CHAPTER 2

Importance of Fluids for the Circulation of Blood, Gas Movement, and Gas Exchange

Read This Chapter to Learn About

- Fluids at Rest
- Fluids in Motion
- Circulatory System
- Gases

This chapter reviews an important topic of physics: fluids. **Fluids** is a term that describes any substance that flows—a characteristic of both liquids and gases. Fluids possess inertia, as defined by their density, and are thus subject to the same physical interactions as solids. All of these interactions as they pertain to fluids at rest and fluids in motion as well as practical examples related to human physiology are discussed in this chapter.

FLUIDS AT REST

Density and Specific Gravity

Density, ρ, is a physical property of a fluid, given as mass per unit volume, or

$$\rho = \frac{\text{mass}}{\text{unit volume}} = \frac{m}{V}$$

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Density represents the fluid equivalent of mass and is given in units of kilograms per cubic meter $\left(\frac{kg}{m^3}\right)$, grams per cubic centimeter $\left(\frac{g}{cm^3}\right)$, or grams per milliliter $\left(\frac{g}{mL}\right)$. Density, a property unique to each substance, is independent of shape or quantity but is dependent on temperature and pressure.

Specific gravity (Sp. gr.) of a given substance is the ratio of the density of the substance ρ_{sub} to the density of water ρ_w, or

$$\text{Sp. gr.} = \frac{\text{density of substance}}{\text{density of water}} = \frac{\rho_{sub}}{\rho_w}$$

where the density of water ρ_w is 1.0 g/cm^3 or 1.0×10^3 kg/m^3. Assuming that equal volumes are chosen, the specific gravity can also be expressed in terms of weight:

$$\text{Sp. gr.} = \frac{\text{weight of substance}}{\text{weight of water}} = \frac{w_{sub}}{w_w}$$

Specific gravity is a pure number that is unitless.

EXAMPLE: Determine the size of container needed to hold 0.7 g of a chemical substance, which has a density of 0.62 g/cm^3.

SOLUTION: The volume of a fluid can be found from the relation for density:

$$V = \frac{m}{\rho} = \frac{0.7\text{ g}}{0.62\ \frac{\text{g}}{\text{cm}^3}} = 1.129\text{ cm}^3 = 1.129\text{ mL}$$

Buoyant Force and Archimedes' Principle

Archimedes' principle states: "A body immersed wholly or partially in a fluid is subjected to a **buoyant force** that is equal in magnitude to the weight of the fluid displaced by the body," or

buoyant force = weight of displaced fluid

If the buoyant force is equal to or greater than the weight of the object, then the object remains afloat. However, if the buoyant force is less than the weight of the object, then the object sinks.

But how would you calculate the weight of displaced fluid in a practical scenario? Let's say that you place an object in a graduated cylinder filled with 40 mL of water and, as a result, the water level rises to 44 mL. Placement of the object into the graduated cylinder caused a change in volume of 4 mL. The mass of the displaced fluid can be determined by the equation for density: $\rho = \frac{m}{V}$ or $m = \rho V$.

Apply this equation to the problem, $m = \rho V = \left(1.00\ \frac{\text{g}}{\text{cm}^3}\right)(4\text{ cm}^3) = 4.0$ g.

The weight of the displaced fluid can be determined by $W = mg = (0.004\text{ kg})\left(9.8\ \frac{\text{m}}{\text{s}^2}\right) = 0.0392$ N.

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EXAMPLE: A humpback whale weighs 5.4×10^5 N. Determine the buoyant force required to support the whale in its natural habitat, the ocean, when it is completely submerged. Assume that the density of seawater is 1030 kg/m^3 and the density of the whale ρ_{whale} is approximately equal to the density of water ($\rho_{\text{water}} =$ 1000 kg/m^3).

SOLUTION: The volume of the whale can be determined from:

$$m = \rho V = \frac{W}{g}$$

Solving for V yields

$$V_{\text{whale}} = \frac{W_{\text{whale}}}{\rho_{\text{whale}} g} = \frac{5.4 \times 10^5 \text{ N}}{\left(1000 \frac{\text{kg}}{\text{m}^3}\right)\left(9.8 \frac{\text{m}}{\text{s}^2}\right)} = 55.1 \text{ m}^3$$

The whale displaces 55.1 m^3 of water when submerged. Therefore, the buoyant force BF, which is equal to the weight of displaced water, is given by:

$$\text{BF} = W_{\text{seawater}} = \rho_{\text{seawater}}\, g V_{\text{whale}} = \left(1030 \frac{\text{kg}}{\text{m}^3}\right)\left(9.8 \frac{\text{m}}{\text{s}^2}\right)\left(55.1 \text{ m}^3\right)$$
$$= 5.6 \times 10^5 \text{ N}$$

