2 Fluid Flow

INTRODUCTION

Fluid flow is an essential element of many pharmaceutical processes. The ability to propel fluids through pipes and to direct materials from one location to another is central to the successful manufacture of many products. Fluids (liquids and gases) are a form of matter that cannot achieve equilibrium under an applied shear stress but deform continuously, or flow, as long as the shear stress is applied.

Viscosity

Viscosity is a property that characterizes the flow behavior of a fluid, reflecting the resistance to the development of velocity gradients within the fluid. Its quantitative significance may be explained by reference to Figure 2.1. A fluid is contained between two parallel planes each of area A m^2 and distance h m apart. The upper plane is subjected to a shear force of F N and acquires a velocity of u m/sec relative to the lower plane. The shear stress, t, is F/A N/m^2. The velocity gradient or rate of shear is given by u/h or, more generally, by the differential coefficient du/dy, where y is a distance measured in a direction perpendicular to the direction of shear. Since this term is described by the units velocity divided by a length, it has the dimension T^{-1} or, in this example, reciprocal seconds. For gases, simple liquids, true solutions, and dilute disperse systems, the rate of shear is proportional to the shear stress. These systems are called Newtonian, and we can write

$$\frac{F}{A} = t = \eta \frac{du}{dy} \tag{2.1}$$

The proportionality constant η is the dynamic viscosity of the fluid: the higher its value, the lower the rates of shear induced by a given stress. The dimensions of dynamic viscosity are M L^{-1} T^{-1}. For the SI system of units, viscosity is expressed in N·sec/m^2. For the centimeter-gram-second (CGS) system, the unit of viscosity is poise (P). One N·sec/m^2 is equivalent to 10 P. The viscosity of water at room temperature is about 0.01 P or 1 centipoise (cP). Pure glycerin at this temperature has a value of about 14 P. Air has a viscosity of 180×10^{-6} P.

Complex disperse systems fail to show the proportionality described by equation (2.1), the viscosity increasing or, more commonly, decreasing with increase in the rate of shear. Viscosity may also depend on the duration of shear and even on the previous treatment of the fluids. Such fluids are termed non-Newtonian.

Equation (2.1) indicated that wherever a velocity gradient is induced within a fluid, a shear stress will result. When the flow of a fluid parallel to some boundary is considered, it is assumed that no slip occurs between the boundary and the fluid, so the fluid molecules adjacent to the surface are at rest ($u = 0$). As

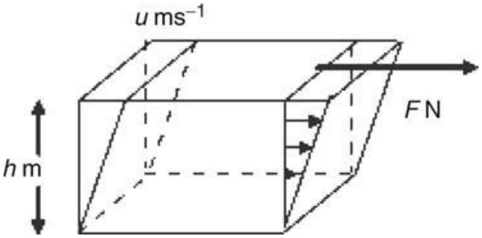


FIGURE 2.1 Schematic of fluid flow depicting the applied force, velocity in the direction of motion, and thickness of the fluid.

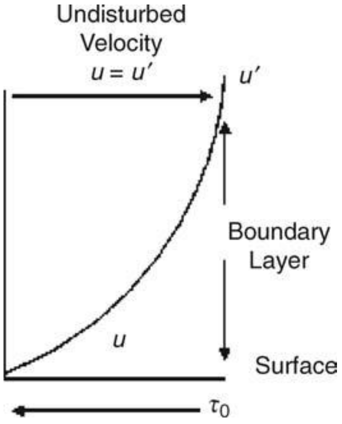


FIGURE 2.2 Distribution of velocities at a boundary layer.

shown in Figure 2.2, the velocity gradient du/dy decreases from a maximum at the boundary ($y = 0$) to zero at some distance from the boundary ($y = y'$) when the velocity becomes equal to the undisturbed velocity of the fluid ($u = u'$). The shear stress must, therefore, increase from zero at this point to a maximum at the boundary. A shear stress, opposing the motion of the fluid and sometimes called fluid friction, is therefore developed at the boundary. The region limited by the dimension y', in which flow of the fluid is perturbed by the boundary, is called the *boundary layer*. The structure of this layer greatly influences the rate at which heat is transferred from the boundary to the fluid under the influence of temperature gradient or the rate at which molecules diffuse from the boundary into the fluid under a concentration gradient. These topics are discussed in chapters 3 and 4.

Compressibility

Deformation is not only a shear-induced phenomenon. If the stress is applied normally and uniformly over all boundaries, then fluids, like solids, decrease in volume. This decrease in volume yields a proportionate increase in density. Liquids can be regarded as incompressible, and changes of density with pressure can be ignored, with consequent simplification of any analysis. This is not possible in the study of gases if significant changes in pressure occur.

Surface Tension

Surface tension, a property confined to a free surface and therefore not applicable to gases, is derived from unbalanced intermolecular forces near the surface of a liquid. This may be expressed as the work necessary to increase the surface by unit area. Although not normally important, it can become so if the free surface is present in a passage of small-diameter orifice or tube. Capillary forces, determined by the surface tension and the curvature of the surface, may then be comparable in magnitude to other forces acting in the fluid. An example is found in the movement of liquid through the interstices of a bed of porous solids during drying.

FLUIDS AT REST: HYDROSTATICS

The study of fluids at rest is based on two principles:

1. Pressure intensity at a point, expressed as force per unit area, is the same in all directions.
2. Pressure is the same at all points in a given horizontal line in a continuous fluid.

The pressure, P, varies with depth, z, in a manner expressed by the hydrostatic equation

$$dP = -\rho g \, dz \tag{2.2}$$

where ρ is the density of the fluid and g is the gravitational constant. Since water and most other liquids can be regarded as incompressible, the density is independent of the pressure, and integration between the limits P_1 and P_2, z_1 and z_2, gives

$$P_1 - P_2 = -\rho g(z_1 - z_2) \tag{2.3}$$

THE MEASURE OF PRESSURE INTENSITY

Application of equation (2.3) to the column of liquid shown in Figure 2.3A gives

$$P_\mathrm{A} - P_1 = -\rho g h$$

and

$$P_1 = P_\mathrm{A} + \rho g h \tag{2.4}$$

The density term should be the difference between the density of the liquid in the column and the density of the surrounding air. The latter is relatively small, and this discrepancy can be ignored. P_1 is the absolute pressure at the point indicated, and P_A is the atmospheric pressure. It is often convenient to refer to the pressure measured relative to atmospheric pressure, that is, $P_1 - P_\mathrm{A}$. This is called the gauge pressure and is equal to $\rho g h$. SI unit for pressure is $\mathrm{N/m^2}$. Alternatively, the gauge pressure can be expressed as the height or head of a static liquid that would produce pressure.

Figure 2.3A represents the simplest form of a manometer, a device widely used for the measurement of pressure. It consists of a vertical tube tapped into the container of the fluid being studied. In this form, it is confined to the

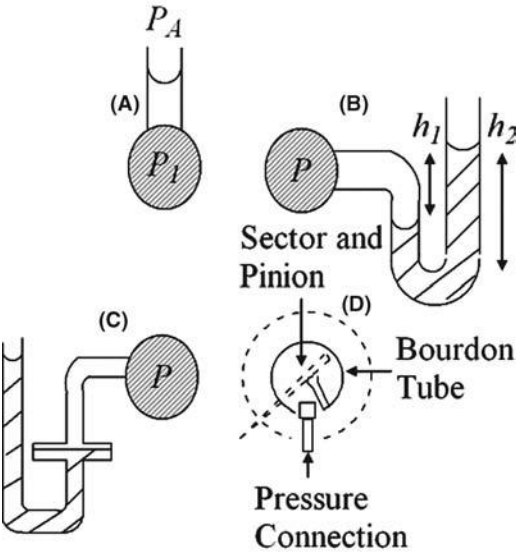


FIGURE 2.3 Pressure measurement apparatus **(A)** vertical; **(B)** U-tube; **(C)** modified U-tube manometers and **(D)** Bourdon gauge.

pressure measurement of liquids. This device is unsuitable for the measurement of very large heads, because of unwieldy construction, or very small heads, because of low accuracy. The U-tube manometer, shown in Figure 2.3B, may be used for the measurement of higher pressures with both liquids and gases. The density of the immiscible liquid in the U-tube, ρ_1, is greater than the density of the fluid in the container, ρ_2. The gauge pressure is given by

$$P = h_1\rho_1 g - h_2\rho_2 g$$

The disadvantage of reading two levels may be overcome by the modification in Figure 2.3C. The cross-sectional area of one limb is many times larger than that of the other, and the vertical movement of the heavier liquid in the wider arm can be neglected and its level is assumed to be constant.

Sloping the reading arm of the manometer can increase the accuracy of the pressure determination for small heads with any of the manometers just described. The head is now derived from the distance moved along the tube and the angle of the slope.

The Bourdon gauge, a compact instrument widely used for the measurement of pressure, differs in principle from the manometer. The fluid is admitted to a sealed tube of oval cross section, the shape of which is shown in Figure 2.3D. The straightening of the tube under internal pressure is opposed by its elasticity. The movement to an equilibrium position actuates a recording mechanism. The gauge is calibrated by an absolute method of pressure measurement.

The principles of pressure measurement also apply to fluids in motion. However, the presence of the meter should minimize perturbation in flow. A calming section, in which a flow regime becomes stable, is present upstream from the pressure tapping, and the edge of the latter should be flush with the inside of the container to prevent flow disturbance.

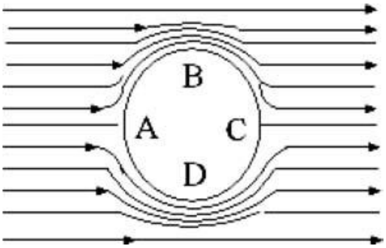


FIGURE 2.4 Flow of a fluid past a cylinder.

FLUIDS IN MOTION

Streamlines are hypothetical lines without width drawn parallel to all points to the motion of the fluid. Figure 2.4 illustrates their use in depicting the flow of a fluid past a cylinder. If the flow at any position does not vary with time, it is steady and the streamlines retain their shape. In steady flow, a change in the spacing of the streamlines indicates a change in velocity because, by definition, no fluid can cross a streamline. In the regions on the upstream side of the cylinder, the velocity of the fluid is increasing. On the downstream side, the reverse occurs. The maximum velocity occurs in the fluid adjacent to regions B and D. At points A and C, the fluid is at rest. As velocity increases, the pressure decreases. The pressure field around an object is the reverse of the velocity field. This may appear to contradict common experience. However, it follows from the principle of conservation of energy and finds expression in Bernoulli's theorem.

BERNOULLI'S THEOREM

At any point in system through which a fluid is flowing, the total mechanical energy can be expressed in terms of the potential energy, pressure energy, and kinetic energy. The potential energy of a body is its capacity to do work by reason of its position relative to some center of attraction. For unit mass of fluid at a height z above some reference level, potential energy $= zg$, where g is the acceleration due to gravity.

The pressure energy or flow energy is an energy form peculiar to the flow of fluids. The work done and the energy acquired in transferring the fluid is the product of the pressure, P, and the volume. The volume of unit mass of the fluid is the reciprocal of the density, ρ. For an incompressible fluid, the density is not dependent on the pressure, so for unit mass of fluid, pressure energy $= P/\rho$ (Fig. 2.5).

The kinetic energy is a form of energy possessed by a body by reason of its movement. If the mass of the body is m and its velocity is u, the kinetic energy is $1/2mu^2$, and for unit mass of fluid, kinetic energy $= u^2/2$.

The total mechanical energy of unit mass of fluid is, therefore,

$$\frac{u^2}{2} + \frac{P}{\rho} + zg$$

The mechanical energy at two points A and B will be the same if no energy is lost or gained by the system. Therefore, we can write

$$\frac{u_A^2}{2} + \frac{P_A}{\rho} + z_A g = \frac{u_B^2}{2} + \frac{P_B}{\rho} + z_B g \tag{2.5}$$

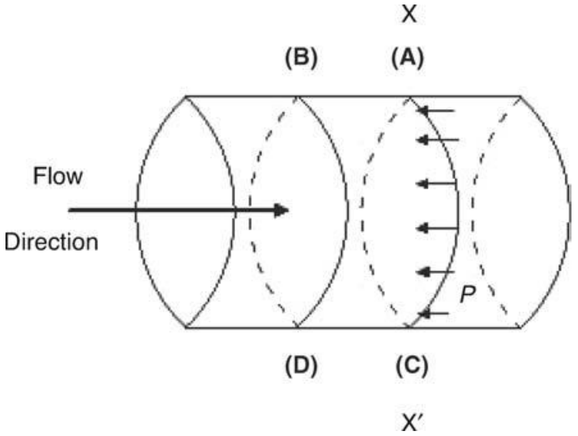


FIGURE 2.5 Pressure energy of a fluid.

This relationship neglects the frictional degradation of mechanical energy, which occurs in real systems. A fraction of the total energy is dissipated in overcoming the shear stresses induced by velocity gradients in the fluid. If the energy lost during flow between A and B is *E*, then equation (2.5) becomes

$$\frac{u_A^2}{2} + \frac{P_A}{\rho} + z_A = \frac{u_B^2}{2} + \frac{P_B}{\rho} + z_B + E \tag{2.6}$$

This is a form of Bernoulli's theorem, restricted in application to the flow of incompressible fluids. Each term is expressed in absolute units, such as N·m/kg. The dimensions are L^2T^{-2}. In practice, each term is divided by g (LT^{-2}) to give the dimension of length. The terms are then referred to as velocity head, pressure head, potential head, and friction head, the sum giving the total head of the fluid as shown in equation (2.2).

$$\frac{u_A^2}{2g} + \frac{P_A}{\rho g} + z_A = \frac{u_B^2}{2g} + \frac{P_B}{\rho g} + z_B + \frac{E}{g} \tag{2.7}$$

The evaluation of the kinetic energy term requires consideration of the variation in velocity found in the direction normal to flow. The mean velocity, calculated by dividing the volumetric flow by the cross-sectional area of the pipe, lies between 0.5 and 0.82 times the maximum velocity found at the pipe axis. The value depends on whether flow is laminar or turbulent, terms that are described later. The mean kinetic energy, given by the term $u^2{}_{\text{mean}}/2$ differs from the true kinetic energy found by summation across the flow direction. The former can be retained, however, if a correction factor, a, is introduced, then the

$$\text{velocity head} = \frac{u^2_{\text{mean}}}{2ga}$$

where a has a value of 0.5 in laminar flow and approaches unity when flow is fully turbulent.

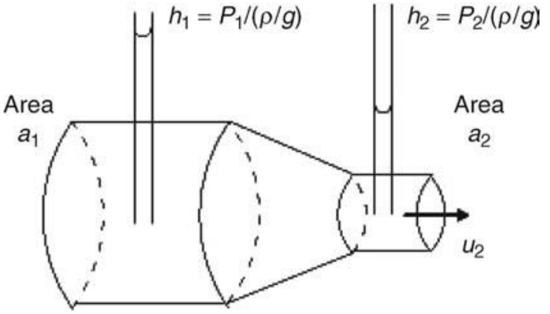


FIGURE 2.6 Flow through a constriction.

A second modification may be made to equation (2.5) if mechanical energy is added to the system at some point by means of a pump. If the work done, in absolute units, on a unit mass of fluid is W, then

$$\frac{W}{g} + \frac{u_A^2}{2g} + \frac{P_A}{\rho g} + z_A = \frac{u_B^2}{2g} + \frac{P_B}{\rho g} + z_B + \frac{E}{g} \tag{2.8}$$

The power required through a system at a certain rate to drive a liquid may be calculated using equation (2.8). The changes in velocity, pressure, height, and the mechanical losses due to friction are each expressed as a head of liquid. The sum of heads, ΔH, being the total head against which the pump must work, is therefore

$$\frac{W}{g} + \Delta H$$

If the work performed and energy acquired by unit mass of fluid is ΔHg, the power required to transfer mass m in time t is given by

$$\text{Power} = \frac{\Delta H g m}{t}$$

Since the volume flowing in unit time Q is $m/\rho t$,

$$\text{Power} = Q \Delta H g \rho \tag{2.9}$$

FLOW MEASUREMENT

The Bernoulli theorem can also be applied to the measurement of flow rate. Consider the passage of an incompressible fluid through the constriction shown in Figure 2.6. The increase in kinetic energy as the velocity increases from u_1 to u_2 is derived from the pressure energy of the fluid, the pressure of which drops from P_1 to P_2, the latter being recorded by manometers. There is no change in height, and equation (2.5) can be rearranged to give

$$\frac{u_2^2}{2} - \frac{u_1^2}{2} = \frac{P_1 - P_2}{\rho} \tag{2.10}$$

The volumetric flow rate $Q = u_1 a_1 = u_2 a_2$. Therefore, by rearrangement,

$$u_1 = u_2 \frac{a_2}{a_1}$$

Substituting for u_1 gives

$$\frac{u_2^2}{2} - \frac{u_2^2(a_2^2/a_1^2)}{2} = \frac{P_1 - P_2}{\rho}$$

and

$$\frac{u_2^2}{2}\left(1 - \frac{a_2^2}{a_1^2}\right) = \frac{P_1 - P_2}{\rho}$$

Therefore,

$$u_2 = \sqrt{\frac{2(P_1 - P_2)}{\rho(1 - a_2^2/a_1^2)}}$$

and

$$Q = a_2\sqrt{\frac{2(P_1 - P_2)}{\rho(1 - a_2^2/a_1^2)}}$$

This derivation neglects the correction of kinetic energy loss due to nonuniformity of flow in both cross sections and the frictional degradation of energy during passage through the constriction. This is corrected by the introduction of a numerical coefficient, C_D, known as the coefficient of discharge. Therefore,

$$Q = C_D a_2\sqrt{\frac{2(P_1 - P_2)}{\rho(1 - a_2^2/a_1^2)}} \qquad (2.11)$$

The value of C_D depends on conditions of flow and the shape of the constriction. For a well-shaped constriction (notably circular cross section), it would vary between 0.95 and 0.99 for turbulent flow. The value is much lower in laminar flow because the kinetic energy correction is larger. The return of the fluid to the original velocity by means of a diverging section forms a flow-measuring device known as a Venturi meter.

