

### SCHOOL OF BIOCHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – I – Mass transfer for Biological Systems –SCH1313

## Introduction to Adsorption

Adsorption is one of the most important surface processes and its knowledge is essential for a chemical engineer due to its wide range of applications in almost all fields of science and technology.

### **Definition:**

Adsorption is defined in many ways, some of the standard definitions of adsorptions are:

- Adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface
- The process by which molecules of a substance, such as a gas or a liquid, collect on the surface of another substance
- Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that phase and a separate (solid) phase.

### **Applications:**

Some of the standard applications of adsorption are:

- Heterogeneous Catalysis- This is probably the most important application relevant to chemical engineering. The reaction mechanism of how a reactant reacts on a catalyst surface revolves around adsorption. Therefore designing catalyst, reactors and studying them requires knowledge of adsorption
- Separation- Adsorption is used as a separation process in many chemical as well as bio chemical industries to separate gaseous or liquid mixtures. Designing adsorption equipment like fixed bed adsorbers, gas drying, pressure swing adsorption etc., chromatography requires knowledge of adsorption.
- Many experiments in the lab use adsorption as a process to calculate various parameters like surface concentration, porosity, change in surface energies, pore surface area etc.

**NOTE:** Adsorption must not be confused with absorption which is a bulk process in which a substance diffuses into the bulk of another substance unlike adsorption which is only a surface process.

### **Adsorption Isotherms**

Now let us study a bit more of the physics of adsorption. Adsorption is usually described through adsorption isotherms that is *the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature*. The adsorption isotherm is the equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent particles at a given temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. Some typical adsorptions are shown in the figure below



### Fig. 7.2: Favourable and unfavourable adsorption

### **Different adsorption isotherms**



Fig. 7.3: Different adsorption isotherms

### Langmuir Adsorption Isotherm

The simplest equation for adsorption under dynamic equilibrium condition was derived by **Irving** Langmuir in 1916. He got the <u>Nobel Prize in 1932</u> in chemistry for his contributions to surface chemistry. It can be used to predict monolayer physisorption as well as chemisorption. Let us derive its equation in terms of partial pressure of the gas (at constant temperature) and the amount of adsobate adsorbed.

### Assumptions

Langmuir made several assumptions in order to simplify his analysis. The main assumptions in Langmuir adsorption isotherm are

- The surface is like a checkerboard and made up of many active (adsorbing) sites (see figure below).
- Each active site can adsorb only one molecule of the adsorbate.
- There cannot be multilayer adsorption. ( In other words the process is adsorption limited)
- All surface sites have constant heat of adsorption (there is no difference between any two active sites)
- Adsorbed molecules don't interact with each other on the surface. (there is no motion of adsorbed molecules on the surface)
- The surface containing the active sites is perfectly like a flat plane with no corrugations.





= gas atom/molecule

Fig. 7.4: Surface of adsorbent

According to Langmuir, the rate of adsorption depends on the following 4 factors

- The rate of collision of the adsorbate molecule of mass 'm' which is at pressure 'p' is proportional to  $\frac{p}{\sqrt{2\pi m k T}}$  per unit surface area at the constant temperature.
- The activation energy  $E^{act}$  of adsorption ,since this determines the fraction of the colliding molecules possessing the necessary energy to be adsorbed (see figure 7.5)



Fig. 7.5: Activation energy diagram for adsorption

• The fractional coverage of the surface  $f(\theta)$  which is the amount of surface that is exposed/available for a single site adsorption =  $(1 - \theta)$ , where

$$\theta = \text{fraction of sites covered} = \frac{number of sites which have absorbed molecules}{total number of sites}$$
(7.1)

σ which is the 'fraction of the total number of colliding molecules which results in adsorption'.

### Shortcomings of the Langmuir adsorption isotherm

- Langmuir assumed that the heat of adsorption is independent of the coverage θ which is not what is observed.
- Multilayer adsorption is not taken into account
- · Lateral interactions on the surface were ignored

### **Non Langmuirian Adsorption Isotherms**

Many corrections to the Langmuir adsorption isotherm were suggested that accounted for its shortcoming. Two of the more famous ones are

• Freundlich isotherm:  $\theta = k.p^n$ .

It can be theoretically derived from Langmuir isotherm by assuming that heat of adsorption falls exponentially as the coverage is increased.

**1. Temkin isotherm:** 
$$\theta = \frac{RT}{\Delta H \alpha} \ln(A_0 p).$$

It can be derived from Langmuir isotherm assuming the heat of adsorption decreases linearly with coverage.

**NOTE:** Langmuir adsorption isotherm can also be derived using basic statistical mechanics principles by considering the grand canonical ensemble and the corresponding Helmholtz free energy.



Fig. 7.6: Langmuir Adsorption isotherm

### **How Does Adsorption occur?**

As mentioned above adsorption is a surface phenomenon. It occurs due to the imbalance of forces at the surface of a material. This lead to formation of bonds (Covalent, ionic, Van der Waals, Hydrogen bonds etc.) between the surface molecules (**adsorbents**) and the molecules in the fluid phase (**adsorbate**).

### **Physisorption**

Adsorption in which the forces involved are intermolecular (i.e., van der Waals, hydrogen bonding) of the same kind as those responsible for the non-ideality of real gases and the condensation of vapours etc. , and which do not involve a significant change in the electronic orbital patterns of the species involved is called physisorption.

### Chemisorption

A chemical process in which a reacting molecule forms a definite chemical bond with an unsaturated atom, or a group of atoms (an active centre) on a catalyst surface, and electron transfer is involved is known as chemisorption.

*Note:* In practice no absolutely sharp distinction can be made between chemisorption and physisorption, although generalities apply.

## Distillation



Distillation is a widely used method for separating mixtures based on differences in the conditions required to change the phase of components of the mixture. To separate a mixture of liquids, the liquid can be heated to force components, which have <u>different boiling points</u>, <u>into the gas phase</u>. The gas is then condensed back into liquid form and collected.

Repeating the process on the collected liquid to improve the purity of the product is called double distillation. Although the term is most commonly applied to liquids, the reverse process can be used to separate gases by liquefying components using changes in temperature and/or pressure.

A plant that performs distillation is called a *distillery*. The apparatus used to perform distillation is called a *still*.

## **Uses of Distillation**

Distillation is used for many commercial processes, such as the production of gasoline, distilled water, xylene, alcohol, paraffin, kerosene, and many other liquids. Gas may be liquefied and separate. For example: nitrogen, oxygen, and argon are distilled from air.

## **Types of Distillation**

Types of distillation include simple distillation, fractional distillation (different volatile 'fractions' are collected as they are produced), and destructive distillation (usually, a material is heated so that it decomposes into compounds for collection).

## **Simple Distillation**

Simple distillation may be used when the boiling points of two liquids are significantly different from each other or to separate liquids from solids or nonvolatile components. In simple distillation, a mixture is heated to change the most volatile component from a liquid into vapor.

The vapor rises and passes into a condenser. Usually, the condenser is cooled (e.g., by running cold water around it) to promote condensation of the vapor, which is collected.

## **Steam Distillation**

Steam distillation is used to separate heat-sensitive components. Steam is added to the mixture, causing some of it to vaporize. This vapor is cooled and condensed into two liquid fractions. Sometimes the fractions are collected separately, or they may have different density values, so they separate on their own. An example is steam distillation of flowers to yield essential oil and a water-based distillate.

### **Fractional Distillation**

Fractional distillation is used when the boiling points of the components of a mixture are close to each other, as determined using Raoult's law. A fractionating column is used to separate the components used a series of distillations called rectification. In fractional distillation, a mixture is heated so vapor rises and enters the fractionating column. As the vapor cools, it condenses on the packing material of the column. The heat of rising vapor causes this liquid to vaporize again, moving it along the column and eventually yielding a higher purity sample of the more volatile component of the mixture.

## **Vacuum Distillation**

Vacuum distillation is used to separate components that have high boiling points. Lowering the pressure of the apparatus also lowers boiling points. Otherwise, the process is similar to other forms of distillation. Vacuum distillation is particularly useful when the normal boiling point exceeds the decomposition temperature of a compound.

## I. Introduction

Membrane filtration can be a very efficient and economical way of separating components that are suspended or dissolved in a liquid. The membrane is a physical barrier that allows certain compounds to pass through, depending on their physical and/or chemical properties. Membranes commonly consist of a porous support layer with a thin dense layer on top that forms the actual membrane. Types of Membrane filtration based on membrane pore sizes are described below;

### 1.1 Types of Membrane Processes

### Ultrafiltration

Ultrafiltration (UF) is the process of separating extremely small particles and dissolved molecules from fluids. The primary basis for separation is molecular size, although in all filtration applications, the permeability of a filter medium can be affected by the chemical, molecular or electrostatic properties of the sample. Ultra filtration can only separate molecules which differ by at least an order of magnitude in size. Molecules of similar size can not be separated by ultra filtration.Materials ranging in size from 1K to 1000K molecular weight (MW) are retained by certain ultrafiltration membranes, while salts and water will pass through. Colloidal and particulate matter can also be retained. Ultrafiltration membranes can be used both to purify material passing through the filter and also to collect material retained by the filter. Materials significantly smaller than the pore size rating pass through the filter and can be depyrogenated, clarified and separated from high molecular weight contaminants. Materials larger than the pore size rating are retained by the filter and can be concentrated or separated from low molecular weight contaminants. Ultrafiltration is typically used to separate proteins from buffer components for buffer exchange, desalting, or concentration. Ultrafilters are also ideal for removal or exchange of sugars, non-aqueous solvents, the separation of free from proteinbound ligands, the removal of materials of low molecular weight, or the rapid change of ionic and/or pH environment (see Figure 1.1). Depending on the protein to be retained, the most frequently used membranes have a nominal molecular weight limit (NMWL) of 3 kDa to 100 kDa. Ultrafiltration is far gentler to solutes than processes such as

precipitation. UF is more efficient because it can simultaneously concentrate and desalt solutes. It does not require a phase change, which often denatures labile species, and UF can be performed either at room temperature or in a cold room.

### Microfiltration

Micro filtration (MF) is the process of removing particles or biological entities in the 0.025 µm to 10.0µm range from fluids by passage through a microporous medium such as a membrane filter. Although micron-sized particles can be removed by use of nonmembrane or depth materials such as those found in fibrous media, only a membrane filter having a precisely defined pore size can ensure quantitative retention. Membrane filters can be used for final filtration or prefiltration, whereas a depth filter is generally used in clarifying applications where quantitative retention is not required or as a prefilter to prolong the life of a downstream membrane. Membrane and depth filters offer certain advantages and limitations. They can complement each other when used together in a microfiltration process system or fabricated device. The retention boundary defined by a membrane filter can also be used as an analytical tool to validate the integrity and efficiency of a system. For example, in addition to clarifying or sterilizing filtration, fluids containing bacteria can be filtered to trap the microorganisms on the membrane surface for subsequent culture and analysis. Microfiltration can also be used in sample preparation to remove intact cells and some cell debris from the lysate. Membrane pore size cut-offs used for these types of separation are typically in the range of 0.05 µm to 1.0 μm.

### **Reverse Osmosis**

Reverse osmosis (RO) separates salts and small molecules from low molecular weight solutes (typically less than 100 daltons) at relatively high pressures using membranes with NMWLs of 1 kDa or lower. RO membranes are normally rated by their retention of sodium chloride while ultrafiltration membranes are characterized according to the molecular weight of retained solutes. Millipore water purification systems employ both reverse osmosis membranes as well as ultrafiltration membranes. Reverse osmosis systems are primarily used to purify tap water to purities that exceed distilled water quality. Ultrafiltration systems ensure that ultrapure water is free from endotoxins as well as nucleases for critical biological research.



Figure 1.1: Types of Membrane filtration processes based on membrane pore sizes.

# WHAT IS A MEMBRANE?



HOW SEPARATION OCCURS

# Difference in permeabilities through a membrane:

- Difference in size,
- Affinity to the membrane,
- Charge, etc.

# **DRIVING FORCES**

- Pressure difference,
- Concentration difference,
- Voltage difference, etc.

# TYPES OF PROCESSES

Classification according to pore size

- Microfiltration
- Ultrafiltration
- Nanofiltration
- Reverse Osmosis

# **REVERSE OSMOSIS**



- only remove some suspended materials larger than 1 micron
- the process eliminates the dissolved solids, bacteria, viruses and other germs contained in the water
- only water molecules allowed to pass via very big pressure
- assymmetric type membranes

- extensive applications:
  - potable water from sea or brackish water
  - ultrapure water for food processing and electronic industries

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Process	Membrane Type and Pore Radius	Membrane Material	Process Diving Force	Applications
Microfiltration	Symmetric microporous, 0.1-10 microns	Cellulose nitrate or acetate, Polyvinylidene difluoride (PVDF), Polyamides, Polysulfone, PTFE, Metal Oxides etc.	Hydro- static pressure difference at approx. 10-500 kPa	Sterile filtration, Clarification
Ultrafiltration	Asymmetric microporous, 1-10 nm	Polysulfone, Polypropylene, Nylon 6, PTFE, PVC, Acrylic Copolymer	Hydrostatic pressure difference at approx. 0.1-1.0 Mpa	Separation of macromolecular solutions
Reverse Osmosis	Asymmetric skin-type, 0.5-1.5 nm	Polymers, Cellulosic acetate, Aromatic Polyamide	Hydrostatic pressure difference at approx. 2-10 Mpa	Separation of salts and microsolutes from solutions
Nanofiltration	Thin-film membranes	Cellulosic Acetate and Aromatic Polyamide	9.3-15.9 bar	Removal of hardness and desalting









# Absorption

**Gas absorption:** It is a mass transfer operation in which one or more gas solutes is removed by dissolution in a liquid. The inert gas in the gas mixture is called "carrier gas". In the absorption process of ammonia from air-ammonia mixture by water, air is carrier gas, ammonia is "solute" and water is absorbent. An intimate contact between solute gas and absorbent liquid is achieved in a suitable absorption equipment, namely, tray tower, packed column, spray tower, venture scrubber, etc. Desorption or stripping operation is the reverse of absorption.

Absorption operation is of two types;

- physical
- and chemical.

## Solute+Carrier gas Solut absorbent+Carrier gas

Solute absorbed in

For the determination of driving force in any mass transfer operation, the solubility of a species in a solvent, i.e., equilibrium distribution between phases is important. With the increase in temperature, solubility of a gas in liquid decreases. Hence, absorption is done at lower temperature. On the contrary, desorption is done at higher temperature.

# Selection of solvent for absorption and stripping

Few criteria for the selection of an absorbent are as follows:

(A) Gas Solubility: High solubility of a gas in the solvent is preferred, utilizing low quantity of solvent. Absorbent should not dissolve carrier gas. Similar chemical nature of solute and absorbent (solvent) gives a good solubility. If chemical reaction takes place between solute and solvent, rate of absorption is extremely high. But the reaction should be reversible to recover solvent during desorption.

(B) Volatility: Low volatility or low vapor pressure of the solvent enhances the adsorption operation as solvent loss with carrier gas is very small. Sometimes, a second less volatile solvent is used to recover the first solvent.

