

## CHAPTER III

### THEORY

#### 3.1 Fick's First Law of Diffusion [21]

Within binary isothermal system of species A, B Bird, Stewart and Lightfoot [22] proposed the definition of an unidirectional diffusion.

$$N_A = -cD_{AB} \frac{dX_A}{dZ} + X_A (N_A + N_B) \dots\dots\dots(3.1)$$

The diffusion flux  $N_A$ , relative to stationary coordinates, is the resultant of two vectors quantities.

The vector  $X_A (N_A + N_B)$  is the molar flux of A resulting from the bulk motion of fluid.

The vector  $-cD_{AB} dX_A / dZ$  is the molar flux of A resulting from the diffusion superimposed on the bulk flow.

The equation (3.1) is the general definition of diffusivity. If the substance A is slightly soluble,  $X_A (N_A + N_B)$  term is neglected.

$$N_A = -c D_{AB} \frac{dX_A}{dZ} \dots\dots\dots(3.2)$$

which is Fick's first law.

### 3.2 General Theories of Mass Transfer [23], [24], [25]

The various mass transfer mechanisms which have been postulated to fit experimental data are based on Fick's law for diffusion processes. Through Fick's first law, which is applicable for steady state conditions, the following relationship is obtained:

$$N' = k(c_s - c) \dots\dots\dots(3.3)$$

The assumption implicit in the use of the difference  $(c_s - c)$  as a driving force is that a saturation concentration always exists at the phase interface. Although this assumption is common in mass transfer work, it is not always valid. It is possible, where mass transfer rates are high, for the interface solute concentration to fall short of saturation. When this occurs, the driving force is not so great as the indicated difference  $c_s - c$ .

#### 3.2.1 The Laminar Film Theory or Two-Film Theory

The oldest of mass transfer theories is the laminar film theory due to Lewis and Whitman. (This theory recognizes the existence of the laminar layer, even in turbulent regime situations. Lewis and Whitman visualized that at the interface of two liquids, the turbulence loses its identity and a laminar sublayer exists on either side of the interface. As in the case when velocity adjacent to a solid surface becomes zero, they assumed that these fictitious layers are stationary for a moment,

during which time the transfer takes place under molecular mechanism.)

The rate constant  $k$  in Equation (3.3) can be interpreted as the ratio of molecular diffusivity to a stagnant film thickness:

$$k = D_v / \delta \dots\dots\dots(3.4)$$

This is the basic concept of the film theory. By this concept, mass transfer into or out of a moving fluid phase occurs by molecular diffusion through a thin film of stagnant fluid at the phase boundary. Mass transfer through the stagnant film is presumed to be slower by orders of magnitude than in the bulk phase and controls the overall single phase rate. As indicated in Equation (3.4), the rate of mass transfer is directly proportional to molecular diffusivity and diffusion is assumed to occur only in a direction perpendicular to the interface.

With the possible exception of mass transfer from spheres of solute suspended in a stagnant solvent, the film theory has never been totally adequate for any transfer process. One of its most serious limitations is that the mass transfer rate is presumed to be constant with time, which follows from Fick's first law. In many transfer processes of practical interest, the contact between phases occurs in a series of intermittent steps and mass transfer rates are functions of the effective contacting times. The penetration theory was developed as an improved model for mass transfer incorporating a correction for such unsteady state behavior.



### 3.2.2 The Penetration Theory

The Penetration Theory was introduced by Higbie. For discontinuous contact between phases he assumed:

- fresh fluid is brought to the phase boundary for each new contact.

- the fluid, during the period of contact, remains quiescent, and mass transfer occurs by molecular diffusion in a direction perpendicular to the interface.

- contacting occurs with a regular frequency, that is, the length of time that each new element of fluid remains in contact with the phase boundary is constant.

The mass transfer coefficient expressed in the relation of

$$k = 2(D_v/\pi t)^{1/2} \dots\dots\dots(3.5)$$

where  $t$  is contact time (t)

This theory is developed and improved by numerous authors such as Danckwert [26] and Harriott [27].