The Venturi meter is shown in Figure 2.7A. The converging cone leads to the narrowest cross section, known as the throat. The change in pressure is measured across this part of the meter and the volumetric flow rate is found by substitution into equation (2.11). Values of the coefficient of discharge are given in the preceding paragraph. The diverging section or diffuser is designed to induce a gradual return to the original velocity. This minimizes eddy formation in the diffuser and permits the recovery of a large proportion of the increased kinetic energy as pressure energy. The permanent loss of head due to friction in both converging and diverging sections is small. The meter is therefore efficient.

When the minimization of energy degradation is less important, the gradual, economic return to the original velocity may be abandoned, compensation for loss of efficiency being found in a device that is simpler, cheaper, and more adaptable than the Venturi meter. The orifice meter, to which this statement applies, consists simply of a plate with an orifice. A representation of flow through the meter is depicted in Figure 2.7B, indicating convergence of the fluid stream after passage through the orifice to give a cross section of minimum area called the *vena contracta*. The downstream pressure tapping is made at this cross

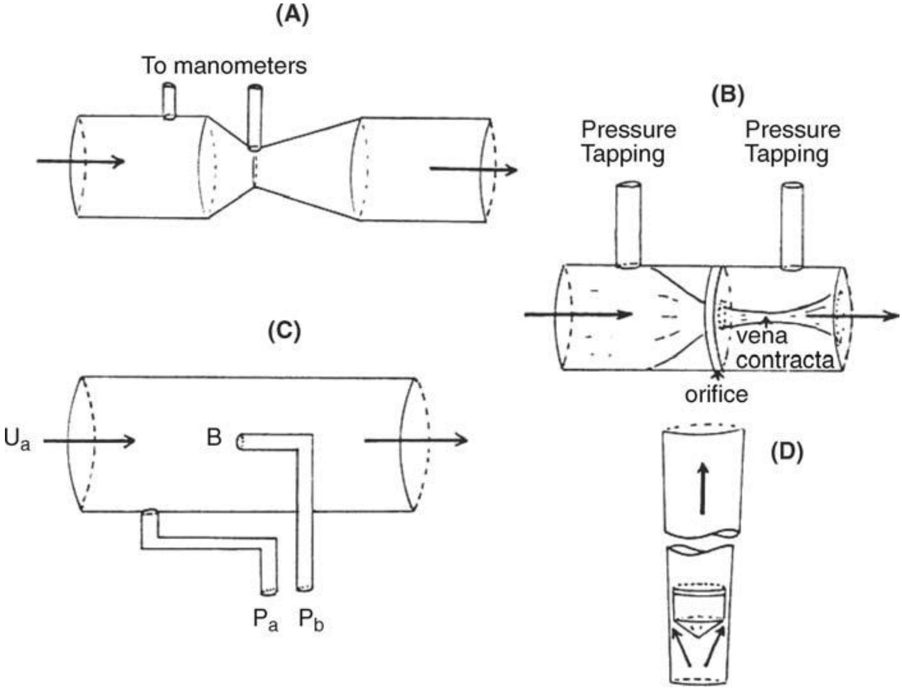


FIGURE 2.7 Flow meters: (**A**) Venturi meter, (**B**) orifice meter, (**C**) Pitot tube, and (**D**) rotameter.

section. The volumetric flow rate would be given by equation (2.6) for which a_2 is the jet area at the *vena contracta*. The measurement of this dimension is inconvenient. It is therefore related to the area of the orifice, a_0, which can be accurately measured by the coefficient of contraction, C_c, defined by the relation

$$C_c = \frac{a_2}{a_0}$$

The coefficient of contraction, frictional losses between the tapping points, and kinetic energy corrections are absorbed in the coefficient of discharge. The volumetric flow rate is then

$$Q = C_D a_0 \sqrt{\frac{2(P_1 - P_2)}{\rho\left(1 - \frac{a_0^2}{a_1^2}\right)}} \tag{2.12}$$

The term $[1 - (a_0^2/a_1^2)]$ approaches unity if the orifice is small compared to the pipe cross section. Since $P_1 - P_2 = \Delta h \rho g$, Δh being the difference in head developed by the orifice, equation (2.12) reduces to

$$Q = C_D\, a_0\, (2\Delta h g)^{1/2} \tag{2.13}$$

The value of C_D for the orifice meter is about 0.6, varying with construction, the ratio a_0/a_1, and flow conditions within the meter. Because of its complexity, it cannot be calculated. After passage through the orifice, flow disturbance during retardation causes the dissipation of most of the excess kinetic energy as heat. The permanent loss of heat is therefore high, increasing as the ratio of a_0/a_1 falls, ultimately reaching the differential head produced within the meter. When constructional requirements and methods of installation are followed, the correcting coefficients can be derived from charts. Alternatively, the meters can be calibrated.

The Bernoulli theorem may be used to determine the change in pressure caused by retardation of fluid at the upstream side of a body immersed in a fluid stream. This principle is applied in the *Pitot tube*, shown in Figure 2.7C. The fluid velocity is reduced from u_a, the velocity of the fluid filament in alignment with the tube, to zero at B, a position known as the stagnation point. The pressure, P_b, is measured at this point by the method shown in Figure 2.7C. The undisturbed pressure, P_a, is measured in this example with a tapping point in the wall connected to a manometer. Since the velocity at B is zero, equation (2.10) reduces to

$$\frac{u_a^2}{2} = \frac{P_b - P_a}{\rho}$$

and u_a can be calculated. Since only a local velocity is measured, variation of velocity in a section can be studied by altering the position of the tube. This procedure must be used if the flow rate in a pipe is to be measured. The mean velocity is derived from velocities measured at different distances from the wall. This derivation and the low pressure differential developed render the Pitot tube less accurate than either the Venturi tube or the orifice meter for flow measurement. However, the tube is small in comparison with the pipe diameter and therefore produces no appreciable loss of head.

The *rotameter* (a variable area meter), shown in Figure 2.7D, is commonly used, giving a direct flow rate reading by the position of a small float in a vertical, calibrated glass tube through which the fluid is flowing. The tube is internally tapered toward the lower end so that the annulus between float and wall varies with the position of the float. Acceleration of the fluid through the annulus produces a pressure differential across the position of the float and an upward force on it. At the equilibrium position, which may be stabilized by a slow rotation of the float, this upward force is balanced by the weight force acting on the float. If the equilibrium is disturbed by increasing the flow rate, the balance of weight force and the pressure differential are produced by movement of the float upward to a position at which the area of the annulus is bigger. For accurate measurement, the rotameter is calibrated with the fluid to be metered. Its use is, however, restricted to that fluid.

LAMINAR AND TURBULENT FLOWS

The translation of the energy of flow from one form to another has been described with little reference to the actual nature of flow. Flow of fluids can be laminar (and may be depicted by streamlines) or turbulent, terms that are best introduced by describing a series of simple experiments performed in 1883 by Osborne Reynolds. The apparatus, shown in Figure 2.8, consisted of a straight glass tube through which the fluid was allowed to flow. The nature of flow may be examined by introducing a dye into the axis of the tube. At low speeds, the dye forms a coherent thread, which grows very little in thickness with distance

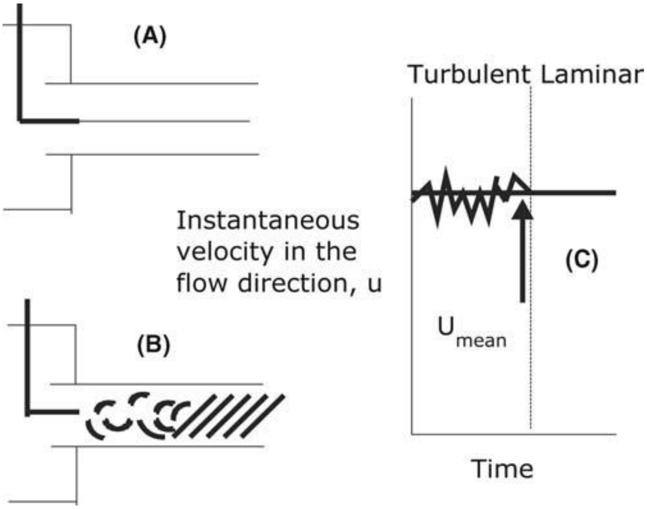


FIGURE 2.8 The Reynold's experiment **(A)** Laminar; **(B)** Turbulent and; **(C)** illustration of the use of a mean velocity for turbulent flow.

down the tube. However, with progressive increase in speed, the line of dye first began to waver and then break up. Secondary motions, crossing and recrossing the general flow direction, occur. Finally, at very high speeds, no filament of dye could be detected and mixing to a dilute color was almost instantaneous. In this experiment, flow changes from laminar to turbulent, the change occurring at a critical speed. Generalizing, in laminar flow, the instantaneous velocity at a point is always the same as the mean velocity in both magnitude and direction. In turbulent flow, order is lost and irregular motions are imposed on the main steady motion of the fluid. At any instant of time, the fluid velocity at a point varies both in magnitude and direction, having components perpendicular as well as parallel to the direction of net flow. Over a period of time, these fluctuations even out to give the net velocity in the direction of flow.

In turbulent flow, rapidly fluctuating velocities produce high-velocity gradients within the fluid. Proportionately large shear stresses are developed, and to overcome them, mechanical energy is degraded and dissipated in the form of heat. The degradation of energy in laminar flow is much smaller.

The random motions of turbulent flow provide a mechanism of momentum transfer not present in laminar flow. If a variation in velocity occurs across a fluid stream, as in a pipe, a quantity of fast-moving fluid can move across the flow direction to a slower-moving region, increasing the momentum of the latter. A corresponding movement must take place in the reverse direction elsewhere, and a complementary set of rotational movements, called an eddy, is imposed on the main flow. This is a powerful mechanism for equalizing momentum. By the same mechanism, any variation in the concentration of a component is quickly eliminated. Admitting dye to the fluid stream in Reynolds' original experiment showed this. Similarly, the gross mixing of turbulent flow quickly erases variations in temperature.

The turbulent mechanism that carries motion, heat, or matter from one part of the fluid to another is absent in laminar flow. The agency of momentum transfer is the shear stress arising from the variations in velocity, that is, the viscosity. Similarly, heat and matter can only be transferred across streamlines on a molecular scale, heat by conduction and matter by diffusion. These mechanisms, which are present but less important in turbulent flow, are comparatively slow. Velocity, temperature, and concentration gradients are, therefore, much higher than that in turbulent flow.

LIQUID FLOW IN PIPES

The many pharmaceutical processes that involve the transfer of a liquid confer great importance on the study of flow in pipes. This study permits the evaluation of pressure loss due to friction in a simple pipe and assesses the additional effects of pipe roughness, changes in diameter, bends, exists, and entrances. When the total pressure drop due to friction is known for the system, the equivalent head can be derived and the power requirement for driving a liquid through the system can be calculated from equation (2.14).

Streamline Flow in a Tube

The mathematical analysis of streamline flow in a simple tube results in the expression known as Poiseuille's law, one form of which is equation (2.14):

$$Q = \frac{\Delta P \pi d^4}{128 \eta l} \tag{2.14}$$

where Q is the volumetric flow rate or discharge, ΔP is the pressure drop across the tube, d and l are the diameter and length of the tube, respectively, and η is the viscosity of the fluid.

Whether flow in the tube is streamline or turbulent, an infinitesimally thin stationary layer is found at the wall. The velocity increases from zero at this point to a maximum at the axis of the tube. The velocity profile of streamline flow is shown in Figure 2.9A. The velocity gradient du/dr is seen to vary from a maximum at the wall to zero at the axis. In flow through a tube, the rate of shear is equal to the velocity gradient, and equation (2.1) dictates the same variation of shear stress.

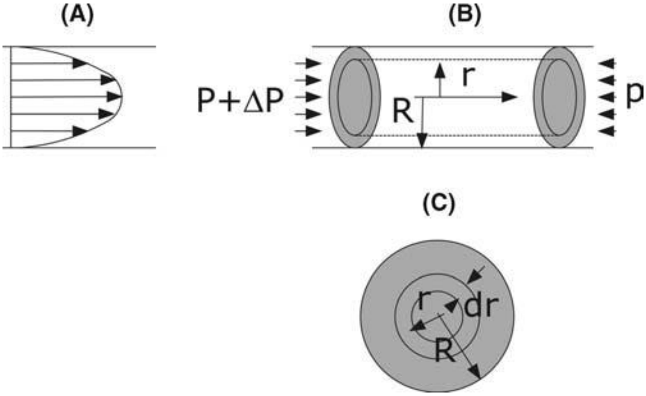


FIGURE 2.9 Streamline flow. **(A)** Velocity profile in a pipe; **(B)** longitudinal terms and **(C)** cross-sectional terms used to define flow properties.

To derive Poiseuille's law, the form of the velocity profile must first be established. For a fluid contained within a radius r flowing in a tube of radius R, this is shown in Figure 2.9B. If the pressure drop across length l is ΔP, the force attributed to the applied pressure driving this section is $\Delta P \pi r^2$. If the flow is steady, this force can only be balanced by opposing viscous forces acting on the "wall" of the section. This force, the product of the shear stress τ and the area over which it acts, is $2t\pi l$. The expression given by equating these forces is

$$\tau = \frac{\Delta P r}{2l}$$

Substituting from equation (2.1) gives

$$-\frac{du}{dr} = \frac{\Delta P r}{2\eta l}$$

The velocity gradient is negative because u decreases as r increases. When $r = R$, $u = 0$. Integration gives

$$\int_0^u du = \frac{\Delta P}{2\eta l}\int_R^r r \cdot dr$$

Therefore,

$$u = \frac{\Delta P}{2\eta l}\left(\frac{R^2 - r^2}{2}\right) \tag{2.15}$$

This relation shows that the velocity distribution across the tube is parabolic. For such a distribution, the maximum velocity is twice the mean velocity. The volumetric flow rate across an annular section between r and $(r + dr)$ shown in Figure 2.9C is

$$Q = 2\pi r \cdot dr \cdot r$$

Substituting for u from equation (2.15) gives

$$Q = \frac{\Delta P \pi}{2\eta l}(R^2 r - r^2) r \cdot dr$$

The total volumetric flow rate is the integral between the limits $r = R$ and $r = 0$:

$$Q = \frac{\Delta P \pi}{2\eta l}\int_0^R (R^2 r - r^3) dr = \frac{\Delta P \pi}{2\eta l} R^2 \left(\frac{r^2}{2} - \frac{r^4}{4}\right)_0^R$$

Therefore,

$$Q = \frac{\Delta P \pi R^4}{8\eta l} = \frac{\Delta P \pi d^4}{128\eta l}$$

which is equation (2.14), where d is the diameter of the tube. Since $Q = u_{\text{mean}}\pi(d^2/4)$, substitution and rearrangement gives

$$\Delta P = \frac{32 u_{\text{mean}} \eta l}{d^2} \tag{2.16}$$

Dimensional Analysis and Flow Through a Tube: A General Approach

The utility of equation (2.16) for evaluating the loss of pressure due to friction in a tube is limited because streamline conditions are rare in practice. The theoretical analysis of turbulent flow, however, is incomplete, and experiments with fluids are necessary for the development of satisfactory relations between the controlling variables, one in terms of the other, while other variables are temporarily held constant. Dimensional analysis is a procedure in which the interaction of variables is presented in such a way that the effect of each variable can be assessed.

The method is based on the requirement that the dimensions of all terms of a physically meaningful equation are the same, that is, an equation must be dimensionally homogeneous. This principle may be usefully illustrated by reference to equation (2.14) written in the form

$$Q \propto \frac{\Delta P d''}{\eta l}$$

Reviewing in basic units of mass, length, and time and using the symbol [ ] to represent dimension of $[Q] = [\mathrm{L}^3\mathrm{T}^{-1}]$, $[\Delta P] = [\mathrm{ML}^{-1}\mathrm{T}^{-2}]$, $[d^n] = [\mathrm{L}^n]$, and $[\eta] = [\mathrm{M\ L}^{-1}\mathrm{T}^{-1}]$, equating gives

$$[\mathrm{L}^3\mathrm{T}^{-2}] = \left[\frac{\mathrm{ML}^{-1}\mathrm{T}^{-2}\mathrm{L}^n}{\mathrm{ML}^{-1}\mathrm{T}^{-1}\mathrm{L}}\right] = [\mathrm{L}^{n-1}\mathrm{T}^{-1}]$$

[M] and [T] are correct, as they must be. Equating [L] gives $[\mathrm{L}^3] = [\mathrm{L}^{n-1}]$ from which $n = 4$.

If no previous knowledge of the combined form of the variable that determines Q is available, dimensional analysis can be applied in the following way. The dependence of Q on ΔP, l, d, and η can be written as

$$Q = f(\Delta P, l, d, \eta)$$

The function f can be expressed as a series, each term of which is the product of the independent variables raised to suitable powers. Taking the first term of the series gives

$$Q = N \cdot \Delta P^w \cdot L^x \cdot D^y \cdot \eta^z$$

where N is a numerical factor (dimensionless). Rewriting terms as $[Q] = [\mathrm{L}^3\mathrm{T}^{-1}]$, $[\Delta P^w] = [\mathrm{M}^w\mathrm{L}^{-w}\mathrm{T}^{-2w}]$, $[l^x] = [\mathrm{L}^x]$, $[d^y] = [\mathrm{L}^y]$, and $[\eta^z] = [\mathrm{M}^z\mathrm{L}^{-z}\mathrm{T}^{-z}]$, the equation $[Q] = [\Delta P^w{\cdot}l^x{\cdot}D^y{\cdot}\eta^z]$ becomes $[\mathrm{L}^3\mathrm{T}^{-1}] = [\mathrm{M}^w\mathrm{L}^{-w}\mathrm{T}^{-2w}{\cdot}\mathrm{L}^x{\cdot}\mathrm{L}^y{\cdot}\mathrm{M}^z\mathrm{L}^z\mathrm{T}^{-z}]$.

Equating powers of M, L, and T gives the following system:

M: $0 = w + z$
L: $3 = -w + x + y - z$
T: $-1 = -2w - z$

Since four unknowns are present in three simultaneous equations, three may be determined in terms of the fourth. Solving gives $w = l$, $z = -1$, and $x + y = 3$. Expressing y as $3 - x$, one gets

$$Q = N\frac{\Delta P}{\eta}d^{3-x}l^x = N\frac{\Delta P d^3}{\eta}\left(\frac{l}{d}\right)^x \tag{2.17}$$

The first part of the example demonstrates the use of dimensions as a partial check on the derivation or completeness of a solution. In the second part, a solution, although incomplete, gives considerable information about discharge of a fluid in streamline flow and its relation to pressure drop, viscosity, and the geometry of the pipe without any theoretical or experimental analysis. For example, if two tubes had the same ratio l/d, the values of $Q/\eta d^3 \Delta P$ would also be the same.