(C) Viscosity: For better absorption, a solvent of low viscosity is required. In mechanically agitated absorber, greater amount of power is required for high viscous solvent and flooding is also caused at lower liquid and gas flow rates.

(D) Corrosiveness: Non-corrosive or less corrosive solvent reduces equipment construction cost as well as maintenance cost.

(E) Cost: The solvent should be cheap so that losses will be insignificant and should be easily available.

(F) Toxicity and Hazard: The solvent should be non-toxic, non-flammable, non-hazardous and should be chemically stable.

Two common gas absorption equipments are packed tower and plate tower. The gas and the liquid phases come in contact in several discrete stages. Thus, a stage wise contact is there in a plate column. But in packed tower, the upflowing gas remains in contact with down-flowing liquid throughout the packing, at every point of the tower. Therefore, packed tower is known as "continuous differential contact equipment



Figure 5.1-2 Equipment for absorption and stripping.

# **Packing Materials:**

Packing materials are utilized to provide large interfacial area of contact between two phases. These are made from either of ceramics, metals or plastics. A number of packing materials with various size, shape and performance are available. These are classified into three types, namely, dumped or random, structured and grid.







(a) Raschig rings;

(b) Lessing rings and modified Raschig rings (Cross-partition rings) (c) Berl saddle

Figure 4.1: First generation dumped or random packing materials





(a) Intalox saddle and modification(b) Pall ring and modificationFigure 4.2: Second generation dumped or random packing materials.

# The packing materials have following characteristics:

- (a) Cost: The cost of the packing materials should be very low.
- (b) Surface area: A large interfacial area of contact is always recommended. In that case, pressure drop will be more.
- (c) Void volume: A high void volume is needed to maintain low pressure drop.
- (d) Fouling resistance: Packing materials should not trap suspended solids present in liquid. Bigger packing materials generally give low fouling resistance.
- (e) Mechanical strength: Good mechanical strength is desired for choosing packing materials as this will not break or deform during filling or operation.
- (f) Uniform flow of streams: Stack of packing materials should have uniform void spaces through which both the streams (gas and liquid) can flow uniformly. Non-uniform flow of streams leads to stagnant liquid pool which in turn gives low mass transfer



### SCHOOL OF BIO&CHEMICAL ENGINEERING

### DEPARTMENT OF CHEMICAL ENGINEERING

**UNIT – II-Mass transfer for Biological Systems-SCH1313** 

### **PRINCILPES OF UNSTEADY -STATE AND CONVECTIVE MASS TRANSFER**

### 1. Introduction

Our discussion of mass transfer in the previous chapter was limited to molecular diffusion, which is a process resulting from a concentration gradient. In system involving liquids or gases, however, it is very difficult to eliminate convection from the overall mass-transfer process.

Mass transfer by convection involves the transport of material between a boundary surface (such as solid or liquid surface) and a moving fluid or between two relatively immiscible, moving fluids.

There are two different cases of convective mass transfer:

- 1. Mass transfer takes place only in a single phase either to or from a phase boundary, as in sublimation of naphthalene (solid form) into the moving air.
- 2. Mass transfer takes place in the two contacting phases as in extraction and absorption.

### **1.1 Convective Mass Transfer Coefficient**

In the study of convective heat transfer, the heat flux is connected to heat transfer coefficient as

$$Q/A = q = h(t_s - t_m)$$
 ------(1.1)

The analogous situation in mass transfer is handled by an equation of the form

$$N_A = k_c (C_{As} - C_A)$$
 ------(1.2)

The molar flux N<sub>A</sub> is measured relative to a set of axes fixed in space. The driving force is the difference between the concentration at the phase boundary,  $C_{AS}$  (a solid surface or a fluid interface) and the concentration at some arbitrarily defined point in the fluid medium,  $C_A$ . The convective mass transfer coefficient  $k_c$  is a function of geometry of the system and the velocity and properties of the fluid similar to the heat transfer coefficient, h.

#### **1.2 Significant Parameters in Convective Mass Transfer**

Dimensionless parameters are often used to correlate convective transfer data. In momentum transfer Reynolds number and friction factor play a major role. In the correlation of convective heat transfer data, Prandtl and Nusselt numbers are important. Some of the same parameters, along with some newly defined dimensionless numbers, will be useful in the correlation of convective mass-transfer data.

The molecular diffusivities of the three transport process (momentum, heat and mass) have been defined as:

Momentum diffusivity 
$$v = \frac{\mu}{\rho}$$
 ------(1.3)  
Thermal diffusivity  $\alpha = \frac{k}{\rho C_p}$  ------(1.4)

and

It can be shown that each of the diffusivities has the dimensions of  $L^2/t$ , hence, a ratio of any of the two of these must be dimensionless.

The ratio of the molecular diffusivity of momentum to the molecular diffusivity of heat (thermal diffusivity) is designated as the Prandtl Number

The analogous number in mass transfer is Schmidt number given as

The ratio of the molecular diffusivity of heat to the molecular diffusivity of mass is designated the Lewis Number, and is given by

$$\frac{\text{Thermal diffusivity}}{\text{Mass diffusivity}} = Le = \frac{\alpha}{D_{AB}} = \frac{k}{\rho C_p D_{AB}} - \dots$$
(1.8)

Lewis number is encountered in processes involving simultaneous convective transfer of mass and energy.

Let us consider the mass transfer of solute A from a solid to a fluid flowing past the surface of the solid. The concentration and velocity profile is depicted .For such a case, the mass transfer between the solid surface and the fluid may be written as

$$N_{A} = k_{c} (C_{As} - C_{A\infty})$$
 ------(1a)

Since the mass transfer at the surface is by molecular diffusion, the mass transfer may also described by

$$N_A = -D_{AB} \left. \frac{dC_A}{dy} \right|_{y=0}$$
 ------(1.9)

When the boundary concentration,  $C_{As}$  is constant, equation (9) may be written as

Equation (4.1a) and (4.10) may be equated, since they define the same flux of component A leaving the surface and entering the fluid

$$k_{c}(C_{As} - C_{A\infty}) = -D_{AB} \frac{d}{dy}(C_{A} - C_{As})\Big|_{y=0}$$
 -------(1.11)

This relation may be rearranged into the following form:

Multiplying both sides of equation(4.12) by a characteristic length, L we obtain the following dimensionless expression:

The right hand side of equation (4.13) is the ratio of the concentration gradient at the surface to an overall or reference concentration gradient; accordingly, it may be considered as the ratio of molecular mass-transport resistance to the convective mass-transport resistance of the fluid. This ratio is generally known as the Sherwood number, Sh and analogous to the Nusselt number Nu, in heat transfer.

### **1.3 Application of Dimensionless Analysis to Mass Transfer**

One of the method of obtaining equations for predicting mass-transfer coefficients is the use of dimensionless analysis. Dimensional analysis predicts the various dimensionless parameters which are helpful in correlating experimental data.

There are two important mass transfer processes, which we shall consider, the transfer of mass into a steam flowing under forced convection and the transfer of mass into a phase which is moving as the result of natural convection associated with density gradients.

### 1.4 Transfer into a stream flowing under forced convection

Consider the transfer of mass from the walls of a circular conduit to a fluid flowing through the conduit. The mass transfer is due to the concentration driving force  $C_{As} - C_A$ .

These variables include terms descriptive of the system geometry, the flow and fluid properties and the quantity of importance,  $k_{c}$ .

By the Buckingham method of grouping the variables, the number of dimensionless  $\pi$  groups is equal to the number of variables minus the number of fundamental dimensions. Hence the number of dimensionless group for this problem will be three.

With D  $_{\text{AB},}\,\rho$  and D as the core variables, the three  $\pi$  groups to be formed are

$$\pi_{1} = D_{AB}^{a} \rho^{b} D^{c} k_{c} \qquad (1.14)$$
$$\pi_{2} = D_{AB}^{d} \rho^{e} D^{f} \mathcal{G} \qquad (1.15)$$

and  $\pi_3 = D_{AB}^{\ g} \rho^h D^i \mu$  ------(1.16)

Substituting the dimensions for  $\pi$  ,

$$\pi_{1} = D_{AB}^{\ a} \rho^{\ b} D^{\ c} k_{c} - \dots$$
(1.17)  
$$1 = \left(\frac{L^{2}}{t}\right)^{a} \left(\frac{M}{L^{3}}\right)^{b} (L)^{c} \left(\frac{L}{t}\right) - \dots$$
(1.18)

Equating the exponents of the fundamental dimensions on both sides of the equation, we have

L: 
$$0 = 2a - 3b + c + 1$$

- t: 0=-a-1
- M : 0 = b

Solving these equations,

a = -1, b = 0 and c = 1

Thus 
$$\pi_1 = \frac{k_c D}{D_{AB}}$$
 which is the Sherwood number.

The other two  $\pi$  groups could be determined in the same manner, yielding

and  $\pi_3 = \frac{\mu}{\rho D_{AB}} = S_c$  ------(1.20)

which is termed as Schmidt Number

Dividing  $\pi_2$  by  $\pi_3$ , we get

which is the Reynolds Number

The result of the dimensional analysis of mass transfer by forced convection in a circular conduit indicates that a correlating relation could be of the form,

 $Sh = \psi$  (Re, Sc) ------(1.22)

Which is analogous to the heat transfer correlation

 $Nu = \psi$  (Re, Pr) -------(1.23)

### 1.5 Transfer into a phase whose motion is due to Natural Convection

Natural convection currents develop if there exists any variation in density within the fluid phase. The density variation may be due to temperature differences or to relatively large concentration differences.

In the case of natural convection involving mass transfer from a vertical plane wall to an adjacent fluid, the variables of importance are listed in the table (4.2)

### Table (4.2)

According to Buckingham theorem, there will be three dimensionless groups. Choosing D<sub>AB</sub>, L and  $\mu$  as the core variables, the  $\pi$  groups to be formed are

$$\pi_{1} = D_{AB}^{\ a} L^{b} \mu^{c} k_{c} - (4.24)$$

$$\pi_{2} = D_{AB}^{\ d} L^{e} \mu^{f} \rho - (4.25)$$
and
$$\pi_{3} = D_{AB}^{\ g} L^{h} \mu^{i} g \Delta \rho_{A} - (4.26)$$

Solving for the dimensionless groups, we obtain

$$\pi_1 = \frac{k_c L}{D_{AB}} = Nu$$
, the Nusselt number -------(4.27)

$$\pi_2 = \frac{\rho D_{AB}}{\mu} = \frac{1}{Sc}$$
, the reciprocal of Schmidt number ------ (4.28)

and 
$$\pi_3 = \frac{L^3 g \Delta \rho_A}{\mu D_{AB}}$$
 ------(4.29)

With the multiplication of  $\pi_2$  and  $\pi_3$ , we obtain a dimensionless parameter analogous to the Grashof number in heat transfer by natural convection

$$\pi_{2} \pi_{3} = \left(\frac{\rho D_{AB}}{\mu}\right) \left(\frac{L^{3} g \Delta \rho_{A}}{\mu D_{AB}}\right)$$
$$= \frac{L^{3} \rho g \Delta \rho_{A}}{\mu^{2}} = Gr_{AB} - \dots (4.30)$$

The result of the dimensional analysis of mass transfer by natural convection indicates that a correlating relation could be of the form,

$$Sh = \psi \left( Gr_{AB}, Sc \right)$$
 ------(4.31)

### 1.6 Analysis among Mass, Heat and Momentum Transfer

Analogies among mass, heat and momentum transfer have their origin either in the mathematical description of the effects or in the physical parameters used for quantitative description.

To explore those analogies, it could be understood that the diffusion of mass and conduction of heat obey very similar equations. In particular, diffusion in one dimension is described by the Fick's Law as

$$J_A = -D_{AB} \frac{dC_A}{dz} \qquad (4.32)$$

Similarly, heat conduction is described by Fourier's law as

$$q = -k \frac{dT}{dz}$$
 (4.33)

Where k is the thermal conductivity.

The similar equation describing momentum transfer as given by Newton's law is

$$\tau = -\mu \frac{dv}{dz} - \dots + (4.34)$$

Where  $\tau$  is the momentum flux (or shear stress) and  $\mu$  is the viscosity of fluid.

At this point it has become conventional to draw an analogy among mass, heat and momentum transfer. Each process uses a simple law combined with a mass or energy or momentum balance.

In this section, we shall consider several analogies among transfer phenomenon which has been proposed because of the similarity in their mechanisms. The analogies are useful in understanding the transfer phenomena and as a satisfactory means for predicting behaviour of systems for which limited quantitative data are available.

The similarity among the transfer phenomena and accordingly the existence of the analogies require that the following five conditions exist within the system

- 1. The physical properties are constant
- 2. There is no mass or energy produced within the system. This implies that there is no chemical reaction within the system
- 3. There is no emission or absorption of radiant energy.
- 4. There is no viscous dissipation of energy.
- 5. The velocity profile is not affected by the mass transfer. This implies there should be a low rate of mass transfer.

### 1.6.1 Reynolds Analogy

The first recognition of the analogous behaviour of mass, heat and momentum transfer was reported by Osborne Reynolds in 1874. Although his analogy is limited in application, it served as the base for seeking better analogies.

Reynolds postulated that the mechanisms for transfer of momentum, energy and mass are identical. Accordingly,

$$\frac{k_c}{v_{\infty}} = \frac{h}{\rho \, v_{\infty} \, C_p} = \frac{f}{2}$$
 (4.35)

Here h is heat transfer coefficient

f is friction factor

 $\nu_{\,\infty}$  is velocity of free stream

The Reynolds analogy is interesting because it suggests a very simple relation between different transport phenomena. This relation is found to be accurate when Prandtl and Schmidt numbers are equal to one. This is applicable for mass transfer by means of turbulent eddies in gases. In this situation, we can estimate mass transfer coefficients from heat transfer coefficients or from friction factors.

### 1.6.2 Chilton – Colburn Analogy

Because the Reynold's analogy was practically useful, many authors tried to extend it to liquids. Chilton and Colburn, using experimental data, sought modifications to the Reynold's analogy that would not have the restrictions that Prandtl and Schmidt numbers must be equal to one. They defined for the j factor for mass transfer as

$$j_D = \frac{k_c}{v_\infty} (Sc)^{2/3}$$
 ------ (4.36)

The analogous j factor for heat transfer is

$$j_H = St Pr^{2/3}$$
 ------(4.37)

where St is Stanton number = 
$$\frac{Nu}{\text{Re Pr}} = \frac{h}{\rho \vartheta_{\infty} C_{p}}$$

Based on data collected in both laminar and turbulent flow regimes, they found

$$j_D = j_H = \frac{f}{2}$$
 ------ (4.38)

This analogy is valid for gases and liquids within the range of 0.6 < Sc < 2500 and 0.6 < Pr < 100.

The Chilton-Colburn analogy has been observed to hold for many different geometries for example, flow over flat plates, flow in pipes, and flow around cylinders.