Pressure: Atmospheric and Hydrostatic

Pressure P is defined as a force F acting perpendicular to a surface area, A, of an object and is given by:

$$\text{pressure} = \frac{\text{force}}{\text{area}} = \frac{F}{A}$$

Pressure is a scalar quantity and is expressed in units of $\frac{\text{N}}{\text{m}^2}$. Two specific types of pressure particularly applicable to fluids include atmospheric pressure and hydrostatic pressure.

Atmospheric pressure P_{atm} represents the average pressure exerted by Earth's atmosphere, and is defined numerically as 1 atm but can also be expressed as 760 millimeters of mercury (mmHg) or 1.01×10^5 pascals (Pa).

Hydrostatic pressure P_{hyd} is the fluid pressure exerted on an object at a depth h in a fluid of density ρ and is given by:

$$P_{\text{hyd}} = \rho g h$$

The total pressure, P, exerted on an object within a contained fluid is the sum of the atmospheric pressure and the hydrostatic pressure:

$$P = P_{\text{atm}} + P_{\text{hyd}} = P_{\text{atm}} + \rho g h$$

EXAMPLE: Given that the density of water is $1.0 \frac{\text{g}}{\text{cm}^3}$, what is the pressure exerted on a swimmer in a swimming pool at a depth of 180 cm? (atmospheric pressure $= 1.013 \times 10^5 \frac{\text{N}}{\text{m}}$)

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SOLUTION: The pressure exerted on a swimmer at a certain depth within a swimming pool depends on the atmospheric pressure as well as the hydrostatic pressure due to the water above the depth in question. The total pressure exerted on the swimmer at a depth of 180 cm, or 1.8 m, is:

$$P_{\text{total}} = P_{\text{atm}} + P_{\text{hyd}} = P_{\text{atm}} + \rho g h$$

where ρ is the density of water, g is the acceleration due to gravity, and h is the height (or depth) of the column of water.

$$P_{\text{total}} = P_{\text{atm}} + P_{\text{hyd}} = \left(1.013 \times 10^5 \,\frac{\text{N}}{\text{m}^2}\right) + \left(1000 \,\frac{\text{kg}}{\text{m}^3}\right)\left(9.8 \,\frac{\text{m}}{\text{s}^2}\right)(1.8\text{ m})$$

$$= 1.19 \times 10^5 \,\frac{\text{N}}{\text{m}^2}$$

Pascal's Principle

Pascal's principle states: "An external pressure applied to a confined fluid will be transmitted equally to all points within the fluid."

EXAMPLE: An example of Pascal's principle is the hydraulic jack, shown in Figure 2-1. If a force of 300 N is applied to a piston of 1-cm^2 cross-sectional area, determine the lifting force transmitted to a piston of cross-sectional area of 100 cm^2.

