



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – I– MASS TRANSFER-I – SCH1401

INTRODUCTION TO MASS TRANSFER

1. Introduction of Mass Transfer

When a system contains two or more components whose concentrations vary from point to point, there is a natural tendency for mass to be transferred, minimizing the concentration differences within a system. The transport of one constituent from a region of higher concentration to that of a lower concentration is called mass transfer.

The transfer of mass within a fluid mixture or across a phase boundary is a process that plays a major role in many industrial processes. Examples of such processes are:

- (i) Dispersion of gases from stacks
- (ii) Removal of pollutants from plant discharge streams by absorption
- (iii) Stripping of gases from waste water
- (iv) Neutron diffusion within nuclear reactors
- (v) Air conditioning

Many of our day-by-day experiences also involve mass transfer, for example:

- (i) A lump of sugar added to a cup of coffee eventually dissolves and then eventually diffuses to make the concentration uniform.
- (ii) Water evaporates from ponds to increase the humidity of passing-air-stream
- (iii) Perfumes present a pleasant fragrance which is imparted throughout the surrounding atmosphere.

The mechanism of mass transfer involves both molecular diffusion and convection.

1.1 Properties of Mixtures

Mass transfer always involves mixtures. Consequently, we must account for the variation of physical properties which normally exist in a given system. When a system contains three or more components, as many industrial fluid streams do, the problem becomes unwieldy very quickly. The conventional engineering approach to problems of

multicomponent system is to attempt to reduce them to representative binary (i.e., two component) systems.

In order to understand the future discussions, let us first consider definitions and relations which are often used to explain the role of components within a mixture.

1.2 Concentration of Species:

Concentration of species in multicomponent mixture can be expressed in many ways. For species A, mass concentration denoted by ρ_A is defined as the mass of A, m_A per unit volume of the mixture.

$$\rho_A = \frac{m_A}{V} \quad \text{-----} \quad (1)$$

The total mass concentration density ρ is the sum of the total mass of the mixture in unit volume:

$$\rho = \sum_i \rho_i$$

where ρ_i is the concentration of species i in the mixture.

Molar concentration of, A, C_A is defined as the number of moles of A present per unit volume of the mixture.

By definition,

$$\text{Number of moles} = \frac{\text{mass of A}}{\text{molecular weight of A}}$$

$$n_A = \frac{m_A}{M_A} \quad \text{-----} \quad (2)$$

Therefore from (1) & (2)

$$C_A = \frac{n_A}{V} = \frac{\rho_A}{M_A}$$

For ideal gas mixtures,

$$n_A = \frac{p_A V}{RT} \quad [\text{from Ideal gas law } PV = nRT]$$

$$C_A = \frac{n_A}{V} = \frac{p_A}{RT}$$

where p_A is the partial pressure of species A in the mixture. V is the volume of gas, T is the absolute temperature, and R is the universal gas constant.

The total molar concentration or molar density of the mixture is given by

$$C = \sum_i C_i$$

1.3 Velocities

In a multicomponent system the various species will normally move at different velocities; and evaluation of velocity of mixture requires the averaging of the velocities of each species present.

If v_i is the velocity of species i with respect to stationary fixed coordinates, then mass-average velocity for a multicomponent mixture defined in terms of mass concentration is,

$$v = \frac{\sum_i \rho_i v_i}{\sum_i \rho_i} = \frac{\sum_i \rho_i v_i}{\rho}$$

By similar way, molar-average velocity of the mixture v^* is

$$v^* = \frac{\sum_i C_i v_i}{C}$$

For most engineering problems, there will be little difference in v^* and v and so the mass average velocity, v , will be used in all further discussions.

The velocity of a particular species relative to the mass-average or molar average velocity is termed as diffusion velocity

(i.e.) Diffusion velocity = $v_i - v$

The mole fraction for liquid and solid mixture, x_A , and for gaseous mixtures, y_A , are the molar concentration of species A divided by the molar density of the mixtures.

$$x_A = \frac{C_A}{C} \quad (\text{liquids and solids})$$

$$y_A = \frac{C_A}{C} \quad (\text{gases}).$$

The sum of the mole fractions, by definition must equal 1;

$$(\text{i.e.}) \quad \sum_i x_i = 1$$

$$\sum_i y_i = 1$$

by similar way, mass fraction of A in mixture is;

$$w_A = \frac{\rho_A}{\rho}$$

1. The molar composition of a gas mixture at 273 K and 1.5×10^5 Pa is:

O₂ 7%

CO 10%

CO₂ 15%

N₂ 68%

Determine

- a) the composition in weight percent
- b) average molecular weight of the gas mixture
- c) density of gas mixture
- d) partial pressure of O₂.

Calculations:

Let the gas mixture constitutes 1 mole. Then

$$\text{O}_2 = 0.07 \text{ mol}$$

$$\text{CO} = 0.10 \text{ mol}$$

$$\text{CO}_2 = 0.15 \text{ mol}$$

$$\text{N}_2 = 0.68 \text{ mol}$$

Molecular weight of the constituents are:

$$\text{O}_2 = 2 * 16 = 32 \text{ g/mol}$$

$$\text{CO} = 12 + 16 = 28 \text{ g/mol}$$

$$\text{CO}_2 = 12 + 2 * 16 = 44 \text{ g/mol}$$

$$\text{N}_2 = 2 * 14 = 28 \text{ g/mol}$$

Weight of the constituents are: (1 mol of gas mixture)

$$\text{O}_2 = 0.07 * 32 = 2.24 \text{ g}$$

$$\text{CO} = 0.10 * 28 = 2.80 \text{ g}$$

$$\text{CO}_2 = 0.15 * 44 = 6.60 \text{ g}$$

$$\text{N}_2 = 0.68 * 28 = 19.04 \text{ g}$$

$$\begin{aligned} \text{Total weight of gas mixture} &= 2.24 + 2.80 + 6.60 + 19.04 \\ &= 30.68 \text{ g} \end{aligned}$$

Composition in weight percent:

$$\text{O}_2 = \frac{2.24}{30.68} * 100 = 7.30\%$$

$$CO = \frac{2.80}{30.68} * 100 = 9.13\%$$

$$CO_2 = \frac{6.60}{30.68} * 100 = 21.51\%$$

$$N_2 = \frac{19.04}{30.68} * 100 = 62.06\%$$

$$\text{Average molecular weight of the gas mixture } M = \frac{\text{Weight of gas mixture}}{\text{Number of moles}}$$

$$M = \frac{30.68}{1} = 30.68 \text{ g/mol}$$

Assuming that the gas obeys ideal gas law,

$$PV = nRT$$

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{n}{V} = \text{molar density} = \rho_m$$

Therefore, density (or mass density) = $\rho_m M$

Where M is the molecular weight of the gas.

$$\begin{aligned} \text{Density} = \rho_m M &= \frac{PM}{RT} = \frac{1.5 * 10^5 * 30.68}{8314 * 273} \text{ kg/m}^3 \\ &= 2.03 \text{ kg/m}^3 \end{aligned}$$

Partial pressure of O₂ = [mole fraction of O₂] * total pressure

$$\begin{aligned}
 &= \frac{7}{100} * (1.5 * 10^5) \\
 &= 0.07 * 1.5 * 10^5 \\
 &= 0.105 * 10^5 \text{ Pa}
 \end{aligned}$$

1.4 Diffusion flux

Just as momentum and energy (heat) transfer have two mechanisms for transport-molecular and convective, so does mass transfer. However, there are convective fluxes in mass transfer, even on a molecular level. The reason for this is that in mass transfer, whenever there is a driving force, there is always a net movement of the mass of a particular species which results in a bulk motion of molecules. Of course, there can also be convective mass transport due to macroscopic fluid motion. In this chapter the focus is on molecular mass transfer.

The mass (or molar) flux of a given species is a vector quantity denoting the amount of the particular species, in either mass or molar units, that passes per given increment of time through a unit area normal to the vector. The flux of species defined with reference to fixed spatial coordinates, N_A is

$$N_A = C_A v_A \text{ ----- (1)}$$

This could be written in terms of diffusion velocity of A, (i.e., $v_A - v$) and average velocity of mixture, v , as

$$N_A = C_A (v_A - v) + C_A v \text{ ----- (2)}$$

By definition

$$v = v^* = \frac{\sum_i C_i v_i}{C}$$

Therefore, equation (2) becomes

$$\begin{aligned} N_A &= C_A (v_A - v) + \frac{C_A}{C} \sum_i C_i v_i \\ &= C_A (v_A - v) + y_A \sum_i C_i v_i \end{aligned}$$

For systems containing two components A and B,

$$\begin{aligned} N_A &= C_A (v_A - v) + y_A (C_A v_A + C_B v_B) \\ &= C_A (v_A - v) + y_A (N_A + N_B) \\ N_A &= C_A (v_A - v) + y_A N \quad \text{----- (3)} \end{aligned}$$

The first term on the right hand side of this equation is diffusional molar flux of A, and the second term is flux due to bulk motion.

1.5 Fick's law:

An empirical relation for the diffusional molar flux, first postulated by Fick and, accordingly, often referred to as Fick's first law, defines the diffusion of component A in an isothermal, isobaric system. For diffusion in only the Z direction, the Fick's rate equation is

$$J_A = -D_{AB} \frac{dC_A}{dZ}$$

where D_{AB} is diffusivity or diffusion coefficient for component A diffusing through component B, and dC_A / dZ is the concentration gradient in the Z-direction.

A more general flux relation which is not restricted to isothermal, isobasic system could be written as

$$J_A = -C D_{AB} \frac{dy_A}{dZ} \text{-----} (4)$$

using this expression, Equation (3) could be written as

$$N_A = -C D_{AB} \frac{dy_A}{dZ} + y_A N \text{-----} (5)$$

1.6 Relation among molar fluxes:

For a binary system containing A and B, from Equation (5),

$$\begin{aligned} N_A &= J_A + y_A N \\ \text{or } J_A &= N_A + y_A N \text{-----} (6) \end{aligned}$$

Similarly,

$$J_B = N_B + y_B N \text{-----} (7)$$

Addition of Equation (6) & (7) gives,

$$J_A + J_B = N_A + N_B - (y_A + y_B) N \text{-----} (8)$$

By definition $N = N_A + N_B$ and $y_A + y_B = 1$.

Therefore equation (8) becomes,

$$\begin{aligned} J_A + J_B &= 0 \\ J_A &= -J_B \end{aligned}$$

$$C D_{AB} \frac{dy_A}{dz} = - C D_{BA} \frac{dy_B}{dz} \text{ ----- (9)}$$

From $y_A + y_B = 1$
 $dy_A = - dy_B$

Therefore Equation (9) becomes,

$$D_{AB} = D_{BA} \text{ ----- (10)}$$

This leads to the conclusion that diffusivity of A in B is equal to diffusivity of B in A.

1.7 Diffusivity

Fick's law proportionality, D_{AB} , is known as mass diffusivity (simply as diffusivity) or as the diffusion coefficient. D_{AB} has the dimension of L^2 / t , identical to the fundamental dimensions of the other transport properties: Kinematic viscosity, $\nu = (\mu / \rho)$ in momentum transfer, and thermal diffusivity, $\alpha (= k / \rho C_p)$ in heat transfer.

Diffusivity is normally reported in cm^2 / sec ; the SI unit being m^2 / sec .

Diffusivity depends on pressure, temperature, and composition of the system.

In table, some values of D_{AB} are given for a few gas, liquid, and solid systems.

Diffusivities of gases at low density are almost composition independent, increase with the temperature and vary inversely with pressure. Liquid and solid diffusivities are strongly concentration dependent and increase with temperature.

General range of values of diffusivity:

Gases :	5×10^{-6}	-----	1×10^{-5}	$\text{m}^2 / \text{sec}.$
Liquids :	10^{-6}	-----	10^{-9}	$\text{m}^2 / \text{sec}.$
Solids :	5×10^{-14}	-----	1×10^{-10}	$\text{m}^2 / \text{sec}.$

In the absence of experimental data, semitheoretical expressions have been developed which give approximation, sometimes as valid as experimental values, due to the difficulties encountered in experimental measurements.

1.8 Diffusivity in Gases:

Pressure dependence of diffusivity is given by

$$D_{AB} \propto \frac{1}{p} \quad (\text{for moderate ranges of pressures, upto 25 atm}).$$

And temperature dependency is according to

$$D_{AB} \propto T^{3/2}$$

Diffusivity of a component in a mixture of components can be calculated using the diffusivities for the various binary pairs involved in the mixture. The relation given by Wilke is

$$D_{1-\text{mixture}} = \frac{1}{\frac{y'_2}{D_{1-2}} + \frac{y'_3}{D_{1-3}} + \dots + \frac{y'_n}{D_{1-n}}}$$

Where $D_{1-\text{mixture}}$ is the diffusivity for component 1 in the gas mixture; D_{1-n} is the diffusivity for the binary pair, component 1 diffusing through component n; and y'_n is the mole fraction of component n in the gas mixture evaluated on a component –1 – free basis, that is

$$y'_2 = \frac{y_2}{y_2 + y_3 + \dots + y_n}$$

9. Determine the diffusivity of CO_2 (1), O_2 (2) and N_2 (3) in a gas mixture having the composition:

CO_2 : 28.5 %, O_2 : 15%, N_2 : 56.5%,

The gas mixture is at 273 K and 1.2×10^5 Pa. The binary diffusivity values are given as: (at 273 K)

$$D_{12} = 1.874 \text{ m}^2/\text{sec}$$

$$D_{13} = 1.945 \text{ m}^2/\text{sec}$$

$$D_{23} = 1.834 \text{ m}^2/\text{sec}$$

Calculations:

Diffusivity of CO_2 in mixture

$$D_{1m} = \frac{1}{\frac{y_2'}{D_{12}} + \frac{y_3'}{D_{13}}}$$

$$\text{where } y_2' = \frac{y_2}{y_2 + y_3} = \frac{0.15}{0.15 + 0.565} = 0.21$$

$$y_3' = \frac{y_3}{y_2 + y_3} = \frac{0.565}{0.15 + 0.565} = 0.79$$

$$\begin{aligned} \text{Therefore } D_{1m} P &= \frac{1}{\frac{0.21}{1.874} + \frac{0.79}{1.945}} \\ &= 1.93 \text{ m}^2 \cdot \text{Pa/sec} \end{aligned}$$

Since $P = 1.2 \times 10^5 \text{ Pa}$,

$$D_{1m} = \frac{1.93}{1.2 \times 10^5} = 1.61 \times 10^{-5} \text{ m}^2/\text{sec}$$

Diffusivity of O_2 in the mixture,

$$D_{2m} = \frac{1}{\frac{y_1'}{D_{21}} + \frac{y_3'}{D_{23}}}$$

$$\text{Where } y_1' = \frac{y_1}{y_1 + y_3} = \frac{0.285}{0.285 + 0.565} = 0.335$$

(mole fraction on-2 free bans).

and

$$y_3' = \frac{y_3}{y_1 + y_3} = \frac{0.565}{0.285 + 0.565} = 0.665$$

and

$$D_{21} P = D_{12} P = 1.874 \text{ m}^2 \cdot \text{Pa}/\text{sec}$$

Therefore

$$D_{2m} P = \frac{1}{\frac{0.335}{1.874} + \frac{0.665}{1.834}} \\ = 1.847 \text{ m}^2 \cdot \text{Pa}/\text{sec}$$

$$D_{2m} = \frac{1.847}{1.2 \times 10^5} = 1.539 \times 10^{-5} \text{ m}^2/\text{sec}$$

By Similar calculations Diffusivity of N_2 in the mixture can be calculated, and is found to be, $D_{3m} = 1.588 \times 10^{-5} \text{ m}^2/\text{sec}$.

1.9 Diffusivity in liquids:

Diffusivity in liquid are exemplified by the values given in table ... Most of these values are nearer to $10^{-5} \text{ cm}^2 / \text{sec}$, and about ten thousand times slower than those in dilute gases. This characteristic of liquid diffusion often limits the overall rate of processes accruing in liquids (such as reaction between two components in liquids).

In chemistry, diffusivity limits the rate of acid-base reactions; in the chemical industry, diffusion is responsible for the rates of liquid-liquid extraction. Diffusion in liquids is important because it is slow.

Certain molecules diffuse as molecules, while others which are designated as electrolytes ionize in solutions and diffuse as ions. For example, sodium chloride (NaCl), diffuses in water as ions Na^+ and Cl^- . Though each ions has a different mobility, the electrical

neutrality of the solution indicates the ions must diffuse at the same rate; accordingly it is possible to speak of a diffusion coefficient for molecular electrolytes such as NaCl. However, if several ions are present, the diffusion rates of the individual cations and anions must be considered, and molecular diffusion coefficients have no meaning.

Diffusivity varies inversely with viscosity when the ratio of solute to solvent ratio exceeds five. In extremely high viscosity materials, diffusion becomes independent of viscosity.

1.10 Diffusivity in solids:

Typical values for diffusivity in solids are shown in table. One outstanding characteristic of these values is their small size, usually thousands of times less than those in a liquid, which are in turn 10,000 times less than those in a gas.

Diffusion plays a major role in catalysis and is important to the chemical engineer. For metallurgists, diffusion of atoms within the solids is of more importance.

1.11 Steady State Diffusion

In this section, steady-state molecular mass transfer through simple systems in which the concentration and molar flux are functions of a single space coordinate will be considered.

In a binary system, containing A and B, this molar flux in the direction of z, as given by Eqn (5) is [section 3.3.1]

$$N_A = -CD_{AB} \frac{dy_A}{dz} + y_A (N_A + N_B) \quad \text{--- (1)}$$

:

12. Oxygen is diffusing in a mixture of oxygen-nitrogen at 1 std atm, 25°C. Concentration of oxygen at planes 2 mm apart are 10 and 20 volume % respectively. Nitrogen is non-diffusing.

- Derive the appropriate expression to calculate the flux oxygen. Define units of each term clearly.
- Calculate the flux of oxygen. Diffusivity of oxygen in nitrogen = $1.89 \times 10^{-5} \text{ m}^2/\text{sec}$.

Solution:

Let us denote oxygen as A and nitrogen as B. Flux of A (i.e.) N_A is made up of two components, namely that resulting from the bulk motion of A (i.e.), Nx_A and that resulting from molecular diffusion J_A :

$$N_A = Nx_A + J_A \text{ ----- (1)}$$

From Fick's law of diffusion,

$$J_A = -D_{AB} \frac{dC_A}{dz} \text{ ----- (2)}$$

Substituting this equation (1)

$$N_A = Nx_A - D_{AB} \frac{dC_A}{dz} \text{ ----- (3)}$$

Since $N = N_A + N_B$ and $x_A = C_A / C$ equation (3) becomes

$$N_A = (N_A + N_B) \frac{C_A}{C} - D_{AB} \frac{dC_A}{dz}$$

Rearranging the terms and integrating between the planes between 1 and 2,

$$\int \frac{dz}{cD_{AB}} = - \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{N_A C - C_A (N_A + N_B)} \text{ ----- (4)}$$

Since B is non diffusing $N_B = 0$. Also, the total concentration C remains constant. Therefore, equation (4) becomes

$$\frac{z}{CD_{AB}} = - \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{N_A C - N_A C_A}$$

$$= \frac{1}{N_A} \ln \frac{C - C_{A2}}{C - C_{A1}}$$

Therefore,

$$N_A = \frac{CD_{AB}}{z} \ln \frac{C - C_{A2}}{C - C_{A1}} \text{----- (5)}$$

Replacing concentration in terms of pressures using Ideal gas law, equation (5) becomes

$$N_A = \frac{D_{AB} P_t}{RTz} \ln \frac{P_t - P_{A2}}{P_t - P_{A1}} \text{----- (6)}$$

where

D_{AB} = molecular diffusivity of A in B

P_T = total pressure of system

R = universal gas constant

T = temperature of system in absolute scale

z = distance between two planes across the direction of diffusion

P_{A1} = partial pressure of A at plane 1, and

P_{A2} = partial pressure of A at plane 2

Given:

$$D_{AB} = 1.89 \times 10^{-5} \text{ m}^2/\text{sec}$$

$$P_t = 1 \text{ atm} = 1.01325 * 10^5 \text{ N/m}^2$$

$$T = 25^\circ\text{C} = 273 + 25 = 298 \text{ K}$$

$$z = 2 \text{ mm} = 0.002 \text{ m}$$

$$P_{A1} = 0.2 * 1 = 0.2 \text{ atm (From Ideal gas law and additive pressure rule)}$$

$$P_{A2} = 0.1 * 1 = 0.1 \text{ atm}$$

Substituting these in equation (6)

$$N_A = \frac{(1.89 * 10^{-5})(1.01325 * 10^5)}{(8314)(298)(0.002)} \ln \left(\frac{1 - 0.1}{1 - 0.2} \right)$$

$$= 4.55 * 10^{-5} \text{ kmol/m}^2 \cdot \text{sec}$$

1.12 Psuedo steady state diffusion through a stagnant film:

In many mass transfer operations, one of the boundaries may move with time. If the length of the diffusion path changes a small amount over a long period of time, a pseudo steady state diffusion model may be used. When this condition exists, the equation of steady state diffusion through stagnant gas' can be used to find the flux.

If the difference in the level of liquid A over the time interval considered is only a small fraction of the total diffusion path, and $t_0 - t$ is relatively long period of time, at any given instant in that period, the molar flux in the gas phase may be evaluated by

$$N_A = \frac{CD_{AB}(y_{A1} - y_{A2})}{zy_{B,lm}} \text{ ----- (1)}$$

where z equals $z_2 - z_1$, the length of the diffusion path at time t .

The molar flux N_A is related to the amount of A leaving the liquid by

$$N_A = \frac{\rho_{A,L}}{M_A} \frac{dz}{dt} \text{ ----- (2)}$$

where $\frac{\rho_{A,L}}{M_A}$ is the molar density of A in the liquid phase

under Psuedo steady state conditions, equations (1) & (2) can be equated to give

$$\frac{\rho_{A,L}}{M_A} \frac{dz}{dt} = \frac{CD_{AB}(y_{A1} - y_{A2})}{zy_{B,lm}} \quad \text{----- (3)}$$

Equation. (3) may be integrated from $t = 0$ to t and from $z = z_{t0}$ to $z = z_t$ as:

$$\int_{t=0}^t dt = \frac{\rho_{A,L} y_{B,lm} / M_A}{CD_{AB}(y_{A1} - y_{A2})} \int_{z_{t0}}^{z_t} z dz$$

yielding

$$t = \frac{\rho_{A,L} y_{B,lm} / M_A}{CD_{AB}(y_{A1} - y_{A2})} \left(\frac{z_t^2 - z_{t0}^2}{2} \right) \quad \text{----- (4)}$$

This shall be rearranged to evaluate diffusivity D_{AB} as,

$$D_{AB} = \frac{\rho_{A,L} y_{B,lm}}{M_A C (y_{A1} - y_{A2}) t} \left(\frac{z_t^2 - z_{t0}^2}{2} \right)$$

1. A vertical glass tube 3 mm in diameter is filled with liquid toluene to a depth of 20mm from the top openend. After 275 hrs at 39.4 °C and a total pressure of 760 mm Hg the level has dropped to 80 mm from the top. Calculate the value of diffusivity.