13. A stream of air at 100 kPa pressure and 300 K is flowing on the top surface of a thin flat sheet of solid naphthalene of length 0.2 m with a velocity of 20 m/sec. The other data are:

Mass diffusivity of naphthalene vapor in air = 6 \*  $10^{-6}$  m <sup>2</sup>/sec

Kinematic viscosity of air =  $1.5 * 10^{-5} \text{ m}^2.\text{sc}$ 

Concentration of naphthalene at the air-solid naphthalene interface =  $1 * 10^{-5}$  kmol/m<sup>3</sup>

### Calculate:

- (a) the overage mass transfer coefficient over the flat plate
- (b) the rate of loss of naphthalene from the surface per unit width

Note: For heat transfer over a flat plate, convective heat transfer coefficient for laminar flow can be calculated by the equation.

$$Nu = 0.664 \text{ Re}_L^{1/2} \text{ Pr}^{1/3}$$

you may use analogy between mass and heat transfer.

### Solution:

Given: Correlation for heat transfer

$$Nu = 0.664 \text{ Re}_L^{1/2} \text{ Pr}^{1/3}$$

The analogous relation for mass transfer is

$$Sh = 0.664 \operatorname{Re}_{L}^{1/2} Sc^{1/3}$$
 -----(1)

where

Sh = Sherwood number =  $kL/D_{AB}$ Re L = Reynolds number =  $Lv\rho/\mu$ Sc = Schmidt number =  $\mu / (\rho D_{AB})$ k = overall mass transfer coefficient L = length of sheet D<sub>AB</sub> = diffusivity of A in B v = velocity of air  $\mu$  = viscosity of air  $\rho$  = density of air, and  $\mu/\rho$  = kinematic viscosity of air.

Substituting for the known quantities in equation (1)

$$\frac{k(0.2)}{6*10^{-6}} = 0.664 \left(\frac{(0.2)(20)}{1.5*10^{-5}}\right)^{1/2} \left(\frac{1.5*10^{-5}}{6*10^{-6}}\right)^{1/3}$$
  
k = 0.014 m/sec

Rate of loss of naphthalene = k ( $C_{Ai} - C_{A\infty}$ )

 $= 0.014 (1 * 10^{-5} - 0) = 1.4024 * 10^{-7} \text{ kmol/m}^2 \text{ sec}$ 

Rate of loss per meter width =  $(1.4024 * 10^{-7}) (0.2) = 2.8048 * 10^{-8} \text{ kmol/m.sec}$ 

= 0.101 gmol/m.hr.

**1.7Convective Mass Transfer Correlations**
Extensive data have been obtained for the transfer of mass between a moving fluid and certain shapes, such as flat plates, spheres and cylinders. The techniques include sublimation of a solid, vapourization of a liquid into a moving stream of air and the dissolution of a solid into water.

These data have been correlated in terms of dimensionless parameters and the equations obtained are used to estimate the mass transfer coefficients in other moving fluids and geometrically similar surfaces.

#### 1.7.1 Flat Plate

From the experimental measurements of rate of evaporation from a liquid surface or from the sublimation rate of a volatile solid surface into a controlled air-stream, several correlations are available. These correlation have been found to satisfy the equations obtained by theoretical analysis on boundary layers,

$$Sh = 0.036 \text{ Re}_{L}^{0.8} Sc^{1/3} (\text{turbulent}) \text{ Re}_{L} > 3 * 10^{5} \dots (4.40)$$

Using the definition of j factor for mass transfer on equation (4.39) and (4.40) we obtain

$$j_D = 0.664 \text{ Re}_L^{-1/2} (\text{laminar}) \text{ Re}_L < 3*10^5$$
 -------(4.41)

$$J_D = 0.037 \text{ Re}_L^{-0.2} (\text{turbulent}) \text{ Re}_L > 3 \times 10^5 \dots$$
 (4.42)

These equations may be used if the Schmidt number in the range 0.6 < Sc < 2500.

7. If the local Nusselt number for the laminar boundary layer that is formed over a flat plate is

$$Nu_x = 0.332 \text{ Re}_x^{1/2} \text{ Sc}^{1/3}$$

Obtain an expression for the average film-transfer coefficient  $\bar{k}_c$ , when the Reynolds number for the plate is

a) Re<sub>L</sub> = 100 000

The transition from laminar to turbulent flow occurs at Re  $_x$  = 3 \* 10<sup>5</sup>.

Derivation:

By definition : 
$$\overline{k}_{c} = \frac{\int_{0}^{L} k_{c} dx}{\int_{0}^{L} dx}$$
  
and  $Nu_{x} = \frac{k_{c} x}{D_{AB}}$ ;  $Re_{x} = \frac{x v \rho}{\mu}$ ;  $Sc = \frac{\mu}{\rho D_{AB}}$ ;

For Re  $_{L}$  = 100 000 ; (which is less than the Reynolds number corresponding to Transition value of 3 \* 10 <sup>5</sup>)

$$\overline{k}_{c} = \frac{\int_{0}^{L} 0.332 \left(\frac{x \, v \, \rho}{\mu}\right)^{\frac{1}{2}} (Sc)^{\frac{1}{3}} \frac{D_{AB}}{x} dx}{L}$$
$$= \frac{0.332 (Sc)^{\frac{1}{3}} \left(\frac{v \, \rho}{\mu}\right)^{\frac{1}{2}}}{L} D_{AB} \int_{0}^{L} \frac{d \, x}{x^{\frac{1}{2}}}$$
$$= \frac{0.332}{\frac{1}{2}L} Sc^{\frac{1}{3}} \left(\frac{v \, \rho}{\mu}\right)^{\frac{1}{2}} D_{AB} \left[x^{\frac{1}{2}}\right]_{0}^{L}$$
(i.e.)  $\frac{\overline{k}_{c} L}{D_{AB}} = 0.664 \operatorname{Re}_{L}^{\frac{1}{2}} Sc^{\frac{1}{3}}$  [answer (a)]

For Re  $_{L}$  = 1500 000 (> 3 \* 10<sup>5</sup>)

$$\overline{k}_{c} = D_{AB} \frac{\begin{pmatrix} L_{t} \\ \int 0.332 \operatorname{Re}_{x} ^{1/2} \operatorname{Sc}^{1/3} \frac{d x}{x} + \int_{L_{t}}^{L} 0.0292 \operatorname{Re}_{x} ^{4/5} \operatorname{Sc}^{1/3} \frac{d x}{x} \end{pmatrix}}{I} \text{ where } L_{t} \text{ is}$$

the

distance from the leading edge of the plane to the transition point where Re  $_x$  = 3 \* 10<sup>5</sup>.

$$\overline{k}_{c} = D_{AB} \frac{\left(0.332 \,\text{Sc}^{1/3} \left(\frac{v \,\rho}{\mu}\right)^{1/2} \int_{0}^{L_{t}} \frac{d \,x}{x^{1/2}} + 0.0292 \,\text{Sc}^{1/3} \left(\frac{v \,\rho}{\mu}\right)^{4/5} \int_{L_{t}}^{L} \frac{d \,x}{x^{1/5}}\right)}{L} \frac{\overline{k}_{c} \,L}{D_{AB}} = 0.664 \,\text{Re}_{t}^{1/2} \,\text{Sx}^{1/3} + \frac{0.0292}{4/5} \,\text{Sc}^{1/3} \left[x^{4/5}\right]_{L_{t}}^{L} \left(\frac{V \,\rho}{\mu}\right)^{4/5} = 0.664 \,\text{Re}_{t}^{1/2} \,\text{Sc}^{1/3} + 0.0365 \,\text{Sc}^{1/3} \left(\text{Re}_{L}^{4/5} - \text{Re}_{t}^{4/5}\right)$$
$$\frac{\overline{k}_{c} \,L}{D_{AB}} = 0.664 \,\text{Re}_{t}^{1/2} \,\text{Sc}^{1/3} + 0.0365 \,\text{Re}_{L}^{4/5} \,\text{Sc}^{1/3} - 0.0365 \,\text{Re}_{t}^{4/5} \,\text{Sc}^{1/3} \,\text{where } \,\text{Re}_{t} = 3 \times 10^{5}$$

#### 1.7.2 Single Sphere

Correlations for mass transfer from single spheres are represented as addition of terms representing transfer by purely molecular diffusion and transfer by forced convection, in the form

$$Sh = Sh_{o} + CRe^{m}Sc^{n}$$
 ------(4.43)

Where C, m and n are constants, the value of n is normally taken as 1/3

For very low Reynold's number, the Sherwood number should approach a value of 2. This value has been derived in earlier sections by theoretical consideration of molecular diffusion from a sphere into a large volume of stagnant fluid. Therefore the generalized equation becomes

$$Sh = 2 + CRe^{m} Sc^{1/3}$$
 ------(4.44)

For mass transfer into liquid streams, the equation given by Brain and Hales

$$Sh = \left(4 + 1.21 \ Pe_{AB}^{2/3}\right)^{1/2}$$
 ------ (4.45)

correlates the data that are obtained when the mass transfer Peclet number, Pe <sub>AB</sub> is less than 10,000. This Peclet number is equal to the product of Reynolds and Schmidt numbers (i.e.)

 $Pe_{AB} = Re Sc$  ------(4.46)

For Peclet numbers greater than 10,000, the relation given by Levich is useful

$$Sh = 1.01 Pe_{AB}^{1/3}$$
 ------ (4.47)

The relation given by Froessling

correlates the data for mass transfer into gases for at Reynold's numbers ranging from 2 to 800 and Schmidt number ranging 0.6 to 2.7.

For natural convection mass transfer the relation given by Schutz

$$Sh = 2 + 0.59 (Gr_{AB} Sc)^{1/4}$$
 ------ (4.49)

is useful over the range

 $2 * 10^{8} < Gr_{AB} Sc < 1.5 * 10^{10}$ 

6. The mass flux from a 5 cm diameter naphthalene ball placed in stagnant air at 40°C and atmospheric pressure, is  $1.47 \times 10^{-3}$  mol/m<sup>2</sup>. sec. Assume the vapor pressure of naphthalene to be 0.15 atm at 40°C and negligible bulk concentration of naphthalene in air. If air starts blowing across the surface of naphthalene ball at 3 m/s by what factor will the mass transfer rate increase, all other conditions remaining the same?

For spheres :

Where Sh is the Sherwood number and Sc is the Schmids number. The viscosity and density of air are  $1.8 \times 10^{-5}$  kg/m.s and 1.123 kg/m<sup>3</sup>, respectively and the gas constant is 82.06 cm<sup>3</sup>. atm/mol.K.

#### **Calculations:**

$$Sh = \frac{k_c L}{D_{AB}}$$
 where L is the characteristic dimension for sphere L = Diameter.

$$Sc = \frac{\mu}{\rho D_{AB}}$$
$$R_c = \frac{D v \rho}{\mu}$$

Mass flux,  $N_A = K_c \Delta c$  -----(1)

$$Sh = 2.0 + 0.6 (Re)^{0.5} (Sc)^{0.33}$$

$$\frac{k_c D}{D_{AB}} = 2.0 + 0.6 \left(\frac{D V \rho}{\rho}\right)^{0.5} \left(\frac{\mu}{\rho D_{AB}}\right)^{0.33}$$
 ------(2)

also N = K<sub>G</sub>  $\Delta p_A$ 

Therefore  $\frac{k_c}{RT} = K_G$ 

Given:

$$N = 1.47 * 10^{-3} \frac{mol}{m^2. sec} = \frac{K_c}{RT} \Delta p_A$$

$$\frac{k_c}{RT} \left( \frac{0.15}{1} - 0 \right) = 1.47 * 10^{-3} * 10^{-4} \frac{mol}{cm^2 \cdot sec}$$

$$k_c = \frac{1.47 * 10^{-7}}{0.15} * 82.06 * (273 + 40)$$

$$= 0.0252 \text{ cm/sec}$$

$$k_c = 2.517 * 10^{-4} \text{ m/sec} -----(3)$$

Estimation of D<sub>AB</sub>:

From (2),

$$\frac{2.517 * 10^{-4} * 5 * 10^{-2}}{D_{AB}} = 2 \text{ (since v = 0)}$$

Therefore  $D_{AB}$  = 6.2925 \* 10<sup>-6</sup> m<sup>2</sup>/sec.

And

$$\frac{k_{c} * 5 * 10^{-2}}{6.2925 * 10^{-6}} = 2 + 0.6 \left(\frac{5 * 10^{-2} * 3 * 1.123}{1.8 * 10^{-5}}\right)^{0.5} \left(\frac{1.8 * 10^{-5}}{1.123 * 6.2925 * 10^{-6}}\right)^{0.33}$$

$$7946 k_{c} = 2 + 0.6 * (96.74) * (1.361)$$

k<sub>c</sub> = 0.0102 m/sec. ----- (4)

$$\frac{(4)}{(3)} \Rightarrow \frac{N_{A2}}{N_{A1}} = \frac{0.0102}{2.517 * 10^{-4}} = 40.5$$

Therefore, rate of mass transfer increases by 40.5 times the initial conditions.

#### 1.7.3 Single Cylinder

Several investigators have studied the rate of sublimation from a solid cylinder into air flowing normal to its axis. Bedingfield and Drew correlated the available data in the form

$$\frac{k_G P Sc^{0.56}}{G_m} = 0.281 \left( \text{Re}^{\,\prime} \right)^{-0.4} - \dots + (4.50)$$

which is valid for  $400 < \text{Re}^{/} < 25000$ 

and 0.6 < Sc < 2.6

Where Re<sup>7</sup> is the Reynold's number in terms of the diameter of the cylinder, G<sub>m</sub> is the molar mass velocity of gas and P is the pressure.

#### 1.7.4 Flow Through Pipes

Mass transfer from the inner wall of a tube to a moving fluid has been studied extensively. Gilliland and Sherwood, based on the study of rate of vapourization of nine different liquids into air given the correlation

$$Sh \frac{p_{B,Im}}{P} = 0.023 \text{ Re}^{0.83} Sc^{0.44}$$
 -------(4.51)

Where  $p_{B, Im}$  is the log mean composition of the carrier gas, evaluated between the surface and bulk stream composition. P is the total pressure. This expression has been found to be valid over the range

2000 < Re < 35000 0.6 < Sc < 2.5

Linton and Sherwood modified the above relation making it suitable for large ranges of Schmidt number. Their relation is given as

$$Sh = 0.023 \text{ Re}^{0.83} Sc^{1/3}$$
 ------(4.52)

and found to be valid for

2000 < Re < 70000

and 1000 < Sc < 2260

8. A solid disc of benzoic acid 3 cm in diameter is spin at 20 rpm and 25 °C. Calculate the rate of dissolution in a large volume of water. Diffusivity of benzoic acid in water is  $1.0 \times 10^{-5}$  cm<sup>2</sup>/sec, and solubility is 0.003 g/cc. The following mass transfer correlation is applicable:

Sh = 0.62 Re 
$$\frac{1}{2}$$
 Sc  $\frac{1}{3}$ 

Where  $Re = \frac{D^2 \omega \rho}{\mu}$  and  $\omega$  is the angular speed in radians/time.

#### **Calculations:**

Where  $N_A$  = mass flux, and

S = surface area for mass transfer

 $N_{A} = k_{c} (C_{As} - C_{A\infty})$  ------(2)

Where  $C_{As}$  is the concentration of benzoic and at in water at the surface of the dose.

