
<td>0.16</td>
<td>0.01248</td>
</tr>
</tbody>
</table>

$\sum K_i \times x_i = 1.0008 = 1$

Then for pressure = 1930 kN/m$^2$, the bubble point is 119.8°C

2- Calculation of dew point temperature, we will assume the mixture is a vapor mixture at $P_T = 1930 \text{ kN/m}^2$, assume $T = 190$ °C

<table>
<thead>
<tr>
<th>component</th>
<th>$K_i$</th>
<th>$y_i$</th>
<th>$\frac{y_i}{K_i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$</td>
<td>3.85</td>
<td>0.28</td>
<td>0.073</td>
</tr>
<tr>
<td>n-C$_4$</td>
<td>2.0</td>
<td>0.24</td>
<td>0.12</td>
</tr>
<tr>
<td>n-C$_5$</td>
<td>1.25</td>
<td>0.24</td>
<td>0.192</td>
</tr>
<tr>
<td>n-C$_6$</td>
<td>0.78</td>
<td>0.08</td>
<td>0.103</td>
</tr>
<tr>
<td>n-C$_8$</td>
<td>0.3</td>
<td>0.16</td>
<td>0.533</td>
</tr>
</tbody>
</table>
\[
\sum \frac{y_i}{k_i} = 1.02 > 1
\]

Then assume a lower temperature
After trial and error the dew point of the mixture = 188.7°C at 1930

Where the \( \sum \frac{y_i}{k_i} = 0.999 \approx 1 \)

3- To find the amounts and the composition of liquid and vapor at 150°C and 1930 kN/m², we will assume \( f_v \) and then find the \( y_i \) of each component using the following equation.
If \( \sum y_i = 1 \) then the assumed \( f_v \) is correct, if not assume a new one.

\[
y_i = \frac{k_i \cdot x_i}{f_v \cdot (k_i - 1) + 1}
\]

Then we must find the \( k \)-value for each component at \( T = 150°C \) and \( P = 1930 \) kN/m²

<table>
<thead>
<tr>
<th>Feed components</th>
<th>( C_3 )</th>
<th>n-C₄</th>
<th>n-C₅</th>
<th>n-C₆</th>
<th>n-C₈</th>
</tr>
</thead>
<tbody>
<tr>
<td>k-value</td>
<td>3</td>
<td>1.42</td>
<td>0.85</td>
<td>0.48</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Assume \( f_v = 0.5 \)

(\text{do not forget } 0 < f_v < 1)

\[
y_{C_3} = \frac{3 \cdot 0.28}{0.5 \cdot (3-1) + 1} = 0.42
\]

\[
y_{n-C_4} = \frac{1.42 \cdot 0.24}{0.5 \cdot (1.42 - 1) + 1} = 0.2817
\]

\[
y_{n-C_5} = \frac{0.85 \cdot 0.24}{0.5 \cdot (0.85 - 1) + 1} = 0.2205
\]

\[
y_{n-C_6} = \frac{0.48 \cdot 0.08}{0.5 \cdot (0.48 - 1) + 1} = 0.0519
\]

\[
y_{n-C_8} = \frac{0.17 \cdot 0.16}{0.5 \cdot (0.17 - 1) + 1} = 0.0465
\]

\( \sum y_i = 1.0206 > 1 \), then assumption is not correct

Assume \( f_v = 0.55 \)

\[
y_{C_3} = \frac{3 \cdot 0.28}{0.55 \cdot (3-1) + 1} = 0.4
\]

\[
y_{n-C_4} = \frac{1.42 \cdot 0.24}{0.55 \cdot (1.42 - 1) + 1} = 0.2768
\]

\[
y_{n-C_5} = \frac{0.85 \cdot 0.24}{0.55 \cdot (0.85 - 1) + 1} = 0.2223
\]

\[
y_{n-C_6} = \frac{0.48 \cdot 0.08}{0.55 \cdot (0.48 - 1) + 1} = 0.0315
\]

\[
y_{n-C_8} = \frac{0.17 \cdot 0.16}{0.55 \cdot (0.17 - 1) + 1} = 0.05
\]