Data:

vapor pressure of toluene at 39.4°C = 7.64 kN / m²,

density of liquid toluene = 850 kg/m³

Molecular weight of toluene = 92



$$D_{AB} = \frac{\rho_{A,L} Y_{B,lm}}{M_A C (y_{A1} - y_{A2}) t} \left(\frac{Z_t^2 - Z_{t0}^2}{2} \right)$$

$$\text{where } Y_{B,lm} = \frac{Y_{B2} - Y_{B1}}{\ln \left(\frac{Y_{B2}}{Y_{B1}} \right)}$$

$$y_{B2} = 1 - y_{A2}$$

$$y_{B1} = 1 - y_{A1}$$

$$y_{A1} = \frac{p_{A1}}{P} = \frac{7.64}{101.3} \quad (760 \text{ mm Hg} = 101.3 \text{ kN/m}^2)$$

$$= 0.0754$$

$$y_{B1} = 1 - 0.0754 = 0.9246$$

$$y_{A2} = 0$$

$$y_B = 1 - y_{A2} = 1$$

$$\text{Therefore } Y_{B,lm} = \frac{1 - 0.9246}{\ln \left(\frac{1}{0.9246} \right)} = 0.9618$$

$$C = \frac{P}{RT} = \frac{1.01325 * 10^5}{8314 * (273 + 39.4)}$$

$$= 0.039 \text{ k mol /m}^3$$

Therefore

$$D_{AB} = \frac{850 * 0.9618}{92 * 0.039 * (0.0754 - 0) * 275 * 3600} \left(\frac{0.08^2 - 0.02^2}{2} \right)$$

$$= 1.5262 * 10^{-3} (0.08^2 - 0.02^2)$$

$$= 9.1572 * 10^{-6} \text{ m}^2/\text{sec}.$$

1.13 Equimolar counter diffusion:

A physical situation which is encountered in the distillation of two constituents whose molar latent heats of vaporization are essentially equal, stipulates that the flux of one gaseous component is equal to but acting in the opposite direction from the other gaseous component; that is, $N_A = -N_B$.

The molar flux N_A , for a binary system at constant temperature and pressure is described by

$$N_A = -CD_{AB} \frac{dy_A}{dz} + y_A (N_A + N_B)$$

or

$$N_A = -D_{AB} \frac{dC_A}{dz} + y_A (N_A + N_B) \quad \text{----- (1)}$$

with the substitution of $N_B = -N_A$, Equation (1) becomes,

$$N_A = -D_{AB} \frac{dC_A}{dz} \quad \text{----- (2)}$$

For steady state diffusion Equation. (2) may be integrated, using the boundary conditions:

$$\begin{array}{ll} \text{at } z = z_1 & C_A = C_{A1} \\ \text{and } z = z_2 & C_A = C_{A2} \end{array}$$

Giving,

$$N_A \int_{z_1}^{z_2} dz = -D_{AB} \int_{C_{A1}}^{C_{A2}} dC_A$$

from which

$$N_A = \frac{D_{AB}}{z_2 - z_1} (C_{A1} - C_{A2}) \quad \text{----- (3)}$$

For ideal gases, $C_A = \frac{n_A}{V} = \frac{p_A}{RT}$. Therefore Equation. (3) becomes

$$N_A = \frac{D_{AB}}{RT(z_2 - z_1)} (P_{A1} - P_{A2}) \quad \text{----- (4)}$$

This is the equation of molar flux for steady-state equimolar counter diffusion.

Concentration profile in these equimolar counter diffusion may be obtained from,

$$\frac{d}{dz} (N_A) = 0 \quad (\text{Since } N_A \text{ is constant over the diffusion path}).$$

And from equation. (2)

$$N_A = -D_{AB} \frac{dC_A}{dz}.$$

Therefore

$$\frac{d}{dz} \left(-D_{AB} \frac{dC_A}{dz} \right) = 0.$$

or
$$\frac{d^2 C_A}{dz^2} = 0.$$

This equation may be solved using the boundary conditions to give

$$\frac{C_A - C_{A1}}{C_{A1} - C_{A2}} = \frac{z - z_1}{z_1 - z_2} \quad \text{----- (5)}$$

Equation, (5) indicates a linear concentration profile for equimolar counter diffusion.

3. Methane diffuses at steady state through a tube containing helium. At point 1 the partial pressure of methane is $p_{A1} = 55 \text{ kPa}$ and at point 2, 0.03 m apart $p_{A2} = 15 \text{ kPa}$. The total pressure is 101.32 kPa, and the temperature is 298 K. At this pressure and temperature, the value of diffusivity is $6.75 \times 10^{-5} \text{ m}^2/\text{sec}$.

- i) calculate the flux of CH_4 at steady state for equimolar counter diffusion.
- ii) Calculate the partial pressure at a point 0.02 m apart from point 1.

Calculation:

For steady state equimolar counter diffusion, molar flux is given by

$$N_A = \frac{D_{AB}}{RTZ} (p_{A1} - p_{A2}) \text{-----} (1)$$

Therefore;

$$\begin{aligned} N_A &= \frac{6.75 * 10^{-5}}{8.314 * 298 * 0.03} (55 - 15) \frac{\text{kmol}}{\text{m}^2 \cdot \text{sec}} \\ &= 3.633 * 10^{-5} \frac{\text{kmol}}{\text{m}^2 \text{ sec}} \end{aligned}$$

And from (1), partial pressure at 0.02 m from point 1 is:

$$3.633 * 10^{-5} = \frac{6.75 * 10^{-5}}{8.314 * 298 * 0.02} (55 - p_A)$$

$$p_A = 28.33 \text{ kPa}$$

11. In a gas mixture of hydrogen and oxygen, steady state equimolar counter diffusion is occurring at a total pressure of 100 kPa and temperature of 20°C. If the partial pressures of oxygen at two planes 0.01 m apart, and perpendicular to the direction of diffusion are 15 kPa and 5 kPa, respectively and the mass diffusion flux of oxygen in the mixture is $1.6 * 10^{-5} \text{ kmol/m}^2 \cdot \text{sec}$, calculate the molecular diffusivity for the system.

Solution:

For equimolar counter current diffusion:

$$N_A = \frac{D_{AB}}{RTZ} (p_{A1} - p_{A2}) \text{-----} (1)$$

where

N_A = molar flux of A ($1.6 * 10^{-5}$ kmol/m².sec):

D_{AB} = molecular diffusivity of A in B

R = Universal gas constant (8.314 kJ/kmol.k)

T = Temperature in absolute scale ($273 + 20 = 293$ K)

z = distance between two measurement planes 1 and 2 (0.01 m)

P_{A1} = partial pressure of A at plane 1 (15 kPa); and

P_{A2} = partial pressure of A at plane 2 (5 kPa)

Substituting these in equation (1)

$$1.6 * 10^{-5} = \frac{D_{AB}}{(8.314)(293)(0.01)} (15 - 5)$$

Therefore, $D_{AB} = 3.898 * 10^{-5}$ m²/sec

2. A tube 1 cm in inside diameter that is 20 cm long is filled with Co₂ and H₂ at a total pressure of 2 atm at 0°C. The diffusion coefficient of the Co₂ – H₂ system under these conditions is 0.275 cm²/sec. If the partial pressure of Co₂ is 1.5 atm at one end of the tube and 0.5 atm at the other end, find the rate of diffusion for:

- i) steady state equimolar counter diffusion ($N_A = - N_B$)
- ii) steady state counter diffusion where $N_B = -0.75 N_A$, and
- iii) steady state diffusion of Co₂ through stagnant H₂ ($N_B = 0$)

$$i) N_A = -C D_{AB} \frac{d y_A}{d z} + y_A (N_A + N_B)$$

Given

$$N_B = - N_A$$

$$\text{Therefore } N_A = -C D_{AB} \frac{dy_A}{dz} = -D_{AB} \frac{dC_A}{dz}$$

(For ideal gas mixture $C_A = \frac{p_A}{RT}$ where p_A is the partial pressure of A; such that $p_A + p_B = P$)

$$\text{Therefore } N_A = -D_{AB} \frac{d(p_A/RT)}{dz}$$

For isothermal system, T is constant

$$\text{Therefore } N_A = \frac{-D_{AB}}{RT} \frac{dp_A}{dz}$$

$$\text{(i.e.) } N_A \int_{Z_1}^{Z_2} dz = -\frac{D_{AB}}{RT} \int_{P_{A1}}^{P_{A2}} dp_A$$

$$N_A = \frac{D_{AB}}{RT Z} (p_{A1} - p_{A2}) \text{ ----- (1)}$$

where $Z = Z_2 - Z_1$

Given: $D_{AB} = 0.275 \text{ cm}^2/\text{sec} = 0.275 * 10^{-4} \text{ m}^2/\text{sec}$; $T = 0^\circ\text{C} = 273 \text{ K}$

$$N_A = \frac{0.275 * 10^{-4}}{8314 * 273 * 0.2} (1.5 * 1.01325 * 10^5 - 0.5 * 1.01325 * 10^5)$$

$$= 6.138 * 10^{-6} \frac{k \text{ mol}}{m^2 \text{ sec}}$$

Rate of diffusion = $N_A S$

Where S is surface area

$$\begin{aligned} \text{Therefore rate of diffusion} &= 6.138 * 10^{-6} * \pi r^2 \\ &= 6.138 * 10^{-6} * \pi (0.5 * 10^{-2})^2 \\ &= 4.821 * 10^{-10} \text{ k mol/sec} \\ &= 1.735 * 10^{-3} \text{ mol/hr.} \end{aligned}$$

$$\text{ii) } N_A = -CD_{AB} \frac{dy_A}{dz} + y_A (N_A + N_B)$$

$$\text{given: } N_B = -0.75 N_A$$

$$\text{Therefore } N_A = -CD_{AB} \frac{dy_A}{dz} + y_A (N_A - 0.75 N_A)$$

$$= -CD_{AB} \frac{dy_A}{dz} + 0.25 y_A N_A$$

$$N_A - 0.25 y_A N_A = -CD_{AB} \frac{dy_A}{dz}$$

$$N_A dz = -CD_{AB} \frac{dy_A}{1 - 0.25 y_A}$$

for constant N_A and C

$$N_A \int_{z_1}^{z_2} dz = -CD_{AB} \int_{y_{A1}}^{y_{A2}} \frac{dy_A}{1 - 0.25 y_A}$$

$$\left[\int \frac{dx}{a + bx} = \frac{1}{b} \ln(a + bx) \right]$$

$$N_A z = (-CD_{AB}) \left(\frac{-1}{0.25} \right) \left[\ln(1 - 0.25 y_A) \right]_{y_{A1}}^{y_{A2}}$$

$$N_A = -\frac{4CD_{AB}}{z} \ln \left(\frac{1 - 0.25 y_{A2}}{1 - 0.25 y_{A1}} \right) \text{----- (2)}$$

Given:

$$C = \frac{p}{RT} = \frac{2 * 1.01325 * 10^5}{8314 * 273} = 0.0893 \text{ K mol/m}^3$$

$$y_{A1} = \frac{p_{A1}}{P} = \frac{1.5}{2} = 0.75$$

$$y_{A2} = \frac{p_{A2}}{P} = \frac{0.5}{2} = 0.25$$

Substituting these in equation (2),

$$N_A = \frac{4 * 0.0893 * 0.275 * 10^{-4}}{0.2} \left[\ln \frac{1 - 0.25 * 0.25}{1 - 0.25 * 0.75} \right]$$

$$= 7.028 * 10^{-6} \frac{\text{kmol}}{\text{m}^2 \text{ sec}}$$

$$\begin{aligned} \text{Rate of diffusion} &= N_A S = 7.028 * 10^{-6} * \pi * (0.5 * 10^{-2})^2 \\ &= 5.52 * 10^{-10} \text{ kmol/sec} \\ &= 1.987 * 10^{-3} \text{ mol/hr.} \end{aligned}$$

$$\text{iii) } N_A = -CD_{AB} \frac{dy_A}{dz} + y_A (N_A + N_B)$$

Given: $N_B = 0$

$$\text{Therefore } N_A = -CD_{AB} \frac{dy_A}{dz} + y_A N_A$$

$$\begin{aligned} N_A \int_{Z_1}^{Z_2} dz &= -CD_{AB} \int_{y_{A1}}^{y_{A2}} \frac{dy_A}{1-y_A} \\ &= \frac{CD_{AB}}{Z} \ln \left(\frac{1-y_{A2}}{1-y_{A1}} \right) \\ &= \frac{0.0893 * 0.275 * 10^{-4}}{0.2} \left[\ln \left(\frac{1-0.25}{1-0.75} \right) \right] \\ &= 1.349 * 10^{-5} \frac{\text{kmol}}{\text{m}^2 \cdot \text{sec}} \end{aligned}$$

$$\text{Rate of diffusion} = 1.349 * 10^{-5} * \pi * (0.5 * 10^{-2})^2$$

$$= 1.059 \text{ Kmol / sec}$$

$$= 3.814 \text{ mol/hr}$$

1.14 Diffusion in Liquids:

Equation derived for diffusion in gases equally applies to diffusion in liquids with some modifications. Mole fraction in liquid phases is normally written as 'x' (in gases as y). The concentration term 'C' is replaced by average molar density, $\left(\frac{\rho}{M} \right)_{av}$.

- a) For steady – state diffusion of A through non diffusivity B:
 $N_A = \text{constant}, N_B = 0$

$$N_A = \frac{D_{AB}}{Z X_{BM}} \left(\frac{\rho}{M} \right)_{av} (x_{A1} - x_{A2})$$

where $Z = Z_2 - Z_1$, the length of diffusion path; and

$$X_{BM} = \frac{X_{B2} - X_{B1}}{\ln \left(\frac{X_{B2}}{X_{B1}} \right)}$$

- b) For steady – state equimolar counter diffusion :

$$N_A = -N_B = \text{const}$$

$$N_A = \frac{D_{AB}}{Z} (C_{A1} - C_{A2}) = \frac{D_{AB}}{Z} \left(\frac{\rho}{M} \right)_{av} (x_{A1} - x_{A2})$$

4. Calculate the rate of diffusion of butanol at 20°C under unidirectional steady state conditions through a 0.1 cm thick film of water when the concentrations of butanol at the opposite sides of the film are, respectively 10% and 4% butanol by weight. The diffusivity of butanol in water solution is $5.9 \times 10^{-6} \text{ cm}^2/\text{sec}$. The densities of 10% and 4% butanol solutions at 20°C may be taken as 0.971 and 0.992 g/cc respectively. Molecular weight of Butanol ($\text{C}_4\text{H}_9\text{OH}$) is 74, and that of water 18.

Calculations

For steady state unidirectional diffusion,

$$N_A = \frac{D_{AB}}{Z} C \frac{(x_{A1} - x_{A2})}{x_{B,lm}}$$

where C is the average molar density.

$$= \left(\frac{\rho}{M} \right)_{avg}$$

Conversion from weight fraction the Mole fraction:

$$x_{A1} = \frac{(0.1/74)}{(0.1/74 + 0.9/18)} = 0.026$$

$$x_{A2} = \frac{(0.04/74)}{(0.04/74 + 0.96/18)} = 0.010$$

Average molecular weight at 1 & 2:

$$M_1 = \frac{1}{(0.1/74 + 0.9/18)} = 19.47 \text{ kg/Kmol}$$

$$M_2 = \frac{1}{(0.04/74 + 0.96/18)} = 18.56 \text{ kg/Kmol}$$

$$\begin{aligned} \left(\frac{\rho}{M} \right)_{avg} &= \frac{(\rho_1/M_1 + \rho_2/M_2)}{2} \\ &= \frac{0.971/19.47 + 0.992/18.56}{2} \\ &= 0.0517 \text{ gmol / cm}^3 \\ &= 51.7 \text{ kmol/m}^3 \end{aligned}$$

$$x_{B,lm} = \frac{x_{B2} - x_{B1}}{\ln(x_{B2}/x_{B1})} = \frac{(1 - x_{A2}) - (1 - x_{A1})}{\ln\left(\frac{1 - x_{A2}}{1 - x_{A1}}\right)}$$

$$\text{(i.e.) } x_{B,lm} = \frac{(1 - 0.01) - (1 - 0.026)}{\ln\left(\frac{1 - 0.01}{1 - 0.026}\right)}$$

$$= \frac{0.016}{0.0163} = 0.982$$

$$\begin{aligned} \text{Therefore } N_A &= \frac{D_{AB}}{2} \left(\frac{\rho}{M} \right)_{avg} \frac{(x_{A1} - x_{A2})}{x_{B,lm}} \\ &= \frac{5.9 * 10^{-6} * 10^{-4} * 51.7}{0.1 * 10^{-2}} * \frac{(0.026 - 0.010)}{0.982} \\ &= 4.97 * 10^{-7} \frac{kmol}{m^2 \text{ sec}} \\ &= 1.789 \frac{gmol}{m^2.hr.} \\ &= 1.789 * 74 \frac{g}{m^2.hr.} \\ &= 132.4 \frac{g}{m^2.hr.} \end{aligned}$$

1.15 Diffusion in solids

In certain unit operation of chemical engineering such as in drying or in absorption, mass transfer takes place between a solid and a fluid phase. If the transferred species is distributed uniformly in the solid phase and forms a homogeneous medium, the diffusion of the species in the solid phase is said to be structure independent. In this cases diffusivity or diffusion coefficient is direction – independent.

At steady state, and for mass diffusion which is independent of the solid matrix structure, the molar flux in the z direction is :

$$N_A = -D_{AB} \frac{dC_A}{dz} = \text{constant, as given by Fick's law.}$$

Integrating the above equation,

$$N_A = \frac{D_{AB} (C_{A1} - C_{A2})}{z}$$

which is similar to the expression obtained for diffusion in a stagnant fluid with no bulk motion (i.e. $N = 0$).

1.16 Diffusion in process solids:

In some chemical operations, such as heterogeneous catalysis, an important factor, affecting the rate of reaction is the diffusions of the gaseous component through a porous solid. The effective diffusivity in the solid is reduced below what it could be in a free fluid, for two reasons. First, the tortuous nature of the path increases the distance, which a molecule must travel to advance a given distance in the solid. Second, the free cross – sectional area is restricted. For many catalyst pellets, the effective diffusivity of a gaseous component is of the order of one tenth of its value in a free gas.

If the pressure is low enough and the pores are small enough, the gas molecules will collide with the walls more frequently than with each other. This is known as Knudsen flow or Knudsen diffusion. Upon hitting the wall, the molecules are momentarily absorbed and then given off in random directions. The gas flux is reduced by the wall collisions.

By use of the kinetic flux is the concentration gradient is independent of pressure ; whereas the proportionality constant for molecular diffusion in gases (i.e. Diffusivity) is inversely proportional to pressure.

Knudsen diffusion occurs when the size of the pore is of the order of the mean free path of the diffusing molecule.



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – II– MASS TRANSFER-I – SCH1401

UNIT-II

Humidification is the process of constituting the water-vapor content in a gas. The reverse of the operation is called dehumidification. Both are important for many industrial operations such as air conditioning, gas cooling, controlled drying of wet solids, comfort heating etc. When a gas is brought in contact with a pure liquid in which it is essentially insoluble, interphase mass and heat transfer takes place.

Four major applications of humidification operations are as follows:

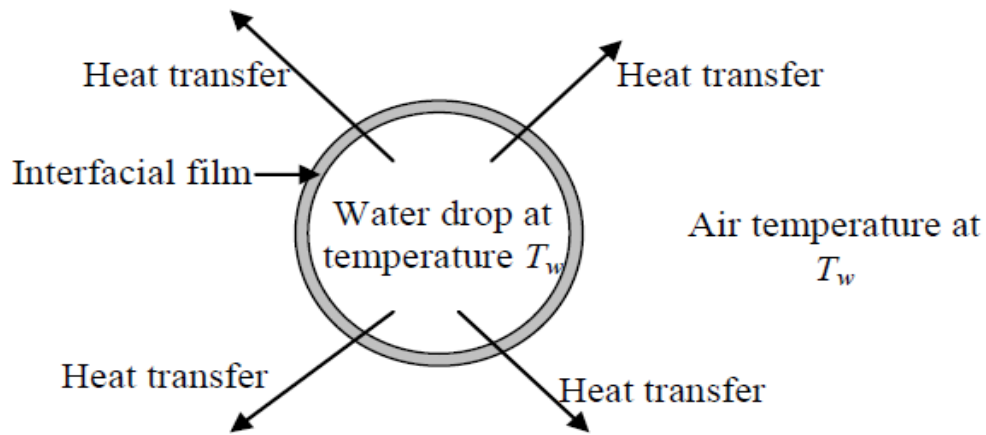
- a) Humidification of gases for controlled drying of wet solids
- b) Dehumidification and cooling of gas in air conditioning
- c) Gas cooling with the help of water
- d) Cooling of liquid (e.g. water) before reuse

Humidification operations: In this operation, water transfers from liquid phase to gas phase. Hence, moisture content of air increases. Air with particular moisture content is useful for drying of a solid under controlled condition.

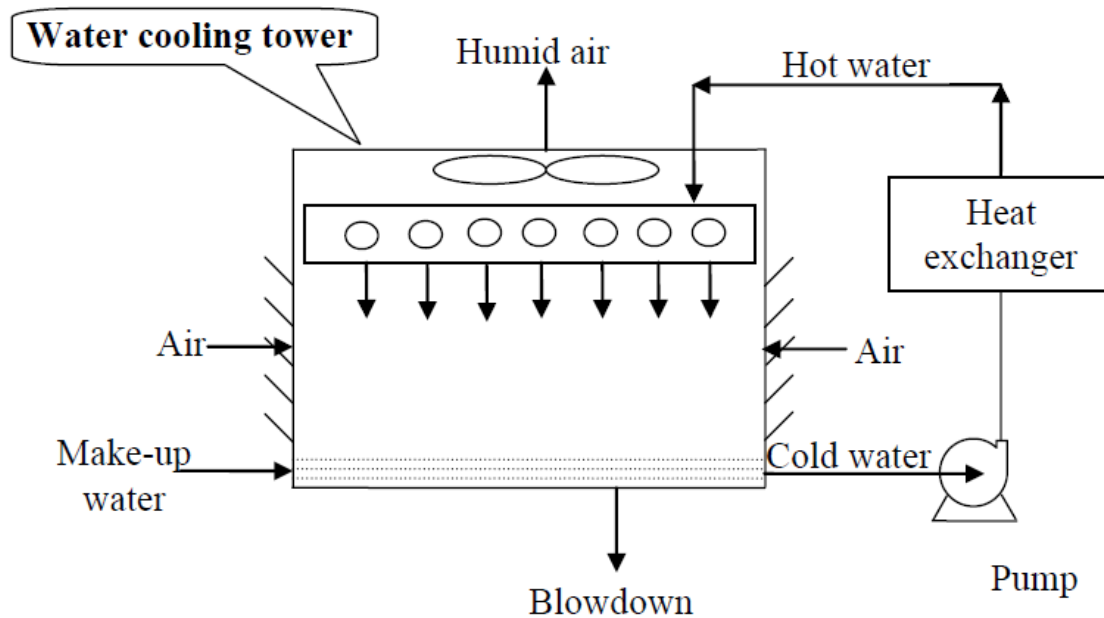
Dehumidification operations: It is the reverse phenomena of humidification. A portion of water vapor from moist warm air is condensed by contacting cold water in air conditioning.

Cooling tower principle and operation

A cooling tower is a special type of heat exchanger in which the warm water and the air are brought in direct contact for '*evaporative cooling*'. It provides a very good contact of air and water in terms of the contact area and mass transfer co-efficient of water vapor while keeping air pressure drop low. Enthalpy of air is lower than enthalpy of water. Sensible heat and latent heat transfer take place from water drop to surrounding air. Schematic of heat transfer from water drop to surrounding air is presented in

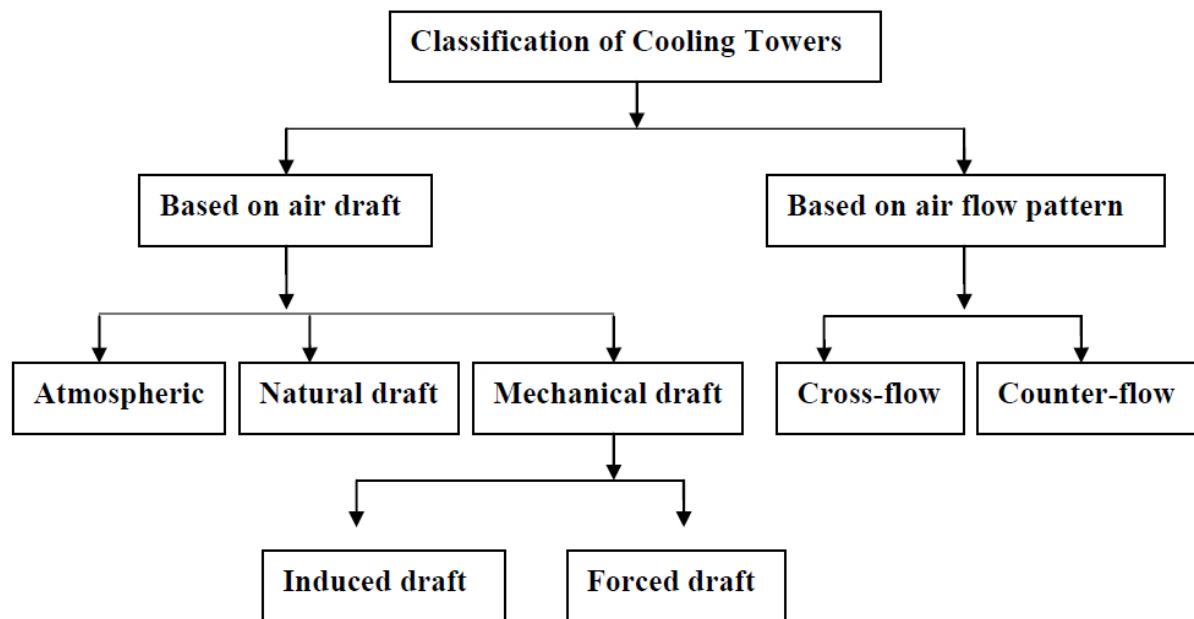


Thus, cooling is accomplished by sensible heat transfer from water to air and evaporation of a small portion of water. A generalized cooling tower system is shown in Figure 6.4. The hot water which is coming from heat exchanger is sprayed at the top of the cooling tower. Air enters through the louvers at the two opposite walls of the cooling tower. During cooling process of water, around 2% water is evaporated. Make water is used to compensate the water loss due to evaporation. Blowdown is there to drain a part of water containing solid deposit. The exit cold water from the cooling tower is used in the heat exchanger or other unit operation.