### 3.2.3 Danckwerts' Modification (Surface Renewal Theory)

Higbie assumed that every fluid element is brought to the interface and exposed to the gas for a short but constant period of time. During this period of time the fluid element

absorbs the same amount of gas. Danckwerts considered the Higbie's model unrealistic for the following two reasons:

- It specifies that all fluid elements spend the same length of time at the surface.

- It specifies the same rate of absorption for all fluid elements.

Danckwerts proposed that the fluid elements were exposed to the gas for varying lengths of time and he proposed infinite ranges of ages for these fluid elements and the average rates of mass transfer depends on the distribution of the elements of the fluids with different age group at the surface.

The mass transfer coefficient expressed in the relation of

$$k = (D_s)^{1/2} \dots\dots\dots(3.6)$$

Other theories of mass transfer coefficient are not mentioned here -i.e., Film-Penetration, Film-Surface Renewal and Boundary Layer Theory.

### 3.3 Definition of Mass Transfer Coefficient [29]

In the case of low flux transfer, the transfer coefficient is defined by the relation

$$dm = k dA \Delta c \dots\dots\dots(3.7)$$

$$\Delta c = c_s - c \dots\dots\dots(3.8)$$

- dm : quantity of dissolved mass per unit time (kg/s)
- k : mass transfer coefficient (m/s)
- dA : exchange area (m<sup>2</sup>)
- Δc : concentration difference (kg/m<sup>3</sup>)
- c<sub>s</sub> : the saturated concentration (kg/m<sup>3</sup>)
- c : concentration (kg/m<sup>3</sup>)

For isothermal system, the concentration c<sub>s</sub> is constant. On the other hand the liquid concentration per time is proportional to the mass of solid dissolved.

$$dm = V dc/dt \dots\dots\dots(3.9)$$

Substituting for dm in Equation (3.7).

$$kA(c_s - c) = V dc/dt \dots\dots\dots(3.10)$$

The term kA/V is constant. Integrating Equation (3.10) gives

$$\ln[(c_s - c)/(c_s - c_o)] = -kAt/V \dots\dots\dots(3.11)$$

or  $k = [V(c - c_o)] / (At \Delta c_{ML}) \dots\dots\dots(3.12)$

where  $\Delta c_{ML} = [(c_s - c_o) - (c_s - c)] / \ln[(c_s - c_o) / (c_s - c)]$   
 $= (c - c_o) / \ln[(c_s - c_o) / (c_s - c)]$



In Equation (3.12),  $V(c-c_0)/t$  is mass transfer rate  
Equation (3.12) becomes:

$$k = m/(A\Delta c_{ML}) \dots\dots\dots(3.13)$$

In Equation (3.13),  $k$  and  $A$  are mean values for the transfer coefficient and surface area, which are supposed constant for integration. In fact, the particle size varies during dissolution, but for this work these variations are slow and never exceeded 10 %.

#### 3.4 Flow Patterns [25]

Agitator are used to produce flow and, subsequently, turbulence in a liquid mass. Each type of agitator causes high velocity liquid to flow through a vessel in a specific path, referred to as a flow pattern. Flat and curved blade turbine, mixing low or moderate viscosity liquids, produce radial flow patterns when used in a baffle vessel. Radial flow, shown in Figure 3.1, is primarily perpendicular to the vessel wall. The marine type propeller and pitched blade turbine produce axial flow patterns when centered in a baffled vessel containing low or moderate viscosity liquids. Axial flow, shown in Figure 3.2, is primarily flow parallel to tank wall.



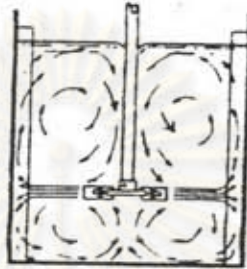
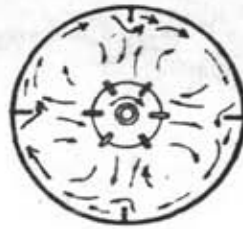


Figure 3.1 Radial flow pattern

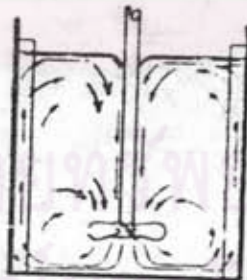


Figure 3.2 Axial flow pattern

If either the marine propeller or any of the impeller agitators are used in an unbaffled vessel containing low viscosity liquid, vortexing develops. The liquid swirls in the direction of the agitator rotating, causing a drop in liquid level around the agitator shaft. Vortexing increases with impeller speed until



eventually the vortex passes through the agitator. Gas bubbles will be sucked into the bulk fluid. The mixing efficiency of vortexing systems is usually lower than for geometrically similar nonvortexing systems. This can be avoided by putting baffles into the vessel. Baffles is fixed perpendicular to the vessel wall.