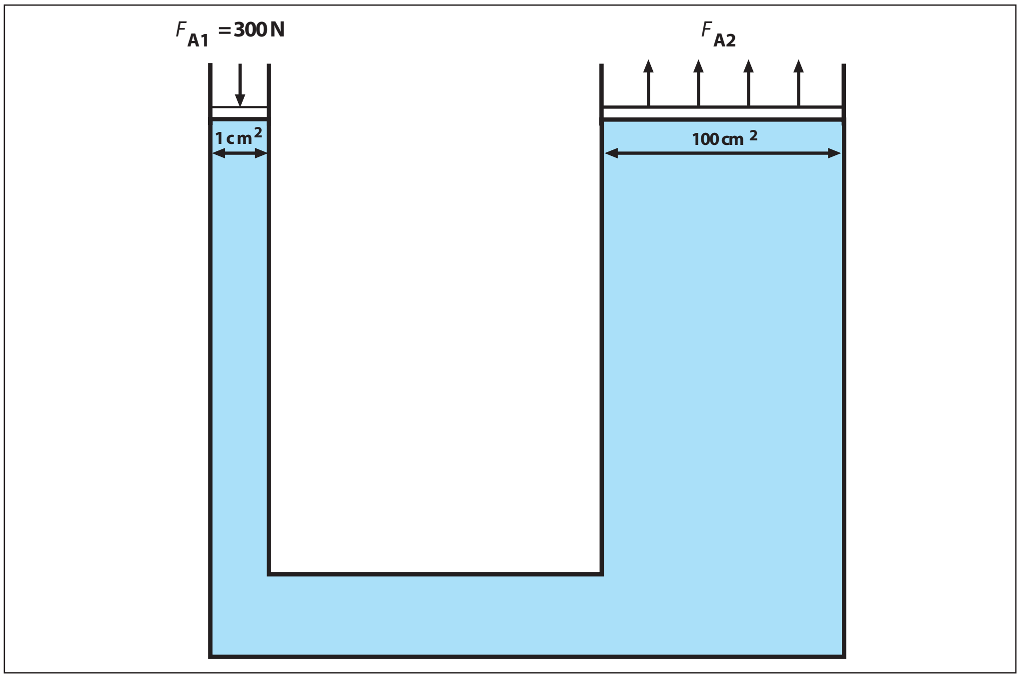

FIGURE 2-1 Hydraulic jack. *Source:* From George Hademenos, *Schaum's Outline of Physics for Pre-Med, Biology, and Allied Health Students*, McGraw-Hill, 1998; reproduced with permission of The McGraw-Hill Companies.

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SOLUTION: According to Pascal's principle,

$$P_{1\,\text{cm}^2} = P_{100\,\text{cm}^2}$$
$$\left(\frac{F}{A}\right)_{1\,\text{cm}^2} = \left(\frac{F}{A}\right)_{100\,\text{cm}^2}$$

Making the appropriate substitutions yields

$$\frac{300\text{ N}}{1\text{ cm}^2} = \frac{F}{100\text{ cm}^2}$$

Solving for F yields

$$F = 30{,}000\text{ N}$$

FLUIDS IN MOTION

Viscosity and Poiseuille's Law

Viscosity η is a measurement of the resistance or frictional force exerted by a fluid in motion. The SI unit of viscosity is newton seconds per square meter $\left(\frac{\text{N}\cdot\text{s}}{\text{m}^2}\right)$. Viscosity is typically expressed in units of poise (P), where

$$1\text{ poise} = 0.1\frac{\text{N}\cdot\text{s}}{\text{m}^2}$$

Fluid flow, Q, through a rigid, cylindrical tube of radius r and length L subjected to a constant external pressure gradient ΔP can be expressed as:

$$Q = \frac{\pi}{8}\frac{\Delta P r^4}{L\eta}$$

where η is fluid viscosity. This equation is known as **Poiseuille's law**. Fluid flow Q is the rate of volume flow through a pipe and is typically expressed in units of $\frac{\text{cm}^3}{\text{s}}$.

EXAMPLE: Determine the change in fluid flow for (1) a decrease in the pressure gradient by one-half, (2) an increase in viscosity by 2, (3) a decrease in vessel length by one-half, and (4) an increase in vessel radius by 2.

SOLUTION: The effect of the various parameters on fluid flow can be determined by analysis of their qualitative dependence according to Poiseuille's law:

$$Q = \frac{\pi}{8}\frac{\Delta P r^4}{L\eta}$$

1. Fluid flow Q is directly dependent on the pressure gradient ΔP. Thus a decrease in pressure gradient by one-half implies:

$$\Delta P = \frac{\Delta P}{2}$$

Substituting into Poiseuille's law gives:

$$Q = \frac{\pi}{8}\frac{(\Delta P/2)r^4}{L\eta} = \frac{1}{2}\left(\frac{\pi}{8}\frac{\Delta Pr^4}{L\eta}\right) = \frac{Q}{2}$$

Thus a decrease in pressure gradient by one-half results in a decrease in fluid flow by one-half.

2. Fluid flow Q is inversely dependent on the fluid viscosity η. Thus an increase in fluid viscosity by 2 implies:

$$\eta = 2\eta$$

Substituting into Poiseuille's law, you have:

$$Q = \frac{\pi}{8}\frac{\Delta Pr^4}{L(2\eta)} = \frac{1}{2}\left(\frac{\pi}{8}\frac{\Delta Pr^4}{L\eta}\right) = \frac{Q}{2}$$

Thus an increase in fluid viscosity by 2 results in a decrease in fluid flow by one-half.

3. Fluid flow Q is inversely dependent on the vessel length L. Thus a decrease in vessel length by one-half implies:

$$L = \frac{L}{2}$$

Substituting into Poiseuille's law yields:

$$Q = \frac{\pi}{8}\frac{\Delta Pr^4}{(L/2)\eta} = 2\left(\frac{\pi}{8}\frac{\Delta Pr^4}{L\eta}\right) = 2Q$$

Thus a decrease in vessel length by one-half results in an increase in fluid flow by 2.