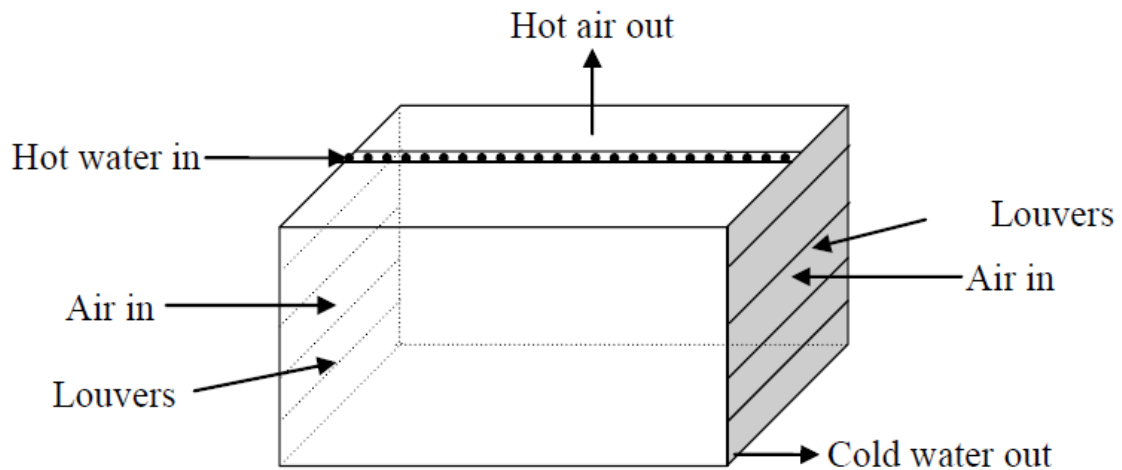


Factors govern the operation of cooling tower

- The dry-bulb and wet-bulb temperatures of air
- Temperature of warm water
- The efficiency of contact between air and water in terms of volumetric mass transfer coefficient.
- Contact time between air and water
- The uniformity of the distribution of the phases within the tower
- Air pressure drop
- Desired temperature of cooled water



It is a big rectangular chamber with two opposite ‘louvered’ walls. Tower is packed with a suitable ‘tower fill’. Atmospheric air enters the tower through louvers driven by its own velocity. Direction and velocity of wind greatly influence its performance.



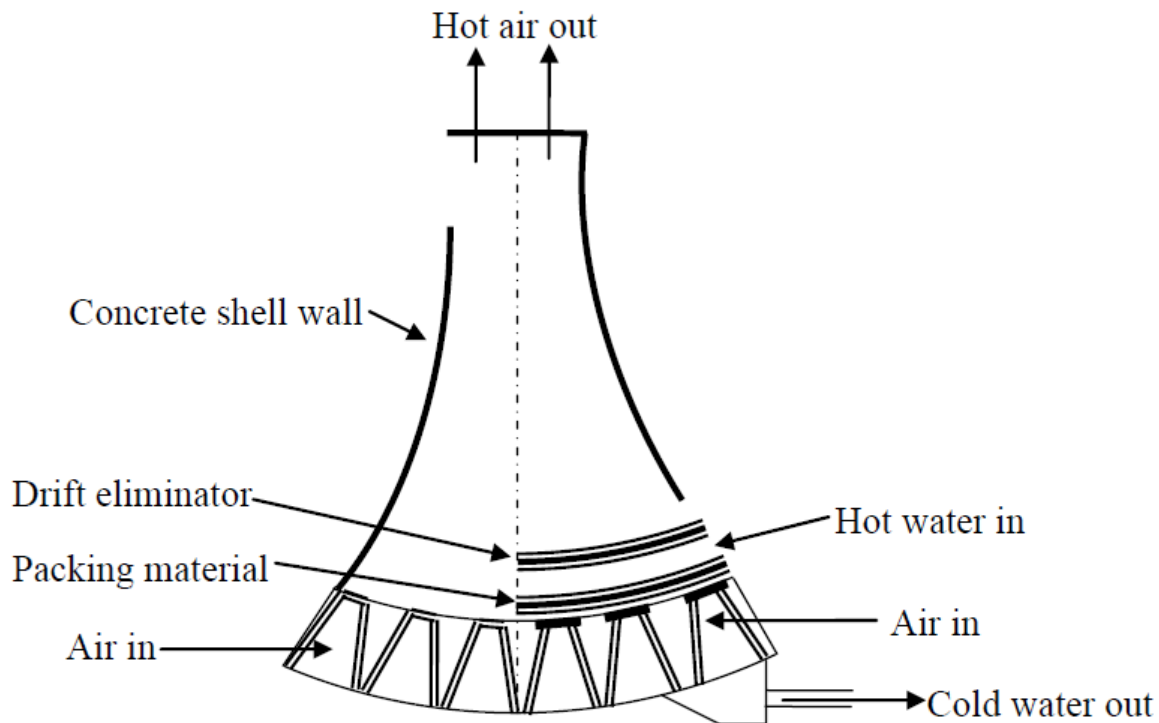
Natural Draft Towers

A natural draft cooling tower has a large reinforced concrete shell of hyperbolic shape (also called ‘hyperbolic tower’). Natural flow of air occurs through the tower; hence it is called natural draft.

Factors responsible for creating natural draft

- A rise in temperature and humidity of air in the column reduces its density
- Wind velocity at the tower bottom

Fan is used to enhance the air flow rate in fan assisted natural draft tower. The typical diameter of tower is 150 m and capacity is 5, 00,000 gpm.



Advantages of hyperbolic shape

- More packing materials can be placed at the bottom
- The entering air gets smoothly directed towards the centre
- Greater structural strength and stability

Forced draft towers:

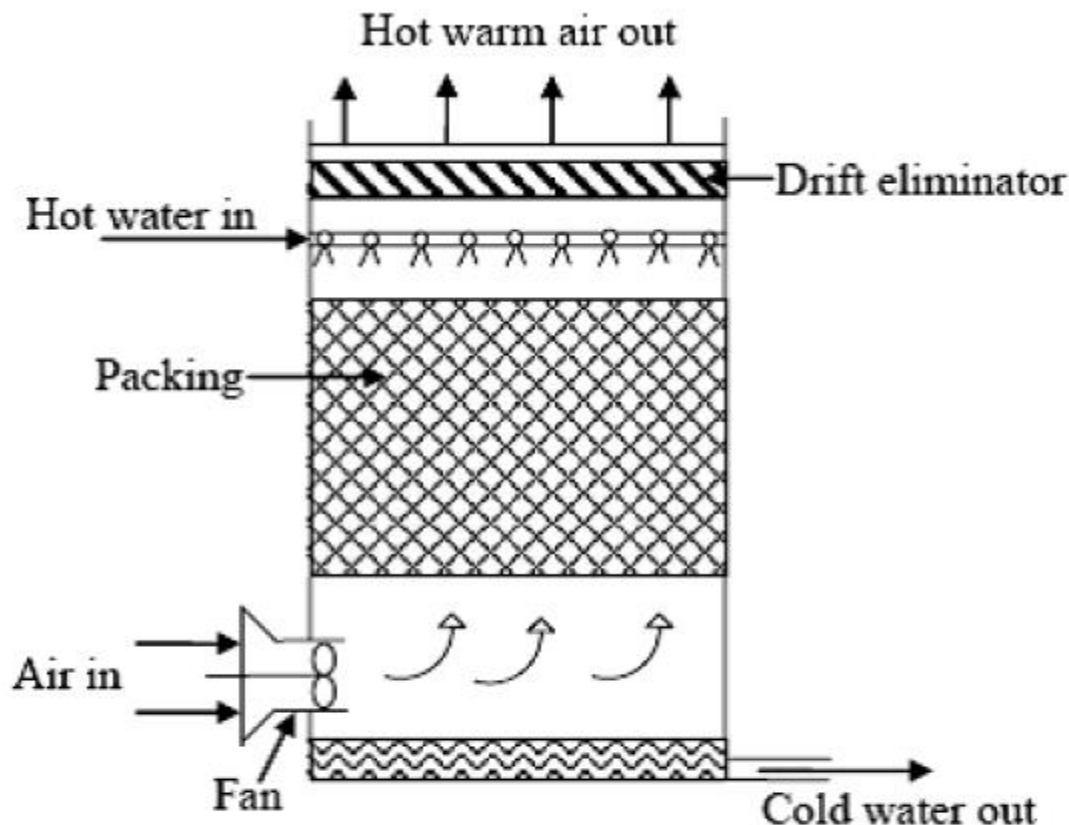
It can be seen from Figure below; that it has one or more fans located at the tower bottom to push air into tower.

Advantages:

- A part of the velocity head of air thrown by the blower is converted to pressure head on entering into the tower. It makes energy efficient than induced draft.
- Less susceptible to vibrations as fans are installed near the ground.

Disadvantages:

- Air flow through the packing may not be uniform
- Some of the warm and humid air may be recirculated back. Recirculation rate becomes low if the wind velocity is high. It is not popular except for small capacities.



Schematic of forced draft towers.

Induced draft towers:

One or more fans are installed at the top of the tower. Depending on the air inlet and flow pattern, induced draft towers are of two types, cross-flow and counter flow towers.

Major advantages of countercurrent induced draft cooling tower

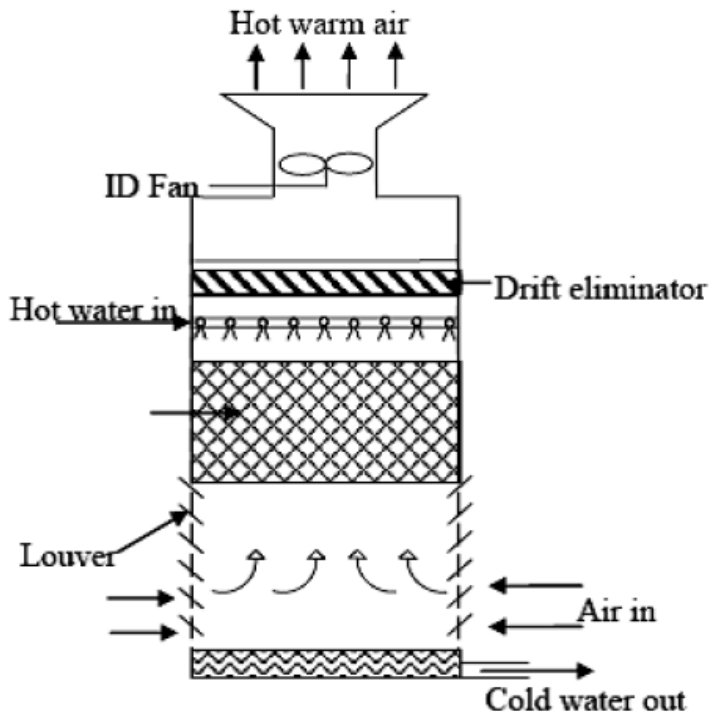
- Relatively dry air contacts the coldest water at the bottom of the cooling tower
- Humid air is in contact with the warm water and hence maximum average driving force prevails for both heat and mass transfer.

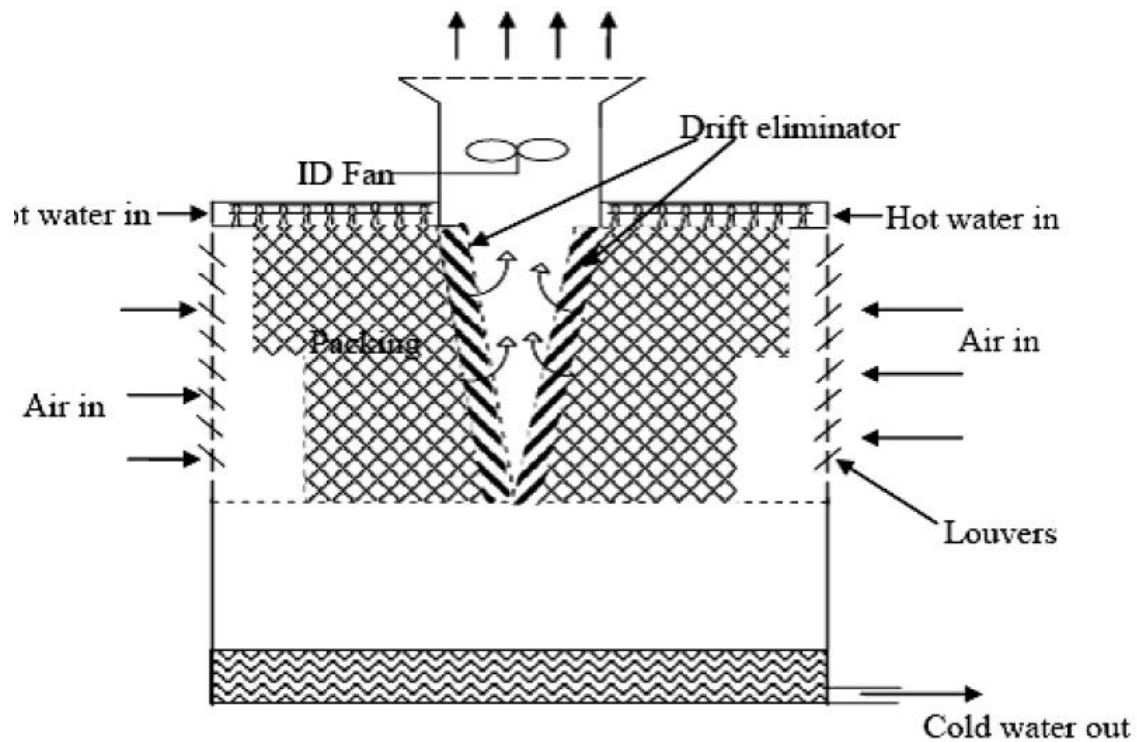
Disadvantage of induced draft towers compared to forced draft towers

- It consumes more horse power. Cross-flow induced draft cooling tower requires less motor horse power than countercurrent induced draft cooling towers.

(B) Cross-current and counter-current

Cross-flow induced draft cooling tower supplies horizontal air flow along the packed height and requires less motor horse power than the counter-flow type. Additional cells may be added to raise the capacity.





Schematic of mechanical draft cross flow tower

SPRAY POND:

A spray pond is a reservoir in which warmed water is cooled for reuse by evaporation of water discharged from nozzles in spray or mist form over the pond.



The warm water is sprayed into cooler air, cooling down as it reaches the water. The spray pond is the predecessor to the natural draft cooling tower, which is much more efficient and takes up less space but has a much higher construction cost. A spray pond requires between 25 to 50 times the area of a cooling tower. However, some spray ponds are still in use today.

SPRAY TOWER:

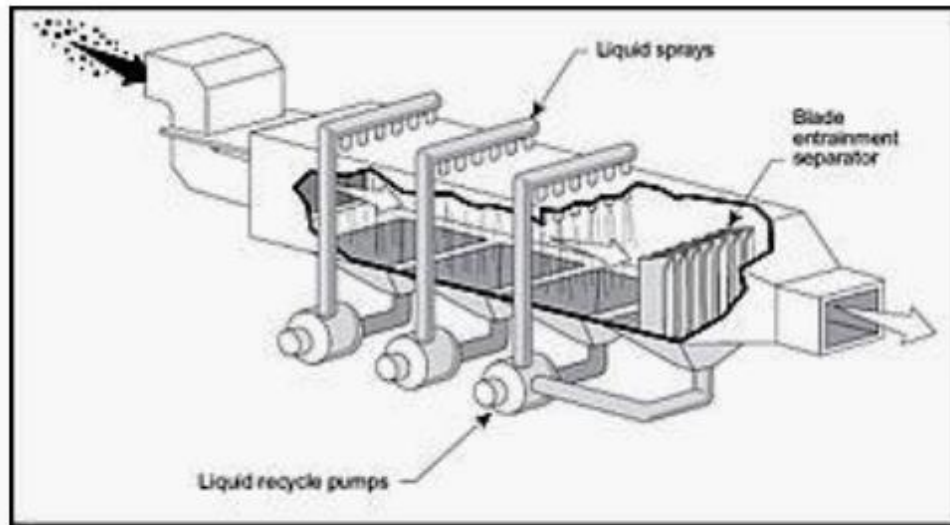
A spray tower (or spray column or spray chamber) is gas-liquid contactor used to achieve the mass and heat transfer between a continuous gas phase (that can contain dispersed solid particles) and a dispersed liquid phase. It consists of empty cylindrical vessel made of steel or plastic and nozzles that spray liquid into the vessel. The inlet gas stream usually enters the bottom of the tower and moves upward, while liquid is sprayed downward from one or more levels. This flow of inlet gas and liquid in the opposite direction is called countercurrent flow.

This type of technology can be used for example as a wet scrubber for air pollution control. Countercurrent flow exposes the outlet gas with the lowest pollutant concentration to the freshest scrubbing liquid. Many nozzles are placed across the tower at different heights to spray all of the gas as it moves up through the tower. The reason for using many nozzles is to maximize the number of fine droplets impacting the pollutant particles and to provide a large surface area for absorbing gas.

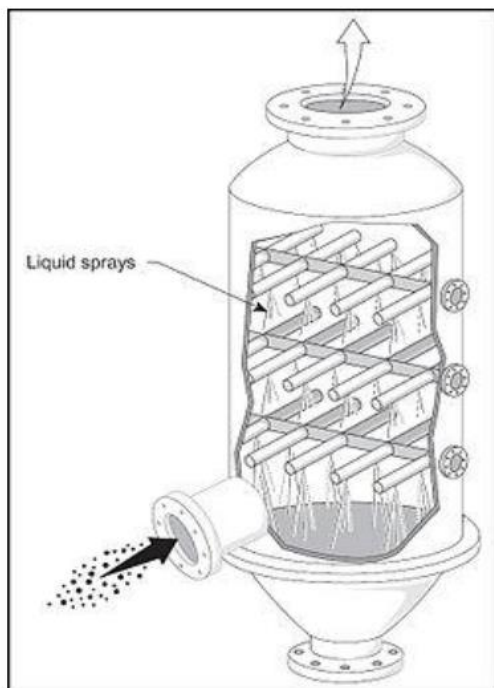
Theoretically, the smaller the droplets formed, the higher the collection efficiency achieved for both gaseous and particulate pollutants. However, the liquid droplets must be large enough to not be carried out of the scrubber by the scrubbed outlet gas stream. Therefore, spray towers use nozzles to produce droplets that are usually 500–1000 μm in diameter. Although small in size, these droplets are large compared to those created in the venturi scrubbers that are 10–50 μm in size. The gas velocity is kept low, from 0.3 to 1.2 m/s (1–4 ft/s) to prevent excess droplets from being carried out of the tower.

In order to maintain low gas velocities, spray towers must be larger than other scrubbers that handle similar gas stream flow rates. Another problem occurring in spray towers is that after the droplets fall short distances, they tend to agglomerate or hit the walls of the tower. Consequently, the total

liquid surface area for contact is reduced, reducing the collection efficiency of the scrubber.



Crosscurrent-flow spray tower



countercurrent-flow spray tower.

In cocurrent-flow spray towers, the inlet gas and liquid flow in the same direction. Because the gas stream does not "push" against the liquid sprays, the gas velocities through the vessels are higher than in countercurrent-flow spray towers. Consequently, cocurrent-flow spray towers are smaller

than countercurrent-flow spray towers treating the same amount of exhaust flow. In crosscurrent-flow spray towers, also called horizontal-spray scrubbers, the gas and liquid flow in directions perpendicular to each other.

Definitions

1. *Definition of humidity.* The humidity H of an air–water vapor mixture is defined as the kg of water vapor contained in 1 kg of dry air. The humidity so defined depends only on the partial pressure p_A of water vapor in the air and on the total pressure P (assumed throughout this chapter to be 101.325 kPa, 1.0 atm abs, or 760 mm Hg). Using the molecular weight of water (A) as 18.02 and of air as 28.97, the humidity H in kg H_2O /kg dry air or in English units as lb H_2O /lb dry air is as follows:

$$H \frac{\text{kg } H_2O}{\text{kg dry air}} = \frac{p_A}{P - p_A} \frac{\text{kg mol } H_2O}{\text{kg mol air}} \times \frac{18.02 \text{ kg } H_2O}{\text{kg mol } H_2O} \times \frac{1}{28.97 \text{ kg air/kg mol air}}$$

$$H = \frac{18.02}{28.97} \frac{p_A}{P - p_A}$$

Saturated air is air in which the water vapor is in equilibrium with liquid water at the given conditions of pressure and temperature. In this mixture the partial pressure of the water vapor in the air–water mixture is equal to the vapor pressure p_{AS} of pure water at the given temperature. Hence, the saturation humidity H_S is

$$H_S = \frac{18.02}{28.97} \frac{p_{AS}}{P - p_{AS}}$$

2. *Percentage humidity.* The percentage humidity H_P is defined as 100 times the actual humidity H of the air divided by the humidity H_S if the air were saturated at the same temperature and pressure.

$$H_P = 100 \frac{H}{H_S}$$

3. *Percentage relative humidity.* The amount of saturation of an air–water vapor mixture is also given as percentage relative humidity H_R using partial pressures.

$$H_R = 100 \frac{P_A}{P_{AS}}$$

4. *Dew point of an air–water vapor mixture.* The temperature at which a given mixture of air and water vapor would be saturated is called the *dew-point temperature* or simply the *dew point*. For example, at 26.7°C (80°F), the saturation vapor pressure of water is $p_{AS} = 3.50$ kPa (0.507 psia). Hence, the dew point of a mixture containing water vapor having a partial pressure of 3.50 kPa is 26.7°C.

5. *Humid heat of an air–water vapor mixture.* The humid heat c_s is the amount of heat in J (or kJ) required to raise the temperature of 1 kg of dry air plus the water vapor present by 1 K or 1°C. The heat capacity of air and water vapor can be assumed constant over the temperature ranges usually encountered at 1.005 kJ/kg dry air · K and 1.88 kJ/kg water vapor · K

$$c_s \text{ kJ/kg dry air} \cdot \text{K} = 1.005 + 1.88H$$

6. *Humid volume of an air–water vapor mixture.* The humid volume v_H is the total volume in m³ of 1 kg of dry air plus the vapor it contains at 101.325 kPa (1.0 atm) abs pressure and the given gas temperature. Using the ideal gas law,

$$\begin{aligned} v_H \text{ m}^3/\text{kg dry air} &= \frac{22.41}{273} T \text{ K} \left(\frac{1}{28.97} + \frac{1}{18.02} H \right) \\ &= (2.83 \times 10^{-3} + 4.56 \times 10^{-3} H) T \text{ K} \end{aligned}$$

7. *Total enthalpy of an air–water vapor mixture.* The total enthalpy of 1 kg of air plus its water vapor is H_y J/kg or kJ/kg dry air. If T_0 is the datum temperature chosen for both components, the total enthalpy is the sensible heat of the air–water vapor mixture plus the latent heat λ_0 in J/kg or kJ/kg water vapor of the water vapor at T_0 . Note that $(T - T_0)^\circ\text{C} = (T - T_0) \text{ K}$ and that this enthalpy is referred to liquid water.

$$H_y \text{ kJ/kg dry air} = c_s(T - T_0) + H\lambda_0 = (1.005 + 1.88H)(T - T_0)^\circ\text{C} + H\lambda_0$$

Terminologies and definitions

Three most important quantities, namely, 'Temperature', 'humidity' and 'enthalpy', are essential terminologies in dealing humidification.