The basic principles which related fluid velocities and equipment geometry are applicable also to rotating impellers in agitated vessels.

### 3.5 Impeller Types [29], [30]

Impeller agitators are divided into two classes: these which generate currents parallel with the axis of the impeller shaft and those which generate currents in a tangential or radial direction. The first are called axial-flow impellers, the second radial-flow impellers.

The three main types of mixing impellers are turbines, propellers and paddles. Each type contains many variations and subtypes for specific purposes, which will not be considered here.

#### 3.5.1 Turbine Agitator

This type of agitator is used for vigorous mixing where high power inputs are necessary. Materials of construction are designed for acid, neutral or alkaline conditions. General applications are chemical reaction between liquids and solids, reagent mixing, neutralisation reactions and mineral surface conditioning. See Figure 3.3.

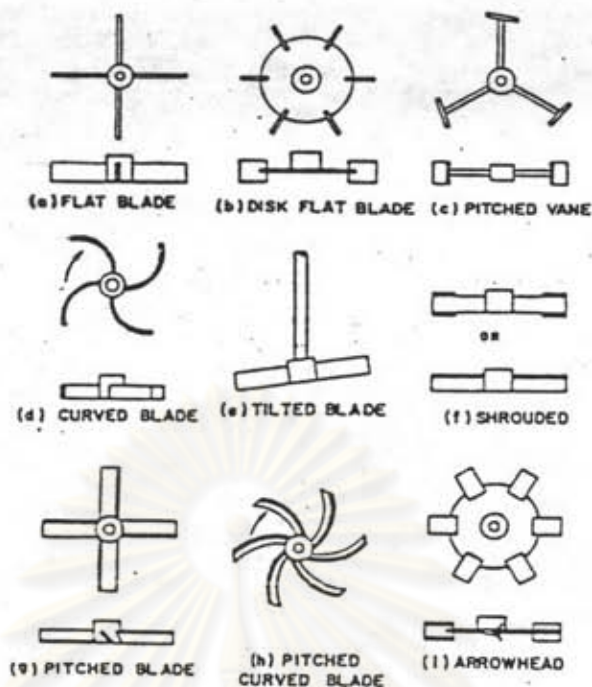


Figure 3.3 Turbine impeller designs

### 3.5.2 Propeller Agitator

This agitator is similar to the turbine type but for less vigorous mixing and lower horsepower input. General applications are slower chemical reactions, reagent mixing, reactions requiring aeration by the creation of a vortex. See Figure 3.4

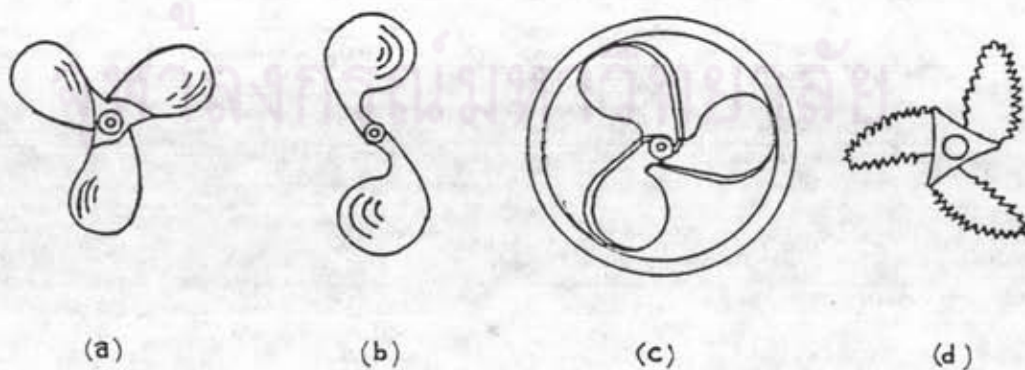


Figure 3.4 Mixing propellers: (a) Standard three-blade (b) Weedles (c) Guarded (d) Saw-toothed