\( \sum y_i = 0.9806 < 1 \), then assumption is not correct

Assume \( f_v = 0.54475 \)

\[
y_{C_3} = \frac{3 \cdot 0.28}{0.54475 \cdot (3-1) + 1} = 0.402
\]
\[ \gamma_{n - C_4} = \frac{1.42 \times 0.24}{0.54475 \times (1.42 - 1) + 1} = 0.2773 \]
\[ \gamma_{n - C_5} = \frac{0.85 \times 0.24}{0.54475 \times (0.85 - 1) + 1} = 0.2215 \]
\[ \gamma_{n - C_6} = \frac{0.48 \times 0.08}{0.54475 \times (0.48 - 1) + 1} = 0.0536 \]
\[ \gamma_{n - C_8} = \frac{0.17 \times 0.16}{0.54475 \times (0.17 - 1) + 1} = 0.0496 \]
\[ \Sigma y_i = 1.004 \approx 1, \text{ then assumption is correct} \]

\[ f_V = \frac{V}{F} \]

\[ F = 100 \text{ kmole/he} \]

Then

\[ V = 54.4475 \text{ kmole/hr} \]

\[ L = 45.5525 \text{ kmole/hr} \]

Then to find the composition of the liquid phase make a material balance for each component as follow:

\[ F * x_{fi} = V * y_i + L * x_i \]

Then

\[ x_i = \frac{F \times x_{Fi} - V \times y_i}{L} \]

\[ x_{C_3} = \frac{100 \times 0.28 - 54.4475 \times 0.402}{45.5525} = 0.1342 \]

\[ x_{n - C_4} = \frac{100 \times 0.24 - 54.4475 \times 0.2773}{45.5525} = 0.1954 \]

\[ x_{n - C_5} = \frac{100 \times 0.24 - 54.4475 \times 0.2215}{45.5525} = 0.2621 \]

\[ x_{n - C_6} = \frac{100 \times 0.08 - 54.4475 \times 0.0536}{45.5525} = 0.1116 \]

\[ x_{n - C_8} = \frac{100 \times 0.16 - 54.4475 \times 0.0496}{45.5525} = 0.292 \]

\[ \Sigma x_i = 0.995 \approx 1 \]

As a final conclusion:
B- fractionating column:

To calculate the number of trays needed in fractionating column, Lewis and Matheson method is used, which is based on Lewis and Sorel method when the composition of liquid on any phase is known, then vapor composition in equilibrium can be calculated from vapor pressures or relative volatilities. So the composition of each component above the feed plate entrance can be calculated from the upper operating line equation and below the feed plate the lower operating line equation must be used.

Keep in mind that for each component an upper operating equation and lower operating equation must be found. In below the steps which must be followed to calculate the number of theoretical plates.

1- Complete the material balance, so the mole flow rate of each component in the two products must be known (i.e. D, and W is calculated and their composition also).

2- Calculate the reflux ratio.

3- Exam the feed condition in order to calculate (q) if it is necessary.

4- Find the U.O.L. & L.O.L. equations for each component.

5- Starting from the bottom, use the equilibrium equation and substitute $x_{Wi}$ in the following equation for each component to find $y_{mi}$

$$y_i = \frac{\sum_{n=1}^{\alpha} \alpha_i x_i}{\sum_{n=1}^{\alpha} \alpha x}$$
6- Substitute \( y_{mi} \) in the L.O.L equation and find \( x_{(m+1)i} \) for each component.

7- Repeat steps 6 & 7 until you reach \( x_{mi} > x_{fi} \) then substitute \( y_{mi} \) obtained from the equilibrium equation in the U.O.L. equation for each component to find \( x_{mi} \) and repeat the same procedure as done in steps 6 & 7 until you reach \( x_{mi} = x_{Di} \). Step off the number of plates required (N).

Theoretical number of plates = N -1

**Minimum reflux ratio**

The method used for determining the minimum reflux ratio for binary mixture graphically can not be used when we deal with multi-component system, as we can not draw an equilibrium curve for this system. There are two methods for determining the minimum reflux:

1- Colburn's Method:-

The following equation was proposed by Colburn to calculate the minimum reflux ratio:

\[
R_{min} = \frac{1}{\alpha_{DL}} \left[ \frac{x_{DL}}{x_{nL}} - \alpha_{DL} \right] \frac{x_{DH}}{x_{nH}}
\]

Where:

\( \alpha_{DL} \): The relative volatility of L.K. component to the H.K. component.

\( x_{DL} \): The mole composition of the L.K. component in the distillate.

\( x_{DH} \): The mole composition of the H.K. component in the distillate.

\( x_{nL} \): The mole composition of the L.K. component in the pinch point.

\( x_{nH} \): The mole composition of the H.K. component in the pinch point.

Where:

\[
x_{nL} = \frac{r_f}{(1 + r_f)(1 + \sum \alpha x_{fh})}
\]

\[
x_{nH} = \frac{x_{nL}}{r_f}
\]

For \( r_f \): is the estimated ratio of the key components on the feed plate.