 $C_{\mbox{\scriptsize A}\infty}$  is the concentration benzoic acid in wate for an from the surface of the disc.

Given:

Sh = 0.62 Re 
$$\frac{1}{2}$$
 Sc  $\frac{1}{3}$ 

(i.e.) 
$$\frac{k_c D}{D_{AB}} = 0.62 \left(\frac{D^2 \omega \rho}{\mu}\right)^{\frac{1}{2}} \left(\frac{\mu}{\rho D_{AB}}\right)^{\frac{1}{3}}$$
------(3)

1 rotation = 2  $\pi$  radian

Therefore 20 rotation per minute = 20 \* 2  $\pi$  radian/min

$$=\frac{20}{60}$$
 \* 2  $\pi$  radian/sec

For water  $\rho = 1 \text{ g/cm}^3 \mu = 1 \text{ centipoise} = 0.01 \text{ g/cm.sec.}$ 

From (3),

$$k_{c} = 0.62 \ D_{AB} \left(\frac{\omega \rho}{\mu}\right)^{\frac{1}{2}} \left(\frac{\mu}{\rho D_{AB}}\right)^{\frac{1}{3}}$$
$$= 0.62 * 1.0 * 10^{5} * \left(\frac{(40 \pi/60) * 1}{0.01}\right)^{\frac{1}{2}} \left(\frac{0.01}{1 * 1.0 * 10^{-5}}\right)^{\frac{1}{3}}$$

= 8.973 \* 10<sup>-4</sup> cm/sec.

From (2),

$$N_A = 8.973 * 10^{-4} (0.003 - 0)$$
  
= 2.692 \* 10<sup>-6</sup> g/cm<sup>2</sup>.sec

From (1),

$$N_A S = N_A * (2\pi r^2)$$
  
= 2.692 \* 10<sup>-6</sup> \* (2\pi \* 1.5<sup>2</sup>)  
= 3.805 \* 10<sup>-5</sup> g/sec  
= 0.137 g/hr.

#### **1.7.5 Mass transfer between phases:**

Instead of a fluid in contact with a solid, suppose we now consider two immiscible fluids, designated 1 and 2, in contact with each other. If fluid 1 has dissolved in it a substance A that is also soluble in fluid 2, then as soon as the two fluids are brought together, substance A will begin to diffuse into fluid 2. As long as the two phases remain in contact, the transport of A will continue until a condition of equilibrium is reached.

The situation discussed here occurs in a variety of engineering processes such as gas absorption, stripping, and in liquid – liquid extraction. In all these separation processes, two immiscible fluids are brought into contact and one or more components are transferred from one fluid phase to the other.

In the system of fluids 1 and 2 with A, the transported component, the concentration gradients in the region of the interface between the two fluids are illustrated in figure. Concentration  $C_{A1}$  and  $C_{A2}$  are the bulk phase concentrations

in fluids 1 and 2, respectively,  $C_{Ai}$  is the concentration of A at the interface, and  $N_A$  is the molar flux of A. For steady state conditions, we can define the flux of A as

$$N_{A} = k_{c1} (C_{A1} - C_{Ai}) = k_{c2} (C_{Ai} - C_{A2}) = K_{c} (C_{A1} - C_{A2})$$

where  $k_c =$  individual mass transfer coefficient defined in terms of the

concentration difference in a single phase.

K<sub>c</sub> = overall mass transfer coefficient defined in terms of the overall

difference in composition.

Equation (1) is analogous to that in heat transfer, where the individual coefficients h are related to the overall coefficient U.

From equation (1),

$$\frac{1}{k_{c_1}} + \frac{1}{k_{c_2}} = \frac{1}{K_c}$$
(2)

In equation (1), the potential for mass transfer is exposed in terms of composition. However, this is not always the most convenient way to express it. For example, if fluid 1 is a gas and fluid 2 a liquid, as in gas absorption, the potential in gas phase is often expressed in terms of partial pressures, while that in the liquid phase may be expressed in terms of concentrations. The expression for the molar flux is then written for the individual phases as:

$$N_{A} = K_{p} \left( P_{AG} - P_{Ai} \right) = K_{c} \left( C_{Ai} - C_{AL} \right)$$
(3)

where

k<sub>p</sub> = individual mass transfer coefficient for the gas phase with the

potential defined in terms of partial pressures.

P<sub>AG</sub>, C<sub>AL</sub> = partial pressure and concentration of A in the bulk gas and liquid

phases, respectively.

 $P_{Ai}$ ,  $C_{Ai}$  = partial pressure and concentration of A, respectively, at the interface.

At the interface, it is usually assumed the two phases are in equilibrium. This means that  $P_{Ai}$  and  $C_{Ai}$  are related by an equilibrium relationship such as 'Henry's law :

$$P_{Ai} = HC_{Ai} \qquad (4)$$

where H is Henry's law constant.

The flux N<sub>A</sub> can also be expressed in terms of overall mass transfer coefficients as,

$$N_{A} = K_{p} \left( P_{AG} - P_{AE} \right) = K_{c} \left( C_{AE} - C_{AL} \right)$$
(5)

where

K  $_{p}$  = overall mass transfer coefficient with the overall potential defined

in terms of partial pressures.

K c = overall mass transfer coefficient with the overall potential defined

in terms of concentrations.

 $P_{AE}$ ,  $C_{AE}$  = equilibrium composition.

 $P_{\,\text{AE}}$  is related to the bulk liquid composition C  $_{\text{AL}}$  AS

$$P_{AE} = HC_{AL} \quad (6)$$

similarly,  $C_{AE} = \frac{P_{AG}}{H}$  (7)

The relationship between the individual and overall coefficients is readily obtained through the use of equations (3) to (7) as

$$\frac{1}{K_{p}} = \frac{1}{k_{p}} + \frac{H}{k_{c}} = \frac{H}{K_{c}}$$
(8)

In many system, mass transfer resistance is mainly in one phase. For example, gases such as nitrogen and oxygen do not dissolve much in liquids. Their Henry's law constant H is very large, thus  $K_c \approx k_c$  is a good approximation. In this case, the liquid phase controls the mass transfer press since mass transfer is slowest there.

Mars Francier Coefficient: -The rate of M.T is propositional to the driving force and alas proportional to the area.

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$$W_{A} \propto A \Delta C$$

$$W_{A} = (K_{c}, A \Delta C)$$

$$M_{T} = W_{T}$$

$$M_{A} = \frac{W_{A}}{A} = K_{C} \Delta C$$

$$(x_{C}) = (x_{C})$$

$$(x_{C}) = (x_{C})$$

$$(x_{C}) = (x_{C})$$

like H-T coeff. it is also on experimental quantity and it can be calculated with the help of dimensionlins numbers.

$$\overline{\text{Tor gauge}} := Colffeesion of H Harryth Harry A Harry B
NA = CDARS CA, -(Ar
Z CBLAN
NA = Kc (CA, -(Ar))
= (CDARS (Yar - Yar)
Z Yourn
NA = Kc (CA, -(Ar))
= (CDARS (Yar - Yar)
Z Yourn
NA = Ky (Yar - Yar)
NA = Ky (Yar - Yar)
NA = Ky (Yar - Yar)
Z Yourn
NA = Kg (Dar - Par)
NA = (DAB (Car - CAR))
NA = (DAB (CAR))
NA = (DAB (CA$$

.

$$k_c = \frac{D_{AB}}{2 \times e_{EM}}$$
  
 $k_y = \frac{c_{DAB}}{2 \times e_{EM}}$   
 $k_a = D_{BB}$ 

RTZ XBLM When I calculate M.T cocff, we will not change the form Here to CRIMON PRIM

$$\frac{\text{For Liquido:}-}{\text{NA} = \frac{C_{AV} \text{ DAB}}{2} \frac{(K_{A_1} - X_{A_2})}{N_{GLM}} \xrightarrow{3} K_{M} = \frac{G_{AV} \text{ DAB}}{2} \frac{(K_{A_1} - X_{A_2})}{N_{GLM}} \xrightarrow{3} K_{M} = \frac{G_{AV} \text{ DAB}}{2} \frac{(K_{A_1} - (A_2))}{N_{BLM}} \xrightarrow{3} K_{L} \xrightarrow{2} \frac{N_{AB}}{2} \frac{N_{AB}}{$$

.

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For gooes and liquido , equimolar counter deffusion :-

$$N_{A} = \frac{C D_{AB}}{Z} \quad Ma_{1} - Ma_{2} \qquad K'y = \frac{C D_{AB}}{Z}$$

$$N_{A} = \frac{D_{AB}}{Z} \quad Ca_{1} - Ca_{2} \qquad K'z = \frac{D_{AB}}{Z}$$

$$N_{A} = \frac{D_{AB}}{ZRT} \quad (Pa_{1} - Pa_{2}) \qquad K'z = \frac{D_{AB}}{ZRT}$$

$$\frac{K'a' = \frac{K'z}{RT} \qquad K'z = \frac{D_{AB}}{ZRT}$$

$$\frac{K'a' = \frac{K'z}{RT} \qquad P$$

$$N_{A} = \frac{Cav}{Z} \frac{D_{AB}}{DA} \quad (M_{A1} - M_{A2}) \qquad K'y = \frac{Cav}{Z} \frac{D_{AB}}{Z}$$

$$\frac{Na = Cav}{Z} \frac{D_{AB}}{Z} \quad (Ca_{1} - Ca_{2}) \qquad K'z = \frac{D_{AB}}{Z}$$

$$\frac{K'y}{RT} = \frac{K'z}{Z}$$

#### 3.4.3 Correlation of mass transfer coefficients for single cylinder

Bedingfield and Drew (1950) studied the sublimation from a solid cylinder into air which is flowing normal to its axis. They developed a correlation for the mass transfer coefficient from their experimental data which can be represented as:

 $\frac{k_0 P}{G_{\mu}} = 0.281 \text{Re}^{-0.4} \text{ Sc}^{-0.56}$ (3.42)

In this case the Reynolds number is defined based on the diameter of the cylinder.  $G_m$  is the molar mass velocity of the gas and P is the total pressure. The correlation is applicable in the range of 400 < Re < 25000 and 0.6 < Sc < 2.6.

#### 3.4.4 Correlation of mass transfer coefficients in circular pipes

In a wetted wall towers as shown in Figure 3.1, the mass transfer from the thin liquid film in the tube wall from the moving fluid has been studied extensively. In the tower a volatile pure liquid flows down inside the surface of the tube wall where a gas is allowed to pass through the central core. Here the evaporation of the liquid into the moving gas stream through the gas liquid surface is referred as mass transfer from liquid to gas Gilliland and Sherwood (1934) developed the following correlation from the experimental data obtained by using different liquid and air as gas in the range of  $2.0 \times 10^3 < \text{Re} < 3.50 \times 10^3$  and 0.6 < Sc < 2.5.

Sh = 0.023 Re<sup>0.83</sup> Sc<sup>0.44</sup>

(3.43)

where the physical properties of the gas are evaluated at the bulk conditions of the moving gas. Sherwood number and Reynolds number are based on tower diameter. Linton and Sherwood (1950) studied the mass transfer by extending the Schmidt number. They developed a correlation with the extended data set and the data set of Gilliland and Sherwood which can be represented as:  $Sh = 0.023 \text{Re}^{0.33} Sc^{1/3}$  (3.44)

In the range of 0.4×10<sup>4</sup> < Re < 7.0×10<sup>4</sup> and 0.6 < Sc < 3.0×10<sup>3</sup>



Figure 3.1: Wetted-wall tower



#### SCHOOL OF BIO&CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – III – Mass Transfer for Biological Systems – SCH1313

#### **EVAPORATION**

#### Introduction

The objective of evaporation is to concentrate a solution consisting of a nonvolatile solute and a volatile solvent. Evaporation is conducted by vaporizing a portion of the solvent to produce a concentrated solution of thick liquor. Evaporation differs from drying in that the residue is a liquid, sometimes a highly viscous one rather than a solid. It differs from distillation in that the vapor usually is a single component, and even when the vapour is a mixture no attempt is made in the evaporation step to separate the vapour into fractions. It differs from crystallization in that emphasis is placed on concentrating a solution rather than forming and building crystals.



## Fig.1.(a),(b)& (c).Evaporation

Normally, in evaporation the thick liquor is the valuable product and the vapour is condensed and discarded. In one specific situation, however, the reverse is true. Mineral bearing water often is evaporated to give a solid free product for boiler feed for special process requirements or for human consumption. This technique is often called water distillation, but technically it is evaporation. Large scale evaporation processes have been developed and used for recovering potable water from seawater.

Here the condensed water is the desired product. Only fraction of the total water in the feed is recovered, and the remainder is returned to the sea.

**51.** Liquid characteristics: The practical solution of an evaporation problem is profoundly affected by the character of the liquor to be concentrated. It is the wide variation in liquor characteristics (which demands judgment and experience in designing and operating evaporators)that broadens this operation from simple heat transfer to a separate art. Some of the most important properties of evaporating liquids are as follows:

# 5.1.1. Concentration

Initially, the solution may be quite dilute and the properties of the solution may be taken as the properties of solvent. As the concentration increases, the solution becomes viscous and heat transfer resistance increases. The crystal may grow on the heating coil or on the heating surface. The boiling points of the solution also rise considerably. Solid or solute contact increases and the boiling temperature of the concentrated solution became higher than that of the solvent as the same pressure (i.e. elevation in boiling point).

## 5.1.2. Foaming

Many of the materials like organic substance may foam during vaporization. If the foam is stable, it may come out along the vapor known as entrainment. Heat transfer coefficient changes abruptly for such systems.

# 5.1.3. Degradation due to high temperature

The products of many chemical, food, pharmaceutical industries etc. are very temperature sensitive and they may get damaged during evaporation. Thus special case or technique is required for concentrating such solution.

# 5.1.4. Scaling

Many solutions have tendency to deposit the scale on the heating surface, which may increase the heat transfer resistance. These scales produce extra thermal resistance of significant value. Therefore, scaling in the equipment should not be ignored thus de-scaling becomes an important and routine matter.

# 5.1.5. Equipment material

The material of the equipment must be chosen considering the solution properties so that the solution should neither be contaminated nor react with the equipment material.

### 52 Evaporator

Equipment, in which evaporation is performed, is known as evaporator. The evaporators used in chemical process industries are heated by steam and have tubular surface. The solution is circulated in the tube and the tubes are heated by steam. In general the steam is the saturated steam and thus it condenses on the outer tube surface in order to heat the tube. The circulation of the solution in the tube has reasonable velocity in order to increase the heat transfer coefficient and removal of scales on the inner surface of the tube. The steam heated tubular evaporators may be classified as natural and forced circulation evaporators.

#### 5.2.1. Single effect and multiple effect evaporation

When a single evaporator is used, the vapour from the boiling liquid is condensed and discarded. This method is called single-effect evaporation, and although it is simple, it utilizes steam ineffectively. To evaporate 1 kg of water from a solution calls for from 1 to 1.3 kg of steam. If the vapour from one evaporator is fed into the steam chest of a second evaporator and the vapour from the second is then sent to a condenser, the operation becomes double effect. The heat in the original steam is reused in the second effect, and the evaporation achieved by a unit mass of steam fed to the first effect is approximately doubled. Additional effects can be added in the same manner. The general method of increasing the evaporation per kg of steam by using a series of evaporators between the steam supply and the condenser is called multiple effect evaporation.