4. Fluid flow Q is dependent on the vessel radius r to the fourth power. Thus an increase in vessel radius by 2 implies:

$$r = (2r)^4 = 16r^4$$

Substituting into Poiseuille's law, you find:

$$Q = \frac{\pi}{8}\frac{\Delta P(2r)^4}{L\eta} = 16\left(\frac{\pi}{8}\frac{\Delta Pr^4}{L\eta}\right) = 16Q$$

Thus an increase in vessel radius by 2 results in an increase in fluid flow by 16.

Continuity Equation

The **equation of continuity** is, in essence, an expression of the conservation of mass for a moving fluid. Specifically, the equation of continuity states that: (1) a fluid maintains constant density regardless of changes in pressure and temperature, and (2) flow measured at one point along a vessel is equal to the flow at another point along the vessel, regardless of the cross-sectional area of the vessel. Fluid flow Q, expressed in

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terms of the cross-sectional area of the vessel A, is given as:

$$Q = Av$$

where v is the velocity of the fluid. Thus the equation of continuity at any two points in a vessel is given as:

$$Q = A_1 v_1 = A_2 v_2 = \text{constant}$$

Laminar and Turbulent Flow

Fluid flow can be characterized according to two different types of flow: laminar flow and turbulent flow. Consider a fluid with density ρ and viscosity η flowing through a tube of diameter d. In **laminar flow,** the fluid flows as continuous layers stacked on one another within a smooth tube and moving past one another with some velocity. However, as the velocity of the fluid increases, fluid particles fluctuate between these ordered layers, causing random motion. When the fluid's velocity exceeds a threshold known as the critical velocity, it now is described as **turbulent flow.** The critical velocity depends on the parameters of the fluid and the vessel according to the relation

$$v = \frac{\eta \text{Re}}{\rho d}$$

where Re is a dimensionless quantity known as the **Reynold's number**.

Surface Tension

Surface tension γ is the tension, or force per unit length, generated by cohesive forces of molecules on the surface of a liquid acting toward the interior. Surface tension is given as force per unit length and defined as the ratio of the surface force F to the length d along which the force acts, or

$$\gamma = \frac{F}{d}$$

Surface tension is given in units of $\frac{\text{N}}{\text{m}}$.

Bernoulli's Principle

Bernoulli's principle, the fluid equivalent of conservation of energy, states that the energy of fluid flow through a rigid vessel by a pressure gradient is equal to the sum of the pressure energy, kinetic energy, and the gravitational potential energy, or

$$E_{\text{tot}} = P + \frac{1}{2}\rho v^2 + \rho g h = \text{constant}$$

An important application of Bernoulli's principle involves fluid flow through a vessel with a region of expansion or contraction. Bernoulli's principle describing fluid flow

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through a vessel with sudden changes in geometry can be expressed as:

$$\left(P + \frac{1}{2}\rho v^2 + \rho g h\right)_1 = \left(P + \frac{1}{2}\rho v^2 + \rho g h\right)_2$$

where 1 describes the energy of fluid flow in the normal region of the vessel and 2 describes the energy of fluid flow in the enlarged or obstructed region. An illustration of these two different scenarios of Bernoulli's principle as applied to vessel disease is seen in Figures 2-2 and 2-3. Note that Bernoulli's principle assumes a smooth transition between the two regions within a vessel with no turbulence in fluid flow. However, in the practical applications depicted in Figures 2-2 and 2-3, there is turbulence noted in Figure 2-2 about the expansion of the blood vessel, and in Figure 2-3 about the surface of the atherosclerotic plaque. Nevertheless, in many cases the vessel expansion in Figure 2-2 and the atherosclerotic plaque in Figure 2-3 are not significantly pronounced, so Bernoulli's principle can still be applied to these scenarios.