- 1) Dry-bulb temperature: It is true temperature of air measured (or, any non-condensable and condensable mixture) by a thermometer whose bulb is dry.
- 2) Wet-bulb temperature: It is the steady-state temperature attained by a small amount of evaporating water in a manner such that the sensible heat transferred from the air to the liquid is equal to the latent heat required for evaporation.
- 3) Relative humidity: It is the ratio of partial pressure of water vapor (p_A) in air at a given temperature to the vapor pressure of water at the same temperature.

$$\%relative\ humidity = \frac{p_A}{p_A^0} \times 100$$

Absolute humidity (simply humidity): It is the direct measurement of moisture content in a gas.

The mass of water vapor per unit mass of dry gas is called absolute humidity, Y' .

$$Y' = \left(\frac{p_A}{P - p_A} \right) \frac{18.02}{28.97}$$

Problem 1

The air in a room is at 26.7°C (80°F) and a pressure of 101.325 kPa and contains water vapor with a partial pressure $p_A = 2.76$ kPa. Calculate the following.

- (a) Humidity, H .
- (b) Saturation humidity, H_S , and percentage humidity, H_P .
- (c) Percentage relative humidity, H_R .

From the steam tables at 26.7°C, the vapor pressure of water is $p_{AS} = 3.50$ kPa (0.507 psia). Also, $p_A = 2.76$ kPa and $P = 101.3$ kPa (14.7 psia). For part (a), using Eq. (9.3-1),

$$H = \frac{18.02}{28.97} \frac{p_A}{P - p_A} = \frac{18.02(2.76)}{28.97(101.3 - 2.76)} = 0.01742 \text{ kg H}_2\text{O/kg air}$$

For part (b), using Eq. (9.3-2), the saturation humidity is

$$H_s = \frac{18.02}{28.97} \frac{p_{AS}}{P - p_{AS}} = \frac{18.02(3.50)}{28.97(101.3 - 3.50)} = 0.02226 \text{ kg H}_2\text{O/kg air}$$

The percentage humidity, from Eq. (9.3-3), is

$$H_P = 100 \frac{H}{H_s} = \frac{100(0.01742)}{0.02226} = 78.3\%$$

For part (c), from Eq. (9.3-4), the percentage relative humidity is

$$H_R = 100 \frac{p_A}{p_{AS}} = \frac{100(2.76)}{3.50} = 78.9\%$$

Problem 2

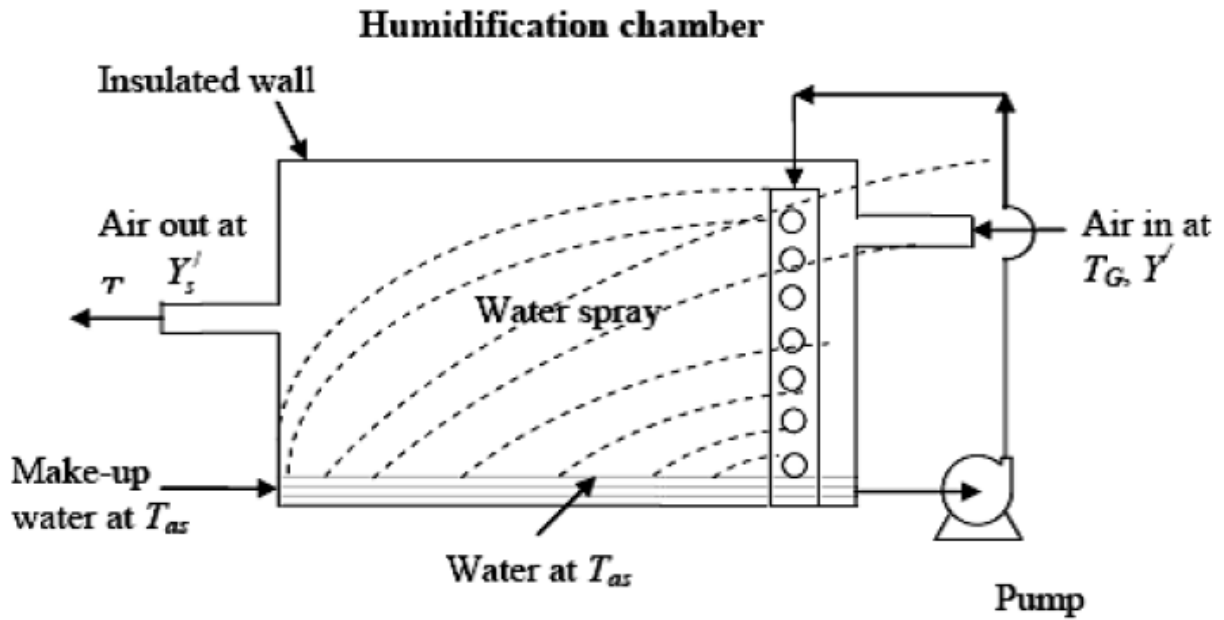
If the total pressure of moist air is 100 kPa (approximately atmospheric) and the humidity is measured as 0.03 kg kg⁻¹, calculate the partial pressure of the water vapour.

Solution:

The molecular weight of air is 29, and of water 18. So the mole fraction of water = $(0.03/18)/(1.00/29 + 0.03/18) = 0.0017/(0.034 + 0.0017) = 0.048$

Therefore the water vapour pressure = $0.048 \times 100 \text{ kPa} = 4.8 \text{ kPa}$.

Adiabatic saturation temperature



Schematic representation of adiabatic saturation of air

The air stream attains thermal equilibrium with water at temperature T_{as} and also gets saturated with water vapor at that temperature before it leaves. A small quantity of water at the temperature T_{as} is fed to the humidification chamber continuously in order to compensate for the vaporization loss of water. The chamber operates adiabatically, wall is well-insulated. The temperature T_{as} attained by air (same as water) is called “*adiabatic saturation temperature, T_{as}* ”.

Enthalpy of inlet air, $H_i' = c_H(T_G - T_{as}) + \lambda_s Y'$

Enthalpy of exit air, $H_o' = c_H(T_{as} - T_{as}) + \lambda_s Y_s' = \lambda_s Y_s'$

At steady state, $H_i' = H_o'$;

Hence,

$$c_H(T_G - T_{as}) + \lambda_s Y' = \lambda_s Y_s'$$

$$(T_G - T_{as}) = \frac{\lambda_s}{c_H} (Y_s' - Y')$$

Determination of relationship between wet-bulb and dry-bulb temperature

Heat flux, $q = h_G(T_G - T_w)$

Molar flux, $N_A = k_G(p_w - p_A)$

Since, heat flux is sufficient to meet requirement of latent heat of vaporization at steady state.

Hence, $h_G(T_G - T_w) = \lambda_w M_w k_G(p_w - p_A) = \lambda_w K_Y'(Y_w' - Y')$

$$(T_G - T_w) = \frac{\lambda_w(Y_w' - Y')}{\left(\frac{h_G}{K_Y'}\right)}$$

$$\frac{h_G}{K_Y'} \approx c_H; \quad \frac{h_G}{c_H K_Y'} \approx 1 \rightarrow \text{Lewis relation}$$

For any system,

$$\frac{h_G}{K_Y'} = 1.231 Sc^{0.56} \text{ kJ/kg.K}$$

Now Equation (6.14) becomes, $(T_G - T_w) = \frac{\lambda_w(Y_w' - Y')}{c_H}$

Equations (6.10) and (6.15) are identical and $T_{as} = T_w$.

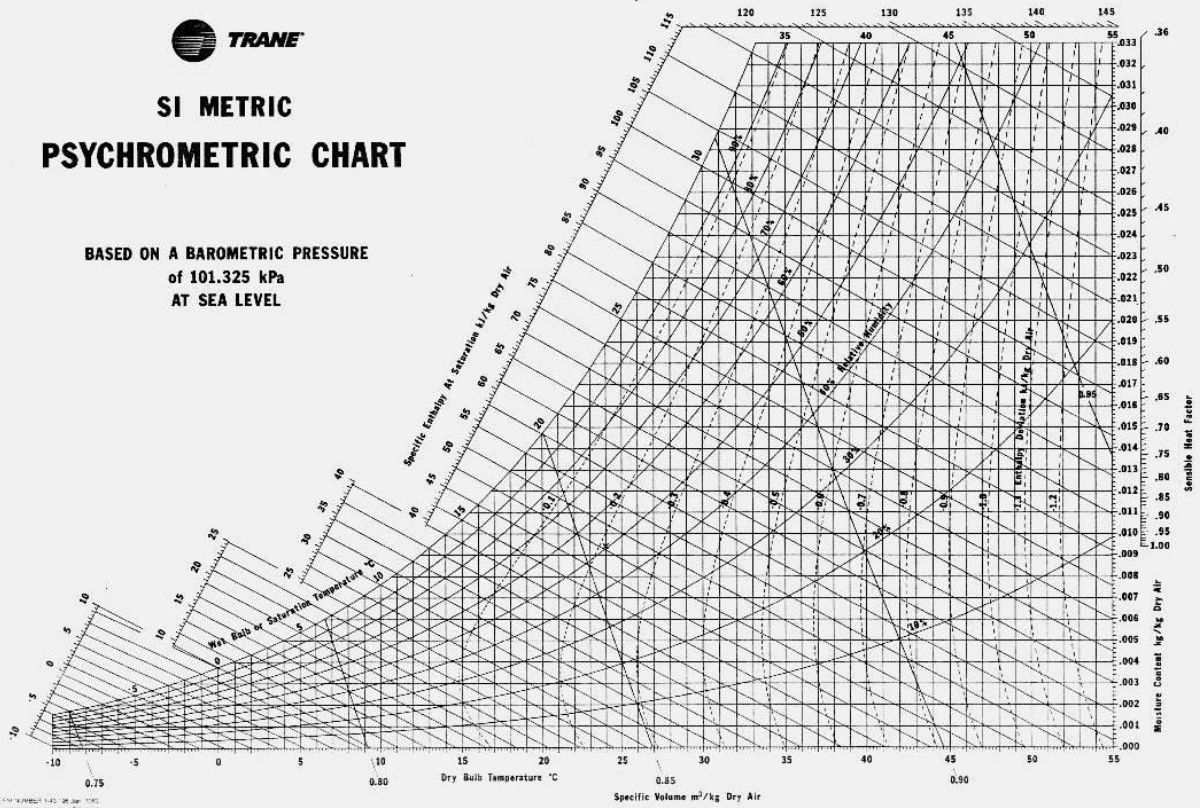
Adiabatic saturation temperature and wet-bulb temperature are nearly equal for air-water system.

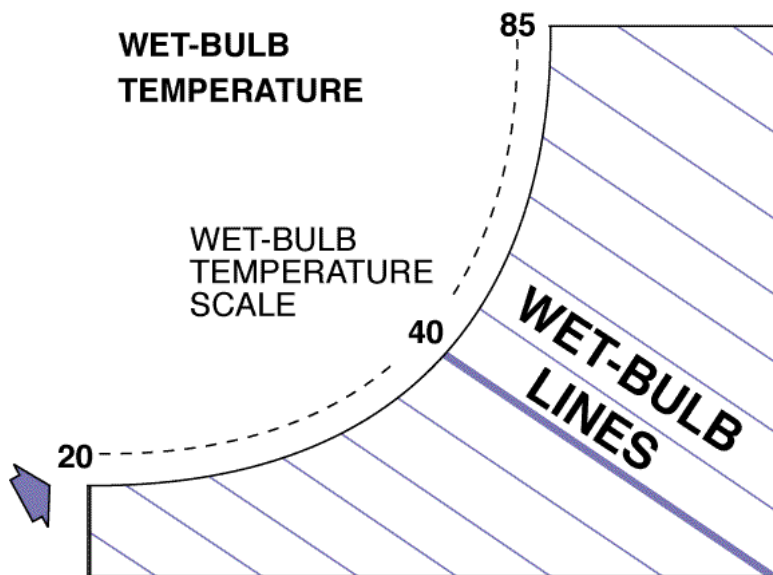
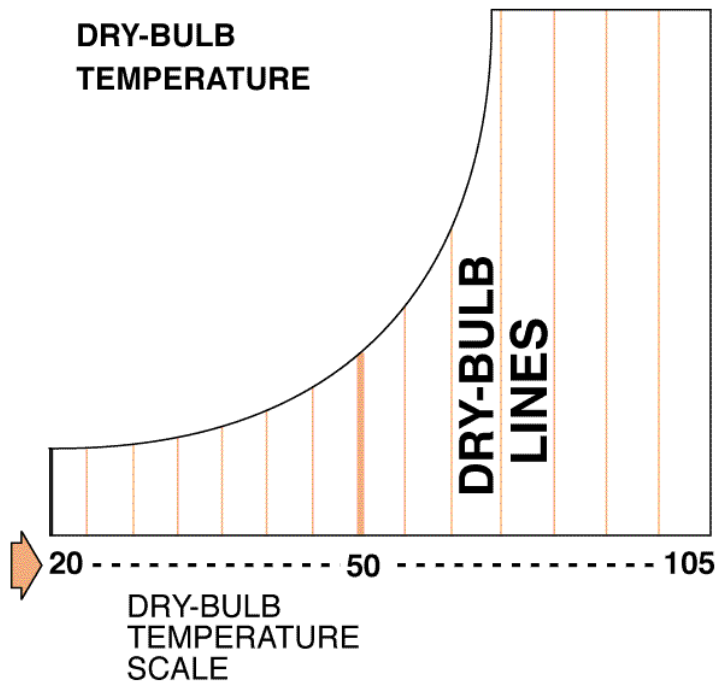
$(T_G - T_w)$ is called wet-bulb depression.

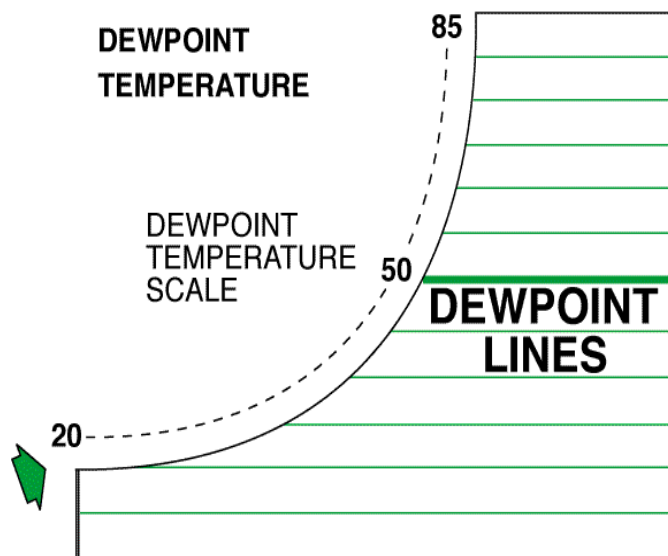
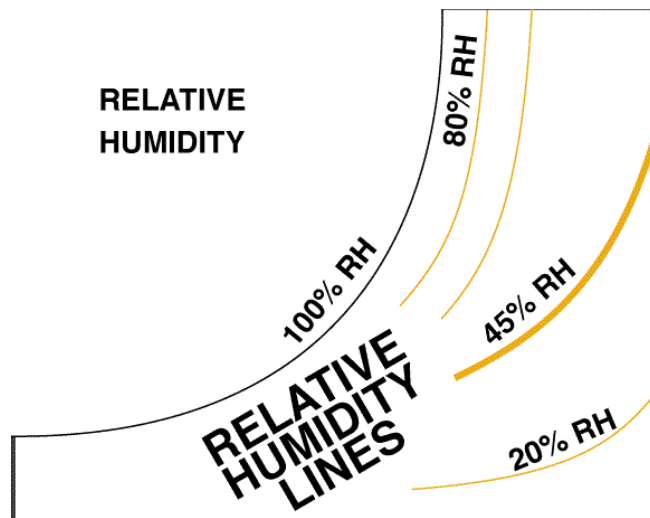


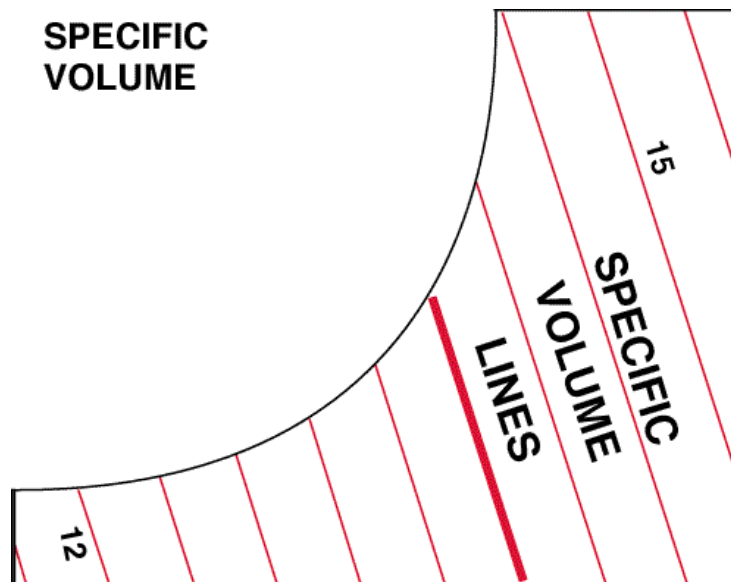
SI METRIC PSYCHROMETRIC CHART

BASED ON A BAROMETRIC PRESSURE
of 101.325 kPa
AT SEA LEVEL





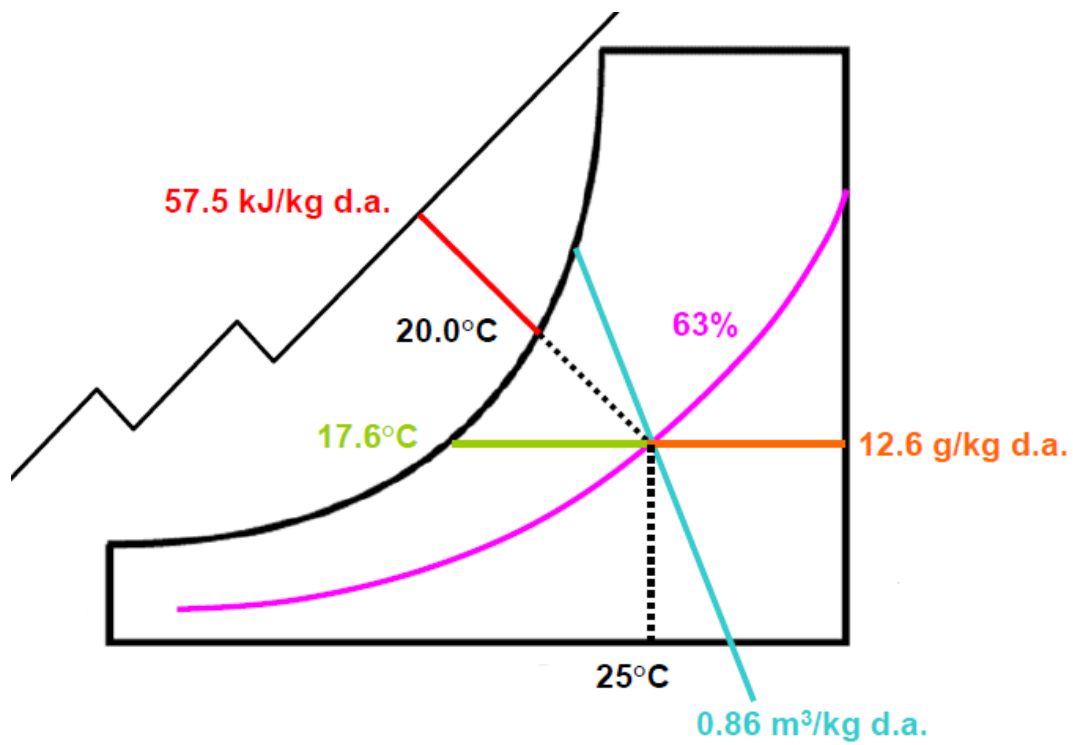




Problem 3

Given: DBT = 25°C WBT = 20°C

Required: (a) RH, (b) Tdp, (c) HR, (d) v , (e) h





SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – III– MASS TRANSFER-I – SCH1401

UNIT-III

INTRODUCTION

The term drying refers generally to the removal of moisture from a substance. It is one of the oldest, most commonly used and most energy consuming unit operation in the process industries.

Drying is often necessary in various industrial operations particularly in chemical process industries to remove moisture from a wet solid, a solution or a gas to make it dry and choice of drying medium is depends on the chemical nature of the materials.

Three basic methods of drying are used today 1) sun drying, a traditional method in which materials dry naturally in the sun, 2) hot air drying in which materials are exposed to a blast of hot air and 3) freeze drying, in which frozen materials are placed in a vacuum chamber to draw out the water.

The fundamental nature of all drying process is the removal of volatile substances (mainly moisture) from mixture to yield a solid product. In general drying is accomplished by thermal techniques and thus involves the application of heat, most commonly by convection from current of air. Throughout the convective drying of solid materials, two processes occur simultaneously namely, transfer of energy from the local environment in the dryer and transfer of moisture from within the solid. Therefore this unit operation may be considered as simultaneous heat and mass transfer operation.

Drying processes and equipment may be categorized according to several criteria, including the nature of material and the method of heat supply and the method of operation. For example In the sugar industry washed and centrifuged sugar crystals are dried to get finished product for packing.

Drying is an important operation in food processing. Milk is dried in a spray chamber to produce milk powder. All the above examples indicate that wet material loses moisture in direct contact with hot air/gas. The hot air/gas supplies the energy required for drying and also carries away the moisture released by the solid. For heat sensitive materials much of the resistance to drying resides within the material. Unduly high heat and mass transfer rates applied at the surface only result in overheating or over drying of the surface layer resulting in quality problems without major increase in the drying kinetics. The rate of migration of the moisture from within the solid to the evaporation front often controls the overall drying rate. Therefore, drying may be defined as an operation in which the liquid, generally water, present in a wet solid is removed by vaporization to get a relatively liquid free solid product. Drying of a solid does not demand or ensure complete removal of the moisture. Sometimes it is desirable to retain a little moisture in the solid after drying. Dryer and drying process selection for a specific operation is a complex problem, and many factors have to be taken into account. Though, the overall selection and design of a drying system for a particular material is dictated by the desire to achieve a favorable combination of a product quality and process economics. In general, with respect to the rate and total drying time, dryer performance is dependent on the factors such as air characteristics, product characteristics, equipment characteristics. But despite the many commercially available

drying techniques at present most dehydrated products (i.e. fruits and vegetables) are still produced by the method of hot air drying. Because this is regarded as the simplest and most economical.

There are other water/liquid removal processes such as filtration, settling, centrifugation, supercritical extraction of water from gels etc. In all these operations liquid is removed by mechanical means but a considerable amount of liquid is still retained in the solid. This residual liquid can be removed by drying. One such example is the production of condensed milk involves evaporation, but the production of milk powder involves drying.

The phase change and production of a solid phase as end product are essential features of the drying process. Drying is an essential operation in chemical, agricultural, biotechnology, food, polymer, pharmaceutical, pulp and paper, mineral processing, and wood processing industries.

PHYSICAL MECHANISM OF DRYING

Drying does not mean only removal of the moisture but during the process, physical structure as well as the appearance has to be preserved. Drying is basically governed by the principles of transport of heat and mass. When a moist solid is heated to an appropriate temperature, moisture vaporizes at or near the solid surface and the heat required for evaporating moisture from the drying product is supplied by the external drying medium, usually air or a hot gas.