Since the exponent x in equation (2.17) is indeterminate, the term in brackets must be dimensionless. Unlike the lengths from which it is derived, it is a pure number and needs no system of units for meaningful expression. Its value is, therefore, independent of the units chosen for its measurement, provided, of course, that the systems of measurement are not mixed. The equation may, therefore, be presented as the relation between two dimensionless groups as

$$\frac{Q\eta}{d^3} = N\left(\frac{l}{d}\right)^x$$

or, since a series of power terms will, in general, form the original unknown function, each of which has different values of N and x,

$$\frac{Q\eta}{d^3 \Delta P} = f\left(\frac{1}{d}\right) \tag{2.18}$$

The study of frictional losses at the wall of a pipe is facilitated by dimensional analysis. The shear stress—that is, the force opposing motion of the fluid acting on each unit of area of the pipe, R—is determined for a given pipe surface by the velocity of the fluid, u, the diameter of pipe, d, the viscosity of the fluid, η, and the fluid density, ρ. The equation of dimensions is

$$[R] = [u^o\, d^q\, \eta^y\, \rho^s]$$

Therefore,

$$\mathrm{ML^{-1}T^{-2}} = \mathrm{L}^p\mathrm{T}^{-p} \cdot \mathrm{L}^q \cdot \mathrm{M}^1\mathrm{L}^{-r}\mathrm{T}^{-r} \cdot \mathrm{M}^s\mathrm{L}^{-3s}$$

Equating M, L, and T, one gets

M: $1 = r + s$
L: $-1 = p + q - r - 3s$
T: $-2 = -p - r$

Solving for p, r, and s in terms of q gives $r = -q$, $s = 1 + q$, and $p = 2 + q$. Therefore,

$$R = N \cdot u^{2+q} \cdot d^q \cdot \eta^{-q} \cdot \rho^{1+q} = N\, u^2 \left(\frac{ud\rho}{\eta}\right)$$

where N is a numerical factor. Generalizing, $R/\rho u^2$, which is the friction factor, is a function of a dimensionless combination of u, d, η, and ρ. This combination gives a parameter known as the Reynolds number, Re. Therefore,

$$\frac{R}{\rho u^2} = f(\mathrm{Re}) \tag{2.19}$$

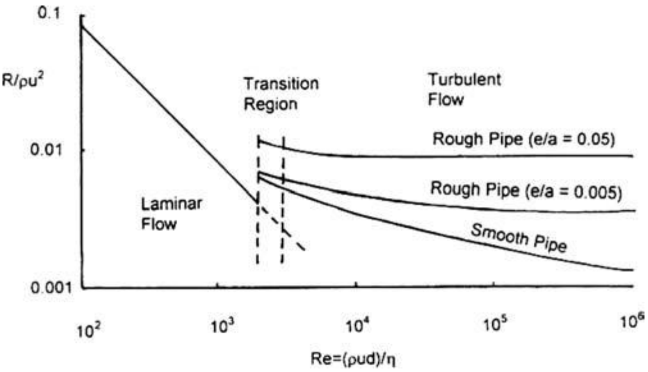


FIGURE 2.10 Pipe friction chart: $R/\rho\mu^2$ versus Reynolds number.

In turbulent flow, the shear stress at the wall depends on the surface, the value being higher for a rough pipe than for a smooth pipe when flow conditions are otherwise the same. Equation (2.19) therefore yields a family of curves when pipes are of differing dimensionless group, e/a, in which e is a linear dimension expressing roughness. Values of e are known for many materials.

The complete dimensionless correlation, plotted on logarithmic coordinates so that widely varying conditions are covered, is given in Figure 2.10. The curve can be divided into four regions. When Re < 2000, flow is streamline and the equation of the line in this region is $R/\rho u^2 = 8/\mathrm{Re}$. This is simply another form of Poiseuille's law. The friction factor is independent of the roughness of the pipe, and all data fall on a single line.

When Re lies between 2000 and 3000, flow normally becomes turbulent. The exact value of the transition depends on the idiosyncrasies of the system. For example, in a smooth pipe, streamline conditions will persist at higher Reynolds number than in a pipe in which disturbances are created by surface roughness.

At higher values of Re, flow becomes increasingly turbulent to give a region in which the friction factor is a function of Re and surface roughness. Ultimately, this merges with a region in which the friction factor is independent of Re. Flow is fully turbulent, and for a given surface, the shear stress at the pipe wall is proportional to the square of the fluid velocity. The onset of the fourth region occurs at a lower Re in rough pipes.

The essential difference between laminar flow and turbulent flow has already been described. In a pipe, the enhanced momentum transfer of the latter modifies the velocity distribution. In laminar flow, this distribution is parabolic. In turbulent flow, a much greater equalization of velocity occurs, the velocity profile becomes flatter, and high-velocity gradients are confined to a region quite close to the wall. In both cases, the boundary layer, the region in which flow is perturbed by the presence of the boundary, extends to the pipe axis and completely fills the tube. In laminar conditions, the structure of the layer is quite simple, layers of fluid sliding one over another in an orderly fashion. In turbulent flow, however, division can be made into three regimes: (*i*) the core of fluid, which is turbulent; (*ii*) a thin layer at the wall, which is a millimeter thick and where laminar conditions persist; this is called the laminar sublayer, and it is separated from the turbulent core by (iii) a buffer layer in which transition from turbulent flow to laminar flow occurs.

This description of the turbulent boundary layer applies generally to the flow of fluids over surfaces. The properties of this layer are central in many aspects of the flow of fluids. In addition, these properties determine the rate at which heat or mass is transferred to or from the boundary. These subjects are described in chapters 3 and 4.

THE SIGNIFICANCE OF REYNOLDS NUMBER, Re

In the Reynolds' experiment, described previously, progressive increase in velocity caused a change from laminar to turbulent flow. This change would also have occurred if the diameter of the tube was increased while maintaining the velocity or if the fluid was replaced by one of higher density. On the other hand, an increase in viscosity could promote a change in the opposite direction. Obviously, all these factors are simultaneously determining the nature of flow. These factors, which alone determine the character of flow, combine to give some value of Re. This indicates that the forces acting on some fluid element have a particular pattern. If some other geometrically similar system has the same Re, the fluid will be subject to the same force pattern.

More specifically, the Reynolds number describes the ratio of the inertia to viscous or frictional forces. The higher the Reynolds number, the greater is the relative contribution of inertial effects. At very low Re, viscous effects predominate and the contribution of inertial forces can be ignored. A clear example of the changing contribution of viscous and inertial or momentum effects and the resulting changes in the flow pattern is given in Figure 2.11. The Reynolds number can also characterize flow in this quite different system.

CALCULATION OF THE PRESSURE DROP IN A PIPE DUE TO FRICTION

If the volumetric flow rate of a liquid of density ρ and viscosity η through a pipe of diameter d is Q, the derivation of the mean velocity, u, from the flow rate and pipe area completes the data required for calculating Re. If the pipe roughness

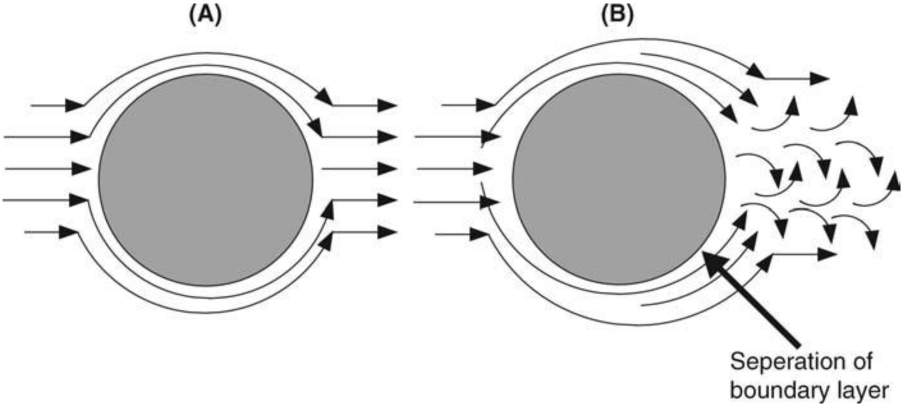


FIGURE 2.11 Flow of fluid past a cylinder **(A)** laminar and **(B)** turbulent.

factor is known, the equivalent value of $R/\rho u^2$ can be determined from Figure 2.10, and the shear stress at the pipe wall can be calculated. The total frictional force opposing motion is the product of R and the surface area of the pipe, πdl, where l is the length of the pipe. If the unknown pressure drop across the pipe is ΔP, the force driving through the pipe is $\Delta P \cdot \pi d^2/4$. Equating pressure force and frictional force gives

$$\Delta P \cdot \frac{\pi d^2}{4} = R\pi dl$$

Therefore,

$$\Delta P = \frac{4Rl}{d} \tag{2.20}$$

Division by ρg gives the pressure loss as a friction head. This form is used in equations (2.7) and (2.8).

FLOW IN TUBES IN NONCIRCULAR CROSS SECTION

Discussion of flow in pipes has been restricted to pipes of circular cross section. The previous exposition may be applied to turbulent flow in noncircular ducts by introducing a dimension equivalent to the diameter of a circular pipe. This is known as the mean hydraulic diameter, d_m, which is defined as four times the cross-sectional area divided by the wetted perimeter. A few examples are as follows:

For a square channel of side b,

$$d_m = \frac{4b^2}{4b} = b$$

For an annulus of outer radius r_1 and inner radius r_2,

$$\frac{4(\pi r_1^2 - \pi r_2^2)}{2\pi r_1 + 2\pi r_2} = 2(r_1 - r_2)$$

This simple modification does not apply to laminar flow in noncircular ducts.

FRICTIONAL LOSSES AT PIPE FITTINGS

Losses occur at the various fittings and valves used in practical systems in addition to the friction losses at the wall of a straight pipe. In general, these losses are derived from sudden changes in the magnitude or direction of flow induced by changes in geometry. They can be classified as loss due to a sudden contraction of enlargement, losses at entrance or exit, and loss due to pipe curvature. Losses can be conveniently expressed as a length of straight pipe offering the same resistance. This is usually in the form of a number of pipe diameters. For example, the loss at a right-angled elbow is equivalent to a length of straight pipe equal to 40 diameters. The sum of the equivalent lengths of all fittings and values is then added to the actual pipe length, and the total frictional loss is estimated by equation (2.20).

MOTION OF BODIES IN A FLUID

When a body moves relative to a fluid in which it is immersed, resistance to motion is encountered and a force must be exerted in the direction of relative body movement. The opposing drag force is made up from two components, viscous drag and form drag. This may be explained by reference to Figure 2.11, which describes the flow past a body, in this case, a cylinder with axis normal to the page, by means of streamlines. As mentioned, streamlines are hypothetical lines drawn tangential at all points to the motion of the fluid. Flow past the cylinder immobilizes the fluid layer in contact with the surface, and the induced velocity gradients result in shear stress or viscous drag on the surface. The crowding of streamlines on the upstream face of the cylinder, the flow pattern, and momentum changes on the downstream surface must be exactly reversed. This is shown in Figure 2.11A, and the entire force opposing relative motion of the cylinder and fluid is viscous drag. However, conditions of increasing pressure and decreasing velocity that exist on the downstream surface may cause the boundary layer to separate. The region between the breakaway streamlines—the wake—is occupied by eddies and vortices, and the flow pattern shown in Figure 2.11B is established. The kinetic energy of the accelerated fluid is dissipated and not recovered as pressure energy on the downstream surface. Under these conditions, there is a second component to the force opposing relative motion. This is known as form drag. Its contribution to the total drag increases as the velocity increases.

Once again, viscous and inertial forces are operating to determine the flow pattern and drag force on a body moving relative to a fluid. Reynolds number, which expresses their ratio, is used as a parameter to predict flow behavior. The relation between the drag force and its controlling variables is presented in a manner similar to that employed for flow in a pipe. If we consider a sphere moving relative to a fluid, the projected area normal to flow is $\pi d^2/4$, where d is the diameter of the sphere. The drag force acting on the unit projected area, R', is determined by the velocity, u, the viscosity, η, and the density, ρ, of the fluid, and the diameter of the sphere, d. Dimensional analysis yields the relation

$$\frac{R'}{\rho u^2} = f(\mathrm{R}e') = f\left(\frac{ud\rho}{\eta}\right) \tag{2.21}$$

The form of Reynolds number, Re$'$, employs the diameter of the sphere as the linear dimension. With the exception of an analysis at very low Reynolds numbers, the form of this function is established by experiment. Results are presented on logarithmic coordinates in Figure 2.12. When $\mathrm{Re}' \leq 0.2$, viscous forces are solely responsible for drag on the sphere and equation (2.21) is

$$\frac{R'}{\rho u^2} = \frac{12}{\mathrm{Re}'}$$

Therefore,

$$\text{Total drag force} = R' \cdot \frac{\pi d^2}{4} = \rho u_2 \cdot \frac{12}{\mathrm{R}e'} \cdot \frac{\pi d^2}{4} = 3\pi\eta du \tag{2.22}$$

This is the normal form of Stokes' law.

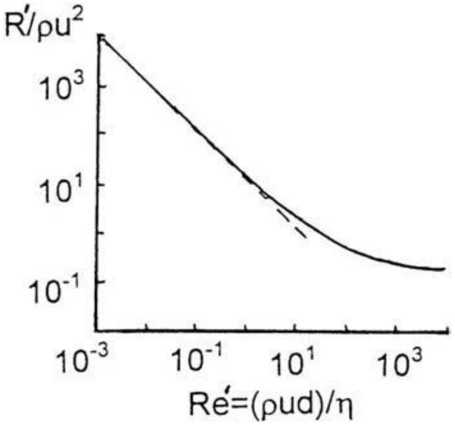


FIGURE 2.12 $R'/\rho\mu^2$ versus Reynolds number for a smooth sphere.

At larger Re′ values, the experimental curve progressively diverges from this relation, ultimately becoming independent of Re′ and giving a value of $R'/\rho u^2 = 0.22$. As Re′ increases, the form drag increases, ultimately becoming solely responsible for the force opposing motion.

For nonspherical particles, the analysis employs the diameter of a sphere of equivalent volume. A correction factor, which depends on the shape of the body and its orientation in the fluid, must be applied.

An important application of this analysis is the estimation of the speed at which particles settle in a fluid. Under the action of gravity, the particle accelerates until the weight force, mg, is exactly balanced by the opposing drag. The body then falls at a constant terminal velocity, u. Equating weight and drag forces gives

$$mg = \frac{\pi}{6} d^3 (\rho_s - \rho) g = R' \cdot \frac{\pi d^2}{4} \tag{2.23}$$

where ρ is the density of the particle.

For a sphere falling under streamline conditions ($\mathrm{Re}' < 0.2$), $R' = \rho u^2 \cdot 12/\mathrm{Re}'$. Substituting in equation (2.23), we obtain

$$u = \frac{d^2 (\rho_s - \rho) g}{18\eta} \tag{2.24}$$

This expression follows more simply from the equation $mg - 3\pi d\eta u$.

FLOW OF FLUIDS THROUGH PACKED BEDS

Fluid flow analysis through a permeable bed of solids is widely applied in filtration, leaching, and several other processes. A first approach may be made by assuming that the interstices of the bed correspond to a large number of discrete, parallel capillaries. If the flow is streamline, the volumetric flow rate, Q, is given for a single capillary by equation (2.14),

$$Q = \frac{\Delta P \pi d^4}{128 \eta l}$$

where l is the length of the capillary, d, its diameter, ΔP is the pressure drop across the capillary, and η is the viscosity of the fluid. The length of the capillary exceeds the depth of the bed of an amount that depends on its tortuosity. The depth of bed, L, is, however, proportional to the capillary length, l, so

$$Q = \frac{\Delta P d^4}{k\eta L}$$

where k is a constant for a particular bed. If the area of the bed is A and it contains n capillaries per unit area, the total flow rate is given by

$$Q = \frac{\Delta P d^4 n A}{k\eta L}$$

Both n and d are not normally known. However, they have certain values for a given bed, so

$$Q = KA\frac{\Delta P}{\eta L} \tag{2.25}$$

where $K = d^4 n/k$. This constant is a permeability coefficient, and $1/K$ is the specific resistance. Its value characterizes a particular bed.

The postulate of discrete capillaries precludes valid comment on the factors that determine the permeability coefficient. Channels are not discrete but are interconnected in a random manner. Nevertheless, the resistance to the passage of fluid must depend on the number and dimensions of the channels. These quantities can be expressed in terms of the fraction of the bed that is void—that is, the porosity—and the manner in which the void fraction is distributed. With reference to a specific example, water would flow more easily through a bed with a porosity of 40% than through a bed of the same material with a porosity of 25%. It would also flow more quickly through a bed of coarse particles than through a bed of fine particles packed to the void fraction or porosity. The latter effect can be expressed in terms of the surface area offered to the fluid by the bed. This property is inversely proportional to the size of the particles forming the bed. Permeability increases as the porosity increases and the total surface of the bed decreases, and these factors may be combined to give the hydraulic diameter, d', of an equivalent channel, defined by

$$d' = \frac{\text{Volume of voids}}{\text{Total surface of material forming bed}}$$

The volume of voids is the porosity, and the volume of solids is $1 - \varepsilon$. If the specific surface area, that is, the surface area of unit volume of solids, is S_0, the total surface presented by unit volume of the bed is $S_0(1 - \varepsilon)$. Therefore,

$$d' = \frac{\varepsilon}{S_0(1-\varepsilon)} \tag{2.26}$$

Under laminar flow conditions, the rate at which a fluid flows through this equivalent channel is given by equation (2.14) as

$$Q = \frac{\Delta P d'^4}{k\eta L}$$

The velocity, u', in the channel is derived by dividing the volumetric flow rate by the area of the channel, $k'd'^2$. Combining the constants produces,

$$u' = \frac{Q}{k'd'^2} = \frac{\Delta P d'^2}{k''\eta L}$$

This velocity, when averaged over the entire area of the bed, solids, and voids, gives the lower value, u. These velocities are related by the equation $u = u'\varepsilon$. Therefore,

$$\frac{u}{\varepsilon} = \frac{\Delta P d'^2}{k''\eta L}$$

Substituting for d' by means of equation (2.26) gives

$$\frac{u}{\varepsilon} = \frac{\Delta P}{k''\eta L} \frac{\varepsilon^2}{(1-\varepsilon)^2 S_0^2}$$

and

$$u = \frac{\Delta P}{k''\eta L} \cdot \frac{\varepsilon^3}{(1-\varepsilon)^2 S_0^2} \tag{2.27}$$

In this equation, known after its originator as Kozeny's equation, the constant k'' has a value of 5 ± 0.5. Since $Q = uA$, where A is the area of the bed, equation (2.27) can be transformed to

$$Q = \frac{\Delta P A}{\eta L} \cdot \frac{\varepsilon^3}{5(1-\varepsilon)^2 S_0^2} \tag{2.28}$$

This analysis shows that permeability is a complex function of porosity and surface area, the latter being determined by the size distribution and shape of the particles. The appearance of specific surface in equation (2.28) offers a method for its measurement and provides the basis of fluid permeation methods of size analysis. This equation also applies to the studies of filtration.