For a liquid feed at its bubble point, \( r_f \) equals to the ratio of the key components in the feed.

\[
r_f = \frac{x_{nL}}{x_{nH}}
\]

Otherwise \( r_f \) is calculated as the ratio of the key component in liquid part of the feed.

\( x_{fh} \): is the mole fraction of each component in liquid portion of feed heavier than heavy key in feed.

\( \alpha \): relative volatility of the components relative to the H.K.

2- Underwood's Method

For conditions where the relative volatilities remain constant, Underwood has developed the following equations from which \( R_{min} \) may be calculated:

\[
\frac{a_A * x_{DA}}{a_A - \theta} + \frac{a_B * x_{DB}}{a_B - \theta} + \frac{a_C * x_{DC}}{a_C - \theta} + \ldots = 1 - q
\]

And

\[
\frac{a_A * x_{DA}}{a_A - \theta} + \frac{a_B * x_{DB}}{a_B - \theta} + \frac{a_C * x_{DC}}{a_C - \theta} + \ldots = R_{min} + 1
\]

Where:
$x_A, x_B, x_C, x_{DA}, x_{DB}, x_{DC}$ … etc are the mole fraction of components A, B, C, … etc in the feed and distillate, A being the light key and B is the heavy key.

$\alpha_A$, $\alpha_B$, $\alpha_C$, are the relative volatilities of components with respect to the heavy key.

$q$: is the heat required to vaporize one mole of feed to the molar latent heat of the feed.

$\theta$: is the root of the first equation where:

$$\alpha_H < \theta < \alpha_L$$

### Number of minimum number of plates:

Using Fensk's equation

$$N_{\text{min}} + 1 = \frac{\log\left([x_L/x_H]_D \cdot \left(x_H/x_L\right)_B\right)}{\log(\alpha_{LH})_{av}}$$

Where:

$$(\alpha_{LH})_{av} = \left[(\alpha_{LH})_f \cdot (\alpha_{LH})_B \cdot (\alpha_{LH})_D\right]^{1/3}$$

### Relation between reflux ratio and number of plates:

The Gilliland's correlation related the reflux ratio $R$ and the number $N$ of plates, in which only the minimum reflux ratio $R_{\text{min}}$ and the number of plates at total reflux (i.e. $N_{\text{min}}$) are required. This is shown in the following equation, where $(R-R_{\text{min}})/(R+1)$ is plotted against the group $[(N+1)-(N_{\text{min}}+1)]/(N+2)$, (the first one represent y-axis while the second one the x-axis). The relation can be given as follow:

$$y = 1 - \exp[1.49 + 0.315 \cdot x - \frac{1.805}{x^{0.1}}]$$

Where $x = \frac{R-R_{\text{min}}}{R+1}$

### Example 10:

Suppose a mixture of hexane, Heptane and Octane to be separate to give products as shown in the table. What will be the value of the minimum reflux ratio, if the feed is liquid at its boiling point? Then find the minimum number of plates required. Investigate the change in $N$ with $R$ and find the number of plates if $R=10$. (Plot $N$ vs. $R$).

<table>
<thead>
<tr>
<th>Component</th>
<th>F mole</th>
<th>$x_f$</th>
<th>D mole</th>
<th>$x_D$</th>
<th>W mole</th>
<th>$x_W$</th>
<th>Relative volatility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>40</td>
<td>0.4</td>
<td>40</td>
<td>0.534</td>
<td>0</td>
<td>0</td>
<td>2.7</td>
</tr>
<tr>
<td>Heptane</td>
<td>35</td>
<td>0.35</td>
<td>34</td>
<td>0.453</td>
<td>1</td>
<td>0.04</td>
<td>2.22</td>
</tr>
<tr>
<td>Octane</td>
<td>25</td>
<td>0.25</td>
<td>1</td>
<td>0.013</td>
<td>24</td>
<td>0.96</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Solution
The L.K. is Heptane, H.K. is Octane
Then $\alpha_{\text{HO}} = 2.7$, $\alpha_{\text{HeoO}} = 2.2$, $\alpha_{\text{OO}} = 1.0$

Using Underwood's method:

$$\frac{\alpha_A * x_{DA} + \alpha_B * x_{DB} + \alpha_C * x_{DC}}{\alpha_A - \theta} + \frac{\alpha_B - \theta}{\alpha_B - \theta} + \frac{\alpha_C - \theta}{\alpha_C - \theta} + \ldots = 1 - q$$

Where $q = 1$ (saturated liquid), then

$$\frac{2.7 * 0.4 + 2.22 * 0.35 + 1 * 0.25}{2.7 - \theta} + \frac{2.22 - \theta}{2.22 - \theta} + \frac{1 - \theta}{1 - \theta} = 0$$