Drying is a diffusional process in which the transfer of moisture to the surrounding medium takes place by the evaporation of surface moisture, as soon as some of the surface moisture vaporizes, more moisture is transported from interior of the solid to its surface. This transport of moisture within a solid takes place by a variety of mechanisms depending upon the nature and type of the solid and its state of aggregation.

Different types of solids may have to be handled for drying crystalline, granular, beads, powders, sheets, slabs, filter-cakes etc. The mechanism of moisture transport in different solids may be broadly classified into (i) transport by liquid or vapour diffusion (ii) capillary section, and (iii) pressure induced transport. The mechanism that dominates depends on the nature of the solid, its pore structure and the rate of drying.

Different mechanisms may come into play and dominate at different stages of drying of the same material. The following terms are commonly used in designing of drying systems.

Moisture content of a substance which exerts an equilibrium vapor pressure less than that of the pure liquid at the same temperature is referred to as *bound moisture*.

Moisture content of the solid which exerts an equilibrium vapor pressure equal to that of pure liquid at the given temperature is the *unbound moisture*.

The moisture content of solid in excess of the equilibrium moisture content is referred to as *free moisture*.

During drying, only free moisture can be evaporated. The free moisture content of a solid depends upon the vapour concentration in the gas.

The moisture contents of solid when it is in equilibrium with given partial pressure of vapour in gas phase is called as *equilibrium moisture content*. Similarly, the moisture content at which the constant rate drying period ends and the falling rate drying period starts is called *critical moisture content*. During the *constant rate drying period*, the moisture evaporated per unit time per unit area of drying surface remains constant and in *falling rate drying period* the amount of moisture evaporated per unit time per unit area of drying surface continuously decreases.

CLASSIFICATION OF DRYERS

Drying equipment is classified in different ways, according to following design and operating features. It can be classified based on mode of operation such as batch or continuous. In case of batch dryer the material is loaded in the drying equipment and drying proceeds for a given period of time, whereas, in case of continuous mode the material is continuously added to the dryer and dried material continuously removed. In some cases vacuum may be used to reduce the drying temperature. Some dryers can handle almost any kind of material, whereas others are severely limited in the style of feed they can accept. Drying processes can also be categorized according to the physical state of the feed such as wet solid, liquid, and slurry. Type of heating system i.e. conduction, convection, radiation is another way of categorizing the drying process. Heat may be supplied by direct contact with hot air at atmospheric pressure, and the water vaporized is removed by the air flowing. Heat may also be supplied indirectly through the wall of the dryer from a hot gas flowing outside the wall or by radiation. Dryers exposing the solids to a hot surface with which the solid is in contact are called adiabatic or direct dryers, while when heat is transferred from an external medium it is known as non-adiabatic or indirect dryers. Dryers heated by dielectric, radiant or microwave energy are also non adiabatic. Some units combine adiabatic and non adiabatic drying; they are known as direct-indirect dryers.

To reduce heat losses most of the commercial dryers are insulated and hot air is recirculated to save energy. Now many designs have energy-saving devices, which recover heat from the exhaust air or automatically control the air humidity. Computer control of dryers in sophisticated driers also results in important savings in energy.

DRYING EQUIPMENT

Batch Type Dryers

Tray Dryer

Schematic of a typical batch dryer is shown in figure 4.1. Tray dryers usually operate in batch mode, use racks to hold product and circulate air over the material. It consists of a rectangular chamber of sheet metal containing trucks that support racks. Each rack carries a number of trays that are loaded with the material to be dried.

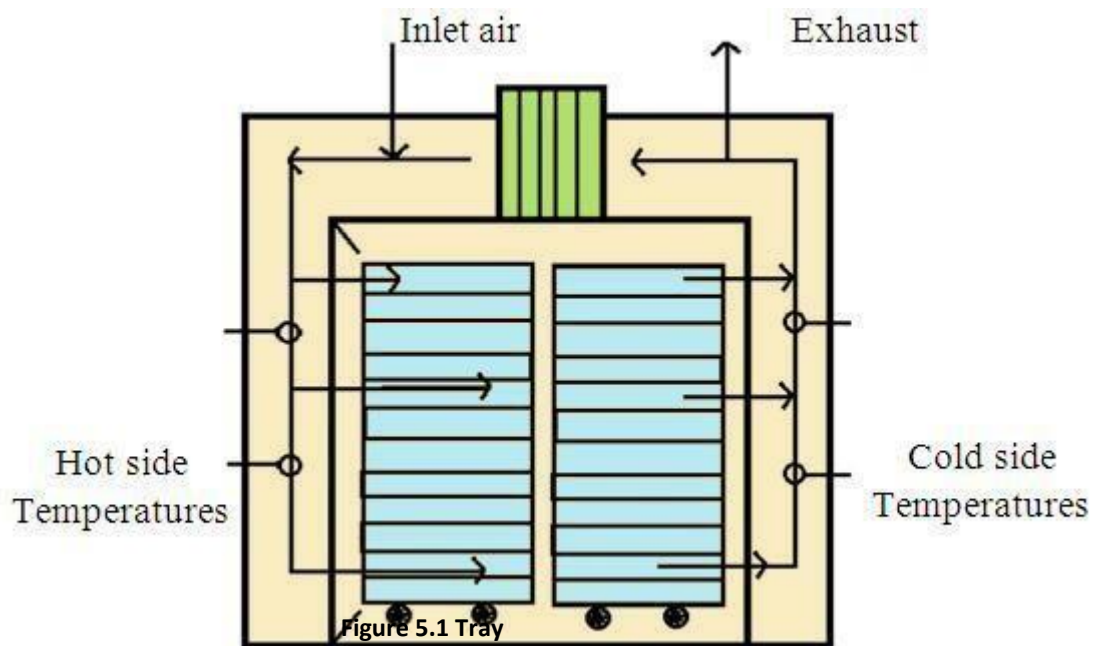


fig:4.1 Tray Dryer

Hot air flows through the tunnel over the racks. Sometimes fans are used to on the tunnel wall to blow hot air across the trays. *Even baffles* are used to distribute the air uniformly over the stack of trays. Some moist air is continuously vented through exhaust duct; makeup fresh air enters through the inlet. The racks with the dried product are taken to a tray-dumping station.

These types of dryers are useful when the production rate is small. They are used to dry wide range of materials, but have high labor requirement for loading and unloading the materials, and are expensive to operate. They find most frequent application for drying valuable products. Drying operation in case of such dryers is slow and requires several hours to complete drying of one batch. With indirect heating often the dryers may be operated under vacuum. The trays may rest on hollow plates supplied with steam or hot water or may themselves contain spaces for a heating fluid. Vapour from the solid may be removed by an ejector or vacuum pump. *Freeze-drying* involves the sublimation of water from ice under high vacuum at temperatures well below 0°C. This is done in special vacuum dryers for drying heat-sensitive products.

Pan Dryer

The atmospheric pan drier has a jacketed round pan in which a stirrer or mill revolves slowly, driven from below. The slow moving stirrer exposes fresh surfaces and thereby raises the rate of evaporation and, hence, of drying. The pan drier is a batch machine and is limited to small batches. Pan driers may be used first to evaporate a solution to its crystallizing concentration and then can function as a crystallizer by sending cold water instead of steam into the jacket. The effect of the stirrer during crystallization prevents the growth of large crystals and promotes formation of small, uniform crystals. The mother liquor is then drained off and the crystals dried in the same apparatus.

Agitated Vacuum Dryer

The agitated vacuum dryer is one of the most versatile in the range and is similar in principle to a pan dryer. The dryer essentially consists of a jacketed cylindrical vessel arranged for hot water, steam or a suitable thermal fluid flow through the jacket for heating. Doors are provided on the shell, at the top for loading the feed material and at the bottom for discharging. The dryers are available in variety of sizes. The entire drying chamber is well machined to insure small clearance with the agitator blade. Thus ensures proper shuffling of the material and avoids localized overheating. Due to the agitation of the product in the agitated vacuum dryer the drying time is substantially reduced.

Rotary Dryer

The rotary drier is basically a cylinder, inclined slightly to the horizontal, which may be rotated, or the shell may be stationary, and an agitator inside may revolve slowly. In either case, the wet material is fed in at the upper end, and the rotation, or agitation, advances the material progressively to the lower end, where it is discharged. Figure 5.2 shows a direct heat rotary drier. Typical dimensions for a unit like this are 9 ft diameter and 45 ft length. In direct-heat revolving rotary driers, hot air or a mixture of flue gases and air travels through the cylinder. The feed rate, the speed of rotation or agitation, the volume of heated air or gases, and their temperature are so regulated that the solid is dried just before discharge

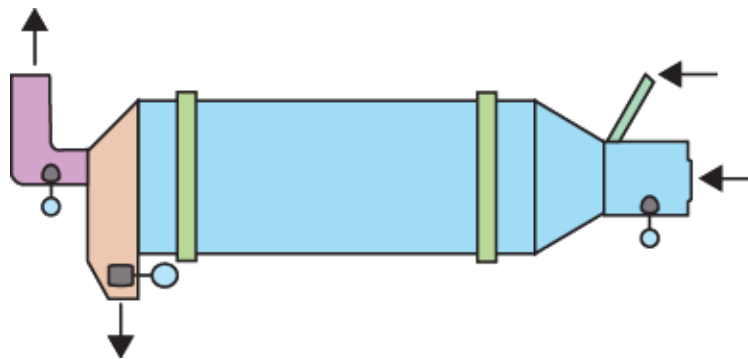


Figure 4.2 Counter current direct heat rotary dryer

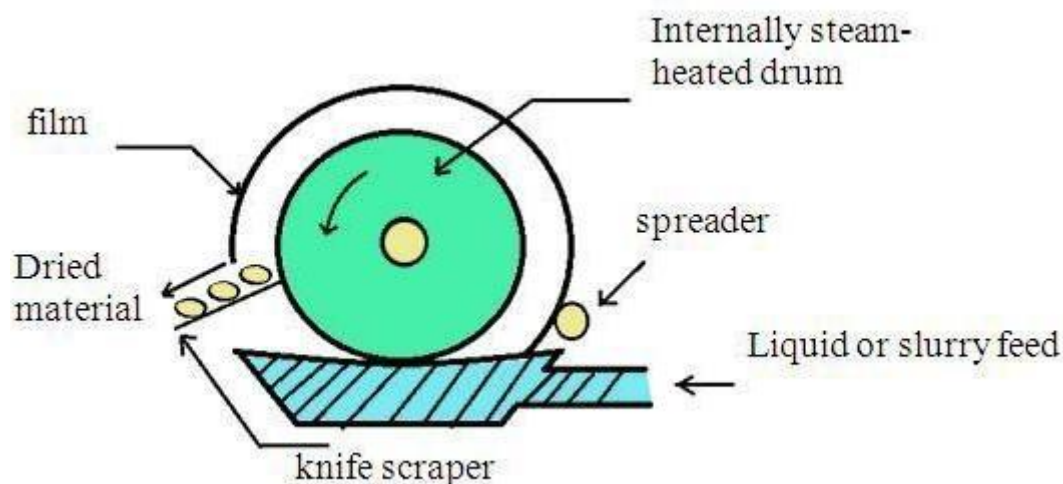
The shell fits loosely into a stationary housing at each end. The material is brought to a chute that runs through the housing; the latter also carries the exhaust pipe. The revolving shell runs on two circular tracks and is turned by a girth gear that meshes with a driven pinion. The inclination is one in sixteen for high capacities and one in thirty for low ones. As the shell revolves, the solid is carried upward one-fourth of the circumference; it then rolls back to a lower level, exposing fresh surfaces to the action of the heat as it does so. Simple rotary driers serve well enough when fuel is cheap. The efficiency is greatly improved by placing longitudinal plates 3 or 4 in. wide on the inside of the cylinder. These are called lifting flights. These carry part of the solid half-way around the circumference and drop it through the whole of a diameter in the central part of the cylinder where the air is hottest and least laden with moisture.

Drum Dryer

In drum dryers (Fig 4.3) a liquid containing dissolved solids or slurry carrying suspended solids forms a thin layer on the outside surface of a large rotating drum. For a single drum unit thickness of the film can be controlled by an adjustable scraping blade.

In case of a double drum unit thickness can be controlled by the gap between the drums (figure 4.3). A gas, normally air may be blown over the surface for rapid removal of moisture. The rotation of the drum adjusted so that all of the liquid is fully vaporized and a dried deposit can be scrapped off with the help of flexible or adjustable knife. This type of dryer mainly handles the materials that are too thick for a spray dryer and too thin for a rotary dryer. The solid collects on an apron in front of the knife and rolls to a container or to a screw conveyor. The operation of the drum drier is continuous. The drum is rotated continuously by a gear driven by a pinion that receives its motion through a belt, a chain, or a reduction gear from. The speed of the drum may be regulated by a variable-speed drive to adopt the speed to any slight variation in the feed quality.

The speed of the drum regulated depending upon the nature of materials (i.e wet or dry), if the product material is wet/dry quite a distance before the knife is reached, the speed should be decreased/increased. The design of the components is similar to that of drum filter. The knife may be held just against the surface. It may be brought closer by turning the adjusting wheels. The knife supports may be turned through part of a circle so that the angle of the blade of the knife relative to the drum surface may be selected for the greatest shearing effect.



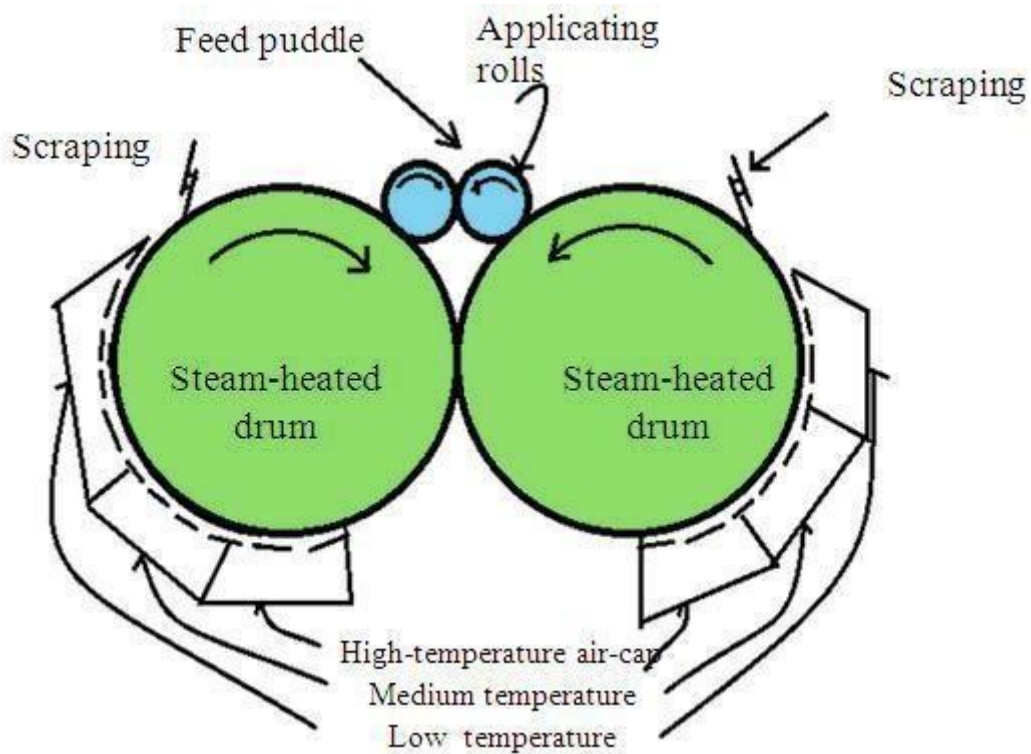


Figure 4.3 Double drum dryer

Flash Dryer

The flash driers (figure 4.4), also called pneumatic dryers, are similar in their operating principle to spray dryer. The materials that are to be dried (i.e. solid or semisolid) are dispersed in finely divided form in an upward flowing stream of heated air. These types of dryer are mainly used for drying of heat sensitive or easily oxidizable materials. The wet materials that are to be dried can be passed into a high-temperature air stream that carries it to a hammer mill or high-speed agitator where the exposed surface is increased. The drying rate is very high for these dryers (hence the term *flash dryers*), but the solid temperature does not rise much because of the short residence time. A flash dryer is not suitable for particles which are large in size or heavy particles. The special advantage of this type of dryer is that no separate arrangement is required for transporting the dried product. The fine particles leave the mill through a small duct to maintain the carrying velocities (drying gas) and reach a cyclone separator.

A solid particle takes few seconds to pass from the point of entry into the air stream to the collector. The inlet gas temperature is high and varies from 50°C to 315°C , for example, in 2 seconds, or from 650°C to 175°C in 4 seconds. The thermal efficiency

this type of dryer is generally low. A material having an initial moisture content of 80 % may be reduced to 5 or 6 % in the dried product.

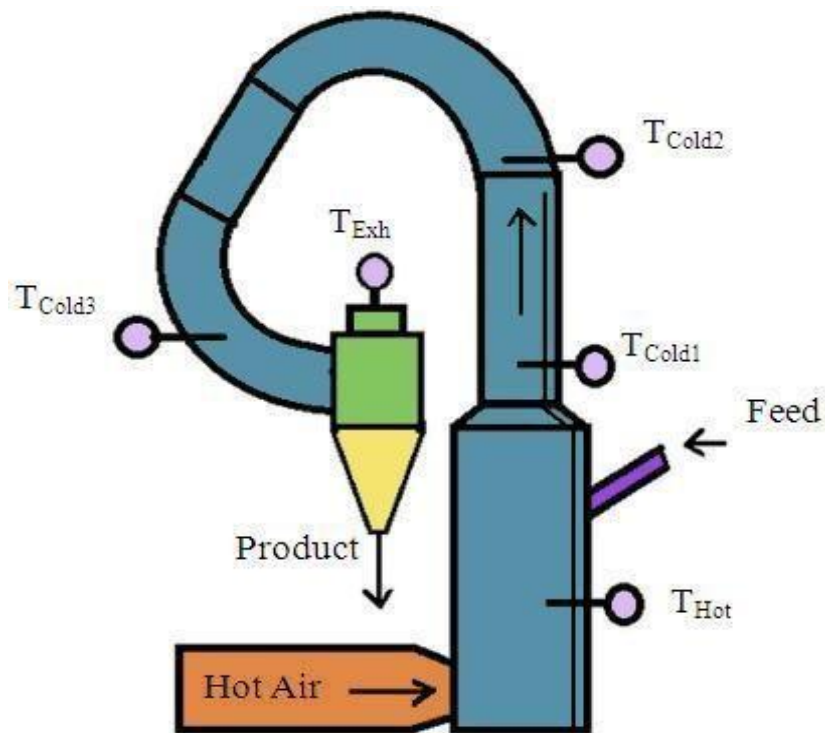


Figure 4.4: Flash dryer

Fluidised Bed Dryer

Fluidized bed dryer consist of a steel shell of cylindrical or rectangular cross section. A grid is provided in the column over which the wet material is rests. In this type of dryer, the drying gas is passed through the bed of solids at a velocity sufficient to keep the bed in a fluidized state. Mixing and heat transfer are very rapid in this type of dryers. The dryer can be operated in batch or continuous mode (figure 4.5). Fluidized bed dryer are suitable for granular and crystalline materials. If fine particles are present, either from the feed or from particle breakage in the fluidized bed, there may be considerable solid carryover with the exit gas and bag filters

are needed for fines recovery. The main advantage of this type of dryer are: rapid and uniform heat transfer, short drying time, good control of the drying conditions.

In case of rectangular fluid-bed dryers separate fluidized compartments are provided through which the solids move in sequence from inlet to outlet. These are known as *plug flow dryers*; residence time is almost the same for all particles in the compartments. But the drying conditions can be changed from one compartment to another, and often the last compartment is fluidized with cold gas to cool the solid before discharge.

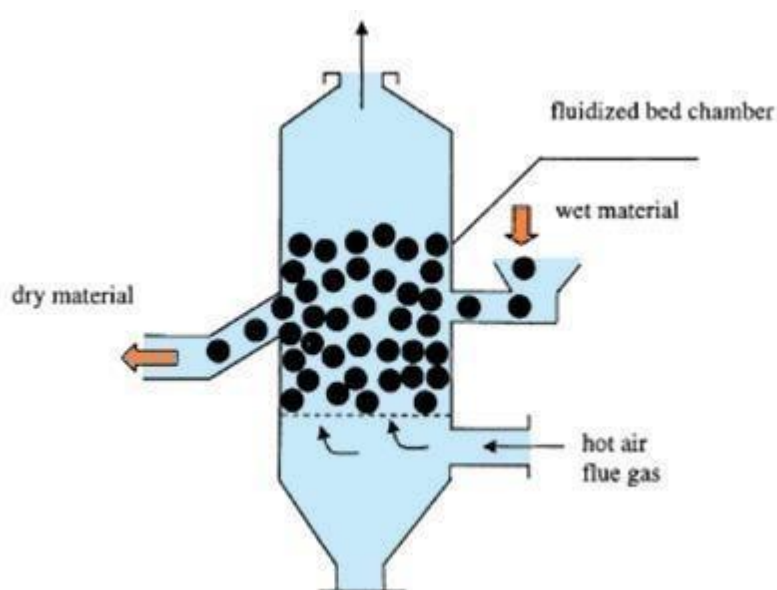


Figure 4.5: Continuous fluidized bed dryer

Screen Conveyor Dryers

Screen conveyor dryer is also called a direct heat continuous type dryer. The solid to be dried are fed on to endless, perforated, conveyor belt through which hot air is forced. The belt is housed in a long rectangular drying chamber or tunnel (figure 4.6). The chamber is divided into series of separate sections, each with its own fan and air heater. Air may be recirculated through, and vented from each section separately or passed from one section to another counter current to the solid movement. The solid is carried through the tunnel and discharged at the opposite end. In order to prevent the higher flow rate of hot air through thinner regions of the bed a uniform feeding rate and distribution of the material over the conveyor is necessary. Coarse granular, flakey, or fibers materials can be dried by through circulation without any pretreatment and without loss of material through the screen. High drying rate can be achieved with good

product quality control. Thermal efficiency of this type of dryer is high and with steam heating, the steam consumption for heating the drying gas can be as low as 1.5 kg per kg of water evaporated. Only disadvantage of this type of dryer are high initial cost and high maintenance cost due to the mechanical belt.