Fig.5.2.Single Effect Evaporation



Fig. 5.3. Multiple effect evaporation

#### 53. Performance of steam heated tubular evaporators

The performance of a steam heated tubular evaporator is evaluated by the capacity

and the economy.

## Capacity and economy

Capacity is defined as the number of kilograms of water vaporized per hour. Economy is the number of kg of water vaporized per kg of steam fed to the unit. Steam consumption is very important to know, and can be estimated by the ratio of capacity divided by the economy. That is the steam consumption (in kg/h) is Steam Consumption = Capacity / Economy

# 5.4. Types of evaporators

The chief types of steam heated tubular evaporators are

1.Long tube vertical evaporators

(i)upward flow (climbing film)

- (ii)Downward flow(falling flow)
- (iii) Forced circulation
- 2. Agitated film evaporators

Based on method of operation evaporators can also be classified as (i)Single effect evaporators (ii)multiple effect evaporators

### 5.4.1. Once through and circulation evaporators

Evaporators may be operated either as once through or as circulation units. In once through operation the feed liquor passes through the tubes only once, releases the vapour, and leaves the unit as thick liquor. All the evaporation is accomplished in a single pass. The ratio of evaporation to feed is limited in single pass units, thus the evaporators are well adapted to multiple effect operation, where the total amount of concentration can be spread over several effects. Agitated film evaporators are always operated once through; falling film and climbing film evaporators can also be operated in this way.

Once through evaporators are especially useful for heat sensitive materials. By operating under high vacuum, the temperature of the liquid can be kept low. With a single rapid passage through the tubes the thick liquor is at the evaporation temperature but a short time and can be quickly cooled as soon as it leaves the evaporator.

In circulation evaporators a pool of liquid is held within the equipment. Incoming feed mixes with the liquid from the pool, and the mixture passes through the tubes. Unevaporated liquid discharged from the tubes returns to the pool, so that only part of the total evaporation occurs in one pass. All forced circulation evaporators are operated in this way. Climbing film evaporators are usually circulation units.

The thick liquor from a circulation evaporator is withdrawn from the pool. All the liquor in the pool must therefore be at the maximum concentration. Since the liquid entering the tubes may contain several parts of thick liquor for each part of feed, its viscosity is high and the heat transfer coefficient tends to be low.

Circulation evaporators are not well suited to concentrating heat sensitive liquids. With a reasonably good vacuum the temperature of the bulk of the liquid may be nondestructive, but the liquid is repeatedly exposed to contact with hot tubes. Some of the liquid, therefore, may be heated to an excessively high temperature. Although the average residence time of the liquid in the heating zone may be short, part of the liquid is retained in the evaporator for considerable time. Prolonged heating of even a small part of a heat sensitive material like a food can ruin the entire product.

Circulation evaporators, can operate over a wide range of concentration between feed and thick liquor in a single unit, and are well adapted to single effect evaporation. They may operate either with natural circulation , with the flow through the tubes induced by density difference, or with forced circulation with flow provided by a pump.

## 5.4.2. Climbing film long tube vertical evaporator

A typical long tube vertical evaporator with upward flow of the liquid is shown in fig.5.4. The essential parts are (i) a tubular exchanger with steam in the shell side and liquid to be concentrated in the tubes (ii) a separator or vapour space for removing entrained liquid from the vapour. When it is operated as a circulation unit a return leg for the liquid from the separator to the bottom of the exchanger is provided. Inlets are provided for feed liquid and steam, and outlets are provided for vapour, thick liquor, steam condensate, and non condensable gases from the steam. The tubular heater operates in exactly the same way as the natural circulation calandria. The tubes , however, are larger than in a calandria, they are typically 25 to 50mm in diameter and 3 to 10m long. Dilute feed enters the system and mixes with the liquid draining from the separator. Concentrated liquor is withdrawn from the bottom of the heater, the remaining liquor is partially vaporized as it rises through the tubes. The mixture of liquid and vapour from the top of the tubes flows into the separator, where its velocity is greatly reduced. To aid in eliminating liquid droplets the vapour impinges on and then passes around sets of baffle plates before leaving the separator.

Long tube vertical evaporators are especially effective in concentrating liquids that tend to foam. Foam is broken when the high velocity mixture of liquid and vapour impinges against the vapour head baffle.

## 5.4.3. Falling film long tube vertical evaporator:

Concentration of highly heat sensitive materials such as orange juice requires a minimum time of exposure to a heated surface. This can be done in once through falling film evaporators, in which the liquid enters at the top, flows downstream inside the heated tubes as a film, and leaves from the bottom. The tubes are large, 50 to 250mm in diameter. Vapour evolved from the liquid is usually carried downward with the liquid and leaves from the bottom of the unit. In appearance these evaporators

resemble long, vertical, tubular exchangers with a liquid-vapour separator at the bottom and a distributor for the liquid at the top.

The chief problem in a falling film evaporator is that of distributing the liquid uniformly as a film inside the tubes, This is done by a set of perforated metal plates above a carefully leveled tube sheet, by inserts in the tube ends to cause the liquid to flow evenly into each tube, or by spider distributors with radial arms from which the feed is sprayed at a steady rate on the inside surface of each tube. Still another way is to use an individual spray nozzle inside each tube.

When recirculation is allowable without damaging the liquid, distribution of liquid to the tubes is facilitated by a moderate recycling of liquid to the top of the tubes. This provides a larger volume of flow through the tubes than is possible in once through operation. For good heat transfer the Reynolds number of the falling film should be greater than 2000 at all the points in the tube. During evaporation, the amount of liquid is continuously reduced as it flows downward, and too great a reduction can lead to dry spots near the bottom of the tubes. Thus the amount of concentration that can be done in a single pass is limited.



Fig.5.4. Long Tube vertical evaporator



(a)

(b) Fig.5.5. Forced circulation Evaporator

#### 5.4.4. Forced circulation Evaporator

In a natural circulation evaporator the liquid enters the tubes at 0.3 to 1.2 m/s. The linear velocity increases greatly as vapour is formed in the tubes, so that in general the rates of heat transfer are satisfactory. With viscous liquids, however, the overall coefficient in a natural circulation unit may be uneconomically low. Higher coefficients are obtained in forced circulation evaporators, an example of which is shown in fig.5.5. Here a centrifugal pump forces the liquid through the tubes at an entering velocity of 2 to 5.5m/s. The tubes are under sufficient static head to ensure that there is no boiling in the tubes, the liquid becomes superheated as the static head is reduced during flow from the heater to the vapor space, and it flashes into a mixture of vapour and spray in the outlet line from the exchanger just before entering the body of the evaporator. The mixture of liquid and vapour impinges on a deflector plate in the vapor space. Liquid returns to the pump inlet, where it meets incoming feed; vapour leaves the top of the evaporator body to a condenser or to the next effect. Part of the liquid leaving the separator is continuously withdrawn as concentrate.

In the design shown in fig.5.5.(b) the exchanger has horizontal tubes and is two pass on both tube and shell sides. In others, vertical single pass exchangers are used(fig.5.5.(a)). In both types the heat transfer coefficients are high, especially with thin liquids, but the greatest improvement over natural circulation evaporators is with viscous liquids. With thin liquids the improvement with forced circulation does not warrant the added pumping costs over natural circulation, but with viscous material the added costs are justified, especially when expensive metals must be used. An example is caustic soda concentration which must be done in nickel equipment. In multiple effect evaporators producing a viscous final concentrate the first effects may be natural circulation units and the later ones handling viscous liquid, forced circulation units. Because of the high velocities in a forced circulation evaporator, the residence time of the liquid in the tubes is short about 1 to 3 s so that moderately heat sensitive liquids can be concentrated in them. They are also effective in evaporating salting liquors or those that tend to foam.

#### 5.4.5. Agitated –film evaporator

The principle resistance to overall heat transfer from the steam to the boiling liquid in an evaporator is on the liquid side. One way of reducing this resistance, especially with viscous liquids, is by mechanical agitation of the liquids film, as in the evaporator shown in fig.5.6. This is a modified falling film evaporator with a single jacketed tube containing an internal agitator. Feed enters at the top of the jacketed section and is spread out into a thin, highly turbulent film by the vertical blades of the agitator. Concentrate leaves from the bottom of the jacketed section, vapour rises from the vapourising zone into an unjacketed separator, which is somewhat larger in diameter than the evaporating tube. In the separator the agitator blades throw entrained liquid outward against stationary vertical plates. The droplets coalesce on these plates and return to the evaporating section. Liquid free vapour escapes through outlets at the top of the unit.

The chief advantage of an agitated film evaporator is its ability to give high rates of heat transfer with viscous liquids. The product may have a viscosity as high as 1000P at the evaporation temperature. As in other evaporators, the overall coefficient falls as the viscosity rises, but in this design the decrease is slow. With highly viscous materials the coefficient is appreciably greater than in forced circulation evaporators and much greater than in natural circulation units. The

agitated film evaporator is particularly effective with such viscous heat sensitive products as gelatin, rubber latex, antibiotics and fruit juices. Its disadvantage are high cost ; the internal moving parts, which may need considerable maintenance and the small capacity of single units, which is far below that of multi tubular evaporators.





## 55. Boiling point elevation

The evaporators produce concentrated solution having substantially higher boiling point than that of the solvent (of the solution) at the prevailing pressure. The increase in boiling point over that of water is known as boiling point elevation (BPE) of the solution. As the concentration increases the boiling point of the solution also increases. Therefore, in order to get the real temperature difference (or driving force) between the steam temperature and the solution temperature, the BPE must be subtracted from the temperature drop. The BPE may be predicted from the steam table (in case water is a solvent).

An empirical rule known as Dühring rule is suitable for estimating the BPE of strong solution. The Dühring rule states that the boiling point of a given solution is a linear function of the boiling point of the pure water at the same pressure. Therefore, if the boiling point of the solution is plotted against that of the water at the same pressure, a straight line results. Different lines are obtained at different concentrations. The fig. 5.7 shows representative Dühring plots for a solution (non-volatile solute in water).



Fig.5.7 Duhring plot for boiling point of sodium chloride solutions

#### 56. Method of feeding in Multiple effect evaporators

The fig. 5.8 a,b,c and d show the four different feeding arrangement of feed to the evaporators. In the fig.5.8 (a) the liquid feed is pumped into the first effect and the partially concentrated solution is sent to the second effect and so on. The heating steam is also sent through the first effect to another effect. This particular strategy is known as forward feed. In the forward feed the concentration of the liquid increases from first effect to the subsequent effects till the last effect. It may be noted that the first effect is that in which the fresh steam is fed, whereas the vapour generated in the first effect is fed to the next evaporator (connected in series with the first effect) is known as second effect and so on. The forward feed requires a pump for feeding

dilute solution to the first effect. The first effect is generally at atmospheric pressure and the subsequent effects are in decreasing pressure. Thus, the liquid may move without the pump from one effect to another effect in the direction of decreasing pressure. However, to take out the concentrated liquid from the last effect may need a pump.

The backward feed arrangement is very common arrangement. A triple-effect evaporator in backward arrangement is shown in the fig. 5.8(b). In this arrangement the dilute liquid is fed to the last effect and then pumped through the successive effects to the first effect. The method requires additional pumps (generally one pump in between two effects) as shown in the fig.5.8.(b). Backward feed is advantageous and gives higher capacity than the forward feed when the concentrated liquid is viscous, because the viscous fluid is at higher temperature being in the first effect. However, this arrangement provides lower economy as compared to forward feed arrangement. The combination of forward-feed and backward-feed is known as mixed feed arrangement. In mixed feed the dilute liquid enters in between effects, flows in forward feed to the end of the effect and then pumped back to the first effect for final concentrated liquid through the first effect, which is having higher temperature among all the effect (being at highest pressure compared to other effects).

Another common evaporator arrangements, which is more common in crystallization is parallel feed where feed is admitted individually to all the effects. Figure 5.8.(d) shows such arrangement.



Fig. 5.8. Methods of feeding in Multiple Effect Evaporator

## 5.7. Enthalpy Balance

## 5.7.1. Single effect evaporator

The latent heat of condensation of the steam is transferred to the boiling solution through the heating surface in order to vaporize the water. Thus, two enthalpy balances are required one for the liquid and another for the steam.

The following assumptions are required, in order to make the enthalpy balance,

- 1. Flow of non-condensable is negligible
- 2. The superheat and sub-cooling of the condensable steam is negligible
- 3. No solid precipitates out from the concentrating solution

The enthalpy balance for the steam side is,

Where,  $q_s$  = rate of heat transfer through heating surface from steam  $\dot{m}_s$  = flow rate of steam

 $\lambda_s$  = latent heat of condensation of steam

 $h_s$  = specific enthalpy of steam

h<sub>c</sub> = specific enthalpy of condensate

Enthalpy balance for the liquor side is,

$$q = (\dot{m}_f - \dot{m})H_v - \dot{m}_f H_f + \dot{m}H$$
(2)

Where, q = Rate of heat transfer from heating surface to the liquid

 $H_v$  = specific enthalpy of vapour

H = specific enthalpy of thick liquor

H<sub>f</sub> = specific enthalpy of feed

 $\dot{m}_f$  = flow rate of liquid feed

 $\dot{m}$  = flow rate of concentrated liquid

The enthalpy balance at steam side and liquid side will be same in the absence of any heat loss. Thus,

$$q = \dot{m}_s \lambda_s = (\dot{m}_f - \dot{m})H_v - \dot{m}_f H_f + \dot{m}H$$
(3)

The area of heat transfer A can be calculated from

$$q = q_s = UA\Delta T \tag{4}$$

When  $\Delta T = (T_b - T_s);$ 

 $T_b$  = Saturated temperature of steam in the shell

 $T_s$  = Boiling point of the solution at the prevailing pressure

U = Overall heat transfer coefficient

### 5.8. Effect of heat of dilution

Most of the solutions when mixed or diluted at constant temperature do not give significant heat effect. It is generally true for organic solutions (like sugar). However, many of the inorganic solutions (like sulfuric acid, potassium hydroxide, calcium

(1)

carbonate etc.) evolve significant heat on dilution. Therefore, an equivalent amount of heat is required (in addition to the latent heat of vaporization), when dilute solutions of these inorganic chemicals are concentrated. Enthalpy-concentration

diagram are helpful in order to find the enthalpy of the solution at different concentration of these chemicals in the solution.



Fig.5.9. Enthalpy concentration diagram

#### 59. Multiple effect evaporators

the equation

The steam goes into I-effect and heat the solution by the latent heat of condensation. The heating surface in the I effect will transmit per hour an amount of heat given by

$$\dot{q}_s = A_1 U_1 \Delta T_1$$

(5)

If the heat required to boil the feed is negligible, it follows that practically all this heat must appear as latent heat in the vapor that leaves the I-effect and enter into II-effect as steam. The temperature of the condensate leaving the II-effect will be very near the temperature  $T_1$  of the vapors from the boiling liquid in the I-effect. Thus, in steady state operation all the heat that was expanded in creating vapor in the I-effect must be given by when this same vapor condenses in the II-effect and so on.