$\alpha_H < \theta < \alpha_L$ or $1 < \theta < 2.22$

The above equation is solved by trial and error, so assume $\theta = 1.15$

$$\sum \frac{\alpha * x_f}{\alpha - \theta} = -0.243$$

Assume $\theta = 1.17$, then

$$\sum \frac{\alpha * x_f}{\alpha - \theta} = -0.024 \approx 0$$ This is an acceptable value

Now substitute the value of $\theta$ in the following equation

$$\frac{\alpha_A * x_{DA} + \alpha_B * x_{DB} + \alpha_C * x_{DC}}{\alpha_A - \theta} + \frac{\alpha_B - \theta}{\alpha_B - \theta} + \frac{\alpha_C - \theta}{\alpha_C - \theta} + \ldots = R_{\text{min}} + 1$$

$$\frac{2.7 * 0.534 + 2.22 * 0.453 + 1 * 0.013}{2.7 - 1.17} + \frac{2.22 - 1.17}{2.22 - 1.17} + \frac{1 - 1.17}{1 - 1.17} = R_{\text{min}} + 1$$

$R_{\text{min}} = 0.827$

The minimum number of plates $N_{\text{min}}$ can be calculated by:

$$N_{\text{min}} + 1 = \frac{\log[(x_{L}/x_{H})_D * (x_{H}/x_{L})_B]}{\log(\alpha_{LH})_{\text{av}}}$$

Here consider $\alpha_{LH}$ is constant for F, D and W, then

$$N_{\text{min}} + 1 = \frac{\log[(0.453/0.013) * (0.96/0.04)]}{\log(2.22)_{\text{av}}}$$

$N_{\text{min}} + 1 = 8.5$

$N_{\text{min}} = 7.5$

Now to find the effect of $R$ on the number of plates use the equation:

$$y = \frac{N - N_{\text{min}}}{N + 2} = 1 - \exp[1.49 + 0.315 * x - \frac{1.805}{x^{0.1}}] \quad \text{Where} \quad x = \frac{R - R_{\text{min}}}{R + 1}$$

Establish a table as shown in below by assuming $R$ starting from $R_{\text{min}}$ to a value of 10 for each value find $x$ for each $R$ and then substitute in equation (*) and find $y$ then evaluate $N$.

Finally plot $N$ vs. $R$ as given in below:

$\theta \approx 0.83$

And $N_{\text{min}} = 7.5$

<table>
<thead>
<tr>
<th>Value of R</th>
<th>$x = \frac{R - R_{\text{min}}}{R + 1}$</th>
<th>$y = 1 - \exp[1.49 + 0.315 * x - \frac{1.805}{x^{0.1}}]$</th>
<th>$N = \frac{2 * y + N_{\text{min}}}{1 - y}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.085</td>
<td>0.547</td>
<td>18.97 ≈ 19</td>
</tr>
<tr>
<td>2</td>
<td>0.39</td>
<td>0.31</td>
<td>11.77 ≈ 12</td>
</tr>
<tr>
<td>5</td>
<td>0.695</td>
<td>0.1504</td>
<td>9.18 ≈ 10</td>
</tr>
<tr>
<td>10</td>
<td>0.833</td>
<td>0.0823</td>
<td>8.35 ≈ 9</td>
</tr>
</tbody>
</table>
Example 11:
A mixture of Ortho, Meta and Para mono-nitro-toluene containing 60, 4 and 36 mol% respectively of the three isomers is to be continuously distilled to give a top product of 98 mol% Ortho, the bottom product is to contain 12.5 mol% Ortho. The mixture is to be distilled at a temperature of 410 K requiring a pressure in the boiler of about 6 kN/m² (0.06 bar). If a reflux ratio of 5 is used, how many theoretical plates will be required and what will be the approximate composition of the top product stream? Given the following data:

\[ \alpha_{OP} = 1.7 \]  
Both at a range of 380 to 415 K

\[ \alpha_{MP} = 1.16 \]

Solution:
As a first estimation, suppose the distillate to contain 0.6 mol% Meta and 1.4 mol% Para. Then by material balance find the composition of the bottom.

Basis 100 kmole of feed
D is the top product with composition of \( x_{DO} \) (mole fraction of Ortho).
W is the bottom product with composition of \( x_{WO} \) (mole fraction of Ortho).