PUMPS

Equations (2.8) and (2.9) examined the power requirement for driving a liquid through a system against an opposing head. This energy is normally added by a pump. In different processes, the quantities to be delivered, the opposing head, and the nature of the fluid vary widely, and many pumps are made to meet these differing requirements. Basically, however, pumps can be divided into positive displacement pumps, which may be reciprocating or rotary, and impeller pumps. Positive displacement pumps displace a fixed volume of fluid with each stroke or revolution. Impeller pumps, on the other hand, impart high kinetic energy to the fluid, which is subsequently converted to pressure energy. The volume discharged depends on the opposing head.

Equipment for pumping gases and liquids is essentially similar. Machines delivering gases are commonly called compressors or blowers. Compressors discharge at relatively high pressures, and blowers, at relatively low pressures. The lower density and viscosity of gases lead to the use of higher operating speeds and, to minimize leakage, smaller clearance between moving parts.

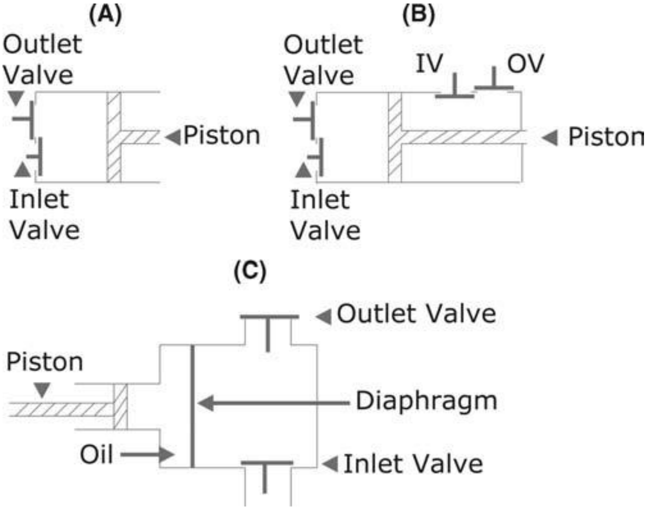


FIGURE 2.13 Positive displacement pumps **(A)** Reciprocating Piston; **(B)** Double Acting Piston and **(C)** Diaphragm pumps.

Positive Displacement Pumps

Positive displacement pumps are most commonly used for the discharge of relatively small quantities of fluid against relatively large heads. The small clearance between moving parts precludes the pumping of abrasive slurries.

The single-acting piston pump in Figure 2.13A exemplifies the reciprocating pump. The fluid is drawn into a cylinder through an inlet valve by movement of the piston to the right. The stroke in the opposite direction drives fluid through the outlet valve. Leakage past the piston may be prevented by rings or packing. Cessation of pumping on the return stroke is overcome in the double-acting piston pump by utilizing the volume on both sides of the piston. Fluid is drawn in on one side by a stroke that delivers the fluid on the other (Fig. 2.13B). In both pumps, delivery fluctuates. Operation, however, is simple, and both are efficient under widely varying conditions. The principle is widely used in gas compressors. In pumping liquids, no priming is necessary because the pump will effectively discharge air present in the pump or feed lines.

A modification, known as the diaphragm pump, is constructed so that reciprocating parts do not contact the pumped liquid (Fig. 2.13C). A flexible disk, fixed at the periphery, expands and contracts the pumping chamber, drawing in and discharging liquid through valves.

Rotary positive displacement pumps operate, presenting an expanding chamber to the fluid that is then sealed and conveyed to the outlet. Both liquids and gases are discharged so that priming is not necessary. The principle is illustrated in Figure 2.14, which describes a gear pump, a lobe pump, and a vane pump. In the gear pump, the liquid is conveyed in the spaces formed between a case and the consecutive teeth of two gears that intermesh at the center of the pump to prevent the return of the liquid to the inlet. The lobe pump, widely used as a liquid pump and as a blower, operates in a similar manner. Each impeller carries two or three lobes that interact with very small clearance to convey fluid from inlet to outlet.

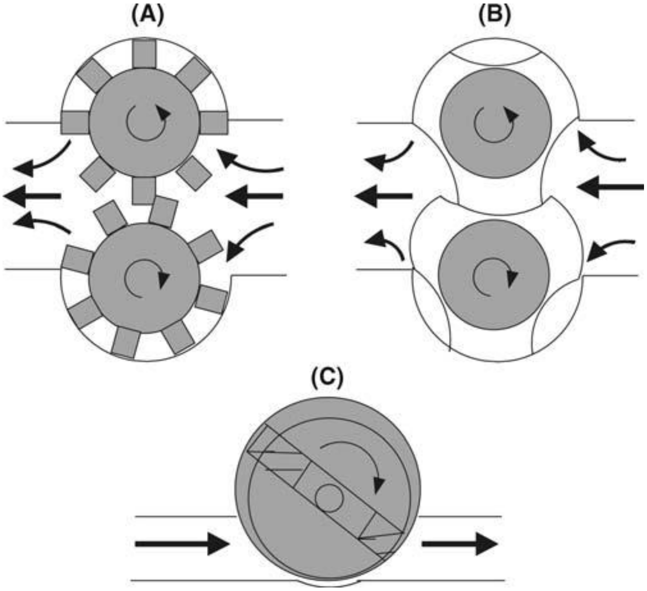


FIGURE 2.14 Rotary Pumps: **(A)** Gear; **(B)** Lobe; and **(C)** Vane.

Sliding vanes, mounted in the surface of an off-center rotor but maintained in contact with the case by centrifugal force or spring loading, provide the pumping action of the vane pump. Fluid is drawn into the chamber created by two vanes at the inlet. The fluid is rotated and expelled by contraction at the outlet. Besides liquid pumping, the principle of the vane pump is used in blowers and, by evacuating at the inlet and discharging to atmosphere at the outlet, in vacuum pumps.

The Mono pump consists of a stator in the form of a double internal helix and a single helical rotor. The latter maintains a constant seal across the stator, and this seal travels continuously through the pump. The pump is suitable for viscous and nonviscous liquids. The stator is commonly made of a rubber or similar material, so slurries are effectively delivered. Discharge is nonpulsating and can be made against very high pressures. The pump is commonly used to drive clarifying and cake filters.

Centrifugal Impeller Pumps

The centrifugal impeller pump is the type most widely used in the chemical industry. The impeller consists of a number of vanes, usually curved backward from the direction of rotation. The vanes may be open or, more commonly, closed between one or two supporting plates. This reduces swirl and increases efficiency. The impeller is rotated at high speeds, imparting radial and tangential momenta to a liquid that is fed axially to the center and that spirals through the impeller. In the simple volute pump (Fig. 2.15A), the liquid is received into a volute chamber. The cross section increases toward the tangential outlet. The liquid, therefore, decelerates, allowing a conversion of kinetic energy to pressure energy. In

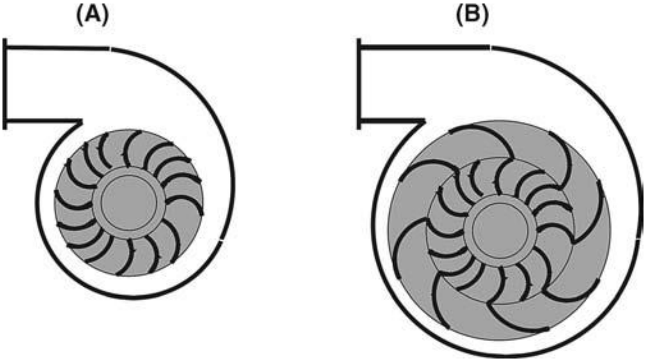


FIGURE 2.15 Centrifugal Impeller Pumps: **(A)** Volute and **(B)** Diffuser.

the diffuser pump, correctly aligned blades of a diffusing ring over which the fluid velocity decreases smoothly receive the liquid from the impeller, and the pressure rises. Flow through a diffuser pump is described in Figure 2.15B.

Because of the less precise control of the direction of the liquid leaving the impeller, the volute pump is less efficient than the diffuser pump. However, it is more easily fabricated in corrosion-resistant materials and is more commonly used. The pump, which is compact and without valves, may be used to pump slurries and corrosive liquid, steadily delivering large volumes against moderately large heads. For large heads, pumps are used in series. Unlike positive displacement pumps, impeller pumps continue to operate if the delivery line is closed, the kinetic energy of the liquid being degraded to heat.

A disadvantage of the centrifugal pump is that the conditions under which a pump of given size will operate with high efficiency are limited. The relation between the quantity discharged and the opposing head for a volute pump operating at a given speed is shown in Figure 2.16. As the head increases, the

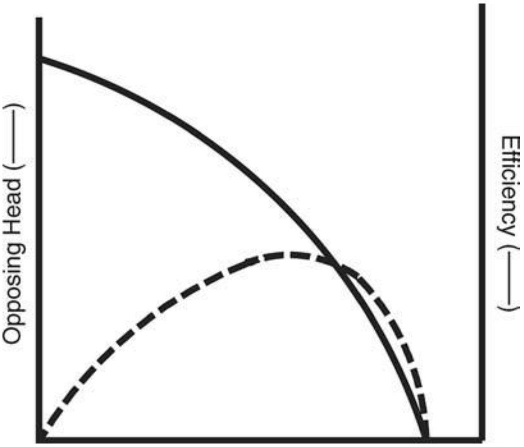


FIGURE 2.16 Performance curve of a volute pump running at fixed speed.

quantity discharged decreases. The mechanical efficiency of the pump is the ratio of the power acquired by the liquid, given by equation (2.9), to the power input. A maximum value is shown in Figure 2.16, indicating optimal operating conditions. The effect on the efficiency when the pump operates at other conditions can be seen from the figure, and to achieve reasonable operating efficiency for a given discharge and opposing head, a pump of suitable size and operating speed must be used.

A second disadvantage of the centrifugal pump lies in priming. If the pump contains air alone, the low kinetic energy imparted by the impeller creates a very small pressure increase across the pump, and liquid is neither drawn into the pump nor discharged. To begin pumping, the impeller must be primed with the liquid to be pumped. Where possible, the pump is placed below the level of the supply. Alternatively, a nonreturn valve could be placed on the suction side of the pump to prevent draining when rotation ceases.

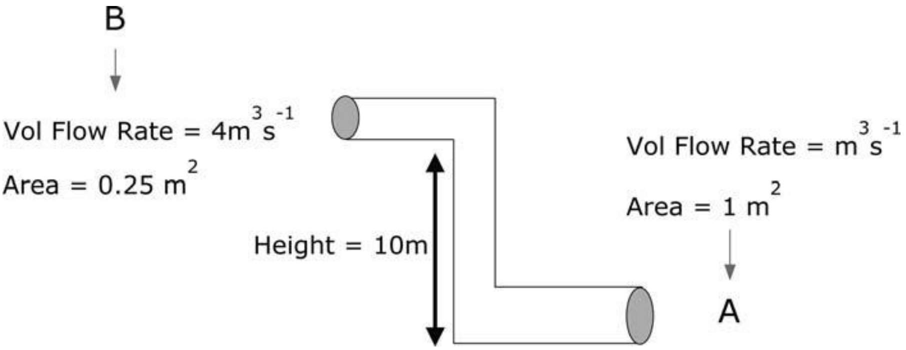
The same principle is employed in centrifugal fans and blowers used to displace large quantities of air and other gases. The gas enters the impeller axially and is moved outward into a scroll. The opposing static head is usually small, and energy appears mainly as the kinetic energy of the moving gas stream.

Other Impeller Pumps

The propeller pump, exemplified by a domestic fan, is used to deliver large quantities of fluids against low heads. These conditions are common in recirculation systems. The principle is also employed in fans used for ventilation, the supply of air for drying, and other similar operations.

Example 1

In the figure, what is the energy loss due to pressure?



Using Bernoulli's equation, we obtain

$$\frac{u_A^2}{2g} + \frac{P_A}{\rho g} + z_A = \frac{u_B^2}{2g} + \frac{P_B}{\rho g} + z_B + \frac{E}{g}$$

Calculate the velocity head and potential head at points A and B.

Velocity head at A is

$$\frac{(4\ \mathrm{m^3/sec})/1\ \mathrm{m^2}}{2(9.8\ \mathrm{m/sec^2})} = 0.82\,\mathrm{m}$$

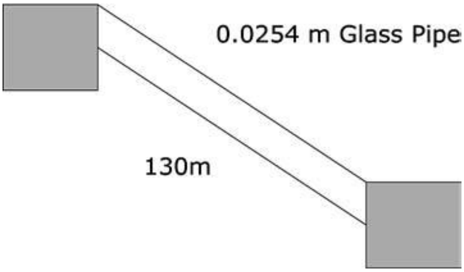
Velocity head at B is

$$\frac{(4\ \mathrm{m^3/sec})/0.25\ \mathrm{m^2}}{2(9.8\,\mathrm{m/\,sec^2})} = 13\,\mathrm{m}$$

Potential head at A = 0 m
Potential head at B = 10 m
Friction head = 0 m

$$\frac{P_\mathrm{B} - P_\mathrm{A}}{\rho g} = 22.18\,\mathrm{m}$$

Example 2
Calculation of pressure drop in a pipe due to friction.



For a smooth 0.08-m pipe, 130-m long, find the friction head. The density of water is 1000 kg/m^3 and the viscosity of water is 9.28×10^{-5} kg·m/sec.

Calculate the Reynolds number.

$$\mathrm{Re} = \frac{(1.8\,\mathrm{m/sec})(0.0254\,\mathrm{m})(1000\,\mathrm{kg/m^3})}{(9.28 \times 10^{-5}\ \mathrm{kg \cdot m/sec})}$$

$$\frac{R}{\rho u^2} = 2.5 \times 10^{-3}$$

$$R = (2.5 \times 10^{-3})(1000\,\mathrm{kg/m^3})(1.8\,\mathrm{N/m^2}) = 8.1\,\mathrm{N/m^2}$$

$$\Delta P = \frac{4RL}{d} = \frac{(4)(8.1\,\mathrm{N/m^2})(130\,\mathrm{m})}{0.0254\,\mathrm{m}} = 17\,\mathrm{m}$$

$$\text{Friction head} = \frac{1.7 \times 10^5\mathrm{N/m^2}}{(1000\,\mathrm{kg/m^3})(9.8\,\mathrm{m/sec^2})} = 17\,\mathrm{m}$$

3 Heat Transfer

INTRODUCTION

Heat transfer is a major unit operation in pharmacy. Heat energy can only be transferred from a region of higher temperature to a region of lower temperature. Understanding heat transfer requires the study of the mechanism and rate of this process. Heat is transferred by three mechanisms: conduction, convection, and radiation. It is unusual for the transfer to take place by one mechanism only.

Conduction: It is the most widely studied mechanism of heat transfer and the most significant one in solids. The flow of heat depends on the transfer of vibrational energy from one molecule to another and, in the case of metals, the movement of free electrons with the occurrence of no appreciable displacement of matter. Radiation is rare in solids, but examples are found among glasses and plastics. Convection, by definition, is not possible in these conditions. Conduction in the bulk of fluids is normally overshadowed by convection, but it assumes great importance at fluid boundaries.

Convection: The motion of fluids transfers heat between them by convection. In natural convection, the movement is caused by buoyancy forces induced by variations in the density of the fluid, caused by differences in temperature. In forced convection, movement is created by an external energy source, such as a pump.

Radiation: All bodies with a temperature above absolute zero radiate heat in the form of electromagnetic waves. Radiation may be transmitted, reflected, or absorbed by matter, the fraction absorbed being transformed into heat. Radiation is of importance at extremes of temperature and in circumstances in which the other modes of heat transmission are suppressed. Although heat losses can, in some cases, equal the losses by natural convection, the mechanism is, from the standpoint of pharmaceutical processing, least important and needs only brief consideration.

Heat transfer in many systems occurs as a steady-state process, and the temperature at any point in the system will not vary with time. In other important processes, temperatures in the system do vary with time. The latter, which is common among the small-scale, batch-operated processes of the pharmaceutical and fine chemicals industry, is known as unsteady heat transfer and, since warming or cooling occurs, the thermal capacity, that is, the size and specific heat, of the system becomes important. Unsteady heat transfer is a complex phenomenon that is difficult to analyze from the first principles at a fundamental level.

THE TRANSFER OF HEAT BETWEEN FLUIDS

The transfer of heat from one fluid to another across a solid boundary is of great importance in pharmaceutical processing. The system, which frequently varies in nature from one process to another, can be divided into constituent parts, and each part is characterized in its resistance to the transfer of heat. The whole system may be considered in terms of the following equation:

$$\text{Rate at which heat is transferred} \propto \frac{\text{Total temperature difference}}{\text{Total thermal resistance}}$$

A hot liquid passing through a heavily lagged metal pipe may be considered as an example. The transfer of heat from the liquid to the pipe, conduction through the pipe wall and across the insulation, and heat loss to the surroundings by natural convection can each be assigned a thermal resistance. A system in which steam is admitted to the outside of a vertical pipe containing a boiling liquid may serve as a second example. This arrangement is common in evaporators, and the evaluation of heat transfer rates demands a study of condensation, conduction across the wall of the tube and any deposited scale, and the mechanism of boiling.