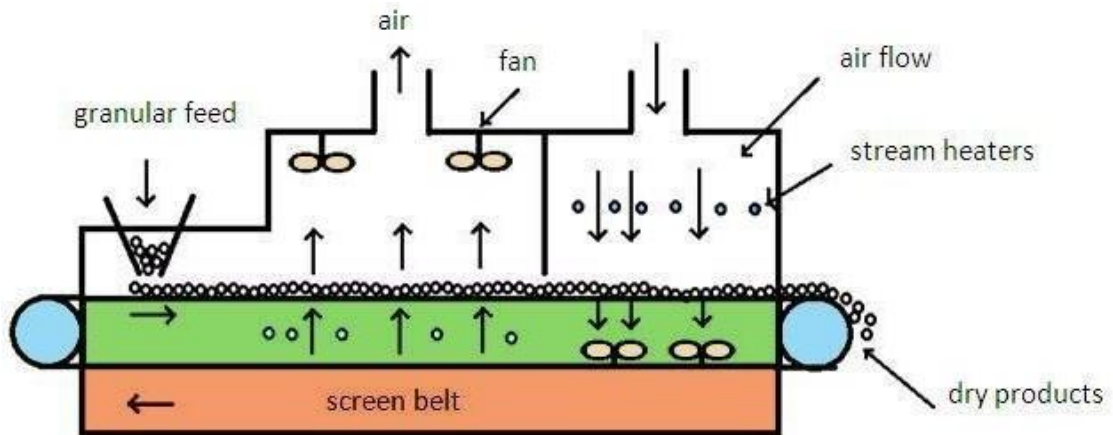
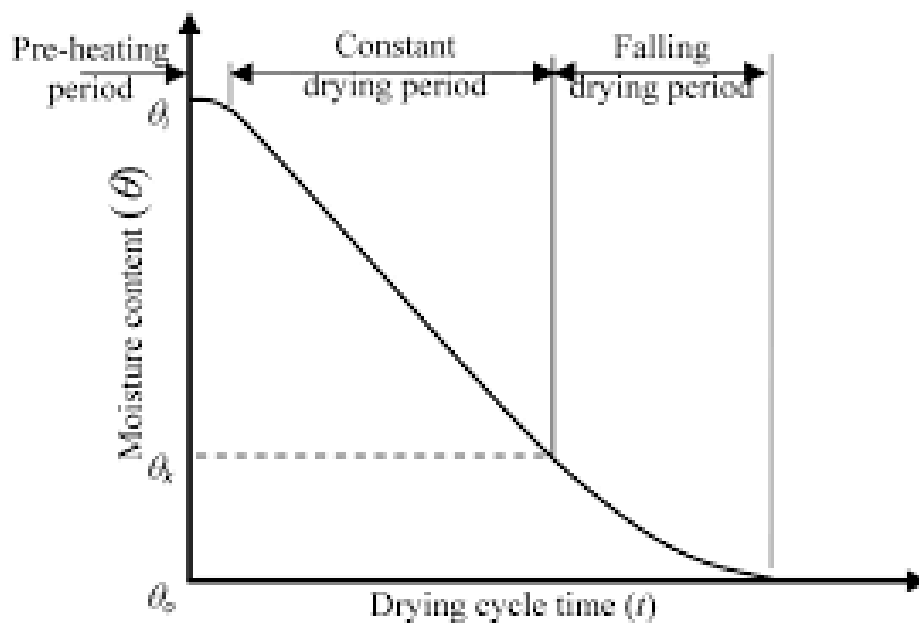


Figure 4.6: Screen conveyor dryer



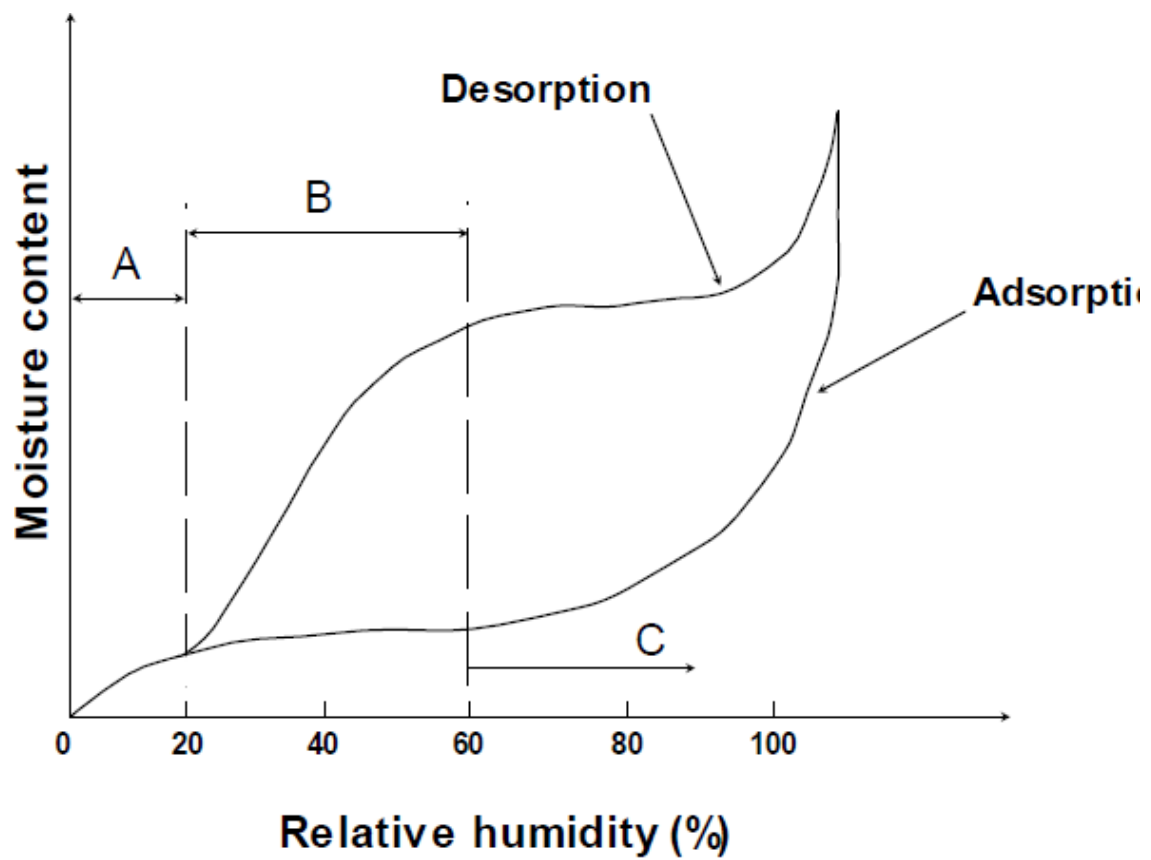


Figure 2 Typical sorption isotherms

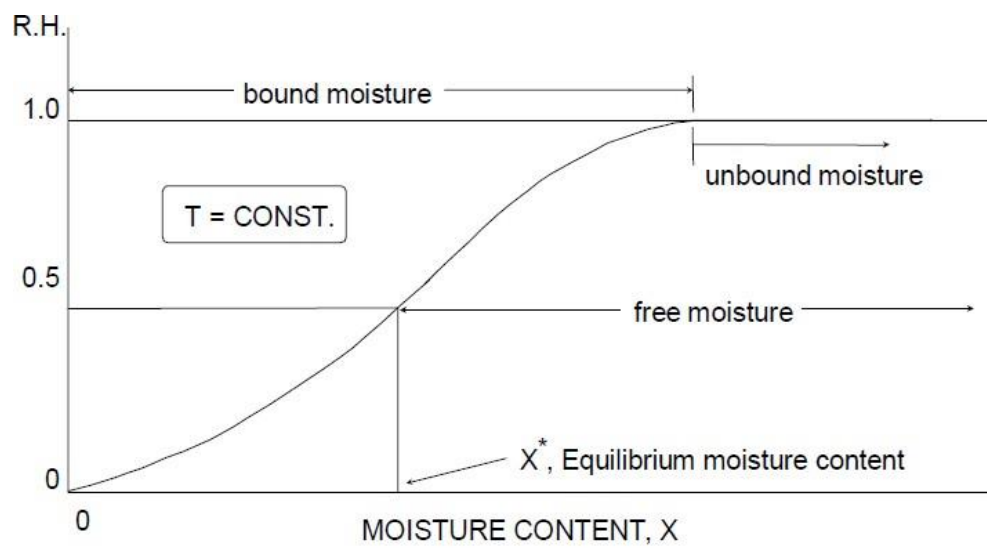


Figure 4 Various types of moisture content

Table 2 Definitions of commonly encountered terms in psychrometry and drying

Term/symbol	Meaning
Adiabatic saturation temperature, T_{as}	Equilibrium gas temperature reached by unsaturated gas and vaporizing liquid under adiabatic conditions. (Note: For air/water system only, it is equal to the wet bulb temperature (T_{wb}))
Bound moisture	Liquid physically and/or chemically bound to solid matrix so as to exert a vapor pressure lower than that of pure liquid at the same temperature
Constant rate drying period	Under constant drying conditions, drying period when evaporation rate per unit drying area is constant (when surface moisture is removed)
Dew point	Temperature at which a given unsaturated air-vapor mixture becomes saturated
Dry bulb temperature	Temperature measured by a (dry) thermometer immersed in vapor-gas mixture
Equilibrium moisture content, X^*	At a given temperature and pressure, the moisture content of moist solid in equilibrium with the gas-vapor mixture (zero for non-hygroscopic solids)
Critical moisture content, X_c	Moisture content at which the drying rate first begins to drop (under constant drying conditions)
Falling rate period	Drying period (under constant drying conditions) during which the rate falls continuously in time
Free moisture, X_f $X_f = X - X^*$	Moisture content in excess of the equilibrium moisture content (hence free to be removed) at given air humidity and temperature
Humid heat	Heat required to raise the temperature of unit mass of dry air and its associated vapor through one degree ($\text{J kg}^{-1} \text{K}^{-1}$ or $\text{Btu lb}^{-1} \text{°F}^{-1}$)
Humidity, absolute	Mass of water vapor per unit mass of dry gas (kg kg^{-1} or lb lb^{-1})
Humidity, relative	Ratio of partial pressure of water vapor in gas-vapor mixture to equilibrium vapor pressure at the same temperature
Unbound moisture	Moisture in solid which exerts vapor pressure equal to that

	of pure liquid at the same temperature
Table 2 Definitions of commonly encountered terms in psychrometry and drying (cont'd)	
Term/symbol	Meaning
Water activity, a_w	Ratio of vapor pressure exerted by water in solid to that of pure water at the same temperature
Wet bulb temperature, T_{wb}	Liquid temperature attained when large amounts of air-vapor mixture is contacted with the surface. In purely convective drying, drying surface reaches T_{wb} during the constant rate period

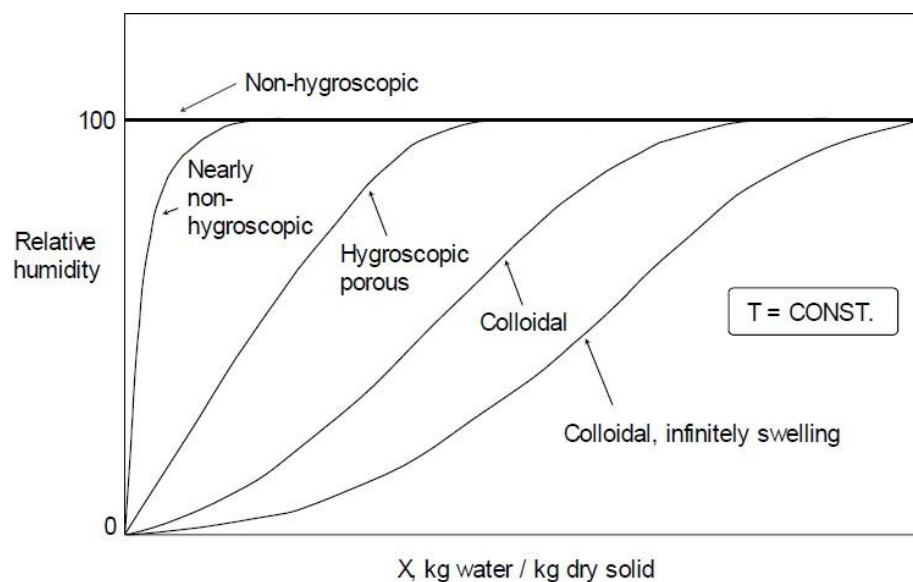


Figure 3 Equilibrium moisture content curves for various types of solids



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – IV– MASS TRANSFER-I – SCH1401

UNIT-IV CRYSTALLIZATION

Crystallization

It is a method of formation of solid particles within a homogeneous phase (vapor phase, liquid melt). Most of the crystalline solid substances are prepared either by solidification from liquid melt or by precipitation in chemical reaction. 'Crystallization' is one of the important unit operations that are taught in undergraduate curriculum of Chemical Engineering and Biochemical Engineering.

This unit operation involves knowledge of mass transfer mechanism, diffusion theory, heat transfer mechanism, hydrodynamics, solubility curves, design of equipment and selection of equipment's on the basis of principles of crystallization. Each manufacturing plant requires many unique features and these must be evaluated on an individual basis in order to achieve optimum result.

It is true that mechanical design of the crystallizer has a significant influence on the nucleation rate due to contact nucleation with the parts of pump, impellor etc. when suspended in a supersaturated solution. This phenomenon yields varying rates of nucleation in scale up and differences in nucleation rate when the same piece of equipment is used to crystallize different materials. All these must be taken care of in order to achieve super saturation of liquid.

Crystallization of a material from solution is important industrially because of the markets' demand due to some advantages of its crystalline solid forms. One of the important advantages of crystallization compared with other means of separation technique is that it produces highly „pure products with good appearance“ from impure solutions.

Energy input is low and products with high bulk density are obtained. Drying requirement is minimum due to low moisture content. Commercial crystallization processes manufacture crystalline products from the standpoint of special demands based on definite crystal shape, size and size range of particles (crystal size distribution, CSD). Generally, narrow size range is desired. Of course, requirements of scientific works are solely restricted to yield of crystal as high as possible and its purity. Crystalline products have high demand in the market due to some reasons and some advantages over liquid form products.

Handling of solid-form products with convenience than solution.

- More economical than liquid form.
- Less degradation, less contamination, more stability than solution.
- More sales appeal than liquid.
- Purity of crystalline product is more than that of a solution.

Crystallization process may be analyzed and judged from the standpoint of following aspects in order to produce good products and avoid problems encountered both within the industry and outside the industry.

1. Yield of a given product
2. Quality of product in terms of size, shape and purity of crystals
3. Uniformity in size and CSD
4. Rate of production of the desired crystals.
5. Energy requirements for cooling and evaporation, etc.

High yield and rate of production of a crystalline product at acceptable cost leads to its economical viability. But, purity of a crystalline material as medicinal compound is mandatory requirement in Pharmaceutical industry. So, purity is the first and foremost demand of the purchaser in Pharmaceutical sector. Size, uniformity in size, crystal size distribution and crystal geometry are characteristics of particles that control many physicochemical factors in making of „formulation drugs“, stability and pharmacological factors.

Crystal geometry

A crystal is the most highly organized type of non-living matter. Molecules, atoms and ions are arranged in a crystal in orderly repetitive arrays called crystal lattices and it appears as polyhedrons having sharp corners and flat sides or faces.. The crystal systems are a grouping of crystal structures according to the axial systems used to describe their lattice. Each crystal system consists of a set of three axes in a particular geometric arrangement. There are seven unique crystal systems. The cubic / isometric system has the symmetry of a cube, that is the three axes are mutually perpendicular and of equal length.

The other six systems in order to decreasing symmetry are as follows:

Hexagonal: Three equal axes are in one plane at 60° to each other, one is at right angles to this plane but not necessarily of the same length as the others. Cross section is hexagonal.

Tetragonal: Three axes are at right angles, one is longer than the other two.

Orthorhombic: It is like tetragonal crystals except not square in cross-section (when viewing the crystal on end), forming rhombic prisms or dipyramids (two pyramids stuck together).

Trigonal: There is single 3-fold axis of rotation instead of the 6-fold axis of hexagonal division.

Monoclinic: Two axes are at right angles in one plane and a third axis at some odd angle to this plane like skewed tetragonal crystals often forming prisms and double pyramids.

Triclinic: Three axes are at odd angles to each other; usually it is not symmetrical from one side to the other, which can lead to some fairly strange shapes. A crystalline substance may have the ability to form more than one form, called polymorphism.

. Crystal size and shape factors

Shape factor or sphericity, ϕ_s is used to calculate the ratio of the total surface (SP) of a crystal to the crystal volume

where $SP = \pi D_p^2$ and $V_p = 1/6 \pi D_p^3$ where D_p is the diameter of crystal.

$$\frac{S_p}{V_p} = \frac{6}{\phi_s D_p} \quad \text{and} \quad L = \phi_s D_p = \frac{6 V_p}{S_p}$$

L is the length of crystal; when $\phi_s = 1$, $L = D_p$. For cubes and spheres, $\phi_s = 1$.

For granular materials range of ϕ_s is from 0.6 to 0.95. The ratio S_p/V_p is very important parameter in any surface related phenomenon. Product containing smaller crystals is more soluble than that of bigger crystals since surface area per unit volume (S_p/V_p) is greater in smaller particles.

Uniformity in size or crystals distribution

Particles of uniform size in a product are desirable for the convenience of selection of filter, washing, uniform time of dissolution and good appearance of product. Besides these, caking tendency of crystals during its storage period can be prevented since number of points of contact between crystalline particles is significantly less in uniform crystals.

Actually a product batch contains various fractions of particles of different particle sizes. Wide range of particle sizes creates problem in many practical situations. So, crystal size range is made narrow by controlling some process parameters like

- adding seed crystals with desired size range.
- avoiding contact nucleation as far as possible
- removing a fraction of small size /finer particles
- dissolving smaller crystals, nuclei either by heating or adding some solvent
- increasing residence time for larger particles.

.

Yield

In crystallization processes, it is often needed to calculate the theoretical yield so that actual yield can be compared with it. Crystals are allowed to grow for sufficient period to reach targeted growth. Finally, mother liquor sheds its super saturation and attains equilibrium at final temperature. Now, solid crystals are separated from mother liquor and further processed.

The yield can be predicted from the difference of concentration of feed solution and solubility of mother liquor (saturated). Predicted yield may not match actual yield due to slow growth longer time required to reach equilibrium, insufficient exposure of surface area when heavier particles settle at the bottom, less growth in the location with poor super saturation, viscous nature of solution etc. In such a situation, the final mother liquor may retain appreciable super saturation and actual yield is always less unless mode of nucleation is changed and above-mentioned causes are solved. The solubility is expressed commonly in terms of anhydrous salt per 100 mass of pure solvent or mass fraction. The calculation of yield of a nonhydrated salt (crystal without water of crystallization) from solution is simple since the amount of solvent in the liquid remains unchanged.

Purity of product

Purity of a crystalline product is judged by many ways, for example determination of melting point of crystalline substance. Generally it is thought that „crystal form“ is the purest form of a substance, but it may retain impurities on its surface due to adherence of impure mother liquor on its surface while separating it from final magma. Smaller crystals will retain relatively more impurities than large crystals due to large specific surface area of the smaller crystals. “Washing of crystal’s surface” is done with the

same solvent to remove impurities. Sometimes mother liquor is occluded within the empty space of an agglomerate / lump that leads to poor quality product. Proper washing of agglomerated crystal is difficult. Formation of agglomerated crystal during crystallization can be minimized by proper agitation.

Nucleation and Crystal growth

In the formation of crystal two-steps is required (1) generation of a new particle (2) its growth to macroscopic size. The first step is called nucleation. Neither formation of a new crystal nor its growth is possible in saturated or unsaturated solution.

Rate of nucleation is very important for controlling crystal size distribution (CSD). The rate of nucleation is the number of new particles formed per unit time per unit volume of magma or solid free mother liquor.

The sequence of stages in the evolution of a crystal is as follows:

Cluster – embryo – nucleus – crystal

Nuclei are in a state of unstable equilibrium if it loses units, it dissolves, if it gains units, it grows and becomes a crystal.

Solubility of large crystal is less than that of smaller crystals in the micrometer range because of significant surface energy per unit mass on smaller crystals. Smaller crystals are in a state of unstable equilibrium in a supersaturated solution. As a result larger crystals grow until the small crystals disappear. This phenomenon is called Ostwald ripening.

The effect of particle size on solubility is a key factor in nucleation. At first, a loose unstable aggregate called „cluster“ is formed when several molecules/atoms of solute come into contact due to random collision. Formation of embryo initiates lattice arrangement and formation of a new and separate phase. Though embryos have short lives but it may grow to a size as that of nucleus, which is the smallest assemblage of particles.

Formation of stable nucleus depends on number of units assemble together. Nucleation may be of three types: Spurious nucleation, primary nucleation and secondary nucleation. Spurious nucleation produces crystals of poor quality with abnormal needle like or whisker like growths from the ends of the crystals. It occurs at large super saturation ($\Delta T > 80^\circ \text{C}$). This is called needle breeding.

Another growth related spurious nucleation called „Veiled growth“ gives the crystal surface „milky“ appearance due to rapid crystal growth and occlusion of mother liquor into the crystal faces. This

problem can be avoided by growing crystals at low super saturation and by using well-designed and operated pumps and agitators. The first, step of „nucleus“ formation is called „nucleation“ or ~~primary~~ nucleation. On an industrial super saturation driving force is necessary to initiate primary nucleation. The second chief mechanism in crystallization is called secondary nucleation. There, crystal growth is initiated with contact.

The formation of nuclei is attributable to fluid shear and to collisions between existing crystals with each other or with the walls of the crystallizer and rotary impellers or agitator blades. On impact with these moving parts of crystallizer, soft or weak crystals can break into fragments and so give new crystals. Attrition is the only source of new crystals that is independent of super saturation.

Crystal growth is a diffusion process; solute molecules reach the growing surface by diffusion through the liquid phase and are organized into space lattice. Growth rate of most crystals is linear with super saturation. The rate of deposition is proportional to driving force between the bulk of the liquor and that wetting the surface of the crystal that is approximately saturated with respect to crystals of that size. The driving force will vary because of the increasing solubility for crystals with lower size range. Crystal growth takes place in metastable zone that lies between saturation and nucleation limits. In this region the solution is supersaturated and no nucleation occurs when crystals are growing.

Miers super saturation theory

In the year 1927, Miers, SIR, H.A. postulated a theory on super saturation. Miers theory explains growth of nuclei with respect to super solubility and solubility curve under some limitations. Let us know first about solubility curve. When equilibrium is attained at final temperature, mother liquor becomes saturated in crystallization process and rate of formation of nucleus is balanced by the rate of dissolution of nucleus. The equilibrium relationship is the solubility curve. Solubility data for different solids had been expressed as function of temperature. Solubility chart displays various types of profiles like curves with positive and high slope (KNO_3), positive and very low slope (NaCl), negative slope ($\text{MnSO}_4\text{--H}_2\text{O}$). For most of the materials, solubility curves follow firstly i.e. high and positive slope. Solubility curve represents the maximum concentration of solutions that can be obtained by bringing solute into equilibrium with solvent. This curve represents final concentration of mother liquor toward which supersaturated solution approaches. Super saturation is attained by decreasing temperature of highly concentrated solution or decreasing amount of solvent by evaporation or by both.

Miers super saturation theory is explained with the help of following figure.

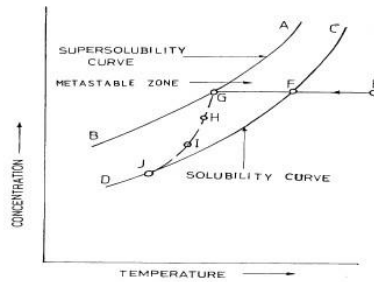


Fig. 1: Miers solubility curve

AB – super solubility curve, CD – solubility curve, E – Feed location, under saturation, F – solution cools to saturation, G – Metastable zone, nucleation begins, H – Concentration of mother liquor decreases with crystal growth, I – Crystal growth during cooling and decrease of concentration of solution, J – Exit location, saturated solution

Super saturation method

1. Super saturation by cooling
2. Super saturation by evaporation of solvent.
3. Super saturation by adiabatic evaporation (cooling plus evaporation)
4. Salting out by adding a substance that reduces the solubility of the substance of interest.

In case of solubility with strong temperature dependencies the cooling method is more attractive whereas with low dependencies on temperature the evaporation method is adopted.

Fig. 2:

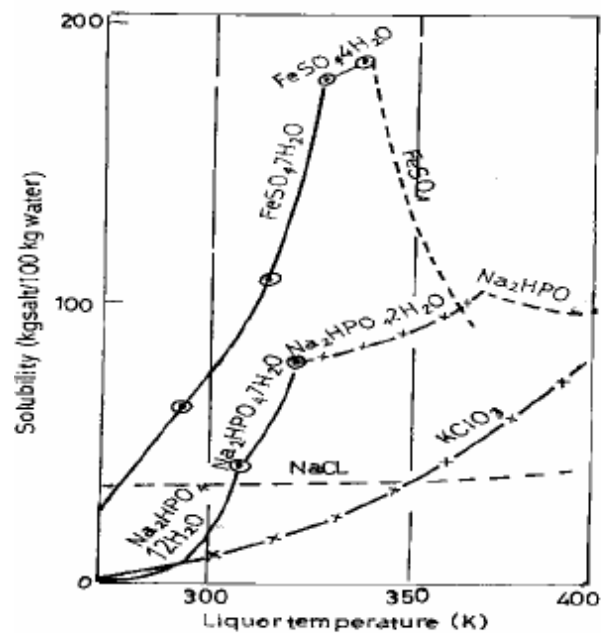


Fig. 2: Solubility curves of salts

When solubility curve decreases appreciably with temperature i.e., rate of decrease of solubility with the decrease of temperature is high, so curve is steeper. KCl, AgNO₃, CuSO₄ · 5H₂O and Na₂HPO₄ · H₂O are the example of crystals that follow Method 1.