The heat delivered into the II-effect will be,

$$\dot{q}_{\nu 1} = A_2 U_2 \Delta T_2 \tag{6}$$

 $\dot{q}_{v1} = q_s$ 

Similarly, for III-effect

$$A_1 U_1 \Delta T_1 = A_2 U_2 \Delta T_2 = A_3 U_3 \Delta T_3 = \dot{q}$$
<sup>(7)</sup>

It can be seen (eq.5.7) that the temperature drops in a multiple effect evaporator is approximately inversely proportional to the heat-transfer coefficient. The total available temperature drop will be given by

$$\sum \Delta T = \Delta T_1 + \Delta T_2 + \Delta T_3$$
$$= (T_s + T_{\nu 3}) - \Sigma BPE$$
(8)

where,

 $T_{s}$  - Steam temperature (I-effect);  $T_{\nu3}$  - Vapor temperature leaving III-effect BPE - boiling point elevation in the solution in various effects

#### **Problems**

**P.No.1**. A single effect evaporator is used to concentrate 9070 kg/hr of 20% caustic soda solution to 50% solids. The gauge pressure of steam is 1.37atm. The absolute pressure in the vapor space is 100 mm Hg. There is a BPE of 22.78 °C. The overall heat transfer coefficient is estimated to be 1400 W/m<sup>2</sup> °C and the feed temperature is 37.8 °C. Calculate the (a) Amount of steam consumed (b) Economy (c) Heating surface required.

Data: Enthalpy of feed at 37.8 °C = 127.9245 kJ/kg Enthalpy of thick liquor = 514.0239 kJ/kg Enthalpy of vapour = 2672.46 kJ/kg Heat of vaporization of steam at 1.37 atm = 2184.0201 KJ/ Kg Condensation temperature of steam = 126.11°C

## Solution:

## Feed:

 $\dot{m}_{f} =$  9070 kg/h

 $x_f = 0.2 \text{ Tf} = 37.8^{\circ}\text{C}$ 



## Thick liquor:

x = 0.5

H = 514.02 kJ/kg

## Vapour:

P= 100mm Hg

H<sub>v</sub>= 2672.46 kJ/kg

#### Steam:

P = 1.37atm

 $\lambda s = 2184.0201 \text{ kJ/ kg}$ 

## **Condensate:**

 $T_{s} = 126.11^{\circ}C$   $Q = \dot{m}_{s}\lambda_{s} = (\dot{m}_{f} - \dot{m})H_{v} - \dot{m}_{f}H_{f} + \dot{m}H$ 

# **Component balance(solid)**

$$m_f x_f = m x$$
  
 $\dot{m} = 3628 \text{ kg/h}$ 



$$\dot{m}_v = 5442 \text{ kg/h}$$

$$q = \dot{m}_s \lambda_s = (\dot{m}_f - \dot{m})H_v - \dot{m}_f H_f + \dot{m}H$$

$$q = \dot{m}_s \lambda_s = (5442 \ x \ 2672 \ .46) - (9070 \ x \ 127 \ .92) + (3628 \ x \ 514 \ .02)$$

 $\dot{m}_s$  = 6981.69 kg/h= 1.9394 kg/s

$$\mathsf{Q} = \mathsf{U} \mathsf{A} \Delta \mathsf{T}$$

A= Q / U ∆T = **57.94 m**<sup>2</sup>

 $\Delta T = Ts - T$ 

## Steam economy:

kg of water vapourised/kg of steam = 5442 / 6981.69 = 0.7795

**P.No.2**. A triple effect forward feed evaporator is used to concentrate a liquid which has marginal elevation in boiling point. The temperature of the stream to the first effect is 105°C, and the boiling point of the solution within third effect is 45°C. The overall heat transfer coefficients are,

2,200 W/m<sup>2</sup>: in the I-effect,

1,800 W/m<sup>2</sup>: in the II-effect,

1,500 W/m<sup>2</sup>: in the III-effect.

Find out at what temperatures the fluid boils in the I and II effects.

## Solution:

#### Assumptions

1. We may assume that there is no elevation in boiling point in the evaporators.

2. Area of all the three evaporators are same  $(A_1 = A_{11} = A_{11} = A)$  Total

temperature drop = (105-45) °C = 60 °C

The temperature drop across I-effect,

$$\Delta T_I = \frac{\frac{1}{2200}}{\frac{1}{2200} + \frac{1}{1800} + \frac{1}{1500}} \times 56 = 15.2 \,^{\circ}C$$

Similarly, the temperature drop across II-effect,

$$\Delta T_{II} = \frac{\frac{1}{1800}}{\frac{1}{2200} + \frac{1}{1800} + \frac{1}{1500}} \times 56 = 18.6 \ ^{\circ}C$$

And the temperature drop across III-effect,

$$\Delta T_{III} = \frac{\frac{1}{1500}}{\frac{1}{2200} + \frac{1}{1800} + \frac{1}{1500}} \times 56 = 22.3 \ ^{\circ}C$$

Therefore, the boiling point in the first effect will be = (105 - 15.2) °C = 89.8 °C Similarly, the boiling point in the second effect will be = (89.8 - 18.6)°C = 71.2 °C.


# SCHOOL OF BIO&CHEMICAL ENGINEERING

# DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – IV – Mass Transfer for Biological Systems-SCH1313

# Introduction

Crystallization "Crystal growth is achieved by the slow dehydration of the water of solvation from the sample in a controlled manner that prevents precipitation and takes the sample out of solution and into a crystalline state."

1840 F.L.Hunfield (German) First documented protein crystallization Earthworm hemoglobin. Obtained plate-like crystals when he pressed the blood of an earthworm between two slides of glass and allowed the blood to dry very slowly.

1851 Otto Funke (German) published a series of papers describing the growing of hemoglobin crystals, by diluting blood with water, alcohol or ether and allowing slow evaporation.

The exact forces governing crystal nucleation are difficult to understand and pinpoint because of the many factors that affect the solubility of the sample in the solvent in which it is dissolved. These factors include the buffer used in the experiment; the pH of the solution; the concentration of the sample and counter ions; the type and concentration of the precipitant used to bring the sample out of solution; the temperature, the surface area of droplet, and the gravity of the system used. In general, when no homologous proteins have been crystallized, all these factors have to be explored before suitable conditions are identified. If a homologous protein has been crystallized, the conditions for the new protein should explore those published and be expanded from this starting point.

A **crystal** is a solid bounded by plane surfaces. Crystallization is important as an industrial process because a large number of commodity chemicals, pharmaceuticals, and specialty chemicals are marketed in the form of crystals. The wide use of crystallization is due to the highly purified and attractive form in which the compounds can be obtained from relatively impure solutions by means of a single processing step. Crystallization can be performed at high or low temperatures, and it generally requires much less energy for separation of pure materials than other commonly used methods of purification do. While crystal- lization may be carried on from vapor or a melt, the most common industrial method is from a solution. A solution is made up of a liquid (solvent) — most commonly water — and one or more dissolved species that are solid in their pure form (solute). The amount of solute present in solution may be expressed in several different units of concentration. For engineering calculations, expressing the solu- bility in mass units is the most useful. The solubility of a material is the maximum amount of solute that can be dissolved in a solvent at a particular temperature. Solubility varies with temperature and,

with most substances, the amount of solute dissolved increases with increasing temperature.

For crystallization to occur, a solution must be supersaturated. **Supersaturation** means that, at a given temperature, the actual solute concentration exceeds the concentration under equilibrium or saturated conditions. A supersaturated solution is metastable, and all crystallization occurs in the metastable region. A crystal suspended in saturated solution will not grow. Supersaturation may be expressed as the ratio between the actual concentration and the concentration at saturated solution (62.1)] or as the difference in concentration between the solution and the saturated solution at the same temperature [Equation (62.2)].

$$S = C/C_{\rm S} \tag{62.1}$$

(62.2)

 $DC = C - C_s$ 

where *C* is the concentration (g/100 g of solution), and  $C_S$  is the concentration (g/100 g of solution) at saturation. This difference in concentration may also be referenced to the solubility diagram and expressed as degrees ( $\infty$ C) of supersaturation.

Nucleation is the birth of a new crystal within a supersaturated solution. Crystal growth is the layer- bylayer addition of solute to an existing crystal. Both of these phenomena are caused by supersaturation. Nucleation is a relatively rapid phenomenon that can occur in a matter of seconds. Growth is a layer- bylayer process on the surface of an existing crystal and takes considerably more time. The ratio of nucleation to growth controls the size distribution of the crystal product obtained. Generating a high level of supersaturation spontaneously leads to both nucleation and growth. The competition between these two processes determines the character of the product produced.

#### 62.1 Methods of Creating Supersaturation

Supersaturation may be created by cooling a solution of normal solubility into the metastable zone. Typically, the amount of supersaturation that can be created in this way without causing spontaneous nucleation is in the range of 1 to 2 °C. Evaporation of solvent at a constant temperature also produces supersaturation by reducing the amount of solvent available to hold the solute. The reaction of two or more chemical species, which causes the formation of a less soluble species in the solvent, can also produce supersaturation. Finally, the addition of a miscible nonsolvent in which the solute is not soluble to a solvent will cause a decrease in the solubility of the solute in the solution. This technique is most often used in pharmaceutical operations involving the addition of alcohol or similar solvents to the primary solvent (water).

#### 62.2 Reasons for the Use of Crystallization

Crystallization is important as an industrial process because a large number of materials can be marketed in the form of crystals that have good handling properties. Typically, crystalline materials can be separated from relatively impure solutions in a single processing step. In terms of energy requirements, the energy required for crystallization is typically much less than for separation by distillation or other means. In addition, crystallization can often be performed at relatively low temperatures on a scale that involves quantities from a few pounds up to thousands of tons per day.

#### 62.3 Solubility Relations

Equilibrium relations for crystallization systems are expressed in the form of solubility data, which are plotted as phase diagrams or solubility curves. The starting point in designing any crystallization process is knowledge of the solubility curve, which is ordinarily plotted in terms of mass units as a function of temperature. An example is given in Figure 62.1 for the solubility of magnesium sulfate in water as a function of temperature. At any concentration and temperature, the information on the diagram allows one to predict the mixture of solids and solution that exists. Note that, in the case of magnesium sulfate, a number of different hydrates can exist in addition to the solution itself, or ice plus the solution. The line that forms a boundary between the solution area and the various crystal hydrate areas is a solubility curve. Starting from point (1) at 50°C and cooling to 30°C at point (2) is a path that crosses the solubility line. During the cooling process, crossing the line in this manner indicates that the solution has become supersaturated for the concentration in question. If the supersaturation is within the metastable range

— which is approximately  $1 \approx C$  — then growth can occur on existing crystals, but no substantial amount of nucleation will occur. If the cooling proceeds further, the system can become unstably supersaturated, and spontaneous nucleation takes place. If spontaneous nucleation takes place, very small crystals or nuclei form, and they will grow as long as the solution remains supersaturated.

As growth takes place, the concentration drops in the direction of point (3), and, as it approaches the solubility line, growth ceases because the driving force approaches zero. Organic and inorganic materials



Solution + MgSO<sub>4</sub> · 7H<sub>2</sub>O MgSO · 7H<sub>2</sub>O  $\sim$  4  $\approx \infty \infty$   $\circ$   $\sim$  4  $\stackrel{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}{\overset{\circ}}}{\overset{\circ}}}$ 

20

10

1 c С

 $\stackrel{\ensuremath{\mathfrak{g}}}{\operatorname{\mathsf{MgSO}}_4} \cdot 12\operatorname{H_2O}$ 



**FIGURE 62.1** Weight fraction of MgSO<sub>4</sub> versus temperature. (*Source:* Courtesy of Swenson Process Equipment Inc.)

have similar solubility curves and they vary in concentration and temperature for each compound. Some materials have no hydrates and others exhibit a wide range of hydrates similar to those shown in Figure

62.1. Solubility information on most compounds is available from the literature in publications, such as the *International Critical Tables* [Campbell and Smith, 1951] and *Lang's Solubility of Inorganic and Organic Compounds* [Linke, 1958], and in various software packages that are becoming available.

## 62.4 Product Characteristics

The shape and size of a crystal are determined by its internal structure as well as external conditions that occur during its growth cycle. These external conditions include growth rate, the solvent system, the level of agitation, and the effect of impurities that may be present. Crystalline material is almost always

separated from its mother liquor before the crystal can be dried or used. The filterability of the crystals, whether separation is done on a centrifuge or filter, is an important characteristic of the product. Generally, larger particles filter more readily, but the average particle size by itself is not an unfailing indication of filterability. The particle size distribution is important because, if it is very broad, small particles may be trapped between the larger particles, making the drainage rates much lower. This could lead to retention of mother liquor, which will degrade the purity of the final product. Broad distributions that increase the amount of mother liquor retained also make the cake less pervious to wash liquids. Products crystallized from continuous crystallizers typically have a coefficient of variation of 45 to 50%. Products made from batch crystallizers, which are fully seeded, often show narrower size distributions with a coefficient of variation of approximately 25 to 30%.

The bulk density of the dried material is affected not only by the crystal density itself, but also by the size distribution. A broader distribution leads to tighter packing and, therefore, a higher bulk density. The flow properties of a crystal product are affected by the crystal shape. Rounded crystals that are formed under conditions of relatively high attrition flow very well, particularly if the particles are in the size range of -8 to +30 U.S. Mesh.

#### 62.5 Impurities Influencing the Product

Since crystallization is generally performed to produce high-purity products, it is important that the crystal be grown in such a way that the impurities that are part of the mother liquor are not carried out with the crystalline particles. Impurities can affect the growth rate and nucleation rate during crystalli- zation and, as a consequence, affect both the mean particle diameter and the habit of the particles being crystallized. Most habit modifiers cause a change in the crystal shape because they are absorbed on one or more of the crystal faces, thereby altering the growth rate of that face and causing that face to either become predominant or largely disappear. Impurities that have this influence can be either ionic, surface- active compounds or polymers.

Under some conditions, the impurities in a product can be increased by lattice incorporation, which occurs when an impurity in the mother liquor substitutes for molecules in the product crystal lattice. Mixed crystals — which are really two separate species crystallizing at the same time — can also be produced. Surface absorption of species that are in the mother liquor not only can add to the impurity level of the product, but can also alter the growth rate and, therefore, the habit of the crystals. Solvent inclusion can occur when rapidly growing crystals form around small volumes of mother liquor that become trapped inside the crystal lattice. The liquor in these inclusions may or may not find its way to the surface during the subsequent drying operations.

Solvent inclusion probably accounts for the largest increase in impurity levels in a crystal, with lattice incorporation generally less, and surface absorption accounting for only very minute amounts of contamination. Normally, recrystallization from a relatively pure solution will eliminate virtually all the impurities, except for a material whose presence is due to lattice incorporation.