HEAT TRANSFER THROUGH A WALL

Heat transfer by conduction through walls follows the basic relation given by Fourier's equation in which the rate of heat flow, Q, is proportional to the temperature gradient, dT/dx, and to the area normal to the heat flow, A.

$$Q = -kA\frac{dT}{dx} \tag{3.1}$$

As the distance, x, increases, the temperature, T, decreases. Hence, measuring in the x direction, the temperature gradient, dT/dx, is algebraically negative. The proportionality constant, k, is the thermal conductivity. Its numerical value depends on the material of which the body is made and on its temperature.

Values of thermal conductivity, k, for a number of materials are given in Table 3.1.

Metals have high conductivity, although values vary widely. The nonmetallic solids normally have lower conductivities than metals. For the porous materials of this group, the overall conductivity lies between that of the homogeneous solid and the air that permeates the structure. Low resultant values lead to their wide use as heat insulators. Carbon is an exception among nonmetals. Its relatively high conductivity and chemical inertness permit its wide use in heat exchangers.

TABLE 3.1 Thermal Conductivity, *k*, of Various Materials (in J/sec m K)

Solids	Temperature (K)	*k*	Liquids	Temperature (K)	*k*
Metals			Mercury	273	8.3
Copper	373	379	Acetone	313	0.17
Silver	373	410	Water	373	0.67
Cast iron	373	46.4			
Stainless steel	373	17.3			
			Gases		
Nonmetals					
Carbon (graphite)	323	138.4	Air	473	0.0311
Glass	373	1.16	Steam	373	0.0235
Building brick	293	0.66	Carbon dioxide	373	0.022
Glass wool	373	0.062	Hydrogen	373	0.215

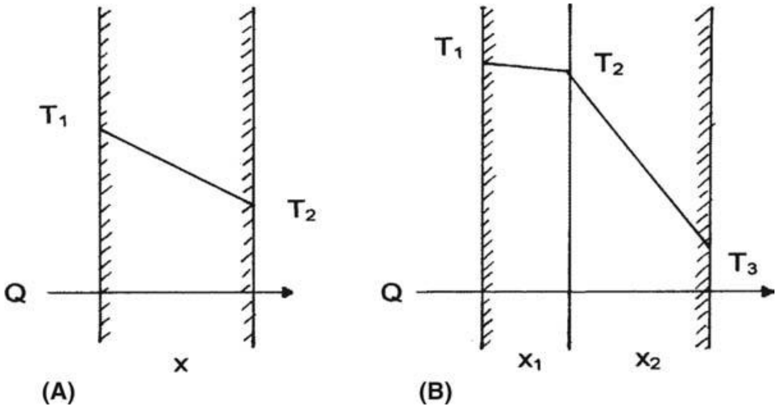


FIGURE 3.1 Conduction of heat through a wall.

Steady nondirectional heat transfer through a plane wall of thickness x and area A is represented in Figure 3.1A. Assuming that the thermal conductivity does not change with temperature, the temperature gradient will be linear and equal to $(T_1-T_2)/x$, where T_1 is the temperature of the hot face and T_2 is the temperature of the cool face. Equation (3.1) then becomes

$$Q = kA\,\frac{T_1 - T_2}{x} \tag{3.2}$$

This may be rearranged as

$$Q = A\,\frac{T_1 - T_2}{x/k} \tag{3.3}$$

where x/k is the thermal resistance. Thus, for a given heat flow, a large temperature drop must be created if the wall or layer has a high thermal resistance.

An increase in thermal resistance will reduce the heat flow promoted by a given temperature difference. This is the principle of insulation by lagging, and it is illustrated by a composite wall shown in Figure 3.1B. The rate of heat transfer will be the same for both materials if steady-state heat transfer exists. Therefore,

$$Q = \frac{k_1A(T_1 - T_2)}{x_1} = \frac{k_2A(T_2 - T_3)}{x_2}$$

The major temperature drop occurs across the distance x_2 since this material provides the major thermal resistance. (In the case of heavily lagged, thin metal walls, the temperature drop and thermal resistance of the metal are so small that they can be ignored.) Rearrangement of this equation and the elimination of the junction temperature give

$$Q = A\,\frac{T_1 - T_3}{(x_1/k_1) + (x_2/k_2)} \tag{3.4}$$

Equations of this form can be applied to any number of layers.

HEAT TRANSFER IN PIPES AND TUBES

Pipes and tubes are common barriers over which heat exchange takes place. Conduction is complicated in this case by the changing area over which heat is transferred. If equation (3.2) is to be retained, some value of A must be derived from the length of the pipe, l, and the internal and external radii, r_1 and r_2, respectively. When the pipe is thin walled and the ratio r_2/r_1 is less than approximately 1.5, the heat transfer area can be based on an arithmetic mean of the two radii. Equation (3.2) then becomes

$$Q = k2\pi \frac{r_2 + r_1}{2} l \frac{T_1 - T_2}{r_2 - r_1} \tag{3.5}$$

This equation is inaccurate for thick-walled pipes. Heat transfer area must then be calculated from the logarithmic mean radius, r_m. The equation for heat transfer is then

$$Q = k2\pi r_m l \frac{T_1 - T_2}{r_2 - r_1} \tag{3.6}$$

where

$$r_m = \frac{r_2 - r_1}{\log_e (r_2/r_1)}$$

HEAT EXCHANGE BETWEEN A FLUID AND A SOLID BOUNDARY

Conduction and convection contribute to the transfer of heat from a fluid to a boundary. The distribution of temperatures at a plane barrier separating two fluids is shown in Figure 3.2. If the fluids are in turbulent motion, temperature gradients are confined to a relatively narrow region adjacent to the wall. Outside this region, turbulent mixing, the mechanism of which is explained in chapter 2, is very effective in the transfer of heat. Temperature gradients are quickly destroyed, and equalization of values T_1 and T_2 occurs. Within the region, there exists a laminar sublayer across which heat is transferred by conduction only. The thermal conductivity of most fluids is small, as shown in Table 3.1. The

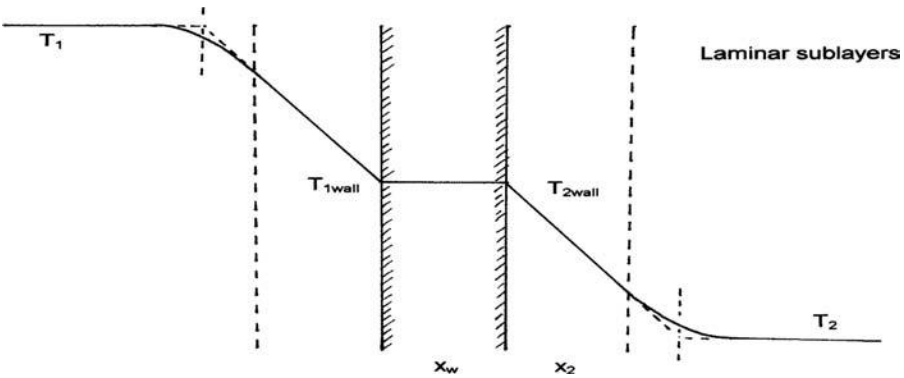


FIGURE 3.2 Heat transfer between fluids.

temperature gradients produced by a given heat flow are correspondingly high. Outside the laminar layer, eddies contribute to the transfer of heat by moving fluid from the turbulent bulk to the edge of the sublayer, where heat can be lost or gained, and by corresponding movements in the opposite direction. The temperature gradients in this region, where both convection and conduction contribute to heat transfer, are smaller than that in the sublayer.

The major resistance to heat flow resides in the laminar sublayer. Its thickness is, therefore, of critical importance in determining the rate of heat transfer from the fluid to the boundary. It depends on the physical properties of the fluid, the flow conditions, and the nature of the surface. Increase in flow velocity, for example, decreases the thickness of the layer and, therefore, its resistance to heat flow. The interaction of these variables is exceedingly complex.

A film transmitting heat only by conduction may be postulated to evaluate the rate of heat transfer at a boundary. This fictitious film presents the same resistance to heat transfer as the complex turbulent and laminar regions near the wall. If, on the hot side of the wall, the fictitious layer had a thickness x_1, the equation of heat transfer to the wall would be

$$Q = kA\,\frac{(T_1 - T_{1\text{wall}})}{x_1}$$

where k is the thermal conductivity of the fluid. A similar equation will apply to heat transfer at the cold side of the wall. The thickness of the layer is determined by the same factors that control the extent of the laminar sublayer. In general, it is not known and the equation above may be rewritten as

$$Q = h_1 A(T_1 - T_{1\text{wall}}) \tag{3.7}$$

where h_1 is the heat transfer coefficient for the film under discussion. It corresponds to the ratio k/x_1 and has units $\text{J/m}^2\cdot\text{sec}\cdot\text{K}$. This is a convenient, numerical expression of the flow of heat by conduction and convection at a boundary. Typical values of heat transfer or film coefficients are given in Table 3.2. The approximate evaluation of these coefficients is discussed in the next section.

The ratio of the temperature difference and the total thermal resistance determines the rate of heat transfer across the three layers of Figure 3.2. Using the film coefficient h_2 to characterize heat transfer from the barrier to the colder fluid,

$$T_1 - T_{1\text{wall}} = \frac{Q}{h_1 A}$$

$$T_{1\text{wall}} - T_{2\text{wall}} = \frac{Q x_\text{w}}{k_\text{w} A}$$

TABLE 3.2 Film Coefficient, h, for Various Fluids (J/m^2 sec K)

Fluid	h
Water	1,700–11,350
Gases	17–285
Organic solvents	340–2,840
Oils	57–680

where k_w is the thermal conductivity of the wall.

$$T_{2\text{wall}} - T_2 = \frac{Q}{h_2 A}$$

Addition and rearrangement of these equations give

$$Q = \frac{A}{(1/h_1) + (x_w/k_w) + (1/h_2)}(T_1 - T_2) \tag{3.8}$$

The quantity

$$\frac{1}{(1/h_1) + (x_w/k_w) + (1/h_2)}$$

is called the overall heat transfer coefficient, *U*. A general expression of the rate of heat transfer then becomes

$$Q = UA\Delta T \tag{3.9}$$

APPLICATION OF DIMENSIONAL ANALYSIS TO CONVECTIVE HEAT TRANSFER

Dimensional analysis offers a rational approach to the estimation of the complex phenomena of convective heat transfer rates.

Free convection describes heat transfer by the bulk movement of fluids induced by buoyancy forces. These arise from the variation of fluid density with temperature. If the surface in contact with the fluid is hotter, the fluid will absorb heat, a local decrease in density will occur, and some of the fluid will rise. If the surface is colder, the reverse takes place. For these conditions, the following factors will influence the heat transferred per unit area per unit time, q. The dimensional form of these factors is given, using the additional fundamental dimensions of temperature, [θ], and heat, [H]. The latter is justified if interchange of heat energy and mechanical energy is precluded. This is approximately true in the subject under discussion, the heat produced by frictional effects, for example, being negligible.

- The viscosity of the fluid, η: $[\mathrm{ML^{-1}T^{-1}}]$
- The thermal conductivity of the fluid, k: $[\mathrm{HT^{-1}L^{-1}\theta^{-1}}]$
- The temperature difference between the surface and the bulk of the fluid, ΔT: $[\theta]$
- The density, ρ: $[\mathrm{ML^{-3}}]$
- The specific heat, Cp: $[\mathrm{HM^{-1}\theta^{-1}}]$
- The buoyancy forces. These depend on the product of the coefficient of thermal expansion, a, and the acceleration due to gravity, g: $[\mathrm{\theta^{-1}LT^{-2}}]$

Normally, only one dimension, of the physical dimensions of the surface, is important. For example, the height of a plane vertical surface has greater significance than the width that only determines the total area involved. The important characteristic dimension is designated l [L].

The equation of dimensions is then

$$[q] = [l^x \Delta T^y k^z \eta^p C_p^q (ag)^r \rho^s]$$

or

$$[\mathrm{HL^{-2}T^{-1}}] = [\mathrm{L}^x\theta^y\mathrm{H}^z\mathrm{T}^{-z}\mathrm{L}^{-z}\theta^{-z}\mathrm{M}^p\mathrm{L}^{-p}\mathrm{T}^{-p}\mathrm{H}^q\mathrm{M}^{-q}\theta^{-q}\theta^{-r}\mathrm{L}^r\mathrm{T}^{-2r}\mathrm{M}^s\mathrm{L}^{-3s}]$$

Equating indices,

H $1 = q + z$
L $-2 = x - p + r - 3s - z$
T $-1 = -p - 2r - z$
θ $0 = y - q - r - z$, and
M $0 = p - q + s$

Solving for x, y, z, p, and s in terms of q and r,

$z = 1 - q$
$y = r + 1$
$p = q - 2r$
$s = 2r$, and
$x = 3r - 1$

Therefore,

$$[q] = [l^{3r-1}\Delta T^{r+1}C_p^q k^{1-q}(ag)^r \rho^{2r}\eta^q - 2r]$$

Collecting into three groups, the variables to the power of one, the power, q, and the power, r, we can write

$$q = \text{Constant}\,\frac{\Delta Tk}{l}\left(\frac{l^3\Delta Tag\rho^2}{\eta^2}\right)^r\left(\frac{C_p\eta}{k}\right)^q$$

or

$$\frac{ql}{\Delta Tk} = \text{Constant}\left(\frac{l^3\Delta Tag\rho^2}{\eta^2}\right)^r\left(\frac{C_p\eta}{k}\right)^q \tag{3.10}$$

Heat transfer by free convection can thus be presented as a relation between three dimensionless groups. $C_p\eta/k$ is known as the Prandtl number; the combination $l^3\Delta Tag\rho^2/\eta^2$ is known as the Grashof number; and $ql/\Delta Tk$ is the Nusselt number. Since the film coefficient, h, is given by $q/\Delta T$, the Nusselt number may also be written as hl/k.

The specific relation in which these groups stand is established for a particular system by experiment. Then, for the same geometric arrangement, in which heat is transferred by free convection, the correlation allows the Nusselt number, Nu, to be determined with reasonable accuracy from known values of the variables that constitute the Grashof number, Gr, and the Prandtl number, Pr. From Nu, the heat transferred per unit area per unit time, q, and the film coefficient, h, can be determined.

The fluid properties Cp, k, η, and ρ are themselves temperature dependent. In establishing a correlation, the temperature at which these properties are to be measured must be chosen. This is usually the temperature of the main body of the fluid or the mean of this temperature and the temperature of the surface.

Experimental correlations for many surface configurations are available. The exponents r and q are usually found to be equal to a value of 0.25 in streamline flow and 0.33 in turbulent flow. The constant varies with the physical configuration. As an example, the heat transfer to gases and liquids from a large horizontal pipe by free convection is described by the relation

$$\frac{qd}{k\Delta T} = 0 \cdot 47 \left(\frac{d^3 \Delta T a g \rho^2}{\eta^2}\right)^{0.25} \left(\frac{C_p \eta}{k}\right)^{0.25} \tag{3.11}$$

The linear dimension in this correlation is the pipe diameter, d. The fluid properties are to be measured at the mean of the wall and bulk fluid temperatures.

In forced convection, the fluid is moved over the surface by a pump or blower. The effects of natural convection are usually neglected. The study of forced convection is of great practical importance, and a vast amount of data has been documented for streamline and turbulent flow in pipes, across and parallel to tubes, across plane surfaces, and in other important configurations such as jackets and coils. Such data is again correlated by means of dimensionless groups.

In forced convection, the heat transferred per unit area per unit time, q, is determined by a linear dimension, which characterizes the surface, l, the temperature difference between the surface and the fluid, ΔT, the viscosity, η, the density, ρ, and the velocity, u, of the fluid, its conductivity, k, and its specific heat, Cp. Dimensional analysis will yield the following relation:

$$\frac{ql}{k\Delta T} = \text{Constant}\left(\frac{C_p \eta}{k}\right)^{x} \left(\frac{ul\rho}{\eta}\right)^{y} \tag{3.12}$$

where $ql/k\Delta T$ is the Nusselt number, Nu, and $C_p\eta/k$ is the Prandtl number, Pr, and $ul\rho/\eta$ is Reynolds number, Re, a parameter discussed in chapter 2. The values of the indices, x and y, and of the constant are established for a particular system by experiment. In the case of turbulent flow in pipes, the correlation for fluids of low viscosity is

$$\mathrm{Nu} = 0 \cdot 023\mathrm{Pr}^{x}\mathrm{Re}^{0.8} \tag{3.13}$$

where x has the values 0.4 for heating and 0.3 for cooling. The linear dimension used to calculate Re or Nu is the pipe diameter, and the physical properties of the fluid are to be measured at the bulk fluid temperature. This relation shows that in a given system, the film coefficient varies as the fluid velocity$^{0.8}$. If the flow velocity is doubled, the film coefficient increases by a factor of 1.7.

Although the correlations given above may appear complex, their use in practice is often simple. A large quantity of tabulated data is available, and numerical values of the variables and their dimensionless combinations are readily accessible. The graphical presentation of these variables or groups will, in many cases, permit an easy solution. In other cases, the correlation can be greatly simplified if it is restricted to a particular system. Free convection to air is an important example.

HEAT TRANSFER TO BOILING LIQUIDS

Heat transfer to boiling liquids occurs in a number of operations such as distillation and evaporation. Heat is transferred by both conduction and convection in a process further complicated by the change of phase that occurs at the heating boundary. When boiling is induced by a heater in contact with a pool of liquid, the process is known as pool boiling. Liquid movement is derived only from heating effects. In other systems, the boiling liquid may be driven through or over heaters, a process referred to as boiling with forced circulation.

POOL BOILING

If a horizontal heating surface is in contact with a boiling liquid, a sequence of events occurs as the temperature difference between the surface and the liquid increases. Figure 3.3 relates heat flux per unit area at the surface, q, to the temperature difference between the surface and boiling water, ΔT. The derived value of the heat transfer coefficient, $h = q/\Delta T$, is also plotted.

When ΔT is small, the degree of superheating of the liquid layers adjacent to the surface is low, and bubble formation, growth, and disengagement, if present, are slow. Liquid disturbance is small, and heat transfer can be estimated from expressions for natural convection given, for example, in equation (3.11). This regime corresponds to section AB of Figure 3.3, over which both q and h increase.