Substances like NaCl, Na₂SO₄, and CaCl₂ follow method 2. Solubility curves of these substances are flat type i.e. solubility does not decrease appreciably with the decrease of temperature. In this case, yield will be very poor if method 1 is followed.

The third method, cooling adiabatically under a vacuum is the most important method for large-scale production. If a hot solution is evaporated under a vacuum, the solvent flashes because total pressure is less than the vapor pressure of the solvent at the temperature at which it is introduced. Now, the solution becomes supersaturated due to evaporation of solvent and adiabatic cooling.

The last method is not very much used. In this method, a foreign substance is deliberately added to reduce the solubility to such an extent that the desired solute crystallizes.

Crystallization Equipments

There are different types of equipments used for making crystals. The design of these equipments is based on the method of super saturation.

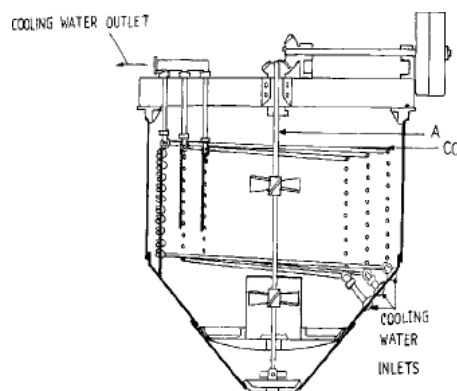
Names of equipments:

1. Super saturation by cooling alone – Tank crystallizer, Agitated batch crystallizer. These two are used in batch process, though tank crystallizer is obsolete one. Swenson Walker crystallizer falls under this category and it is used in continuous process.
2. Super saturation by adiabatic cooling: Different kinds of vacuum crystallizers are used to make crystals by this method.
3. Super saturation by evaporation: Krystal evaporator and salting evaporator are two examples under this type of super saturation.

All these equipments are made of stainless steel.

Description of some crystallizers:

(i) Agitated batch crystallizer: The crystallizer body is equipped with a centrally located agitator, cooling pipes. The upper part of the vessel is cylindrical and closed at the top. The lower part of the vessel is conical and its bottommost part is used to drain out final magma. Magma is defined as the slurry containing product crystal and saturated mother liquor. Hot concentrated solution of a substance is induced in the crystallizer and it is agitated with the impeller. Cold water flows through the cooling coils to transfer heat from the hot solution. Cold water transfers heat due to heat of crystallization too. As temperature drops, super saturation is achieved that initiates crystallization. Agitator facilitates heat transfer operation throughout the solution and maintains uniformity of temperature in the solution and keeps the growing crystals in suspension so that these can grow uniformly. Thus agitator prevents formation of aggregates.



A – Impellor, CC- cooling coil

Fig. 3: Agitated batch crystallizer

Rate of production of crystals is low due to batch process. Since temperature at the surface of cooling coil is least so rapidly formed crystals get deposited on the surface of cooling coil and cause hindrance in heat transfer rate. These are the disadvantages of agitated batch crystallizer. After certain period of growth, magma is transferred to centrifuge where crystals are separated from mother liquor.

The Swenson–Walker crystallizer: It consists of an open semi cylindrical trough, bottom part of which is welded with a jacket to run cold water through the jacket in counter current direction to that of solution. It is equipped with a slow speed long pitched spiral agitator moving at 7 r.p.m., that is fitted as

close to the bottom of the trough as possible i.e. a narrow clearance is maintained. A single unit (trough) is 24 inch wide and 10 feet long. Length of crystallizer may be increased up to 40 feet by joining 4 units. If more units are required, these can be arranged one above another and solution fall from the upper row to the next lower one.

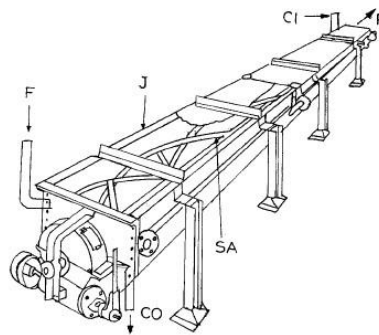


Fig. 4: Swenson Walker Crystallizer: F-feed, J- Jacket, CI-coldwater inlet, CO-coldwater outlet, SA-spiral agitator, P- product.

The hot concentrated solution is fed at one end of the trough and flows to the other end slowly. When solution is cooled to desired degree of super saturation, crystals start forming. At the end of the crystallizer, crystals along with mother liquor overflow to a draining table that separates mother liquor from crystals. Mother liquor is returned to the process and wet crystals are conveyed to a centrifuge.

The spiral agitator functions by conveying crystals in the forward direction and it keeps particles in suspension and prevents accumulation of crystals at the bottom of trough. This agitator lifts the deposited crystals from the bottom and spreads throughout the solution and thus keeps these crystals in suspension facilitating uniform growth of crystals.

Vacuum Crystallizer: This falls in the category of modern type crystallizers. It is closed vessel, at its top vacuum is maintained by a condenser with the help of a steam jet vacuum pump or booster. Large quantity of material can be processed in small floor space and labor cost is also saved in this type of crystallizer.

Vacuum crystallizer consists of a cone-bottomed vessel, which is fitted with a barometric condenser at the top and propellers in the conical part, elutriation leg at the bottom of the vessel. Hot saturated solution (feed) well above the boiling point at the pressure in the crystallizer is introduced into the main crystallizer body via a slow speed low head circulating pump and a heater, through a tangentially cut inlet pipe that causes a swirling motion within solution. Liquid level in the crystallizer body is maintained up to certain mark. At the top of liquid, vacuum is maintained that corresponds to be boiling point of the solution lower than the feed temperature.

The solution so introduced into a vessel in which a vacuum is maintained, the solution flashes and solvent, evaporates due to adiabatic evaporation. As a result solution gets cooled spontaneously to equilibrium temperature; since it is adiabatically cooled i.e. both the enthalpy of cooling and the enthalpy of crystallization provide enthalpy of vaporization. Super saturation is generated due to both cooling and evaporation.

Temperature gradient and concentration gradient thus formed due cooling and evaporation are two driving potential to create nucleation. Vapors are formed in the empty space above the solution and discharged through the top outlet. It is evident that the vapor from the crystallizer cannot be condensed at low pressure with the usual cooling water temperatures available.

This vapor is compressed and then condensed by ordinary cooling water. The crystals so formed in the body due to super saturation, fall through the conical bottom of vessel into elutriation leg that helps to classify and separate bigger size particles.

Now, product magma (crystal along with mother liquor) is discharged through outlet and fed to centrifuge, part of mother liquor is re-circulated. Function of tangential inlet of the pipe is that it creates swirling motion and thus facilitates flashing of solvent and equilibrates magma within the vapor. The simple vacuum crystallizers are not equipped with propellers. So, the effect of static head due to solution creates problem in generating adequate nucleation.

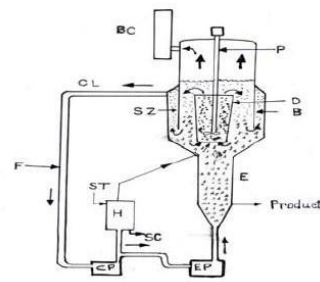


Fig. 5: Vacuum Crystallizer: B- barometric condenser, D- Downpipe, F- feed
ST-steam inlet, SC- steam condensate, H-heater, PM- Pump, C-centrifuge, M-
mother liquor, P-product crystal.

Draft tube baffle (DTB) crystallizer: Draft tube baffle crystallizer is based on the same principle as that of vacuum crystallizer but it is more versatile and effective equipment. The main crystallizer body is equipped with a condenser at the top, elutriation leg at the conical bottom, a recycling loop at the side of the body, a centrally located propeller, a draft tube around the propeller and an annular space within the crystallizer body.

A pump assembly is used to maintain circulation of fluid. Hot solution enters the main crystallizer body. The solution is super saturated adiabatically under the vacuum maintained at the top, due to evaporation of solvent and decrease of temperature of solution.

Draft tube acts as battle. It controls circulation by promoting axial flow of fluid thus facilitating maintenance of temperature and concentration gradient throughout the solution and allowing fine particles to flow in the upstream. In this crystallizer, all the fine particles are not grown simultaneously. Some fraction of fine particles is removed in the upstream.

When fluid enters the annular zone, bigger particles are settled here due to baffling effect and very finer particles float in the upstream and thus unwanted nuclei are removed through the recycle loop. In this way magma density is sharply increased within the body. A part of this recycled liquid is mixed with the fresh feed and is pumped to the main crystallizer body via a heater and another part of liquid is introduced into the elutriation leg via an elutriation pump.

Elutriation leg facilitates in classification of crystals according to size while flowing in the upward direction through it. Upward stream carries away some smaller particles into the main crystallizer body

for further growth. Product is discharged through the outlet and fed to the centrifuge to separate out crystals from mother liquor.

This type of crystallizer produces crystals with narrow crystal size distribution. Draft Tube Baffle Crystallizer is an elaborated Mixed Suspension Mixed Product Removal (MSMPR) design, which has proven to be well suited for vacuum cooling and for processes exhibiting a moderate evaporation rate. MSMPR is an idealized crystallizer model that follows some stringent requirements. The DTB crystallizer has proven to be suitable for many products such as boric acid, Glauber salt, citric acid

The Krystal Crystallizer: The Krystal or Oslo crystallizer is extensively used where large quantities of crystals of controlled size are required. The basic principle is to flow a supersaturated solution to bed of crystals which are maintained in a fluidised state. The Krystal crystallizer consists of a vapor head (A) that is attached with a condenser at the top and connected with a long specially designed discharge tube (E) extended well to the bottom of crystal growth chamber B.

Feed solution is usually introduced into the suction of pump C and then it is sent to vapor head through heater. Vapor formed at the top is released and discharged into condenser and vacuum pump. The hot solutions in the chamber A become supersaturated due to evaporation but crystals are not formed in this chamber.

Super saturation produced in chamber A is discharged on the crystals suspended in an upward flowing stream of liquid at the bottom of Krystal growth chamber. When the liquid becomes saturated at equilibrium, it leaves the chamber through F for recirculation. Coarser particles remain at the bottom and finer particles remain at the top of crystal bed and re-circulated liquid carries away finest particles and enters the vapor chamber via the heater and pump.

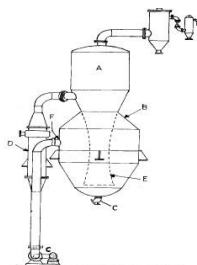


Fig.7: Krystal crystallizer: A- vapor head, B-crystal growth chamber, C- circulating pump, D- heater or cooler, E- discharge tube, F- overflow to circulating pump, G- product outlet.



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited "A" Grade by NAAC | 12B Status by UGC | Approved by AICTE

www.sathyabama.ac.in

SCHOOL OF BIO AND CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – V– MASS TRANSFER-I – SCHA1401

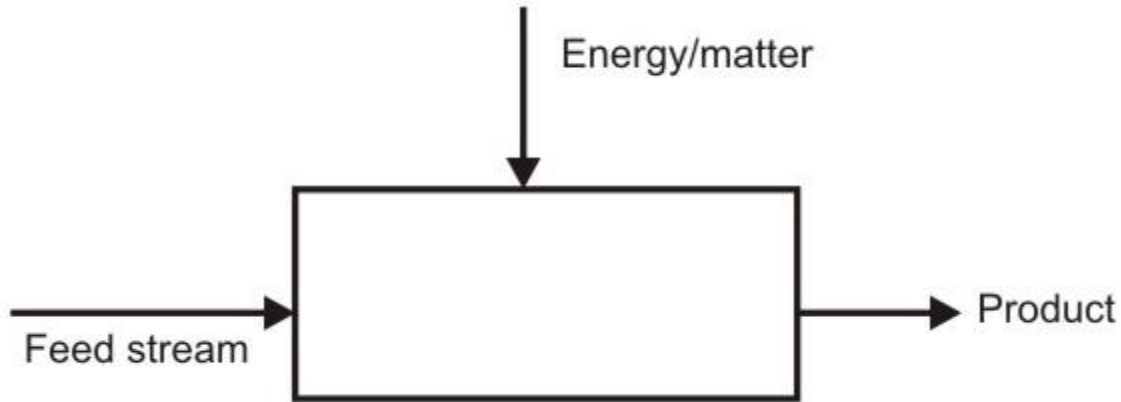
UNIT-V

MEMBRANE SEPERATION

In most of the chemical engineering systems, separation processes are integral part of the entire process flowsheet. If we consider a reactive system, where, certain products are of primary interest, separation units are either put in the upstream or downstream. In such a system, the reactor is the heart of the system. It may happen that the reactants are gaseous and should be devoid of moisture. In such cases, a separation unit must be present as an upstream unit. On the other hand, if a particular product is kept in mind, a separation unit must be placed at the downstream of the flowsheet. There may be processes, where, the separation is the only objective. For example, if we consider a treatment process of an industrial effluent, separation is the only process that is involved. There may be a number of separation processes involved in a system. In an effluent treatment process, there are three steps, namely, primary, secondary and tertiary treatment processes. All these processes are primarily separation processes. Primary treatment processes include coagulation, flocculation, etc. Secondary treatment processes are mainly oxidation ponds, etc. Tertiary treatment processes involve adsorption, membrane separation, etc. In food and juice processing industries, separations are primary stages of operation. Most of the pharmaceutical industries have separation units as integral parts in the downstream or they are the main units. In milk processing separation processes are primary.

Most of the separation processes involve, either separation of solutes from the solvent or, separation of a mixture of solutes. It may be noted that the components those need to be separated are in a mixture naturally. In order to effect separation, one has to put either energy or an extra material from outside to disturb stability. This is equivalent to the concept of exceeding the activation energy of separation by an external agent (agent may be energy or matter). This point can be elaborated by some examples. Consider a case of separation of salt from sea water. In this system, thermal energy is added to the system and water is evaporated leaving behind the salts. Consider another case of separation of charged colloidal particles which are stable in a solution. In such systems, a coagulant, like potassium alum or ferric chloride or calcium oxide (selection depends upon the operating pH) is added. These coagulants are generally of opposite charges of

the colloids. These colloids get themselves attached to the coagulants by electrostatic attractive forces and the whole assembly becomes heavier and settles down.



The extent of separation is defined by separation factor. Separation factor between two species 'i' and 'j' is defined as

$$\alpha_{ij} = \frac{x_{i1}/x_{j1}}{x_{i2}/x_{j2}} \quad (1.1)$$

Where, 1 and 2 are two streams. If $\alpha_{ij} = 1$, no separation occurs. If $\alpha_{ij} < 1$, stream '1' is concentrated in 'j' and stream '2' is concentrated in 'i'. If $\alpha_{ij} > 1$, stream '1' is concentrated in 'i' and stream '2' is concentrated in 'j'.

Grossly, the separation processes are divided into two categories, namely, equilibrium governed separation processes and rate governed separation processes. In equilibrium governed separation processes, the product phases are in equilibrium with the inlet phases. On the other hand, in rate governed separation processes, product phase composition or separation occurs due to the difference of rate of physical transport of species alone. Distillation, absorption etc. are examples of equilibrium governed separation processes. On the other hand, membrane based processes are rate governed separation process.

Chemical potential in interfacial mass transfer

A species of molecules is said to be in equilibrium when there does not exist a chemical potential gradient across the boundaries of the system. Chemical potential (μ) of a system is defined as the amount of change of energy on introduction of a new species in the system keeping the entropy and volume unchanged. Typically the partial molar Gibbs energy is referred as the chemical potential of the system. In the absence of any external force field, the total energy change of the

system is

$$dG = -SdT + VdP + \sum_{i=1}^c \mu_i dN_i$$

$$\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T, P, N_{j \neq i}} = \left(\frac{\partial U}{\partial N_i} \right)_{S, V, N_{j \neq i}}$$

The above expression clearly shows that μ_i is the partial molar Gibbs energy of the system. At equilibrium, for a constant temperature and pressure, μ of each of the species are constant and equal.

Mass transfer is inherently a non-equilibrium process, characterized by the net motion of molecules down a chemical potential gradient (concentration gradient). The mass transfer often takes place across an interface between the two phases. At the interface between two phases, the chemical potential of the diffusing components of the two phases are equal to each other. One can imagine of an infinitely thin region where the phases are in equilibrium with this plane. The energy changes in mass transfer processes include internal entropy, volume and interfacial changes, which occur simultaneously and as a result of the mass transfer.

In mass transfer processes, the molar or mass potential provides the total energy density change, i.e. per mole or per unit mass. Thus, at equilibrium, it is this total energy density that must be constant, whereas in non-equilibrium systems its gradient provides a driving force for mass transfer.

Most of the membrane based processes are the rate governed. The main crux of the separation lies in the difference of transport of various species through the membrane. The driving force of such

transport is generally gradient of chemical potential. If we recall the definition of gradient of chemical potential, it is composed of four parts. These are concentration gradient, pressure gradient, temperature gradient and electrochemical potential gradient. Presence of these causes (one or more of such gradients) results into effects (the difference in separation and hence effects). Some of these systems are described below.

Osmosis is observed when a solution is separated from the solvent by a semipermeable (only solvent is permeable species) membrane. Apparently, difference in osmotic pressure across the membrane causes the transport of the solvent. Actually, osmotic pressure is a colligative property and it is a function of concentration. Therefore, the concentration (or more generally activity) gradient of the solvent is the main driving force in osmosis. In this case, the solvent flows from the solvent side to the solution side until, the solvent activity becomes almost equal in both the sides. This results in generation of hydrostatic pressure difference between the two sides, known as osmotic pressure. If the initial concentration of solute is more in the solution side, more solvent will flow in from the solvent side to equalize the solvent activity on both the sides, resulting in more osmotic pressure difference.

It must be understood that osmosis is a natural phenomenon. In case of reverse osmosis, pressure is applied on the solution side externally (using a pump or a compressor), so that the osmotic pressure is overcome and the solvents are forced out of the solution side. The efficiency of this process depends on the porosity, morphology and thickness of the membrane. These factors influence the transport of the solvent through the membrane immensely and thereby, dictating the throughput of the process and the quality of the product. Since, reverse osmosis membranes have very small pore size, this is used for separation of lower molecular weight species, like, salts. A salt having very osmotic pressure, the operating pressure in the feed side of a reverse osmosis process is therefore extremely high. This will lead to deposition of salts near the membrane surface, leading to build up

of a concentration boundary layer. Therefore, the pressure gradient in this system leads to concentration difference.

In this case, two liquid streams are separated by a permeable barrier or membrane. In the feed side, a specific set of solutes are permeated through the membrane to the other side. The upstream feed is known as the feed side and the downstream is known as the dialysate. Typically, dialysate stream is pure distilled water. Thus, the concentration gradient between the two streams is the maximum. The transport is effected by the concentration gradient between two streams. The duration of separation entirely depends on the rate of the solutes through the membrane. An example is removal of urea, creatinin from blood stream.

It is an interface that separates the two phases and restricts the transport of various chemical species through it. Membrane can be homogeneous, heterogeneous, symmetric, asymmetric, charged, neutral.

- Pore size is 2-10 Å
- Diffusion is controlling mechanism.
- Typical RO membrane

Pore size is 10-1000 Å

- Both convection and diffusion are dominant mechanism.

In this case, a thin polymeric skin is cast on another polymeric support. It is shown schematically in Fig. 3.1. The skin acts like a membrane. Since the thickness of the skin is really small, the resistance offered is less and one can expect a higher flux compared to homogeneous membranes.

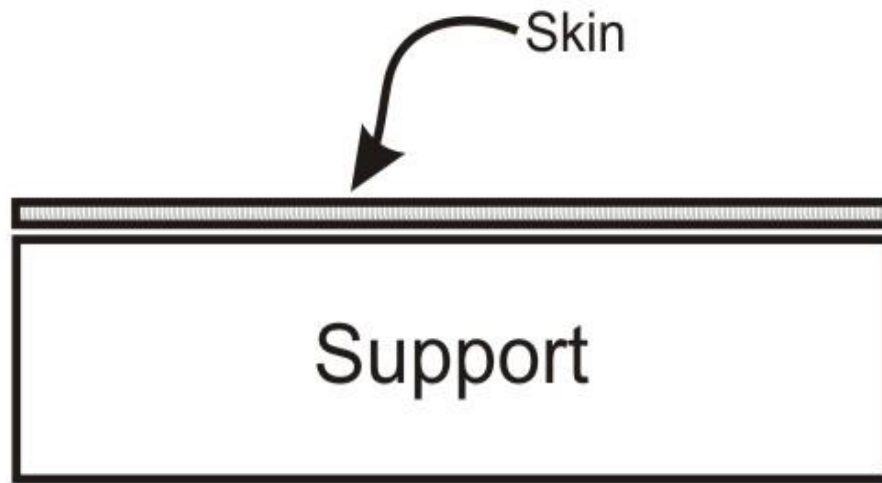


Fig. 3.1: Schematic of an asymmetric membrane

Transmembrane permeate flux is inversely proportional to the membrane thickness. If homogeneous barrier is the skin, microporous barrier may be the support.

1. Dissolution of permeating molecules in the membrane
2. Diffusion of dissolved molecules
3. Desorption of penetrant molecules to the downstream side.

Single gaseous molecules diffuse under rarefied conditions so that the mean free path is longer than the pore diameter.

Viscous flow through the pores of ultrafiltration and microfiltration.



Small solute particles to be separated.

Molecular weight < 100

Pore size: 2 – 10 Å

Pressure: > 25 atm.

Permeation is main transport mechanism

Example: Filtration of salt solution

Particles to be separated with Molecular weight: 200 – 1000

Pore size: 5 – 20 Å

Pressure: 15 – 25 atm.

Particle retention of salts.

Example: Filtration of dyes, small molecular weight organics, etc.

Molecular weight of particles : 10³ - 10⁵

Pore size: 20 – 1000 Å

Pressure: 6 – 8 atm.

Transport Mechanism: Convection (main) + diffusion

Example: Filtration of protein, Red blood cells, polymers, etc.

Molecular weight > 1 lakh

Pore size: more than 1000 \AA^0

Pressure: 2 – 4 atm.

Example: Filtration of clay solution, latex, paint, etc.

Some useful definitions are presented below.

Osmosis means craving for water.

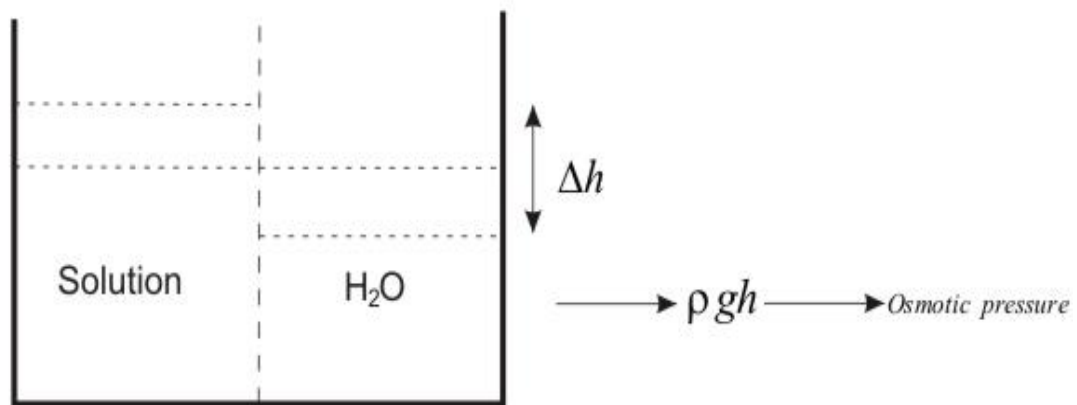


Fig.3.2: A schematic presentation of the osmosis process

Fig. 3.2 shows that a semipermeable barrier separates a solution having some solute in one side and pure solvent (water in this case) at the other side. Due to presence of difference in

concentration of solvent in both sides, water from solution side permeate through the membrane to the solvent side. Therefore, the level of water in solvent side goes down and that in the solution side goes up. At equilibrium, there exists a difference in hydrostatic pressure in both the chambers, although the chemical potential of the solvent is equal across the membrane. The developed hydrostatic head is called osmotic pressure. If the solute concentration in the solution is more, the solution is more “thirsty” of water and equilibrium hydrostatic pressure head is more.