#### 62.6 Kinds of Crystallization Processes

Crystallization can be carried on in either a batch or continuous manner, irrespective of whether evaporation, cooling, or solvent change is the method of creating supersaturation. Batch processes are almost always used for small capacities and have useful application for large capacities when a very narrow particle size distribution is required, such as with sugar, or when materials (e.g., pharmaceuticals) that require very accurate inventory control are being handled. A continuous crystallization process normally must operate around the clock because the retention times typically used in crystallizers range from about 1 to 6 h. As such, it takes at least four to six retention times for the crystallizer to come to equilibrium, which means there may be off-spec product when the system is started up. To minimize this, the unit should be kept running steadily as long as

possible. The cost of at least three operators per day and the instrumentation required to continuously control the process represent a substantially greater investment than what is required for batch processing. This disadvantage can only be overcome by utilizing that labor and investment at relatively high pro- duction rates.

#### 62.7 Calculation of Yield in a Crystallization Process

In order to calculate the yield in a crystallization process, it is necessary that the concentration of feed, mother liquor, and any change in solvent inventory (evaporation) be known. In most crystallization processes, the supersaturation in the residual mother liquor is relatively small and can be ignored when calculating the yield. With some materials, such as sugar, a substantial amount of supersaturation can exist, and under such circumstances the exact concentration of the solute in the final mother liquor must be known in order to make a yield calculation. The product crystal may be hydrated, depending on the compound and temperature at which the final crystal is separated from the mother liquor.

Shown below is a formula method for calculating the yield of a hydrated crystal from a feed solution

[Myerson, 1993].

$$\frac{100W - S(H - E)}{0}$$

$$\frac{P = R - 0}{100 - S(R - 1)}$$
(62.3)

#### where

P = weight of product

*B* = <u>mole weight of hydrate crystal</u>

mole weight of anhydrous crystal

S = solubility at the mother liquor (final) temperature in units/100 units of solvent

*W*<sub>0</sub> = weight of anhydrous solute in feed

 $H_o$  = weight of solvent in feed

E = evaporation

#### 62.8 Mathematical Models of Continuous Crystallization

Randolph and Larsen [1988] developed a method of modeling continuous crystallizers in which the growth rate is independent of size and the slurry is uniformly mixed. Such crystallizers are often referred to as the mixed-suspension mixed-product removal (MSMPR) type. For operation under steady condi- tions, the population density of an MSMPR crystallizer (FC and DTB types shown in Figure 62.2 and Figure 62.3. respectively) is

$$n = n^{O} e^{-L/GT}$$
(62.4)

## where

- *n* = population density, number/mm
- G = growth rate, mm/h
- T = retention time, h
- L = characteristic length, mm
- $n^{O}$  = nuclei population density (i.e., intercept at size L = O)

A plot of the  $\ln n$  versus *L* will be a straight line if the system is operating under the conditions assumed above. The nucleation rate and the mean particle size (by weight) are

$$B^{O} = Gn^{O} \tag{62.5}$$



FIGURE 62.2 Swenson forced-circulation crystallizer. (Source: Courtesy of Swenson Process Equipment Inc.)

$$L_q = 3.67GT$$
 (62.6)

where

 $L_q$  = average particle by weight

B<sup>O</sup> = nucleation rate, number/cc-sec

It is possible to calculate the particle size distribution by weight if the assumptions above are valid and if the plot of  $\ln n$  versus *L* is a straight line. The weight fraction up to any size *L* is

where

x = L/GT

 $W_X$  = cumulative weight fraction up to size L



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particles being used as seed (when used), as well as the product population balance.

In solving Equation (62.4) and Equation (62.5), it must be remembered that the growth rate and the nucleation rate must be measured under the same conditions. In evaluating performance of crystallization equipment, it is necessary to know the heat balance, material balance, and population balance of the

FIGURE 62.3 Swenson draft-tube baffle crystallizer. (Source: Courtesy of Swenson Process Equipment Inc.)

# 62.9 Equipment Designs

While many solvent systems are possible, most large-scale industrial crystallizers crystallize solutes from water. Organic solvents are sometimes encountered in the petroleum industry, and alcohol solutions or mixtures of alcohol and water are found in pharmaceutical applications. Typically, water solutions have

viscosities in the range of 1 to 25 cp and boiling point elevations from 1 up to 12°C. The viscosity of a solution is very important because it determines the settling rates of particles within the solution and heat transfer rates in heat exchange equipment required for heating or cooling the solution. The boiling point elevation represents a temperature loss in an evaporative system where condensation of the vapor in a multiple-stage evaporative crystallizer or condenser is required.

The evaporation rate is determined from the basic process requirements and the heat balance around the system. The evaporation rate and the temperature at which evaporation occurs determine the min- imum body diameter. The specific volume of water vapor is strongly influenced by pressure and tem- perature. Low temperatures, which represent relatively high vacuum for water at its boiling point, require larger bodies than do systems operating at atmospheric pressure. The other consideration in sizing the body is the minimum volume required to provide the retention time required for crystal growth.

Shown in Figure 62.2 is a forced-circulation evaporator-crystallizer, which is often used for the pro-duction of sodium chloride, citric acid, sodium sulfate, sodium carbonate, and many other inorganic compounds produced by evaporative crystallization. The body diameter and straight side are determined by the vapor release rate and retention time required to grow crystals of the desired size. The sizes of the circulating pipe, pump, heat exchanger, and recirculation pipe are based on the heat input required to cause the evaporation to take place. Crystals in the solution circulated throughout the body are kept in suspension by the action of the recirculating liquor. Tube velocities, heat transfer rates, and circulation rates are determined by the particular application and the physical properties of the solution. Slurry leaving the crystallizer is pumped by the product discharge pump into a centrifuge, filter, or other separation equipment. This type of crystallizer is often referred to as an MSMPR type, and the crystal size distribution can be described by the mathematical model described in Equation (62.4) through Equation (62.7). The crystal size typically produced in equipment of this type is in the range of 30 to

100 Mesh, and slurry discharge densities typically handled in such equipment range from about 20 to

## 40% by weight solids.

Shown in Figure 62.3 is a draft-tube baffle (DTB) crystallizer of the evaporative type, including an elutriation leg. Slurry within the crystallizer body is pumped to the surface by means of a slow propeller and recirculates to the suction of the propeller where it is mixed with heated solution exiting the heating element. Surrounding the body of slurry in the crystallizer is an annular space between the skirt baffle and the settler. Liquid is pumped from this annular space at a controlled rate so that small crystal particles from the body can be removed, but the bulk of the circulated liquor and crystals enters the propeller suction. The flow from the annular area is pumped through a circulating pipe by a circulating pump through the heat exchanger, where the temperature rise destroys small particles that are present. This continuous removal and dissolution of small particles by temperature increase serves two purposes:

- 1. The heat required for the evaporation is transferred into the liquid so that a constant vaporization rate can be maintained.
- 2. Small particles are continuously removed so as to limit the seed crystals in the body to values low enough so that the production can be obtained in a coarse crystal size.

When the crystals become too large to be circulated by the propeller, they settle into the elutriation leg, where they are washed by a countercurrent stream of mother liquor pumped from behind the baffle. Crystals leaving the leg are therefore classified generally at a heavier slurry density than would be true if they were pumped from the body itself. This combination of removal of unwanted fines for destruction and classification of the particle size being discharged from the crystallizer encourages the growth of larger particles than would be obtained in a crystallizer such as the forced circulation type in Figure 62.2. Typically, the

DTB crystallizer is used for products in the range of 8 to 20 Mesh with materials such as ammonium sulfate and potassium chloride.

Shown in Figure 62.4 is a surface-cooled crystallizer, which is frequently used at temperatures close to ambient or below. Slurry leaving the body is pumped through a heat exchanger and returns to the body through a vertical inlet. Surrounding the circulating slurry is a baffle that permits removal of unwanted fine crystals or provides for the removal of clarified mother liquor to increase the slurry density





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FIGURE 62.4 Swenson surface-cooled crystallizer. (Source: Courtesy of Swenson Process Equipment Inc.)

within the crystallizer body. Slurry pumped through the tubes of the cooler is chilled by a coolant that is circulated outside the tubes. The temperature difference between the coolant and the slurry flowing through the tubes must be limited to approximately 3 to  $8 \times C$ . The temperature drop of the slurry passing through the tubes is normally about  $0.5 \times C$ . These very low values are required in order to minimize the growth of solids on the tubes. Crystallizers of this type produce a product that ranges between 20 and

150 Mesh in size. Common applications are for the production of copper sulfate pentahydrate, sodium chlorate, sodium carbonate decahydrate, and sodium sulfate decahydrate.

Shown in Figure 62.5 is a reaction-type DTB crystallizer. This unit, while in many respects similar to the DTB crystallizer shown in Figure 62.3, has the important difference that no heat exchanger is required to supply the heat required for evaporation. The heat of reaction of the reactants injected into the crystallizer body

supplies this heat. Typically, this type of equipment is used for the production of ammonium sulfate, where sulfuric acid and gaseous ammonia are mixed in the draft tube of the crys-tallizer so as to produce supersaturation with respect to ammonium sulfate. The heat of reaction is removed by vaporizing water, which can be recirculated to the crystallizer and used for the destruction of fines. Whenever a chemical reaction causes a precipitation of crystalline product, this type of equipment is worth considering because the conditions used in crystallization are compatible with low temperature rises and good heat removal required in reactors. By combining the reactor and crystallizer, there is better control of the particle size with an obvious decrease in equipment costs.

# 62.10 Evaporation

When a solution is boiled (evaporated) at constant pressure, the total pressure above the solution represents the sum of the partial pressures of the liquids that are boiling. If only water is present, then the pressure above the solution at any temperature corresponds to water at its boiling point at that pressure. If there is more than one component present and that component has a vapor pressure at the temperature of the liquid, then the total pressure represents the vapor pressure of water plus the vapor



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FIGURE 62.5 Swenson reaction-type DTB crystallizer. (Source: Courtesy of Swenson Process Equipment Inc.)

pressure of the other component. Vapor leaving such a system, therefore, represents a mixture of solvents in the ratio of their partial pressures. In a sense, an evaporator is a single plate distillation column. In most applications, the vapor pressure of the solute is negligible and only water is removed during boiling, which can be condensed in the form of a pure solution. However, when volatile compounds are present (e.g., H<sub>3</sub>BO<sub>3</sub>, HNO<sub>3</sub>), some of the volatile material will appear in the overhead vapor.

Since the heat required to vaporize water is approximately 556 cal/kg (1000 Btu/lb), it is important

to reduce the amount of energy required as much as possible so as to improve the economics of the process. For this reason, multiple-effect evaporators were developed in the middle of the 19th century and continue today as an important means for achieving good economy during evaporation or crystal-lization. A multiple-effect falling-film evaporator consisting of three vessels and a condenser is shown in Figure 62.6. In this type of equipment, the vapor boiled from the first effect (the vessel where the steam enters) is conducted to the heat exchanger of the second effect, where it acts as the heating medium. Vapor boiled in the second effect is conducted to the third effect, where it again acts as the heating medium. Vapor leaving the third effect, in this case, is condensed in a condenser utilizing ambient-







temperature water. The flow of feed solution to the evaporator can be either forward, backward, or parallel. In a forward feed evaporator, the feed enters the first effect, then passes to the second effect, and is ultimately removed from the third effect as concentrated liquor. With this type of flowsheet, heat exchange means must be employed to minimize the sensible heat required for the liquid fed to the first effect. In a backward feed evaporator, this is not normally done.

An alternative means for reducing energy consumption during evaporation is shown in the recompression evaporative crystallizer in Figure 62.7. The technique can be employed on both evaporation and crystallization equipment. In this case, a single vessel is employed, and the vapor boiled out of the solvent is compressed by a centrifugal compressor and used as the heating medium in the heat exchanger. The compressed vapor has a higher pressure and a higher condensing temperature so that there is a change in temperature between the vapor being condensed in the heater and the liquid being heated in the heat exchanger. In utilizing this technique, it must be remembered that the boiling point elevation decreases the pressure of the vapor above the liquid at any given temperature and, thereby, represents a pressure barrier that must be overcome by the compressor. The efficiency of this process varies greatly with the boiling point elevation. As a practical matter, such techniques are limited to those liquids which have boiling point elevations of less than about 13°C. Typically, such compressors are driven at constant speed by an electric motor. The turndown ratio on a constant speed compressor is about 40%. A variable-speed drive would give a greater range of evaporative capacity.

During the last 100 years, a wide variety of evaporator types has evolved, each offering advantages for certain specific applications. The forced-circulation crystallizer shown in Figure 62.2 is utilized for many applications where no crystallization occurs, but the liquids being handled are viscous, and use of the circulation system is needed to promote heat transfer. A number of evaporator types have been developed that require no external circulating system. For the most part, these rely upon thermo-syphon effects to promote movement of liquid through the tubes as an aid to heat transfer. The calandria evaporator (or Roberts type) shown in Figure 62.8 is a design that has been widely used since the 19th century for both crystallization and evaporation applications. It relies on natural circulation in relatively short tubes (1 to 2 m) to maintain heat transfer rates; a relatively large amount of recirculation occurs through the tubes. Since there is no recirculation pump or piping, this type of equipment is relatively simple to operate and requires a minimum of instrumentation. The volume of liquid retained in this vessel is much larger than in some of the rising or falling film designs and, therefore, in dealing with heat-sensitive materials where concentration must proceed at relatively short retention times, the calandria would be





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a poor choice. In many situations, however, especially where some crystallization may occur, this evaporator may be operated successfully in a semi-batch or continuous manner.

The falling-film evaporator shown in Figure 62.9 is similar to the rising-film evaporator, except that there must be sufficient liquid at all times entering the heater at the feed inlet to wet the inside surface of the tubes in the heat exchanger bundle. With insufficient circulation, solute material can dry on the tubes and cause a serious reduction in heat transfer. Many falling-film evaporators operate with a recir- culating pump between the concentrated liquor outlet and the feed inlet to be certain that the recirculation rate is adequate to maintain a film on the tubes at all times. If this is done, the system can operate stably through a wide range of capacities and achieve very high rates of heat transfer, often 50 to 100% more than are obtained in a rising-film evaporator. The other advantage of the falling film evaporator is that it can operate with very low temperature differences between the steam and the liquid since there is no hydrostatic pressure drop of consequence within the tubes to prevent boiling at the inlet end of the heat exchanger. As a result, this type of design has found wide application as a recompression evaporator.

Even though evaporators are typically used where no precipitation of solids occurs, there is often a trace of precipitation in the form of scaling components that coat the inside of the tubes over a relatively long period of time. This scaling is analogous to that which occurs in boilers and many other types of heat transfer equipment. Typically it is due to either a small amount of precipitation or, because of the composition of the materials being concentrated, some inverted solubility components. Such scaling may often be reduced by a technique known as "sludge recirculation." This is commonly done in cooling tower blowdown evaporation and in the evaporation of salt brines where scaling components are present.



FIGURE 62.9 Swenson falling-film evaporator. (Source: Courtesy of Swenson Process Equipment Inc.)