### 3.5.3 Paddle Agitator

The paddle agitator is essentially a low horsepower input type with slow paddle speeds to maintain solids in suspension without necessarily maintaining a homogeneous pulp density. The paddle is relatively close to the bottom of the tank which makes this type ideal for pulp or liquid storage. Applications include the storage of solid-liquid suspensions such as lime slurries, flotation concentrates and pulps for intermittent or batch processes. See Figure 3.5.

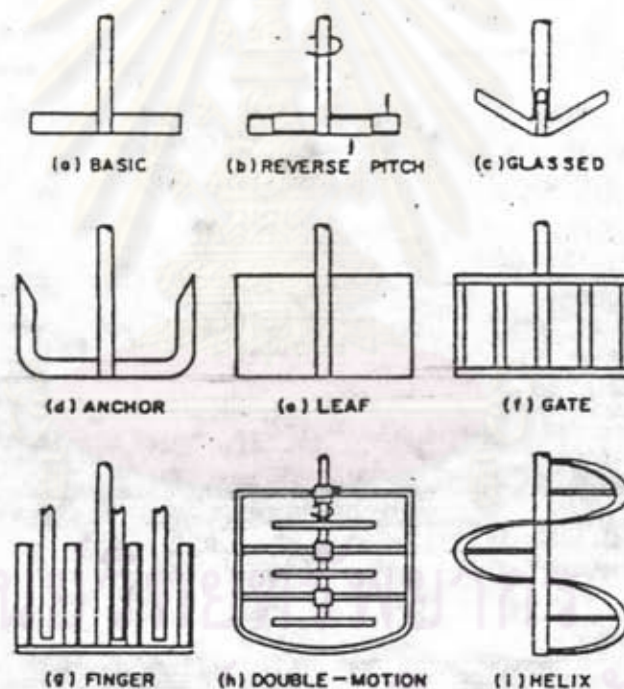


Figure 3.5 Paddle impeller designs

### 3.6 Standard Tank Configuration [31]

The vessel configuration, shown in Figure 3.6 are known as the Standard Tank Configuration. The Standard Tank Configuration has the following geometrical relationships:



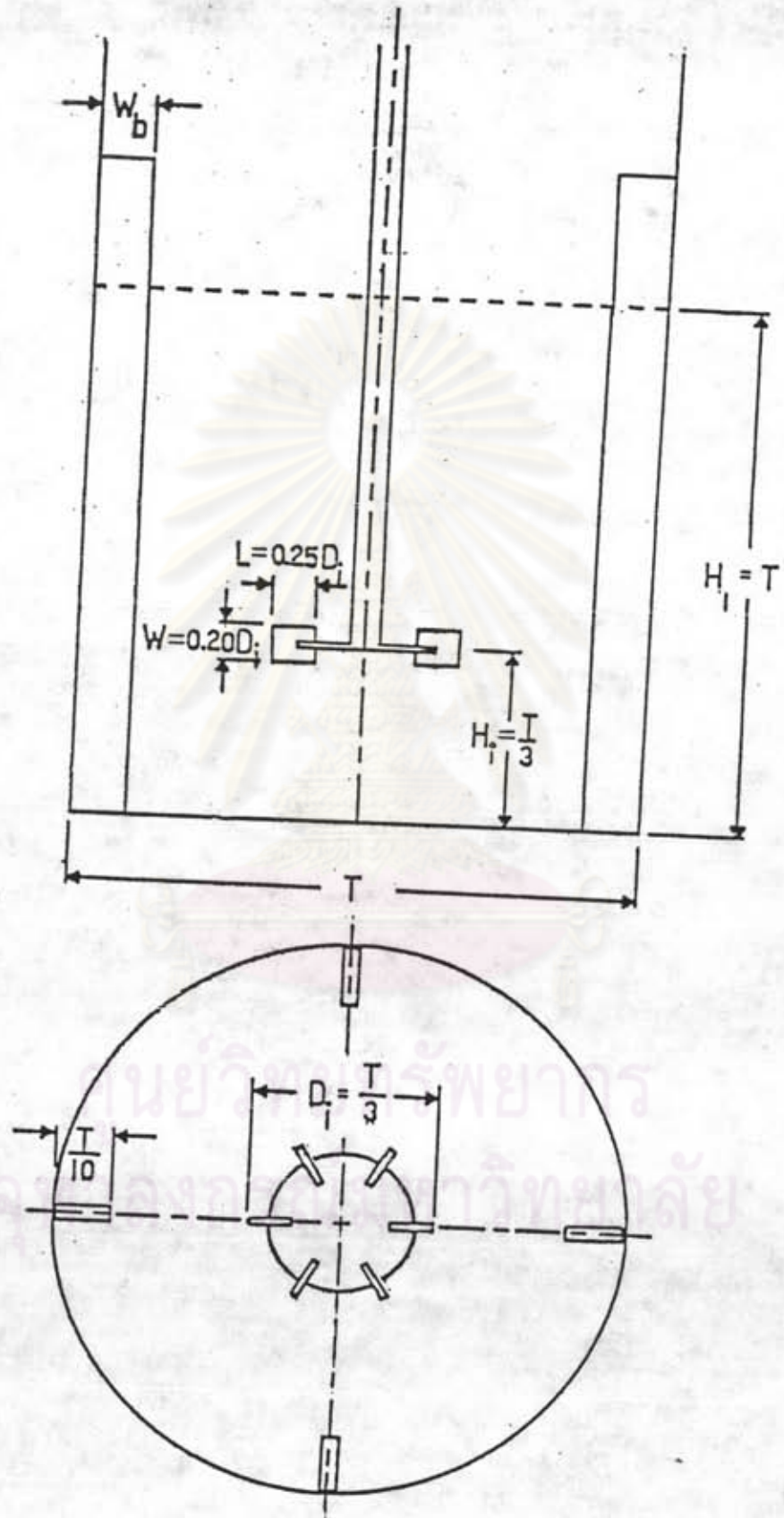


Figure 3.6 Standard tank configuration

1. The agitator is a standard six-bladed turbine (Figure 3.7).
2. Impeller diameter  $D_1 = 1/3$  tank diameter  $T$ .
3. Impeller height from the tank bottom  $H_1 = 1.0$  impeller diameter.
4. Impeller blade length  $L = 1/4$  impeller diameter.
5. Impeller blade width  $W = 1/5$  impeller diameter.
6. Liquid height  $H_1 = 1.0$  tank diameter.
7. Baffle number = 4, vertically mounted at the tank wall and extending from the tank bottom to above the liquid surface.
8. Baffle width  $W_b = 1/10$  tank diameter.

### 3.7 Solids Suspension [25]

Solid suspension is probably the most common application in mixing technology. The state of complete suspension of solid particles in liquid refers to the instant at which all solids are in circulation and none is resting on the vessel bottom. Suspension of solids in a liquid medium will be obtained when the rising velocity of the liquid phase equal or exceeds the settling velocity of the particles. Fluid velocity and direction are function of impeller selection and of vessel configuration. Particle settling velocity is a function of gravitation force, fluid drag, properties of solids (i.e. density, size, shape), solid concentration and several hindering factors such as density difference.