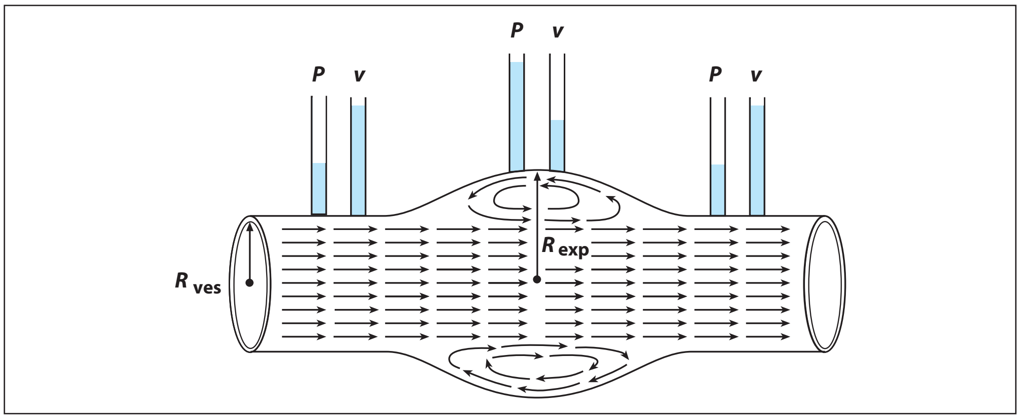

FIGURE 2-2 Bernoulli's principle as applied to the expansion of a blood vessel. *Source:* From George Hademenos, *Schaum's Outline of Physics for Pre-Med, Biology, and Allied Health Students,* McGraw-Hill, 1998; reproduced with permission of The McGraw-Hill Companies.

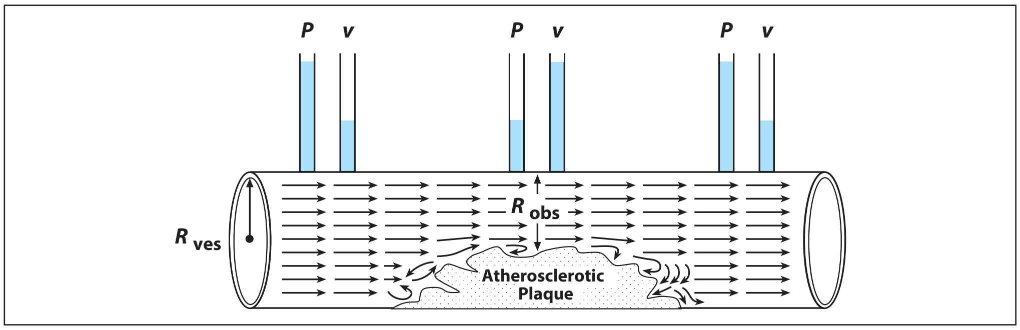

FIGURE 2-3 Bernoulli's principle as applied to an obstruction within a blood vessel. *Source:* From George Hademenos, *Schaum's Outline of Physics for Pre-Med, Biology, and Allied Health Students,* McGraw-Hill, 1998; reproduced with permission of The McGraw-Hill Companies.

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APPLICATIONS OF BERNOULLI'S PRINCIPLE: VENTURI EFFECT AND THE PITOT TUBE

Two extensions involving the application of Bernoulli's principle are the Venturi effect and the pitot tube.

The **Venturi effect** can be seen through the working principles of a Venturi meter. A **Venturi meter**, shown in Figure 2-4, is a device that measures fluid flow through a pipe. As the fluid of density ρ moves from the entrance of the pipe with a known cross-sectional area A_1, the fluid's pressure P_1 is at its maximum (causing a greater push and reduced height of the fluid in the U-tube attachment) and its velocity, v, is at its minimum. As the fluid continues through the pipe and encounters a constriction, the cross-sectional area at the narrowed region A_2 is decreased, the velocity increases, causing the fluid's pressure, P_2, to decrease, resulting in an increase in the height of the fluid in the U-tube attachment. The fluid's flow velocity through the constriction of the pipe, v_2, can be determined from the relationship:

$$v_2 = \sqrt{\frac{2g\left(h_1 - h_2\right)}{1 - \left(\frac{A_2}{A_1}\right)^2}}$$