O. M. B.
\[ F = D + W \]

[Ortho] O. M. B.
\[ 60 = D \times x_{DO} + W \times x_{WO} \]
\[ 60 = (100-W) \times 0.98 + 0.125 \times W \]
Then \( D = 55.56 \) kmole and \( W = 44.44 \) kmole

The M. B. will give the compositions and amounts of all streams as shown in the following table:

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed</th>
<th>Distilled</th>
<th>Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kmole</td>
<td>Mol%</td>
<td>kmole</td>
</tr>
<tr>
<td>Ortho (O)</td>
<td>60</td>
<td>60</td>
<td>54.44</td>
</tr>
<tr>
<td>Para (P)</td>
<td>36</td>
<td>36</td>
<td>0.79</td>
</tr>
<tr>
<td>Meta (M)</td>
<td>4</td>
<td>4</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Now find the operating lines equations for each component:
Above the feed
Liquid flow rate \( L_n = R \times D = 55.56 \times 5 = 277.8 \) kmole
Vapor flow rate \( V_n = D \times (R + 1) = 55.56 \times (5 + 1) = 333.4 \) kmole
Assuming the feed enters as saturated liquid, then
Below the feed
Liquid flow rate \( L_M = L_n + F = 277.8 + 100 = 377.8 \) kmole
Vapor flow rate \( V_M = L_M - W = 377.8 - 44.4 = 333.4 \) kmole
Therefore the lower operating lines for each component will be as:
\[
y_m = \frac{L_{m+1}}{V_m} \times x_m - \frac{W}{V_{m+1}} \times x_W
\]
For Ortho
\[
y_{Om} = \frac{377.8}{333.4} \times x_{Om+1} - \frac{44.4}{333.4} \times 0.125
\]
\[
y_{Om} = 1.133 \times x_{Om+1} - 0.01666 \quad ...1
\]
For Meta
\[
y_{Mm} = 1.133 \times x_{Mm+1} - 0.011 \quad ...2
\]
For Para
\[
y_{Pm} = 1.133 \times x_{Pm+1} - 0.105 \quad ...3
\]
The upper operating lines are:
For Ortho
\[
y_{On} = 0.833 \times x_{On+1} + 0.163 \quad ...4
\]
For Meta
\[
y_{Mn} = 0.833 \times x_{Mn+1} + 0.001 \quad ...5
\]
For Para
\[
y_{Pn} = 0.833 \times x_{Pn+1} + 0.002 \quad ...6
\]
Starting from the bottom, the composition of liquid leaving the still is in equilibrium with the vapor entering the column; therefore the composition of this vapor \( y_{Si} \) is found from the equation of relative volatility:
\[
y_i = \frac{\alpha_{ij} \times x_i}{\sum_{n=i}^{n=1} \alpha \times x}
\]
For Ortho
\[
y_{SO} = \frac{\alpha_{OP} \times x_{SO}}{\alpha_{OP} \times x_{SO} + \alpha_{MP} \times x_{SM} + \alpha_{PP} \times x_{SP}} = 0.193
\]
\[
y_{SP} = \frac{1.7 \times 0.125}{1.7 \times 0.125 + 1.16 \times 0.08 + 1 \times 0.792}
\]
For Meta
\[
y_{SM} = \frac{\alpha_{MP} \times x_{SM}}{\alpha_{OP} \times x_{SO} + \alpha_{MP} \times x_{SM} + \alpha_{PP} \times x_{SP}} = 0.0875
\]
\[
y_{SP} = \frac{1.7 \times 0.125 + 1.16 \times 0.08 + 1 \times 0.792}{1.7 \times 0.125 + 1.16 \times 0.08 + 1 \times 0.792}
\]
For Para

\[
y_{SP} = \frac{\alpha_{PP} * x_{SP}}{1 * 0.792}
\]

\[
y_{SP} = 1.70.125 + 1.16 * 0.08 + 1 * 0.792 = 0.7195
\]

Use these values of \( y_{si} \) in the lower operating lines equations (equations 1, 2 and 3) to find the \( x_{1i} \)

Then

\[
x_{1O} = 0.185
\]
\[
x_{1M} = 0.087
\]
\[
x_{1P} = 0.728
\]

Now find \( y_{1i} \) by reusing the equilibrium equations and then re-substitute in the L.O.L. equations to find \( x_{2i} \), the following table is established