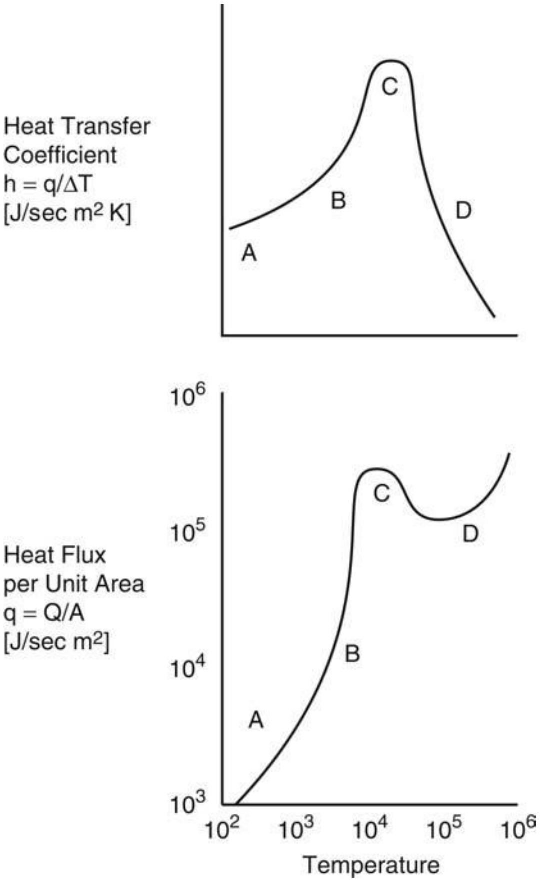


FIGURE 3.3 Variation in heat transfer coefficient and heat flux per unit area.

In section BC of Figure 3.3, vapor formation becomes more vigorous and bubble chains rise from points that progressively increase in number and finally merge. This movement increases liquid circulation, and both *q* and *h* rise rapidly. This phase is called nucleate boiling and is the practically important regime. For water, approximate values of *q* and *h* may be read from Figure 3.3. At point C, a peak flux occurs and a maximum heat transfer coefficient is obtained. ΔT at this point is known as the critical temperature drop. For water, the value lies between 25 and 32 K. The critical temperature drop for organic liquids is somewhat higher. Beyond C, vapor formation is so rapid that escape is inadequate and a progressively larger fraction of the heating surface becomes covered with a vapor film, the low conductivity of which leads to a decrease in *q* and *h*. This represents a transition from nucleate boiling to film boiling. When this transition is complete (D), the vapor entirely covers the surface, film boiling is fully established, and the heat flux again rises.

The low heat transfer coefficient renders film boiling undesirable, and equipment is designed for and operated at temperature differences that are less than the critical temperature drop. If a constant temperature heat source, such as steam or hot liquid, is employed, exceeding the critical temperature drop results simply in a drop in heat flux and process efficiency. If, however, a constant heat input source is used, as in electrical heating, decreasing heat flux as the transition region is entered causes a sudden and possibly damaging increase in the temperature of the heating element. Damage is known as boiling burnout. Under these circumstances, the region CD of Figure 3.3 is not obtained.

Boiling heat transfer coefficients depend on both the physical character of the liquid and the nature of the heating surface. Through the agencies of wetting, roughness, and contamination, the latter greatly influences the formation, growth, and disengagement of bubbles in the nucleate boiling regime. There is, at present, no reliable method of estimating the boiling coefficients of heat transfer from the physical properties of the system. Coefficients, as shown for water in Figure 3.3, are large, and higher resistances elsewhere will often limit the rate at which heat can be transferred through a system as a whole.

BOILING INSIDE A VERTICAL TUBE

Heat transfer to liquids boiling in vertical tubes is common in evaporators. If a long tube of suitable diameter, in which liquid lies at a low level, is heated, the pattern of boiling shown in Figure 3.4 is established (Coulson and McNelly). At low levels, boiling may be suppressed by the imposed head (Fig. 3.4A). Higher in the tube, bubbles are produced, which rise and coalesce (Fig. 3.4B). Slug formation due to bubble coagulation occurs (Fig. 3.4C, D). The slugs finally break down (Fig. 3.4E). Escape is hindered, and both liquid and vapor move upward at an increasing speed. Draining leads to separation of the phases, giving an annular film of liquid dragged upward by a core of high-velocity vapor (Fig. 3.4F). In long tubes, the main heat transfer takes place in this region by either forced convection or nucleate boiling. At low temperature differences between wall and film, heat transfer occurs quietly, as in forced convection. This is the normal regime in a climbing film evaporator, and heat flux can be calculated from correlations of the type given in equation (3.12). At higher temperature differences, nucleate boiling takes place in the film and the vigorous movement leads to an increase in heat transfer coefficient.

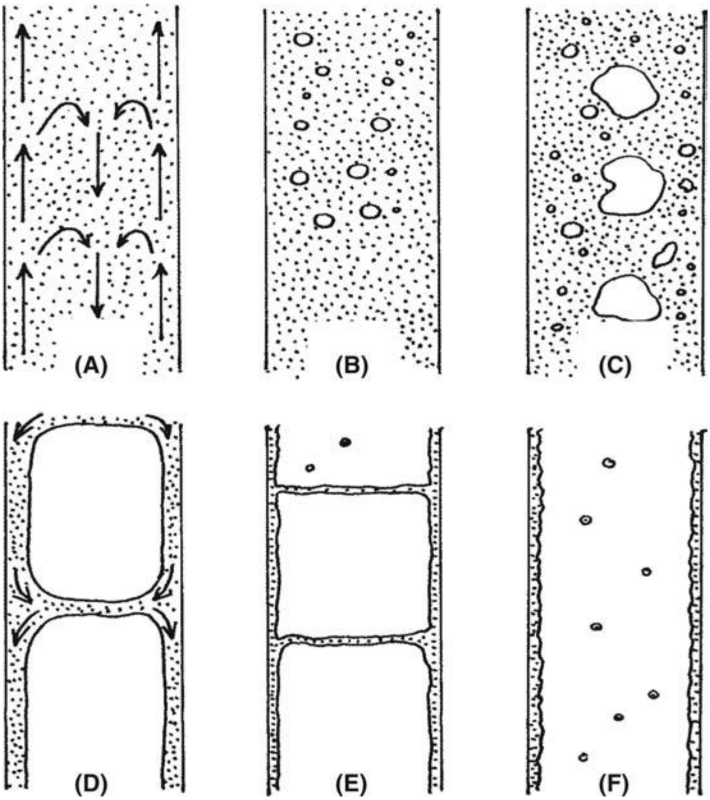


FIGURE 3.4 Boiling in narrow vertical tube.

BOILING WITH FORCED CIRCULATION

In many systems, movements other than those caused by boiling are imposed. For example, boiling in agitated vessels is common in many batch processes. The boiling heat transfer coefficients depend on the properties of the liquid, the nature of the surface, and the agitation used. Coefficients obtained are slightly higher than those of pool boiling. Inside tubes, the pattern of forced circulation boiling is similar to that described in the previous section. Coefficients, however, are higher because the velocities attained are higher.

HEAT TRANSFER FROM CONDENSING VAPORS

When a saturated vapor is brought into contact with a cool surface, heat is transferred to the surface and a liquid condenses. The vapor may consist of a single substance or a mixture, some components of which may be noncondensable.

The process is described by the following sequence: The vapor diffuses to the boundary where actual condensation takes place. In most cases, the condensate forms a continuous layer over the cooling surface, draining under the influence of gravity. This is known as film condensation. The latent heat liberated is transferred through the film to the surface by conduction. Although this film offers considerable resistance to heat flow, film coefficients are usually high.

DROPWISE CONDENSATION

Under some surface conditions, the condensate does not form a continuous film. Droplets are formed, which grow, coalesce, and then run from the surface. Since a fraction of the surface is always directly exposed to the vapor, film resistance is absent and heat transfer coefficients that may be ten times those of film condensation are obtained. This process is known as dropwise condensation. Although highly desirable, its occurrence, which depends on the wettability of the surface, is not predictable and cannot be used as a basis for design.

CONDENSATION OF A PURE VAPOR

For film condensation, a theoretical analysis of the laminar flow of a liquid film down an inclined surface and the progressive increase in thickness due to condensation yields the following expression for the mean heat transfer coefficient, h_{m}:

$$h_{\mathrm{m}} = \mathrm{Constant}\left(\frac{\rho^2 k^3 \lambda g}{\Delta T \eta x}\right)^{0.25} \tag{3.14}$$

where λ is the latent heat of vaporization, and ρ, k, and η are the density, the thermal conductivity, and the viscosity of the liquid, respectively. ΔT is the difference in temperature between the surface and the vapor. Experimentally determined coefficients confirm the validity of equation (3.14). In practice, however, coefficients are somewhat higher because of disturbance of the film arising from a number of factors. As the condensation rate rises, the thickness of the condensate layer increases and the film coefficient falls. However, a point may be reached in long vertical tubes at which flow in the layer becomes turbulent. Under these conditions, the coefficient again rises and equation (3.14) is not valid. Coefficients may also be increased if high vapor velocities induce ripples in the film.

CONDENSATION OF MIXED VAPORS

If a mixture of condensable and noncondensable gases is cooled below its dew point at a surface, the former condenses, leaving the adjacent layers richer in the latter, thus creating an added thermal resistance. The condensable fraction must diffuse through this layer to reach the film of condensate, and heat transfer coefficients are normally very much lower than the corresponding value for the pure vapor. For example, the presence of 0.5% of air has been found to reduce the heat transfer by condensation of steam by as much as 50%.

HEAT TRANSFER BY RADIATION

There is continuous interchange of energy between bodies by the emission and absorption of radiation. If two adjacent surfaces are at different temperatures, the hotter surface radiates more energy than it receives, and its temperature falls. The cooler surface receives more energy than it emits, and its temperature rises. Ultimately, thermal equilibrium is reached. Interchange of energy continues, but gains and losses are equal.

Of the radiation that falls on a body, a fraction, a, is absorbed, a fraction, r, is reflected, and a fraction, t, is transmitted. These fractions are called the absorptivity, the reflectivity, and the transmissivity, respectively. Most industrial solids are opaque so that the transmissivity is zero and

$$a + r = 1 \tag{3.15}$$

Reflectivity and, therefore, *absorptivity*, depend greatly on the nature of the surface. The limiting case, that of a body that absorbs all and reflects none of the incident radiation, is called a blackbody.

EXCHANGE OF RADIATION

The exchange of radiation is based on two laws. The first, known as Kirchhoff's law, states that the ratio of the emissive power to the absorptivity is the same for all bodies in thermal equilibrium. The emissive power of a body, E, is the radiant energy emitted from unit area in unit time (J/m^2 sec). A body of area A_1 and emissivity E_1, therefore, emits energy at a rate E_1A_1. If the radiation falling on unit area of the body is E_b, the rate of energy absorption is $E_b a_1 A_1$, where a_1 is the absorptivity. At thermal equilibrium, $E_b a_1 A_1 = E_1 A$. For another body in the same environment, $E_b a_2 A_2 = E_2 A_2$. Therefore,

$$E_b = \frac{E_1}{a_1} = \frac{E_2}{a_2} \tag{3.16}$$

For a blackbody, $a = 1$. The emissive power is therefore E_b. The blackbody is a perfect radiator, and it is used as the comparative standard for other surfaces. The emissivity of a surface is defined as the ratio of the emissive power, E, of the surface to the emissive power of a blackbody at the same temperature, E_b.

$$e = \frac{E}{E_b} \tag{3.17}$$

The emissivity is numerically equal to the absorptivity. Since the emissive power varies with wavelength, the ratio should be quoted at a particular wavelength. For many materials, however, the emissive power is a constant fraction of the blackbody radiation, that is, the emissivity is constant. These materials are known as gray bodies.

The second fundamental law of radiation, known as the Stefan–Boltzmann law, states that the rate of energy emission from a blackbody is proportional to the fourth power of the absolute temperature, T.

$$E = \sigma T^4 \tag{3.18}$$

where E *is* the total emissive power and σ is the Stefan–Boltzmann constant, the numerical value of which is 5.676×10^{-8} J/m^2·sec·K^4. It is sufficiently accurate to say that the heat emitted in unit time, Q, from a blackbody of area A is given by

$$Q = \sigma A T^4$$

and for a body that is not perfectly black by

$$Q = \sigma e A T^4 \tag{3.19}$$

where e is the emissivity.

The net energy gained or lost by a body can be estimated with these laws. The simplest case is that of a gray body in black surroundings. These conditions, in which none of the energy emitted by the body is reflected back, are approximately those of a body radiating to atmosphere. If the absolute temperature of the body is T_1, the rate of heat loss is $\sigma e A T_1^4$ [equation (3.19)], where A is the area of the body and e is its emissivity. Surroundings at a temperature T_2 will emit radiation proportional to σT_2^4, and a fraction, determined by area and absorptivity, a, will be absorbed by the body. This heat will be $\sigma a A T_2^4$, and since absorptivity and emissivity are equal,

$$\text{Net heat transfer rate} = \sigma e A(T_1^4 - T_2^4) \tag{3.20}$$

If part of the energy emitted by a surface is reflected back by another surface, the calculation of radiation exchange is more complex. Equations for various surface configurations are available. These take the general form

$$Q = F_1 F_2 \sigma A(T_A^4 - T_B^4)$$

where F_1 and F_2 are factors determined by the configuration and emissivity of surfaces at temperatures T_A and T_B.

Example Problems

Example 1

A stainless steel pipe has an internal radius of 0.019 m and an external radius of 0.024 m. The thermal conductivity of stainless steel is 34.606 J/m·sec·K. Steam at 422 K surrounds the pipe that is lagged with 0.051 m of insulation with a conductivity of 0.069 J/m·sec·K. The temperature of the outer surface of the insulation is 311 K. What is the heat loss per meter of pipe?

For the wall of the pipe,

$$\frac{0.024\,\text{m}}{0.019\,\text{m}} = 1.3 < 1.5$$

Therefore, the arithmetic mean best defines the radius.

$$r = \frac{0.019\,\text{m} + 0.024\,\text{m}}{2} = 0.022\,\text{m}$$

For the insulation,

$$\frac{0.051\text{m}}{0.024\text{m}} = 2.1 > 1.5$$

Therefore, the logarithmic mean best defines the radius.

$$r_m = \frac{0.051 - 0.024}{2.3 \log(0.051/0.024)} = 0.036\,\text{m}$$

For the pipe,

$$\begin{aligned} Q &= (34.606\,\text{J/m}\cdot\text{sec}\cdot\text{K})(2\pi)(0.022\,\text{m})(1\,\text{m})\left(\frac{T_1 - T_2}{0.024\,\text{m} - 0.019\,\text{m}}\right) \\ &= 975(T_1 - T_2) \end{aligned}$$

For the insulation,

$$Q = (0.069\ \mathrm{J/m \cdot sec \cdot K})(2\pi)(0.036\mathrm{m})(1\mathrm{m})\left(\frac{T_2 - T_3}{0.051\mathrm{m} - 0.024\,\mathrm{m}}\right) = 0.578(T_2 - T_3)$$

Rearranging these equations gives the following:

$$T_1 - T_2 = \frac{Q}{957}$$

$$T_2 - T_3 = \frac{Q}{0.578}$$

$$T_1 - T_3 = 111\,\mathrm{K} = \frac{Q}{957} + \frac{Q}{0.578}$$

$$Q = \frac{111}{(1/957 + 1/0.578)} = 64\,\mathrm{J/sec}$$

Example 2

A 0.051-m uninsulated horizontal pipe is carrying steam at 389 K to the surroundings at 294 K. The emissivity, *e*, of the pipe is 0.8. Absolute zero is 273 K. Find the heat loss by radiation.

$$\frac{\text{Heat loss}}{\text{Unit length}} = (5.676 \times 10^{-8}\,\mathrm{J/m^2 \cdot sec \cdot\ K^4})(0.058\,\mathrm{m})(\pi)(0.8)[(116\mathrm{K})^4 - (21\mathrm{K})^4]$$

$$= 1.50\,\mathrm{J/m \cdot\ sec}$$

4 Mass Transfer

INTRODUCTION

The following is a brief review of mass transfer to complete the overview of unit processes in pharmacy. Mass transfer is conceptually and mathematically analogous to heat transfer, as will be seen in the following exposition. Many processes are adopted so that a mixture of materials can be separated into component parts. In some, purely mechanical means are used. Solids may be separated from liquids by the arrest of the former in a bed permeable to the fluid. This process is known as filtration. In other examples, a difference in density of two phases permits separation. This is found in sedimentation and centrifugation. Many other processes, however, operate by a change in the composition of a phase due to the diffusion of one component in another. Such processes are known as diffusional or mass transfer processes. Distillation, dissolution, drying, and crystallization provide examples. In all cases, diffusion is the result of a difference in the concentration of the diffusing substance, this component moving from a region of high concentration to a region of low concentration under the influence of the concentration gradient.

In mass transfer operations, two immiscible phases are normally present, one or both of which are fluid. In general, these phases are in relative motion and the rate at which a component is transferred from one phase to the other is greatly influenced by the bulk movement of the fluids. In most drying processes, for example, water vapor diffuses from a saturated layer in contact with the drying surface into a turbulent airstream. The boundary layer, as described in chapter 2, consists of a sublayer in which flow is laminar and an outer region in which flow is turbulent. The mechanism of diffusion differs in these regimes. In the laminar layer, movement of water vapor molecules across streamlines can only occur by molecular diffusion. In the turbulent region, the movement of relatively large units of gas, called eddies, from one region to another causes mixing of the components of the gas. This is called eddy diffusion. Eddy diffusion is a more rapid process, and although molecular diffusion is still present, its contribution to the overall movement of material is small. In still air, eddy diffusion is virtually absent and evaporation occurs only by molecular diffusion.

MOLECULAR DIFFUSION IN GASES

Transport of material in stagnant fluids or across the streamlines of a fluid in laminar flow occurs by molecular diffusion. In Figure 4.1, two adjacent compartments, separated by a partition, are drawn. Each compartment contains a pure gas, A or B. Random movement of all molecules occurs so that after a period of time molecules are found quite remote from their original positions. If the partition is removed, some molecules of A will move toward the region occupied by B, their number depending on the number of molecules at the point considered. Concurrently, molecules of B diffuse toward regions formerly occupied by pure A.