When water is forced through a concentrated solution (by applying pressure), the osmotic pressure resists. The energy required to overcome this resistance is called osmotic energy.

As discussed above, osmotic pressure is a colligative property, directly proportional to concentration.

$$\pi \propto \frac{1}{M_w} \quad \text{and} \quad \pi \propto C$$

and hence,

$$\pi = \frac{RTC}{M_w} \tag{3.1}$$

The above equation is van't Hoff's equation for dilute solutions.

It may be mentioned that any solution has its own osmotic pressure, but it can only be realized in presence of a semipermeable barrier or membrane. For example, a glass of saline water has its own osmotic pressure but it can only be realized, if we place it across a semipermeable barrier.

This property indicates the extent of separation of a membrane can produce with respect to the solute concentration in the feed. Thus, observed retention is defined as,

$$R_o = 1 - \frac{C_p}{C_o} \quad (3.2)$$

C_p = Solute concentration in permeate

C_o = Solute concentration in feed

If $R_o \rightarrow 1.0$, solute is completely retained by the membrane.

Real retention is a constant that defines the partition of the solute concentration across the membrane, i.e., between the the membrane-solution interface and the permeate side. Since, this definition is not masked by any physical phenomenon like concentration polarization, (defined later) etc., this definition indicates the true separation efficiency of the solute by the membrane.

$$R_r = 1 - \frac{C_p}{C_m} \quad (3.3)$$

C_m = Solute concentration in membrane solution interface C It may be mentioned here that since, membrane surface concentration of solute is always greater than the bulk concentration, real retention is always greater than observed retention. For complete solute retention, $R_r = 1.0$.

Molecular weight cut off is another concept to characterize a membrane. In this case, generally neutral solutes of various molecular weights are considered to conduct experiments. The operating conditions of these experiments are low transmembrane pressure drop, high turbulence and low feed concentration. Experiments are conducted using each of these solutes and the observed retention values at the steady state are measured. The observed retention values are then plotted against the molecular weight of the solutes in a semi-log plot. The typical solutes are glucose (molecular weight 180), sucrose (molecular weight 342), various fractions of

polyethylene glycol (molecular weights: 200, 400, 600, 1000, 1500, 2000, 4000, 60000, 10000, 30000), dextran (molecular weight 40000, 1,50,000), etc. The molecular weight at 90% solute retention indicates roughly the molecular weight cut off of the membrane. The molecular weight cut off curves are shown in Figs. 3.3 and 3.4

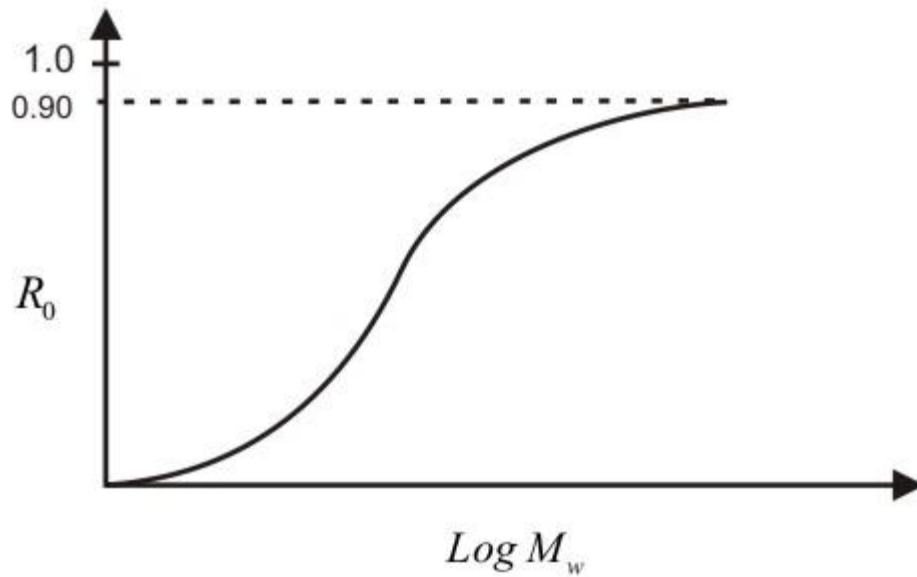


Fig.3.3: Typical molecular cut off curve of a membrane

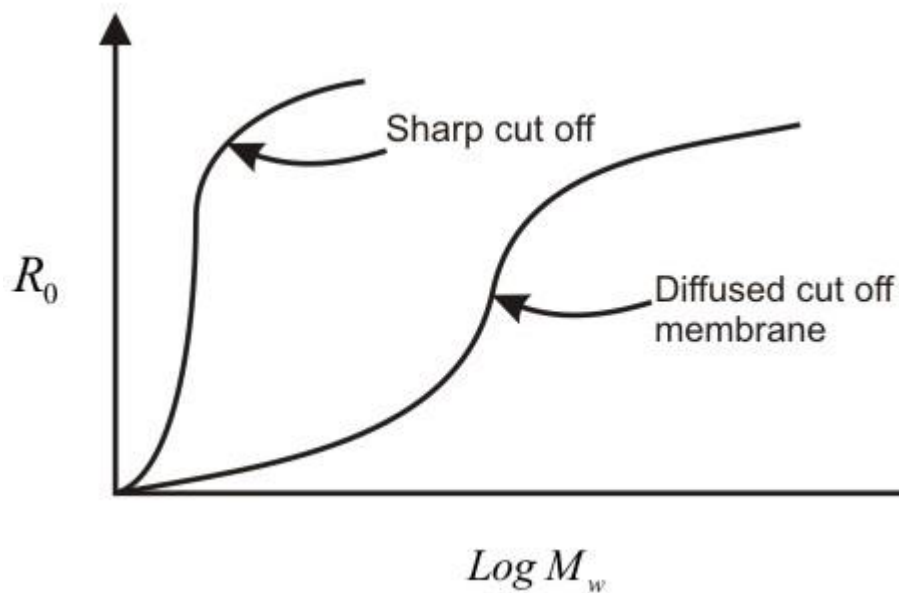


Fig.3.4: Sharp and diffused molecular cut off curves

Molecular weight cut off curves may be a sharp cut off or a diffused cut off. If the retention curve raises sharply to 90% level over a small span of molecular weight regime, then the cut off curve is called a sharp cut off curve. If the retention curve rises over a wide span of molecular weight region, it is a diffused cut off curve. One has to have an accurate control over the operating conditions to achieve the sharp cut off membranes. In fact, most of the commercial membranes are diffused type.

This parameter shows how porous the membrane is. If L_p is more, then the membrane is more

porous. Mathematically, L_p is defined as,
$$L_p = \frac{J^0}{\Delta P}$$
 where, J^0 is the pure water flux and ΔP is transmembrane pressure drop. This concept is elaborated in detail in the subsequent sections.

Retention:

Observed retention (R_o): Estimate by direct experimental measurement

Real retention (R_r): One has to conduct batch experiments at high stirring speed, low feed concentration and low operating pressure. In that case, it is assumed that there is no formation of concentrated solute layer over the membrane surface and in absence of polarized layer, observed retention is almost same as retention retention.

Permeability:

Membrane permeability is measured by distilled water runs. Experiments are conducted using distilled water at various transmembrane pressure drops values. At various pressure drops, the water flux is measured. A plot of permeate flux versus operating pressure would be a straight line through the origin, as shown in Fig. 3.5. The slope of this curve indicates the permeability (L_p) of the membrane. It may be noted here that the permeability of a membrane is its pressure

history only. In other words, permeability of the membrane is independent of turbulence (stirring speed or cross flow velocity) in the flow channel. The unit of permeability

is $\frac{m^3}{m^2 \cdot Pa \cdot s}$ or $\frac{m}{Pa \cdot s}$.

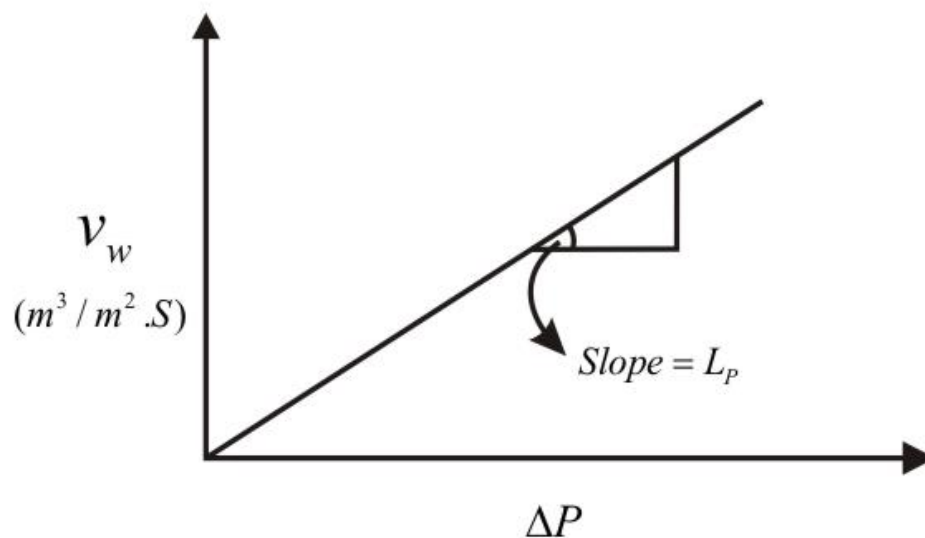


Fig.3.5: A typical flux versus pressure plot for distilled water as feed

The practical equipment where the actual membrane-based separation occurs is known as membrane modules. The basic aim of development of these modules is to provide maximum membrane area in relatively smaller volume, so that the permeate flux i.e., the productivity of the system is maximum. These membrane modules are of four types, (i) plate and frame module, (ii) hollow fiber module, (iii) spiral wound and (iv) tubular modules. Each of these modules is described below:

The heart of plate-frame module is the support plate that is sandwiched between two flat sheet membranes. The membranes are sealed to the plate, either gaskets with locking devices, glue

or directly bonded. The plate is internally porous and provides a flow channel for the permeate which is collected from a tube on the side of the plate. Ribs or grooves on the face of the plate provide a feed side flow channel. The feed channel can be a clear path with channel heights from 0.3 to 0.75 mm. The higher channel heights are necessary for high viscosity feeds; reduction in power consumption of 20 to 40% can be achieved by using a 0.6 mm channel compared to a 0.3 mm channel. Alternatively, retentate separator screens (20 or 50 mesh polypropylene) can be used. Commercial plate-frame units are usually horizontal with the membrane plates mounted vertically. They can be run with each plate in parallel plates in two or three series. Laboratory are also available as preformed stacks up to 10 plates. A typical plate and frame module is shown in Fig. 3.5a.

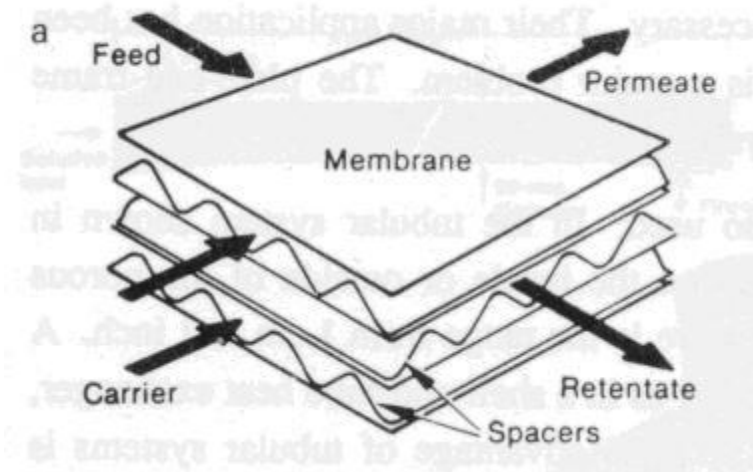


Fig.3.5a: A plate and frame module

In such modules, the membrane is cast on the inside surface of a porous tube. Tubular membranes operate in tangential, or cross-flow, design where process fluid is pumped along the membrane surface in a sweeping type action. The feed solution is pumped through the center of the tube at velocities as high as 6 m/s. These cross-flow velocities minimize the formation of a concentration polarization layer on the membrane surface, promoting high and stable flux and easy cleaning, especially when the objective is to achieve high suspended solids

in the MF, UF or NF concentrate. Permeate is driven through the membrane to be directed out of the system or back into the process depending on the application. There are many advantages in tubular membrane configurations. Besides their rugged construction, they have a distinct advantage of being able to process high suspended solids, and concentrate product successfully and repeatedly to relatively high end point concentration levels without plugging. A common objective of an end-of-pipe waste treatment UF system is to reduce waste volume as much as possible to reduce concentrate hauling costs. For juice clarification applications, tubular membrane systems produce the greatest yields and the highest final suspended solids concentration levels. Tubular MF, UF and NF systems do not require significant prefiltration. Some tubular products have the ability to be mechanically cleaned with spongeballs. Spongeballs can be used in process, and are also used to enhance chemical cleaning by reducing time and cleaning chemicals. Tubular membranes are ideally suited to treatment of metalworking oily waste, wastewater minimization and recovery from industrial processes, juice clarification, treatment of pulp and paper industry waste, etc. Tubular membranes typically have life upto 2 to 10 years. The following figure (Fig. 3.5 b) shows some tubular membranes.



Fig.3.5b: Pictures of tubular modules

In hollow fiber module, lots of hollow fibers (each fiber is a tubular module) are kept in a large pipe. Geometry allows a high membrane surface area to be contained in a compact module. This means large volumes can be filtered, while utilizing minimal space, with low power consumption. Hollow fiber membranes can be designed for circulation, dead end and single

pass operation. Some of the many hollow fiber membrane filtration applications include, potable water treatment, juice clarification, wine filtration, dairy processing, etc. The advantages of such modules include reduction in space requirement, lowering in labor cost, lowering in chemical cost, delivery of high quality product water, etc. Hollow fiber membranes offer the unique benefits of high membrane packing densities, sanitary designs and, due to their structural integrity and construction, can withstand permeate back pressure thus allowing flexibility in system design and operation. Most KMS hollow fiber products are available in (i) 1" diameter laboratory test cartridges ranging up to 10" diameter for commercial products, (ii) Standard commercial cartridge lengths of 25", 43", 48", 60" and 72", (iii) Nominal separation ranges from 0.2 micron down to 1,000 MWCO, (iv) Fiber inside diameters from 0.02"(.5mm) up to 0.106"(2.7mm), (v) Various materials of construction including polysulfone and polyacrylonitrile.

The following figure (Fig. 3.5c) shows some hollow fiber cartridges of 5, 8 and 10" diameter with endcaps.



Fig.3.5c: Pictures of hollow fiber modules with end cap

Benefits of hollow fiber membranes include (i) controlled flow hydraulics, (ii) tangential flow along the membrane surface limits membrane fouling, (iii) membranes can be backflushed to remove solids from the membrane inside surface, thus extending the time between two chemical cleaning cycles, (iv) high membrane packing density resulting in high throughput, (v) modular in structure so that future extension of the plant becomes easier. The flow pattern in a typical hollow fiber module takes place as shown in Fig. 3.5d.

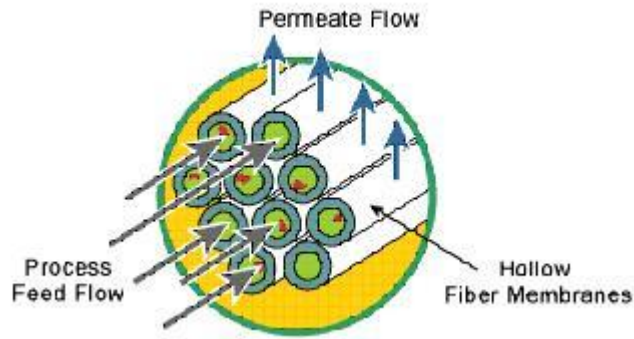


Fig.3.5d: Flow pattern in hollow fiber module

In spiral wound membrane, membrane is cast as a film onto flat sheet. Membranes are sandwiched together with feed spacers (typical thickness 0.03 to 0.1 inch) and permeate carrier. They are sealed at each edge and wound up around a perforated tube. The module diameter ranges from 2.5 to 18 inch and length varies from 30 to 60 inch. The typical cross section of the spiral wound module is shown below:

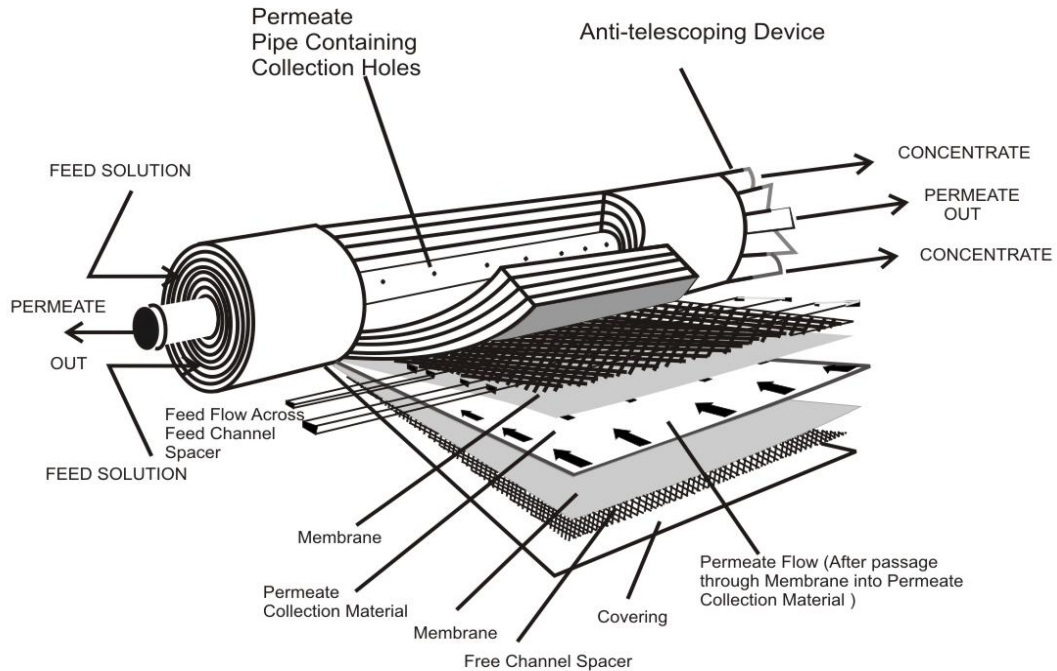


Fig.3.5e: Flow pattern in spiral wound module

The application of spiral wound module includes, seawater desalination, brackish water treatment, potable water treatment, dairy processing, electrocoat paint recovery, protein separation, whey protein concentration, etc.

Therefore, it can be identified that the modeling of plate and frame and spiral wound module can be done by considering the flow through a rectangular channel. On the other hand, that for a tubular and hollow fiber module are done by considering flow through a tube.

Separation in membrane is the result of differences in the transport rates of chemical species through it.

Transport rate is determined by the driving force acting on individual components, their mobility, concentration of solute in membrane phase, etc..

Mobility: Depending on solute size and structure of membrane.

Concentration: Chemical compatibility of solute & interface material.

Let us consider an experiment, where, a solvent and a solution are separated by a semi-permeable membrane as shown in fig. 3.9.

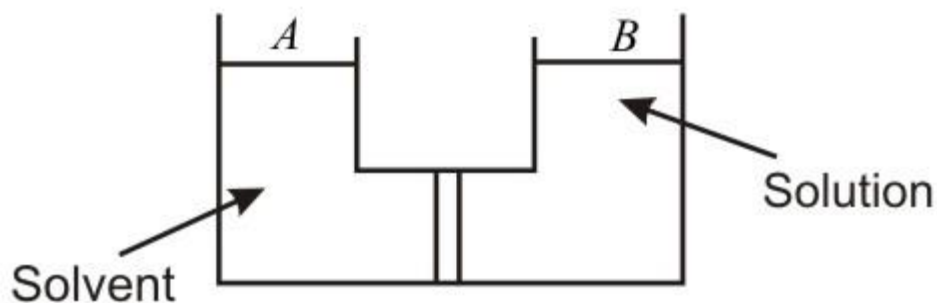


Fig. 3.9: Solution and solvent are separated by a semi-permeable barrier

Osmotic equilibrium means chemical potential of solvent at both chambers are equal.

Let us use the notation, '2' is for solvent and '1' is for solute. P₁ is pressure in chamber A and P₂ is pressure in chamber B.

$$\mu_2 \text{ (at } P_1) = \mu_2 \text{ (at } P_2) \quad (3.4)$$

The above equation can be written as,

$$\mu_2 = \mu_2^0 + RT \ln a_2 \quad (3.5)$$

Where, μ_2^0 is for pure solvent and a_2 is solvent activity.

Following hypothetical experiment is conducted.

Both chambers have pure water and initially at pressure P₁, μ_2 is same at both chambers. Now small amount of solute is added in chamber B.

ELECTROPHORETIC METHODS

Different rates of migration of charged particles/molecules in an electric field are useful for separation. This principle can be utilised quite effectively for the separation of biomolecules as most of them are having charges. Each such molecule has a characteristic pH, known as isoelectric pH, at which, the biomolecule is neutral. One can control the operating pH by addition of few drops of acid or alkali. Thus, if the operating pH is set above the isoelectric pH (pI), the molecule becomes negatively charged and if the operating pH is set below the isoelectric pH, it is positively charged.

<u>Compound</u>	<u>Mw</u>	<u>pI(250C)</u>
Aspartic acid		2.77
Lysine		9.74
Ovalbumin	43000-45000	4.7
Bovine serum albumin	68000	4.95
Hemoglobin	~17000	7.33
Cytochrome C	~12000	9.28

As discussed in Chapter 4, the electrophoretic mobility of a charged spherical ion in an electrolytic solution becomes,

$$u = \frac{v}{E} = \frac{ze}{6\pi\eta R_p} \quad (9.1)$$

For charged colloids, the system contains small amount of electrolytes to carry appreciable current. This causes redistribution of counter and co-ions around charged colloids i.e., within electrical double layer.

$$\text{If } \kappa R_p < 0.1, \text{ then } u = \frac{2\epsilon_0\epsilon\zeta}{3\eta} \quad (9.2)$$

$$\text{If } \kappa R_p > 0.1, \text{ then } u = \frac{\epsilon_0\epsilon\zeta}{\eta} \quad (9.3)$$

Typical values for electrophoretic mobility in free solution are in the orders of 10^{-8} m²/s.V for ions and 10^{-9} m²/s.V for proteins. The mobility increases as size of ion increases.

To prevent the natural convection, electrophoresis is conducted in a stabilizing porous media, *e.g.*, gel or membrane. This method is known as zone electrophoresis. This system behaves exactly like, chromatography. Some stabilizing media should be used. These should have the following characteristics:

1. Inert, should not react with species.
2. No residual charges on the media so that no ion exchange or electroosmosis takes place.
3. Pore size should be greater than the molecular size so that no hindered transport occurs.

1. A thin layer of gel is polymerized onto support plate (glass).
2. Support plate is placed on coolant plate so that joule heating is prevented.
3. Gel layer should be 5mm for better heat dissipation.
4. Cover is to control evaporation and safety reason as high voltage may be used.

a. A small sample is placed in the sample well in the center of gel slab. When current is on, solute particle migrate towards cathode/anode.

b. Since the width of feed sample is small so that each solute migrates as a zone, with velocity u_i . the zones eventually separates out from each other.

c. Products are often detected by UV absorbance, RI, etc..;

The most common electrophoresis is polyacrylamide gel electrophoresis (PAGE). The advantages of this method are listed below:

The most common electrophoresis is polyacrylamide gel electrophoresis (PAGE).

The advantages of this method are listed below:

1. It is an excellent anti-convective gel.
2. Easy to polymerize in place
3. Can be polymerized in the variety of pore sizes.

4. Little residual charge on the polymer.