<table>
<thead>
<tr>
<th>Component</th>
<th>( x_S )</th>
<th>( \alpha * x_S )</th>
<th>( y_S )</th>
<th>( x_1 )</th>
<th>( \alpha * x_1 )</th>
<th>( y_1 )</th>
<th>( x_2 )</th>
<th>( \alpha * x_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho o</td>
<td>0.125</td>
<td>0.2125</td>
<td>0.193</td>
<td>0.185</td>
<td>0.3145</td>
<td>0.275</td>
<td>0.257</td>
<td>0.4369</td>
</tr>
<tr>
<td>Meta M</td>
<td>0.083</td>
<td>0.0963</td>
<td>0.0875</td>
<td>0.087</td>
<td>0.1009</td>
<td>0.088</td>
<td>0.087</td>
<td>0.1018</td>
</tr>
<tr>
<td>Para P</td>
<td>0.792</td>
<td>0.792</td>
<td>0.719</td>
<td>0.728</td>
<td>0.728</td>
<td>0.637</td>
<td>0.656</td>
<td>0.656</td>
</tr>
<tr>
<td>Sum</td>
<td>1.0</td>
<td>1.1008</td>
<td>1.0</td>
<td>1.0</td>
<td>1.1434</td>
<td>1.0</td>
<td>1.0</td>
<td>1.1947</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>( y_2 )</th>
<th>( x_3 )</th>
<th>( \alpha * x_3 )</th>
<th>( y_3 )</th>
<th>( x_4 )</th>
<th>( \alpha * x_4 )</th>
<th>( y_4 )</th>
<th>( x_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho o</td>
<td>0.366</td>
<td>0.338</td>
<td>0.5746</td>
<td>0.46</td>
<td>0.421</td>
<td>0.7157</td>
<td>0.547</td>
<td>0.4975</td>
</tr>
<tr>
<td>Meta M</td>
<td>0.085</td>
<td>0.085</td>
<td>0.0988</td>
<td>0.079</td>
<td>0.079</td>
<td>0.09164</td>
<td>0.07</td>
<td>0.0715</td>
</tr>
<tr>
<td>Para P</td>
<td>0.549</td>
<td>0.577</td>
<td>0.577</td>
<td>0.461</td>
<td>0.5</td>
<td>0.383</td>
<td>0.431</td>
<td></td>
</tr>
<tr>
<td>Sum</td>
<td>1.0</td>
<td>1.0</td>
<td>1.2502</td>
<td>1.0</td>
<td>1.0</td>
<td>1.30734</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>( \alpha * x_5 )</th>
<th>( y_5 )</th>
<th>( x_6 )</th>
<th>( \alpha * x_6 )</th>
<th>( y_6 )</th>
<th>( x_7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho o</td>
<td>0.847575</td>
<td>0.622</td>
<td>0.5636</td>
<td>0.95812</td>
<td>0.6821</td>
<td>0.617</td>
</tr>
<tr>
<td>Meta M</td>
<td>0.08299</td>
<td>0.061</td>
<td>0.0635</td>
<td>0.07366</td>
<td>0.0524</td>
<td>0.056</td>
</tr>
<tr>
<td>Para P</td>
<td>0.431</td>
<td>0.317</td>
<td>0.3729</td>
<td>0.3729</td>
<td>0.2655</td>
<td>0.327</td>
</tr>
<tr>
<td>Sum</td>
<td>1.35969</td>
<td>1.0</td>
<td>1.0</td>
<td>1.40468</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Here we have exceeded the composition of the feed, then by using the same procedure replacing the L.O.L. with the U.O.L. equations and continue the calculation as