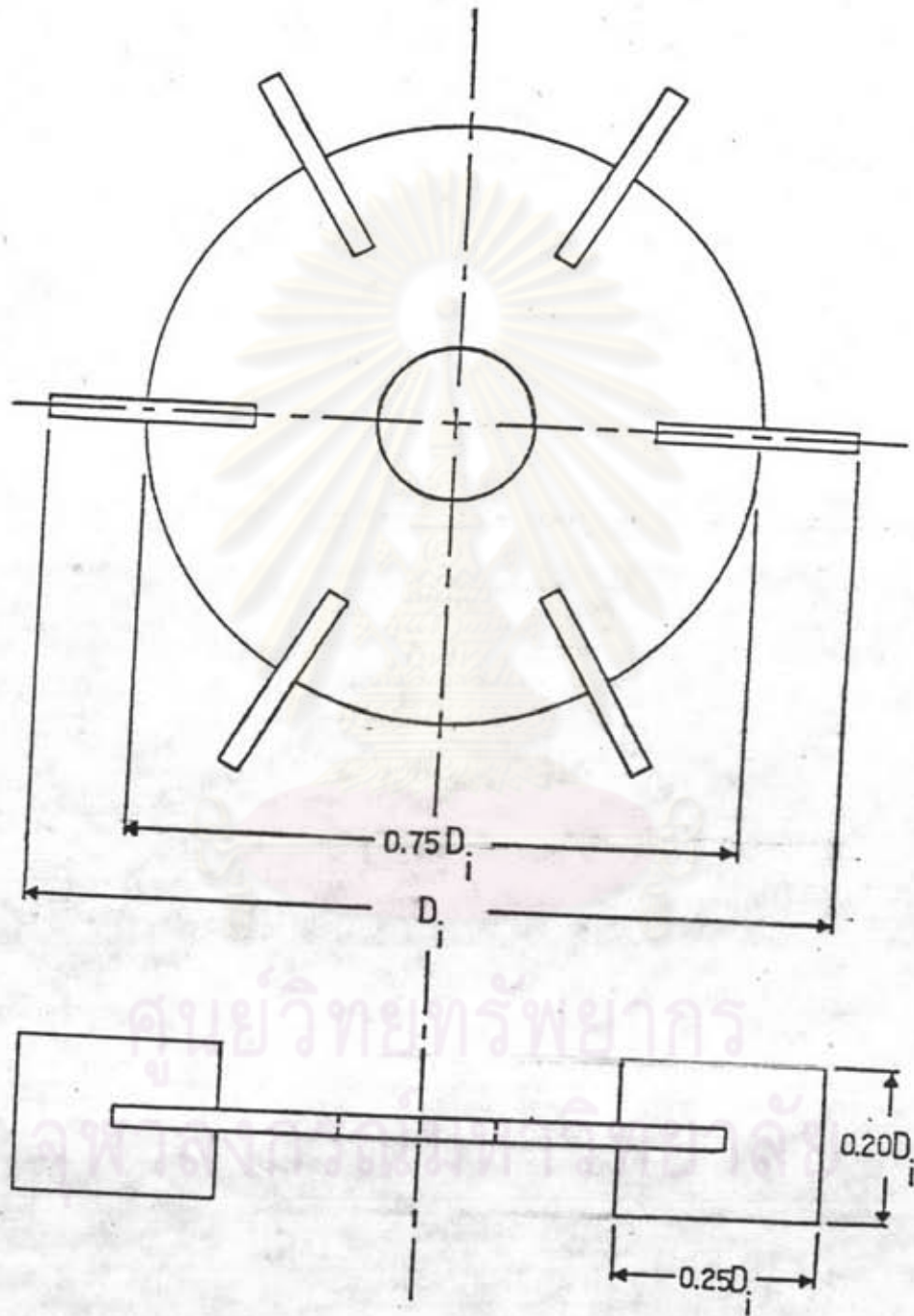


Figure 3.7 Standard six-bladed turbine



### 3.8 Solid-Liquid Mass Transfer

A study of solid-liquid mass transfer considers the effect of mixing on the surface area of the solids (which is often a minimal effect) and the effect of mixing on the fluid film around the solid particles.

Three major correlation methods have been tried by various investigators. One method, using dimensional analysis, usually takes the form:

$$kT/D_v = rRe_T^p Sc^q \dots\dots\dots(3.14)$$

where

$Re_T$  = Reynolds number referred to tank

$Sc$  = Schmidt number

Several investigators have tried using this equation in their correlations, but the constant  $r$  and exponents  $p$  and  $q$  vary with impeller type and system geometry. Therefore, other geometric ratios and groups are needed, as well as the functional relationships between correlating parameters.

A second method involves the particle Sherwood number  $kd_p/D_v$  as a function of particle Reynolds number and Schmidt number.

The third correlation method is based on the slip velocity and terminal velocity of the particle. In a reactor in which the solid particles are fully suspended, Harriott [18] shows

that the relative particle liquid velocity is related to, and is always greater than, the free-fall terminal velocity of the solid particles in static liquid.



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