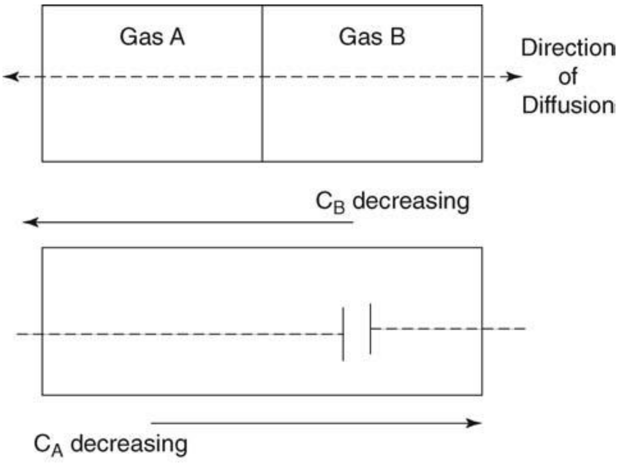


FIGURE 4.1 Molecular diffusion of gases A and B.

Ultimately, complete mixing will occur. Before this point in time, a gradual variation in the concentration of A will exist along an axis, designated x, which joins the original compartments. This variation, expressed mathematically, is $-dC_A/dx$, where C_A is the concentration of A. The negative sign arises because the concentration of A decreases as the distance x increases. Similarly, the variation in the concentration of gas B is $-dC_B/dx$. These expressions, which describe the change in the number of molecules of A or B over some small distance in the direction indicated, are concentration gradients. The rate of diffusion of A, N_A, depends on the concentration gradient and on the average velocity with which the molecules of A move in the x direction. Fick's law expresses this relationship.

$$N_A = -D_{AB}\frac{dC_A}{dx} \tag{4.1}$$

where D is the diffusivity of A in B. It is a property proportional to the average molecular velocity and is, therefore, dependent on the temperature and pressure of the gases. The rate of diffusion, N_A, is usually expressed as the number of moles diffusing across unit area in unit time. In the SI system, which is used frequently for mass transfer, N_A would be expressed as moles per square meter per second. The unit of diffusivity then becomes m^2/sec. As with the basic equations of heat transfer, equation (4.1) indicates that the rate of a process is directly proportional to a driving force, which, in this context, is a concentration gradient.

This basic equation can be applied to a number of situations. Restricting discussion exclusively to steady-state conditions, in which neither dC_A/dx nor dC_B/dx changes with time, equimolecular counterdiffusion is considered first.

EQUIMOLECULAR COUNTERDIFFUSION

If no bulk flow occurs in the element of length dx, shown in Figure 4.1, the rates of diffusion of the two gases, A and B, must be equal and opposite, that is,

$$N_A = -N_B$$

The partial pressure of A changes by dP_A over the distance dx. Similarly, the partial pressure of B changes by dP_B. Since there is no difference in total pressure across the element (no bulk flow), dP_A/dx must equal $-dP_B/dx$. For an ideal gas, the partial pressure is related to the molar concentration by the relation

$$P_A V = n_A RT$$

where n_A is the number of moles of gas A in a volume V. Since the molar concentration, C_A, is equal to n_A/V,

$$P_A = C_A RT$$

Therefore, for gas A, equation (4.1) can be written as

$$N_A = -\frac{D_{AB}}{RT}\frac{dP_A}{dx} \tag{4.2}$$

where D_{AB} is the diffusivity of A in B. Similarly,

$$N_B = -\frac{D_{BA}}{RT}\frac{dP_B}{dx} = \frac{D_{AB}}{RT}\frac{dP_A}{dx}$$

It therefore follows that $D_{AB} = D_{BA} = D$. If the partial pressure of A at x_1 is P_{A1} and that at x_2 is P_{A2}, integration of equation (4.2) gives

$$N_A = -\frac{D}{RT}\frac{P_{A2} - P_{A1}}{x_2 - x_1} \tag{4.3}$$

A similar equation may be derived for the counterdiffusion of gas B.

DIFFUSION THROUGH A STATIONARY, NONDIFFUSING GAS

An important practical case arises when a gas A diffuses through a gas B, there being no overall transport of gas B. It arises, for example, when a vapor formed at a drying surface diffuses into a surrounding gas. At the liquid surface, the partial pressure of A is dictated by the temperature. For water, it would be 12.8 mmHg at 298 K. Some distance away, the partial pressure is lower and the concentration gradient causes diffusion of A away from the surface. Similarly, a concentration gradient for B must exist, the concentration being lowest at the surface. Diffusion of this component takes place toward the surface. There is, however, no overall transport of B so that diffusional movement must be balanced by bulk flow away from the surface. The total flow of A is, therefore, the diffusional flow of A plus the transfer of A associated with this bulk movement.

MOLECULAR DIFFUSION IN LIQUIDS

Equations describing molecular diffusion in liquids are similar to those applied to gases. The rate of diffusion of material A in a liquid is given by equation (4.1).

$$N_A = -D\frac{dC_A}{dx}$$

Fick's law for steady-state, equimolal counterdiffusion is then

$$N_A = -D\frac{C_{A2} - C_{A1}}{x_2 - x_1} \qquad (4.4)$$

where C_{A2} and C_{A1} are the molar concentrations at points x_2 and x_1, respectively.

Equations for diffusion through a layer of stagnant liquid can also be developed. The use of these equations is, however, limited because diffusivity in a liquid varies with concentration. In addition, unless the solutions are very dilute, the total molar concentration will vary from point to point. These complications do not arise with diffusion in gases.

Diffusivities in liquids are very much less than diffusivities in gases, commonly by a factor of 10^4.

MASS TRANSFER IN TURBULENT AND LAMINAR FLOW

As already explained, movement of molecules across the streamlines of a fluid in laminar flow can only occur by molecular diffusion. If the concentration of a component, A, varies in a direction normal to the streamlines, the molar rate of diffusion will be given by equation (4.1).

When a fluid flows over a surface, the surface retards the adjacent fluid region, forming a boundary layer. If flow throughout the fluid is laminar, the equation for molecular diffusion may be used to evaluate the mass transferred across the boundary layer. In most important cases, however, flow in the bulk of the fluid is turbulent. The boundary layer is then considered to consist of three distinct flow regimes. In the region of the boundary layer most distant from the surface, flow is turbulent and mass transfer is the result of the interchange of large portions of the fluid. Mass interchange is rapid, and concentration gradients are low. As the surface is approached, a transition from turbulent to laminar flow occurs in the transition or buffer region. In this region, mass transfer by eddy diffusion and molecular diffusion are of comparable magnitude. In a fluid layer at the surface, a fraction of a millimeter thick, laminar flow conditions persist. This laminar sublayer, in which transfer occurs by molecular diffusion only, offers the main resistance to mass transfer, as shown in Figure 4.2.

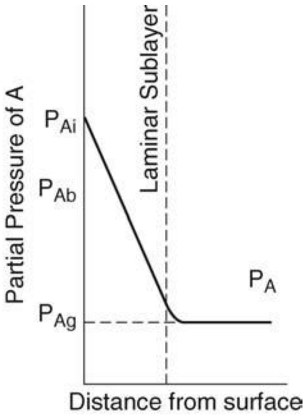


FIGURE 4.2 Mass transfer at a boundary.

As flow becomes more turbulent, the thickness of the laminar sublayer and its resistance to mass transfer decrease.

One approach to the evaluation of the rate of mass transfer under these conditions lies in the postulation of a film, the thickness of which offers the same resistance to mass transfer as the combined laminar, buffer, and turbulent regions. The analogy with heat transfer by conduction and convection is exact, and quantitative relations between heat and mass transfer can be developed for some situations. This, however, is not attempted in this text. The postulate of an effective film is explained by reference to Figure 4.2.

A gas flows over a surface, and equimolecular counterdiffusion of components A and B occurs, A away from the surface and B toward the surface. The variation in partial pressure of A with distance from the surface is shown in the figure. At the surface, the value is P_{Ai}. A linear fall to P_{Ab} occurs over the laminar sublayer. Beyond this, the partial pressure falls less steeply to the value P_{A} at the edge of the boundary layer. P_{Ag}, a value slightly higher than this, is the average partial pressure of A in the entire system. In general, the gas content of the laminar layer is so small that P_{A} and P_{Ag} are virtually equal. If molecular diffusion were solely responsible for diffusion, the partial pressure, P_{Ag}, would be reached at some fictitious distance, x', from the surface, over which the concentration gradient $(P_{\mathrm{Ai}} - P_{\mathrm{Ag}})/x'$ exists. The molar rate of mass transfer would then be

$$N_{\mathrm{A}} = \frac{D}{RT}\frac{P_{\mathrm{Ai}} - P_{\mathrm{Ag}}}{x'}$$

x' is not known, however, and this equation may be written as

$$N_{\mathrm{A}} = \frac{k_{\mathrm{g}}}{RT}(P_{\mathrm{Ai}} - P_{\mathrm{Ag}}) \tag{4.5}$$

where k_{g}, is a mass transfer coefficient, the unit of which is m/sec. Since $C_{\mathrm{A}} = P_{\mathrm{A}}/RT$, we can also write

$$N_{\mathrm{A}} = k_{\mathrm{g}}(C_{\mathrm{Ai}} - C_{\mathrm{Ag}})$$

where C_{Ai} and C_{Ag} are the gas concentrations at either side of the film. Similar equations describe the diffusion of B in the opposite direction.

Diffusion across a liquid film is described by the equation

$$N_{\mathrm{A}} = k_{\mathrm{l}}(C_{\mathrm{Ai}} - C_{\mathrm{Al}}) \tag{4.6}$$

where C_{Ai} is the concentration of component A at the interface and C_{Al} is its concentration in the bulk of the phase.

In all cases, the mass transfer coefficient will depend on the diffusivity of the transferred material and the thickness of the effective film. The latter is largely determined by the Reynolds number of the moving fluid, that is, its average velocity, its density, its viscosity, and some linear dimension of the system. Dimensional analysis will give the following relation:

$$\frac{kd}{D} = \mathrm{Constant}(\mathrm{Re})^{q} \cdot \left(\frac{\eta}{\rho D}\right)^{r}$$

where Re is the Reynolds number, k is the mass transfer coefficient, D is the diffusivity, and d is a dimension characterizing the geometry of the system.

This relation is analogous to the expression for heat transfer by forced convection given in chapter 3. The dimensionless group kd/D corresponds to the Nusselt group in heat transfer. The parameter $\eta/\rho D$ is known as the Schmidt number and is the mass transfer counterpart of the Prandtl number. For example, the evaporation of a thin liquid film at the wall of a pipe into a turbulent gas is described by the equation

$$\frac{kd}{D} = 0.023\,\mathrm{Re}^{0.8}\,\mathrm{Sc}^{0.33}$$

where Sc is the Schmidt number. Although the equation expresses experimental data, comparison with equation (13) from the heat transfer section again demonstrates the fundamental relation of heat and mass transfer.

Similar relations have been developed empirically for other situations. The flow of gases normal to and parallel to liquid surfaces can be applied to drying processes, and the agitation of solids in liquids can provide information for crystallization or dissolution. The final correlation allows the estimation of the mass transfer coefficient with reasonable accuracy.

INTERFACIAL MASS TRANSFER

So far, only diffusion in the boundary layers of a single phase has been discussed. In practice, however, two phases are normally present and mass transfer across the interface must occur. On a macroscopic scale, the interface can be regarded as a discrete boundary. On the molecular scale, however, the change from one phase to another takes place over several molecular diameters. Because of the movement of molecules, this region is in a state of violent change, the entire surface layer changing many times a second. Transfer of molecules at the actual interface is, therefore, virtually instantaneous, and the two phases are, at this point, in equilibrium.

Since the interface offers no resistance, mass transfer between phases can be regarded as the transfer of a component from one bulk phase to another through two films in contact, each characterized by a mass transfer coefficient. This is the two-film theory and is the simplest of the theories of interfacial mass transfer. For the transfer of a component from a gas to a liquid, the theory is described in Figure 4.3. Across the gas film, the concentration, expressed as partial pressure, falls from a bulk concentration P_{Ag} to an interfacial concentration P_{Ai}. In the liquid, the concentration falls from an interfacial value C_{Ai} to a bulk value C_{Al}.

At the interface, equilibrium conditions exist. The break in the curve is due to the different affinities of component A for the two phases and the different units expressing concentration. The bulk phases are not, of course, at equilibrium, and it is the degree of displacement from equilibrium conditions that provides the driving force for mass transfer. If these conditions are known, an overall mass transfer coefficient can be calculated and used to estimate the rate of mass transfer.

Transfer of a component from one mixed phase to another, as described above, occurs in several processes. Liquid-liquid extraction, leaching, gas absorption, and distillation are examples. In other processes, such as drying, crystallization, and dissolution, one phase may consist of only one component. Concentration gradients are set up in one phase only, with the concentration at the interface given by the relevant equilibrium conditions. In drying, for

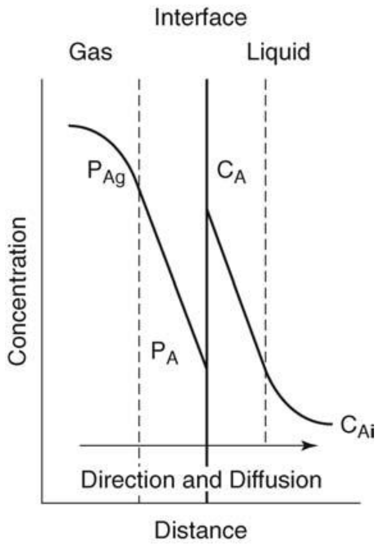


FIGURE 4.3 Interfacial mass transfer.

example, a layer of air in equilibrium, that is, saturated, with the liquid is postulated at the liquid surface and mass transfer to a turbulent airstream will be described by equation (4.5). The interfacial partial pressure will be the vapor pressure of the liquid at the temperature of the surface. Similarly, dissolution is described by equation (4.6), the interfacial concentration being the saturation concentration. The rate of solution is determined by the difference between this concentration, the concentration in the bulk solution, and the mass transfer coefficient.

5 Powders

INTRODUCTION

Powders are employed in many pharmaceutical processes. They are more difficult to handle and process than liquids and gases primarily because their flow properties are fundamentally different. Unlike fluids, a particulate mass will resist stresses less than a limiting value without continuous deformation, and many common powders will not flow because the stresses imposed, for example, by gravity are insufficiently high. Often additional processes that improve flow, such as granulation and fluidization, are adopted to facilitate powder transport and powder feeding.

Another important property of powders is the manner in which the particles of a powder pack together to form a bed and its influence on bulk density. The latter is the ratio of the mass of the powder to its total volume, including voids. Unlike fluids, it varies greatly with the size, size distribution, and shape of the particles because these affect the closeness of packing and the fraction of the bed that is void. Vibration and tapping, which cause rearrangement of the particles and a decrease in the void fraction, increase the bulk density. In several processes, these factors are important because the powder is subdivided and measured by volume. Variation of bulk density then causes variation in weight and dose. The variation in the weight of compressed tablets is an excellent example of this effect. The manner of packing also influences the behavior of a bed when it is compressed.

Finally, in a static condition, there is no leveling at the free surface of a bed of powder. Nor is pressure transmitted downward through the bed. Instead, the walls of the containing vessel carry the weight of the bed.

PARTICLE PROPERTIES

Origins

To understand particle properties it is important to consider their origins. Particles may be produced by different processes that can be regarded as constructive or destructive (Hickey, 1993). Constructive methods include crystallization, precipitation, and condensation, and destructive methods include milling and spray drying.

The most common methods of bulk manufacture are crystallization and precipitation from saturated solutions. These solutions are saturated by exceeding the solubility limit in one of several ways (Martin, 1993). Adding excess solid in the form of nucleating crystals results in crystallization from saturated solution. This can be controlled by reducing the temperature of the solution, thereby reducing solubility. For products that can be melted at relatively low temperatures, heating and cooling can be used to invoke a controlled crystallization. The addition of a cosolvent with different capacity to dissolve the solute may also be used to reduce the solubility and result in precipitation. In the extreme, a chemical reaction or complexation occurs to produce a precipitate (e.g., amine-phosphate/sulfate interactions; Fung, 1990). Condensation from vapors is a technical possibility and has been employed for aerosol products (Pillai et al., 1993), but has little potential as a bulk manufacturing process.

Milling (Carstensen, 1993) and spray drying (Masters, 1991) may be described as destructive methods since they take bulk solid or liquid and increase the surface area by significant input of energy, thereby producing small discrete particles or droplets. The droplets produced by spraying may then be dried to produce particles of pure solute. A variety of mills are available distinguished by their capacity to introduce energy into the powder. Spray dryers are available that may be utilized to produce powders from aqueous or nonaqueous solutions (Sacchetti and Van Oort, 2006).

Structure

The structure of particles may be characterized in terms of crystal system and crystal habit. The crystal system can be defined by the lattice group spacing and bond angles in three dimensions. Consequently, in the simplest form, a crystal may be described by the distance between planes of atoms or molecules in three dimensions (a, b, and c) and by the angles between these planes (α, β, and γ), where each angle is opposite the equivalent dimension (e.g., α opposite a). These angles and distances are determined by X-ray diffraction utilizing Bragg's law (Mullin, 1993). Crystals may be considered as polygons wherein the numbers of faces, edges, and vertices are defined by Euler's law. There are more than 200 possible permutations of crystal system based on this definition. In practice, each of these geometries can be classified into seven specific categories of crystal system: cubic, monoclinic, triclinic, hexagonal, trigonal, orthorhombic, and tetragonal.

Once the molecular structure of crystals has been established, the manner in which crystal growth occurs from solution is dictated by inhibition in any of the three dimensions. Inhibition of growth occurs because of differences in surface free energy or surface energy density. These differences may be brought about by regions of different polarity at the surface, charge density at the surface, the orientation of charged side groups on the molecules, the location of solvent at the interface, or the adsorption of other solute molecules (e.g., surfactant). Crystal growth gives rise to particles of different crystal habit. It is important to recognize that different crystal habits, or superficial appearance, do not imply different lattice group spacing, as defined by crystal system. Also it is possible that any of the methods of production may result in particles that have no regular structure or specific orientation of molecules, which are, by definition, amorphous.

Properties

Properties dictated by the method of manufacture include particle size and distribution, shape, specific surface area, true density, tensile strength, melting point, and polymorphic form. Arising from these fundamental physicochemical properties are other properties such as solubility and dissolution rate.