<table>
<thead>
<tr>
<th>Component</th>
<th>( x_7 )</th>
<th>( \alpha * x_7 )</th>
<th>( y_7 )</th>
<th>( x_8 )</th>
<th>( \alpha * x_8 )</th>
<th>( y_8 )</th>
<th>( x_9 )</th>
<th>( \alpha * x_9 )</th>
<th>( y_9 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho o</td>
<td>0.617</td>
<td>1.0489</td>
<td>0.728</td>
<td>0.678</td>
<td>1.1526</td>
<td>0.7771</td>
<td>0.737</td>
<td>1.2529</td>
<td>0.822</td>
</tr>
<tr>
<td>Meta M</td>
<td>0.056</td>
<td>0.06496</td>
<td>0.045</td>
<td>0.053</td>
<td>0.0615</td>
<td>0.0415</td>
<td>0.048</td>
<td>0.05563</td>
<td>0.037</td>
</tr>
<tr>
<td>Para P</td>
<td>0.327</td>
<td>0.327</td>
<td>0.227</td>
<td>0.269</td>
<td>0.269</td>
<td>0.1814</td>
<td>0.215</td>
<td>0.215</td>
<td>0.141</td>
</tr>
<tr>
<td>Sum</td>
<td>1.0</td>
<td>1.44086</td>
<td>1.0</td>
<td>1.0</td>
<td>1.4831</td>
<td>1.0</td>
<td>1.0</td>
<td>1.52358</td>
<td>1.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>( x_{10} )</th>
<th>( \alpha * x_{10} )</th>
<th>( y_{10} )</th>
<th>( x_{11} )</th>
<th>( \alpha * x_{11} )</th>
<th>( y_{11} )</th>
<th>( x_{12} )</th>
<th>( \alpha * x_{12} )</th>
<th>( y_{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho o</td>
<td>0.791</td>
<td>1.3447</td>
<td>0.862</td>
<td>0.839</td>
<td>1.4263</td>
<td>0.875</td>
<td>0.879</td>
<td>1.4943</td>
<td>0.922</td>
</tr>
<tr>
<td>Meta M</td>
<td>0.043</td>
<td>0.05</td>
<td>0.032</td>
<td>0.037</td>
<td>0.04292</td>
<td>0.027</td>
<td>0.031</td>
<td>0.03596</td>
<td>0.022</td>
</tr>
<tr>
<td>Para P</td>
<td>0.166</td>
<td>0.166</td>
<td>0.106</td>
<td>0.124</td>
<td>0.124</td>
<td>0.078</td>
<td>0.09</td>
<td>0.09</td>
<td>0.056</td>
</tr>
<tr>
<td>sum</td>
<td>1.0</td>
<td>1.5607</td>
<td>1.0</td>
<td>1.0</td>
<td>1.59322</td>
<td>1.0</td>
<td>1.0</td>
<td>1.62026</td>
<td>1.0</td>
</tr>
</tbody>
</table>
And that is the end of calculation because the composition of the product D exceed the given value (0.98)
Therefore the final approximate composition is:
Ortho: 0.983
Meta: 0.007
Para: 0.01
And the theoretical number of plates required = 17 - 1 = 16 plates

Example 12(stage by stage method)
A mixture of benzene and toluene containing 40 mole% of benzene is to be separated to give a product of 90 mole % of benzene at the top, and a bottom product with not more than 10 mole% of benzene. The feed is heated so that it enters the column at its boiling point, and the vapor leaving the column is condensed but not cooled, and provides reflux and product. It is proposed to operate the unit with reflux ratio of 3 kmol / kmol product. It is required to find the number of theoretical plates needed and the position of entry of the feed. The equilibrium data are given in the table below:

<table>
<thead>
<tr>
<th>x_{13}</th>
<th>α * x_{13}</th>
<th>y_{13}</th>
<th>x_{14}</th>
<th>α * x_{14}</th>
<th>y_{14}</th>
<th>x_{15}</th>
<th>α * x_{15}</th>
<th>y_{15}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho</td>
<td>0.911</td>
<td>1.5487</td>
<td>0.943</td>
<td>0.936</td>
<td>1.5912</td>
<td>0.959</td>
<td>0.955</td>
<td>1.6235</td>
</tr>
<tr>
<td>Meta</td>
<td>0.025</td>
<td>0.029</td>
<td>0.018</td>
<td>0.02</td>
<td>0.0232</td>
<td>0.014</td>
<td>0.015</td>
<td>0.01755</td>
</tr>
<tr>
<td>Para</td>
<td>0.064</td>
<td>0.064</td>
<td>0.039</td>
<td>0.044</td>
<td>0.044</td>
<td>0.027</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>sum</td>
<td>1.0</td>
<td>1.6417</td>
<td>1.0</td>
<td>1.0</td>
<td>1.6584</td>
<td>1.0</td>
<td>1.0</td>
<td>1.67105</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>x_{16}</th>
<th>α * x_{16}</th>
<th>y_{16}</th>
<th>x_{17}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho</td>
<td>0.971</td>
<td>1.6507</td>
<td>0.983</td>
</tr>
<tr>
<td>Meta</td>
<td>0.01</td>
<td>0.0116</td>
<td>0.007</td>
</tr>
<tr>
<td>Para</td>
<td>0.019</td>
<td>0.019</td>
<td>0.01</td>
</tr>
<tr>
<td>sum</td>
<td>1.0</td>
<td>1.6813</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Solution:
Basis 100 kmole of feed
A total material balance gives:
100 = D + W
[Benzene M. B.]
100 * 0.4 = 0.9 * D + 0.1 * W
Thus:
40 = 0.9 * (100- W) + 0.1 * W
Whence:
W = 62.5 kmole and D = 37.5 kmole
R = \frac{L_n}{D}
L_n = 3 * D = 112.5
And
V_n = L_n + D = 150
Thus, the upper operating line equation is:

\[ y_n = \frac{112.5}{150} \times x_{n+1} + \frac{37.5}{150} \times 0.9 \]

Or

\[ y_n = 0.75 \times x_{n+1} + 0.225 \]

Since the feed is all at its boiling point, it will all run down as increased reflux to the plate below.