In these cases, the evaporator flowsheet is designed in such a way that a thickened slurry of the scaling component can be recirculated from the discharge of the evaporator back to the feed side. By maintaining an artificial slurry density of the scaling component, which is higher than the natural slurry density, it is often possible to reduce the growth of scale which occurs on heat transfer surfaces.

## **Defining Terms**

- **Crystal** A solid bounded by plane surfaces that has an internal order with atoms or molecules in a fixed lattice arrangement.
- **Crystallizer** An apparatus for causing the crystallization of solutes from solvents by means of changes in heat or solvent inventory.
- **Evaporator** An apparatus for causing water or other solvents to be removed from a solution in order to increase the concentration of the solution.

**Nucleation** — The birth of a new crystal within a supersaturated solution.

**Recompression** — A process for collecting the vapor boiled from the solution in an evaporator or crystallizer and compressing to a higher pressure, where it can be used as the heating medium for said evaporator or crystallizer.

Supersaturation — A metastable condition in a solution that permits nucleation and growth of crystals to occur.



# SCHOOL OF BIO&CHEMICAL ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING

UNIT – V – Mass transfer for Biological Systems – SCH1313

# **1. 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 dependent 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 categorised 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 indicates 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 mositure 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 perticular material is dictated by the desire to achieve a favourable 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 cheracteristics, eqipment 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 soild 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.

# 2. PHYSICAL MECHANISM OF DRYING

Drying does not mean only removal of the moisture but during the process, physical structure as well as the apperance 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 term are commonly used in designing of drying systems.

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

Moisture content of the solid which exters an equillibrium vapour 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 as *free moisture*. During drying, only free moisture can be evporated. 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*. Similalry, 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 evporated per unit time per unit area of drying surface remains constant and in *falling rate drying period* the amount of moisture evporated per unit time per unit area of drying surface continuously decreases.

## **3. CLASSIFICATIONOF 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.

# 4. DRYING EQUIPMENT

# 4.1 Batch Type Dryers

# 4.1.1 Tray Dryer

Schematic of a typical batch dryer is shown in figure 2.1. 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. 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 ba*ffles 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.



Figure 2.1: Tray dryer

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 vaccum. 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<sup>0</sup>C. This is done in special vacuum dryers for drying heat-sensitive products.

# 4.1.2 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.

# 4.1.3 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 over heating. Due to the agitation of the product in the agitated vacuum dryer the drying time is substantially reduced. A choice of the agitator design which can be arranged with or without heating depends on the material characteristics and process requirements. While designing the shell one has to consider the external pressure and the shaft

designing includes fatigue consideration. Designing the impeller needs consideration of characteristics of the material before and after drying.

#### 4.2Continuous Dryer

#### 4.2.1 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 (2.2) 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 2.2: 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. By bending the edge of the lifter slightly inward, some of the material is delivered only in
the third quarter of the circle, producing a nearly uniform fall of the material throughout the cross section of the cylinder. The heated air streams through a rain of particles. This is the most common form of revolving rotary cylinder. It has high capacity, is simple in operation, and is continuous.

#### 4.2.2 Drum Dryer

In drum dryers (Fig 2.3a, b) 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 2.3a). 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. In recent years, double drum dryers have replaced single drum dryer in several applications (figure 2.3b), due to their more efficient operation, wide range of products and high production rates.



Figure 2.3b: Double drum dryer

## 4.2.3 Flash Dryer

The flash driers (figure 2.4), 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 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

650°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 5.4: Flash dryer

## 4.2.4 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 2.5). 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 2.5: Continuous fluidized bed dryer

## 4.2.5 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 2.6). 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 2.6: Screen conveyor dryer

## 6. NOVEL DRYING TECHNOLOGIES

Newer technologies focus on saving in energy consumption that result in considerable overall improvement in energy efficiency. In addition, the final quality of the product is greatly influenced by the drying technique and strategy. A brief overview of some novel drying techniques is given below:

#### 5.1 Microwave Drying

Microwave heating is a direct drying method. High-frequency radio waves are utilized in microwave drying. A highfrequency generates the waves and wave channel guides them in to an oven that is designed to prevent the waves from leaving the chamber. In microwave drying, heat is generated by directly transforming the electromagnetic energy in to kinetic molecular energy, thus the heat is generated deep within the material to be dried. Selection of proper wavelength is necessary to ensure thorough penetration into the material. Apart from these, other parameters such as material type and depth of material being exposed also affect the penetration. Therefore, selection of proper wavelengths and dehydration condition for each product is selected individually.

This type of heating is instantaneous, uniform and penetrating throughout the material, which is a great advantage for the processing of pharmaceutical compounds. In case of microwave drying the waves bounce from wall to wall, until the product absorbs eventually all of the energy, generating heat within the material, resulting in dehydration. Vapour from the liquid evaporating inside the product is emitted through the pore structure of the solid material"s macro-capillary system, resulting in a high drying rate. This type of dryer is highly efficient and power utilization efficiencies are generally greater than 70 %. Important commercial aspects of this dryer includes the ability to maintain colour, moisture and quality of the natural food.

## 6.2Supercritical Fluid Extraction and its application to Drying

The supercritical fluid (SCF) is a substance at a temperature and pressure above its critical point. It can effuse through solids like a gas, and dissolve materials like a liquid. Supercritical fluids possess unique properties that enable them to extract components selectively from a mixture. This ability has been investigated as an alternative to currently used separation processes such as distillation or liquid extractions. In addition, close to the critical point, small changes in pressure or

temperature result in large changes in density, allowing many properties of a supercritical fluid to be "fine-tuned". Above the critical point, this increased density produces enhanced solvency, approaching that of a liquid. It is this solvency that makes SCF extraction a feasible alternative. Mass transfer properties resembling that of gases are also a significant factor in SCF extraction. An application of SCF extraction that has seemingly gone unexplored is to the drying of food products. Since moisture content influences texture, chemical reactions, and susceptibility to microbial spoilage, drying is a way to retain quality and prolong shelf life. A complication associated with drying of food products is that they may undergo changes that alter the physical or chemical structure, thus changing the integrity of the product. SCF extraction avoids this problem because it allows the food product to be dehydrated without undergoing a phase change from liquid water to water vapour. Also, if a solvent such as supercritical carbon dioxide is used, it will not be necessary to heat the product above ambient temperatures.

## 7. SELECTION OF DRYING EQUIPMENT

In view of the enormous choice of dryer types one could possibly deploy for most products, selection of the best type is a challenging task that should not be taken lightly. The first consideration in selecting a dryer is its operability. Above all else, the equipment must produce the desired product in the desired form at the desired rate. The quality required in a finished product, and its necessary physical characteristics, are determined by its end use. A wrong dryer for a given application is still a poor dryer, regardless of how well it is designed. Although variety of commercial dryers are available in the market, the different types mare largely complementary, not competitive, and the nature of the drying problem dictates the type of dryer that must be used, or at least limits the choice to perhaps two or three possibilities. The final choice is then made on the basis of capital and operating costs. Attention must be paid, however, to the costs of the entire drying system, not just the drying unit alone.

There are some general guidelines which need to be followed to select a dryer, but it should be recognized that the rules are far from rigid and exceptions not uncommon. Often batch dryers are used when the production rate of dried product is less than 150 to 200 kg/h, while continuous dryers are suitable for production rates greater than 1 or

2 tons/h. To handle intermediate production rates other factors must be considered.

The dryer must also operate reliably, safely, and economically. Operation and maintenance costs must not be excessive; pollution must be controlled; energy consumption must be minimized. As with other equipment these requirements may be conflict with one another and a compromise needs to be reached in finding the optimum dryer for a given service. As far as the drying operation itself is concerned, adiabatic dryers are generally less expensive than non-adiabatic dryers, in spite of the lower thermal efficiency of adiabatic units. Unfortunately there is usually a lot of dust carry over from adiabatic dryers, and these entrained particles must be removed from the drying gas. Elaborate particle-removal equipment may be needed, equipment that may cost as much as the dryer itself. This often makes adiabatic dryers less commercially attractive than a "buttoned-up" non-adiabatic system in which little or no gas is used.

## Lecture 3: DESIGN CONSIDERATION OF DRIERS

## 8. DESIGN OF DRYER

Design of a rotary dryer only on the basis of fundamental principle is very difficult. Few of correlations that are available for design may not prove to be satisfactory for many systems. The design of a rotary dryer is better done by using pilot plant test data and the full scale operating data of dryer of similar type if available, together with the available design equations. A fairly large number of variables are involved such as solid to be dried per hour, the inlet and exit moisture contents of the solid, the critical and equilibrium moisture contents, temperature and humidity of the drying gas. The design procedure based on the basic principles and available correlations is discussed below. In this case we assume that the solid has only unbound moisture and as shown in fig 2.7 in stage II the solid is at the wet bulb temperature of the gas.





- 1. Heat losses from dryer surfaces are neglected.
- Once the capacity of the dryer is known, the drying gas flow rate, its temperature and humidity are decided considering a number of factors. And the following moisture & enthalpy balances need to be satisfied.

Gs 
$$(Y_1 - Y_2) = Ms (X_1 - X_2)$$

$$Gs (Hg_2 - Hg_1) = Ms (H_{S2} - Hs_1)$$

Here,  $G_S$  = flow rate of air (dry basis, kg/h), Ms = flow rate of solid (kg/h, dry basis), H<sub>S</sub> = humidity of air (kg/H<sub>2</sub>O/kg dry air)

3. The gas and solid temperatures at the stage boundaries are obtained by moisture and energy (enthalpy) balances. The number of heat transfer unit for each zone is calculated. for the stage II. The number of heat transfer units is

given by

4. The total length of dryer is given by

 $L = (L_T)_1 (N_{tG})_1 + (L_T)_{II} (N_{tG})_{II} + (L_T)_{III} (N_{tG})_{III}$ 

5. The shell diameter is calculated from the dry gas flow rate (from step I) and suitable gas flow velocity or gas mass flow rate

Some useful correlations for the design of a rotary dryer are given below. Volumetric gas-solid heat transfer coefficient.

Here,  $G^{"}$  = gas mass flow rate (kg/m<sup>2</sup>.h) and d, dryer diameter

Length of transfer unit  $LT = G^{"}CH / \overline{U}_{a}$ 

Here, c<sub>H</sub> = average humid heat, and d = dryer diameter

**Example 2.1**: Size of the rotary dryer can be estimated for the following case. A moist non hygroscopic granular solid at  $26^{\circ}C$  is to be dried from 20% initial moisture to 0.3% final moisture in a rotary dryer at a rate of 1500 kg/h. The hot air enters the dryer at  $135^{\circ}C$  with a humidity of 0.015. With condition that the temperature of the solid leaving the dryer must not exceed  $110^{\circ}C$  and the air velocity must not exceed

1.5 m/s in order to avoid dust carry over.  $C_{ps} = 0.85$  kJ/kg.K. Recommend the diameter, length and other parameters of the dryer.

## Solution:

Basis of calculation is 1 hr operation

Solid contains 20% initial moisture

Moisture in the wet solid =  $X_1 = 20/80 = 0.25$ 

Moisture in the dry solid =  $X_2 = 0.3/99.7 = 0.00301$ 

Water evaporated, ms, evaporated = Ms  $(X_1 - X_2)$ 

= 1200 (0.25 - 0.00301) = 296.4 Kg

Given data:

 $\mathsf{T}_{\mathsf{S1}} = 26^{0}\mathsf{C}; \quad \mathsf{T}_{\mathsf{G2}} = 135^{0}\mathsf{C}; \quad \mathsf{Y}_{\mathsf{2}} = 0.015$ 

Let us assume that the exit temperature of the gas is  $T_{G1} = 60^{\circ}C$  and for solid  $T_{S2} =$ 

100<sup>0</sup>C

Now enthalpy of different streams (suppose ref temp =  $0^{\circ}$ C) H<sub>S1</sub> = [C<sub>PS</sub> + (4.187) X<sub>1</sub>] [T<sub>S1</sub> - 0]

= [0.85 + (4.187) 0.25] [26 - 0] = 49.31 KJ/kg dry air

 $H_{S2} = [C_{PS} + (4.187) X_1] [T_{S1} - 0]$ 

= [0.85 + (4.187) 0.0.00301] [100 - 0] = 86.2 KJ/kg dry solid

 $H_{g2} = [1.005 + (1.88) 0.015] [135 - 0] + (0.015) (2500) = 177 KJ/kg$ 

 $H_{g1} = [1.005 + (1.88) Y_1] [60 - 0] + Y_1 (2500) = 60.3 + 2613 Y_1$ 

Overall mass balance

GS  $(Y_1 - Y_2) = MS (X_1 - X_2)$  GS  $(Y_1 - Y_2) = 296.4$ 

 $\Longrightarrow$ 

 $G_S = 296.4/(Y_1 - 0.015)$ 

```
M_{S}[H_{S2} - H_{S1}] = G_{S}[H_{g2} - H_{g1}]
```

 $1200[86.2 - 49.31] = 296.4/(Y_1 - 0.015) \times (177 - 60.3 - 2613Y_1)$ 

 $Y_1 = 0.04306$  and  $G_S = 296.4/(Y_1 - 0.015) = 10560$  Kg/h

## **Shell Diameter**

Volume of humid inlet gas (135 $^{0}$ C and Y<sub>2</sub> = 0.015)

$$V_{H2} = 1.183 \text{ m}^3/\text{Kg} dry air$$

Volume of humid exit gas ( $60^{\circ}$ C and Y<sub>1</sub> = 0.04306)

The max. volumetric gas flow rate  $= G_S.V_{H2}$ 

$$= 10560 \times 1.183 = 12490 \text{ m}^3/\text{h}$$

The working velocity i.e. superficial velocity  $= 1.5 - 0.2 \times 1.5$ 

= 1.2 m/s 2 2 / 4 × d<sup>2</sup> (1.2) = d = 1.98 m, *say 2.0 m* 

## **Heat Transfer Unit**

Dryer is divided into three zones and therefore, the stage wise calculation of temperature and humidity of the stream can be obtained by material and energy balance.

Stage III

Very less water left for vaporization in stage III. Consider solid is at TSB, the wet bulb temperature of the air at location between III & II.

assume TSB = TSA = 
$$41^{\circ}$$
C

Enthalpy of solid at the inlet to stage III

H<sub>SB</sub> = [0.85 + (0.00301) (4.187)] (41-0)

= 35.37 KJ/kg dry solid

Humid heat of gas entering stage III

C<sub>HB</sub> = [1.005 + (1.88) (0.015)]

= 1.003 KJ/kg.K

Heat balance over stage III

Adiabatic saturation temperature of air entering stage II (129<sup>0</sup>C & humidity of 0.015)

is 41.3<sup>0</sup>C.

At the boundary B,  $\Delta T_B = 129 - 41 = 88^{\circ}C$  At end 2,

 $\Delta T_2 = 135 - 100 = 35^{\circ}C$ 

LMTD<sub>III</sub> =  $(\Delta T)_m$  = 88-35/ln(88/35) = 57.5<sup>0</sup>C (N<sub>tG</sub>)<sub>III</sub> = T<sub>2</sub> -T<sub>GB</sub>/( $\Delta T$ )<sub>m</sub> = 135 -129/57.5 = 0.104

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