Polymorphism, or the ability of crystals to exhibit different crystal lattice spacings under different conditions (usually of temperature or moisture content), can be evaluated by thermal techniques. Differential scanning calorimetry may be used to determine the energy requirements for rearranging molecules in the lattice as they convert from one form to another. This difference between polymorphic forms of the same substance can also be detected by assessing their solubility characteristics.

PARTICLE INTERACTIONS

The attraction between particles or between particles and a containing boundary influences the flow and packing of powders. If two particles are placed together, the cohesive bond is normally very much weaker than the mechanical strength of the particles themselves. This may be due to the distortion of the crystal lattice, which prevents the correct adlineation of the atoms or the adsorption of surface films. These prevent contact of the surfaces and usually but not always decrease cohesion. Low cohesion is also the result of small area of contact between the surfaces. On a molecular scale, surfaces are very rough, and the real area of contact will be very much smaller than the apparent area. Finally, the structure of the surface may differ from the interior structure of the particle. Nevertheless, the cohesion and adhesion that occur with all particles are appreciable. It is normally ascribed to nonspecific Van der Waal's forces, although, in moist materials, a moisture layer can confer cohesiveness by the action of surface tension at the points of contact. For this reason, an increase in humidity can produce a sudden increase in cohesiveness and the complete loss of mobility in a powder that ceases to flow and pour. The acquisition of an electric charge by frictional movement between particles is another mechanism by which particles cohere together or adhere to containers.

These effects depend on both the chemical and physical forms of the powder. They normally oppose the gravitational and momentum forces acting on a particle during flow and therefore become more effective as the weight or size of the particle decreases. Cohesion and adhesion increase as the size decreases because the number of points in contact in a given area of apparent contact increases. The effects of cohesion will often predominate at sizes less than 100 μm and powders will not pass through quite large orifices, and vertical walls of a limited height appear in a free surface. The magnitude of cohesion also increases as the bulk density of the powder increases.

Cohesion also depends on the time for which contact is made. This is not fully understood but may be due to the gradual squeezing of air and adsorbed gases from between the approaching surfaces. The result, however, is that a system that flows under certain conditions may cease to flow when these conditions are restored after interruption. This is of great importance in the storage and intermittent delivery of powders. Fluctuating humidity can also destroy flow properties if a water-soluble component is present in the powder. The alternating processes of dissolution and crystallization can produce very strong bonds between particles, which cement the mass together.

Measurement of the Effects of Cohesion and Adhesion

The measurement of the cohesion between two particles or the adhesion of a particle to a boundary is difficult, although several methods can be used. More commonly, these effects are assessed by studying an assembly of particles in the form of a bed or a heap. Flow and other properties of the powder are then predicted from these studies (Crowder and Hickey, 2000).

The most commonly observed and measured property of a heap is the maximum angle at which a free powder surface can be inclined to the

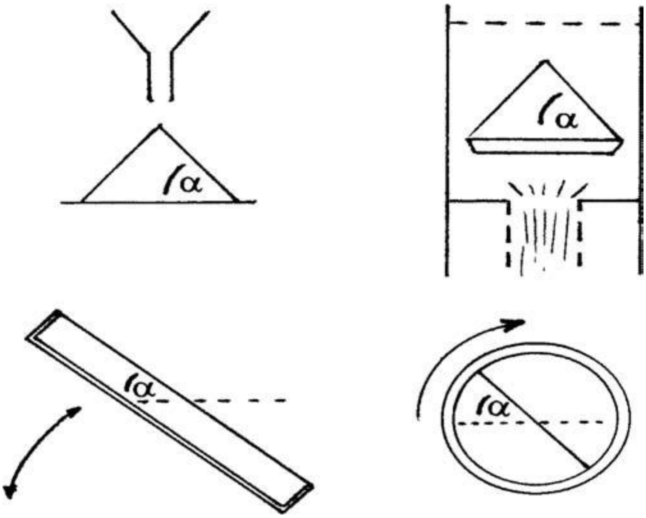


FIGURE 5.1 Measurement of the angle of repose, α.

horizontal. This is the angle of repose, and it can be measured in a number of ways, four of which are shown in Figure 5.1. The angle depends to some extent on the method chosen and the size of the heap. Minimum angles are about 25°, and powders with repose angles of less than 40° flow well. If the angle is over 50°, the powder flows with difficulty or does not flow at all.

The angle, which is related to the tensile strength of a powder bed, increases as the particle shape departs from sphericity and as the bulk density increases. Above 100 μm, it is independent of particle size, but below this value, it increases sharply. The effect of humidity on cohesion and flow is reflected in the repose angle. Moist powders form an irregular heap with repose angles of up to 90°.

A more fundamental measure is the tensile stress necessary to divide a powder bed. The powder may be dredged on to a split plate or, in a more refined apparatus, contained within a split cylinder and carefully consolidated. The stress is found from the force required to break the bed and the area of the divided surface. The principles of this method are shown in Figure 5.2A, and stresses of up to 100 N/m^2 are necessary to divide a bed of fine powders. Values increase as the bulk density increases. Changes in cohesiveness with time and the severe changes in the flow properties of some powders that occur when the relative humidity exceeds 80% can be assessed with this apparatus.

Apparatus for shearing a bed of powder is shown diagrammatically in Figure 5.2B. The shear stress at failure is measured while the bed is constrained under a normal stress. The latter can be varied. The relation between these stresses, a subject fully explored in the science of soil mechanics, is used in the design of bins and hoppers for the storage and delivery of powders.

The adhesion of particles to surfaces can be studied in a number of ways. Measurement of the size of the particles retained on an upturned plate is a useful qualitative test. A common method measures the angle of inclination at which a powder bed slides on a surface, the bed itself remaining coherent.

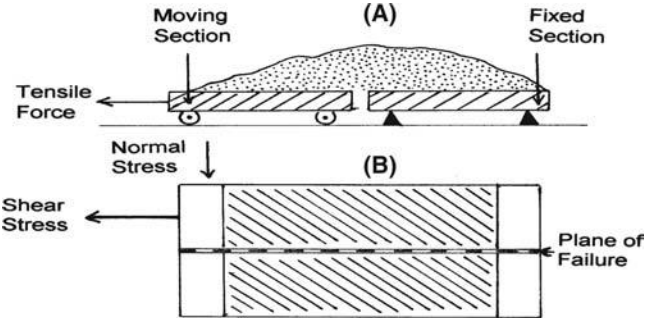


FIGURE 5.2 Measuring the (**A**) tensile and (**B**) shear strength of a powder bed.

FLOW OF POWDERS

The gravity flow of powders in chutes and hoppers and the movement of powders through a constriction occur in tabletting, encapsulation, and many processes in which a powder is subdivided for packing into final containers. In many cases, the accuracy of weight and dose depends on the regularity of flow. The flow of powders is extremely complex and is influenced by many factors. A profile, in two dimensions, of the flow of granular solids through an aperture is shown in Figure 5.3. Particles slide over A while A itself slides over B. B moves slowly over the stationary region E. Material is fed into zone C and moves downward and inward to a tongue D. Here, packing is less dense, particles move more quickly, and bridges and arches formed in the powder collapse. Unless the structure is completely emptied, powder in region E never

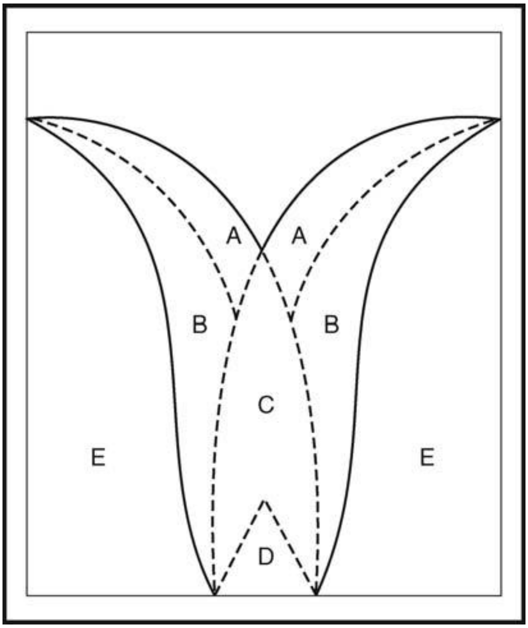


FIGURE 5.3 Profile of the flow of granules through an orifice.

flows through the aperture. If, in use, a container is partially emptied and partially filled, this material may spoil. If the container is narrow, region E is absent and the whole mass moves downward, the central part of region C occupying the entire tube (Brown and Richards).

For granular solids, the relation between mass flow rate, *G*, and the diameter of a circular orifice, D_o, is expressed by the equation

$$G = \text{Constant}\, D_o^a H^b$$

where *H* is the height of the bed and *a* and *b* are constants. For a wide variety of powders, the constant *a* lies between 2.5 and 3.0. If the height of the bed is several times that of the orifice, *H* lies between 0 and 0.05. The absence of a pressure-depth relation, already observed in a static bed, therefore, seems to persist in dynamic conditions.

The relation between mass flow rate and particle size is more complex. With an orifice of given size and shape, the flow increases as the particle size decreases until a maximum rate is reached. With further decrease in size and increase in cohesiveness, flow decreases and becomes irregular. Arches and bridges form above the aperture, and flow stops. The determination of the minimum aperture through which a powder will flow without assistance is a useful laboratory exercise. The distribution of particle sizes also affects the flow in a given system. Often, the removal of the finest fraction will greatly improve flow. On the other hand, the addition of very small quantities of fine powder can, in some circumstances, improve flow. This is probably due to adsorption of these particles onto the original material, preventing close approach and the development of strong cohesional bonds. Magnesia and talc, for example, promote the flow of many cohesive powders. These materials, which can be called glidants, are useful additives when good flow properties are required of a powder.

Vibration and tapping may maintain or improve the flow of cohesive powders by preventing or destroying the bridges and arches responsible for irregular movement or blockage. Vibration and tapping to initiate flow are less satisfactory because the associated increase in bulk density due to closer packing renders the powder more cohesive.

PACKING OF POWDERS

Bulk density, already defined, and porosity are terms used to describe the degree of consolidation in a powder. The porosity, ε, is the fraction of the total volume that is void, often expressed as a percentage. It is related to the bulk density, ρ_b, by the equation

$$\varepsilon = 1 - \frac{\rho_b}{\rho} \tag{5.1}$$

where ρ is the true density of the powder.

When spheres of equal size are packed in a regular manner, the porosity can vary from a maximum of 46% for a cubical arrangement to a minimum of 26% for a rhombohedral array. These extremes are shown in Figure 5.4. For ideal systems of this type, the porosity is not dependent on the particle size. In practice, of course, packing is not regular. Cubic packing, obtained when the next layer is placed directly on top of the four spheres above, is the most open

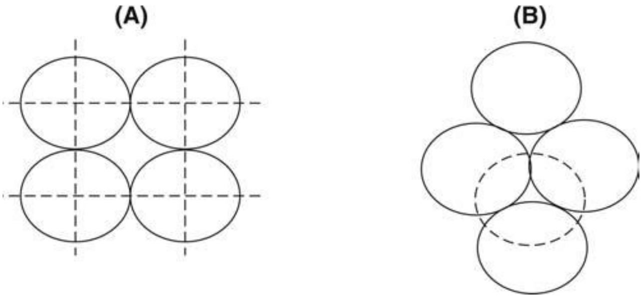


FIGURE 5.4 Systematic packing of spheres **(A)** open (cubic) and; **(B)** closed (rhombohedral) structure.

packing, as shown in Figure 5.4A. Rhombohedral packing, obtained when the next layer is built around the sphere shown in a broken line in Figure 5.4B, is the closest packing.

Nevertheless, for coarse, isodiametric particles with a narrow range of sizes, the porosity is remarkably constant at between 37% and 40%. Lead shot, for example, packs with the same porosity as a closely graded sand. With wider size distributions, the porosity decreases because some packing of fine particles in the interstices between the coarsest particles becomes possible. These effects are absent in fine powders. Because of their more cohesive nature, the porosity increases as the particles become finer and variation in the size distribution has little effect.

In any irregular array, the porosity increases as particle shape departs from sphericity because open packing and bridging become more common. A flaky material, such as crushed mica, packs with a porosity of about 90%. Roughness of the surface of the particles will increase porosity.

In operations in which powders are poured, chance packing occurs and the porosity is subject to the speed of the operation and the degree of agitation. If the powder is poured slowly, each particle can find a stable position in the developing surface. Interstitial volumes will be small, the number of contacts with neighboring particles will be high, and the porosity will be low. If pouring is quick, there is insufficient time for stable packing, bridges are created as particles fall together, and a bed of higher porosity is formed. Vibration opposes open packing and the formation of bridges. It is often deliberately applied when closely packed powder beds are required.

Packing at a boundary differs from packing in the bulk of a powder. The boundary normally creates a region of more open packing, several particle layers in extent. This is important when particles are packed into small volumes. If the particles are relatively large, the region of expanded packing and low bulk density will be extensive, and for these conditions, the weight of material that fills the volume will decrease as the particle size increases. With finer powders, the opposite is true and cohesiveness causes the weight of powder that fills a volume to decrease as the particle size decreases. There is, therefore, some size of particle for which the capacity of a small volume is a maximum. This depends on the dimensions of the space into which the particles are packed.

GRANULATION

Granulation is a term given to a number of processes used to produce materials in the form of coarse particles. In pharmacy, it is closely associated with the preparation of compressed tablets. Here discussion is limited to a general account of the process.

Ideally, granulation yields coarse isodiametric particles with a very narrow size distribution. The several advantages of this form can be inferred from the discussion above. Granules flow well. They will feed evenly from chutes and hoppers and will pack into small volumes without great variation of weight. Segregation in a mixture of powders is prevented if the mixture of powders is granulated. Each granule contains the correct proportions of the components so that segregation of granules cannot cause inhomogeneity in the mixture. The hazards of dust are eliminated, and granules are less susceptible to lumping and caking. Finally, granular materials fluidize well and a material may be granulated to gain the advantages of this process.

The starting materials for granulation vary from fine powders to solutions. Methods can be classified as either wet or dry granulation. In the latter, a very coarse material is comminuted and classified. If the basic material is a fine powder, it is first aggregated by pressure with punches and dies to give tablets or briquettes, or by passage through rollers to give a sheet that is then broken.

In wet methods, a liquid binder is added to a fine powder. If the proportion added converts the powder to a crumbly, adhesive mass, it can be granulated by forcing it through a screen with an impeller. The wet granules are then dried and classified. If a wetter mass is made, it can be granulated by extrusion. Alternatively, the powder can be rotated in a pan and granulating fluid is added until agglomeration occurs. Granule growth depends critically on the amount of fluid added, and other variables, such as particle size, pan speed, and the surface tension of the granulating fluid, must be closely controlled.

Granular materials are also prepared by spray drying and by crystallization.

FLUIDIZATION

The movement of fluids through a fixed bed was described in chapter 2. If the fluid velocity is low, the same situation is found when fluid is driven upward through a loose particulate bed. At higher velocities, however, frictional drag causes the particles to move into a more expanded packing, which offers less resistance to flow. At some critical velocity, the particles are just touching and the pressure drop across the bed just balances its weight. This is the point of incipient fluidization, and beyond it true fluidization occurs, the bed acquiring the properties of surface leveling and flow.

If the fluid is a liquid, increase in velocity causes the quiescent bed to rock and break, allowing individual particles to move randomly in all directions. Increase in velocity causes progressive thinning of this system. In fluidization by gases, the behavior of the bed is quite different. Although much of the gas passes between individual particles in the manner already described, the remainder passes in the form of bubbles so that the bed looks like a boiling liquid. Bubbles rise through the bed, producing an extensive wake from which material is continually lost and gained, and breaking at the surface distributes powder widely. This is an effective mixing mechanism, and any nonhomogeneity in the bed is quickly destroyed. Rates of heat and mass transfer in the bed are therefore high.

Bubble size and movement vary in different systems. In general, both decrease as the particle size decreases. As the size decreases and the powder becomes more cohesive, fluidization becomes more difficult. Eventually, bubbles do not form and very fine powders cannot be fluidized in this way.

The final stage of fluidization occurs at very high velocities when in both liquid and gaseous systems, the particles become entrained in the fluid and are carried along with it. These conditions are used to convey particulate solids from one place to another.

MIXING AND BLENDING

Mixing and blending may be achieved by rotating or shearing the powder bed. Mixing two or more components that may differ in composition, particle size, or some other physicochemical property is brought about through a sequence of events. Most powders at rest occupy a small volume such that it would be difficult to force two static powder beds to mix. The first step in a mixing process, therefore, is to dilate the powder bed. The second step, which may be concurrent with the first, is to shear the powder bed. Ideally, shearing occurs at the level of planes separated by individual particles. The introduction of large interparticulate spaces is achieved by rotating the bed. A V-blender or barrel roller are classical examples of systems which, by rotating through 360°, dilate the powder bed while, through the influence of gravity, shear planes of particles. A planetary mixer uses blades to mechanically dilate and shear the powder. Each of these systems is a batch process. A ribbon blender uses a screw, or auger, action to rotate and shear the bed from one location to another in a continuous process.

Since the shearing of particles in a bed to achieve a uniform mix of blend is a statistical process, it must be monitored for efficiency. Sample thieves are employed to probe the powder bed, with minimal disturbance, and draw samples for analysis. These samples are then analyzed for the relevant dimension for mixing, for example, particle size, drug, or excipient content. Statistical mixing parameters have been derived based on the mean and standard deviation of samples taken from various locations in a blend at various times during processing (Carstensen, 1993). In large-scale mixers random number tables may be employed to dictate sample sites. There is a considerable science of sampling that can be brought to bear on this problem (Thompson, 2002). The sample size for pharmaceutical products is ideally of the scale of the unit dose. This is relevant as it relates to the likely variability in the dose that in turn relates to the therapeutic effect. In the case of small unit doses, the goal should be to sample at a size within the resolution of the sample thief.

CONCLUSION

The origins, structure, and properties of particles within a powder dictate their dynamic performance. Gathering information on the physicochemical properties of the powders is a prerequisite for interpreting and manipulating their flow and mixing properties. Flow properties are important to many unit processes in pharmacy, including transport and movement through hoppers, along conveyor belts, in granulators, and in mixers. Ultimately, the packing and flow properties can be directly correlated with the performance of the unit dose. Filling of capsules, blisters, or tablet dies; compression of tablets; and dispersion of powder aerosols all relate to powder properties.