Thus

\[ L_m = L_n + F = 112.5 + 100 = 212.5 \]

\[ V_m = L_m - W \]

\[ V_m = 212.5 - 62.5 = 150 = V_n \]

Thus, the lower operating line will be

\[ y_m = \frac{212.5}{150} \times x_{m+1} - \frac{62.5}{150} \times 0.1 \]

Or

\[ y_m = 1.415 \times x_{m+1} - 0.042 \]

Continue as described in the lectures.

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**Example 13**

A liquid mixture of Benzene – Toluene is to be distilled in a fractionating column. The feed of 100 kmole/hr is liquid containing 45 mol% Benzene enters the column at a temperature 39 K below its bubble point.

The top product contains 95 mol% Benzene and the bottom product contain 10 mol% Benzene. The reflux ratio is 4:1.

The specific heat of the feed is 159 \( \text{kJ/(kmol.K)} \). the molar latent heat of vaporization of both Benzene and Toluene may be assumed constant and equal 32100 \( \text{kJ/kmol} \). Equilibrium data for Benzene – Toluene mixture is:

<table>
<thead>
<tr>
<th>( x_{\text{Benzene}} )</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( y_{\text{Benzene}} )</td>
<td>0</td>
<td>0.2</td>
<td>0.38</td>
<td>0.51</td>
<td>0.63</td>
<td>0.71</td>
<td>0.78</td>
<td>0.85</td>
<td>0.91</td>
<td>0.96</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Calculate:

1- The number of theoretical plates required.
2- The vapor flow rates inside the column.
3- The liquid flow rates inside the column.
4- The heat transfer rate in the re-boiler in (kJ/hr).
Steam distillation

Where the material to be distilled has a high boiling point, and particularly where decomposition might occur if direct distillation were employed, the process of steam distillation can be used. Steam is passed directly into the liquid in the still; the solubility of steam in the liquid must be very low. Steam distillation is perhaps the most common example of differential distillation.

Two cases are possible. The steam may be superheated and provide sufficient heat to vaporize the material concerned, without itself condensing. Alternatively, some of the steam may condense, producing a liquid water phase. In either case, assuming the gas laws to apply, the composition of the vapor produced can be obtained from the following relationship:

\[
\frac{m_\text{A}}{m_\text{B}} = \frac{P_\text{A}}{P_\text{B}} = \frac{y_\text{A}}{y_\text{B}} = \frac{P_\text{A}}{P - P_\text{A}}
\]

Where the subscript A refers to the component being recovered and B to steam, and:
- \( m \) = mass
- \( M \) = molecular weight
- \( P_\text{A}, P_\text{B} \) = partial pressure of A, B
- \( P \) = total pressure

Azeotropic and extractive distillation

In the processes so far considered, the vapor becomes steadily richer in the more volatile component on successive plates. There are two types of mixtures where this steady increase in the concentration of the more volatile component either does not take place, or else takes place so slowly that an uneconomical number of plates are required. If, for instance, a mixture of ethyl alcohol and water is distilled, the concentration of the alcohol steadily increase until it reaches 96 wt%, when the composition of the vapor equals that of the liquid, and no further enrichment occurs. This mixture is called an azeotrope, and cannot be separated by straightforward distillation. Such a condition is shown in the y-x curves in below where it is seen that the equilibrium curve crosses the diagonal, indicating the existence of an azeotrope. A large number of Azeotropic mixture have been found, some of which are of great industrial importance, e.g. water – nitric acid, water – hydrochloric acid, and water – many alcohols.

The second type of problem occurs where the relative volatility of binary mixture is very low, in which case continuous distillation of the mixture to give nearly pure products will require high reflux ratios with correspondingly high heat requirements; in addition, it will necessitate a tower of
large cross-section containing many trays. An example of the second type of problem is the separation of n-heptane from methyl cyclohexane. Here the relative volatility is only 1.08 and a large number of plates are required to achieve separation.

The principle of Azeotropic and of extractive distillation lies in the addition of a new substance to the mixture so as to increase the relative volatility of the two key components, and thus make separation relatively easy. Benedict and Rubin have defined these two processes in the following way. In Azeotropic distillation the substance added forms an azeotrope with one or more of the components in the mixture, and as a result is present on most of the plates of the column in appreciable concentration. With extractive distillation the substance added is relatively non-volatile compared with the components to be separated, and it is therefore fed continuously near the top of the column. This extractive agent runs down the column as reflux and is present in appreciable concentration on all the plates.

The third component added to the binary mixture is sometimes known as the entrainer or the solvent.