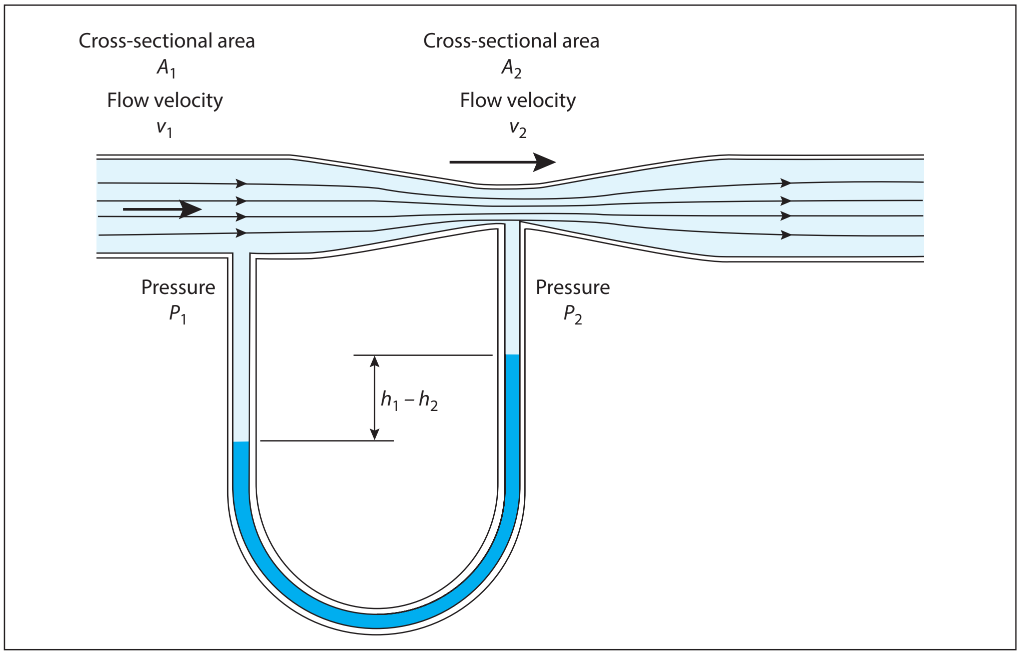

FIGURE 2-4 Venturi meter.

A **pitot tube** is an L-shaped, tubular device used to measure the velocity of airflow through a pipe. The pitot tube has two small holes—one hole is aligned parallel to the direction of the movement of air and is used to measure the stagnation pressure of the airflow. The second hole is located on the side of the parallel portion of the tube

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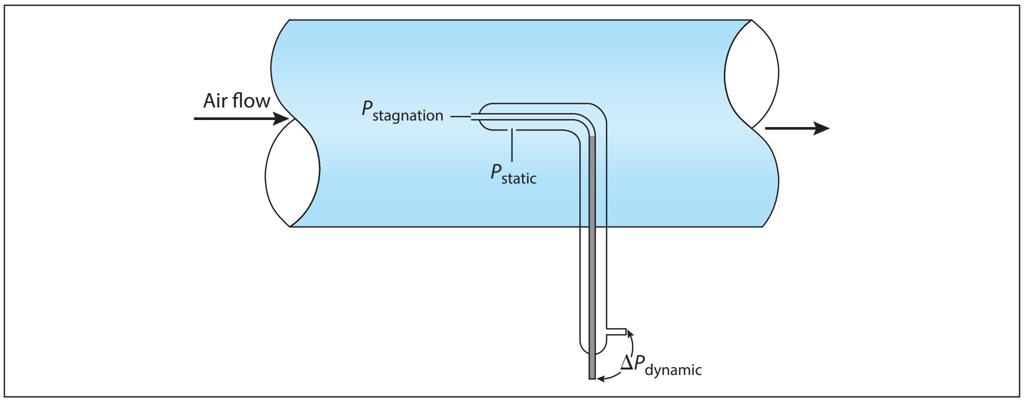

FIGURE 2-5 Pitot tube.

and used to measure the static pressure at that location relative to the airflow. The difference between the stagnation and static pressure values, $\Delta P_{dynamic}$, recorded at the end of the perpendicular segment of the pitot tube provides a measure of the dynamic pressure, which can then be used to calculate the velocity of airflow using Bernoulli's equation. See Figure 2-5.

CIRCULATORY SYSTEM

Arterial and Venous Systems

Beginning at the early stages of embryonic development until death, the circulatory system is responsible for circulating blood through the human body. The circulatory system consists of a vast array of different types of blood vessels, arranged in a complex, intricate, yet efficient design to allow optimal permeation of blood to every point within the human body. The primary purpose of the circulatory system is to deliver oxygen and nutrients to all of the organs and tissues of the human body and to remove cellular metabolic waste products within the body.

The circulatory system is composed primarily of three types of blood vessels: arteries, veins, and capillaries. **Arteries** transport oxygen-rich blood from the heart under high pressure to beds of **capillary vessels** embedded in tissues and organs of the human body. The role of the **veins** is the exact opposite of arteries in that they transport oxygen-poor blood away from the capillary bed under low pressure and return to the heart.

Pressure and Blood Flow Characteristics of the Circulatory System

Blood is pumped from the left ventricle of the heart into the aorta under a pressure of approximately 120 mm Hg (see Figure 2-6.) As blood moves farther into the circulatory

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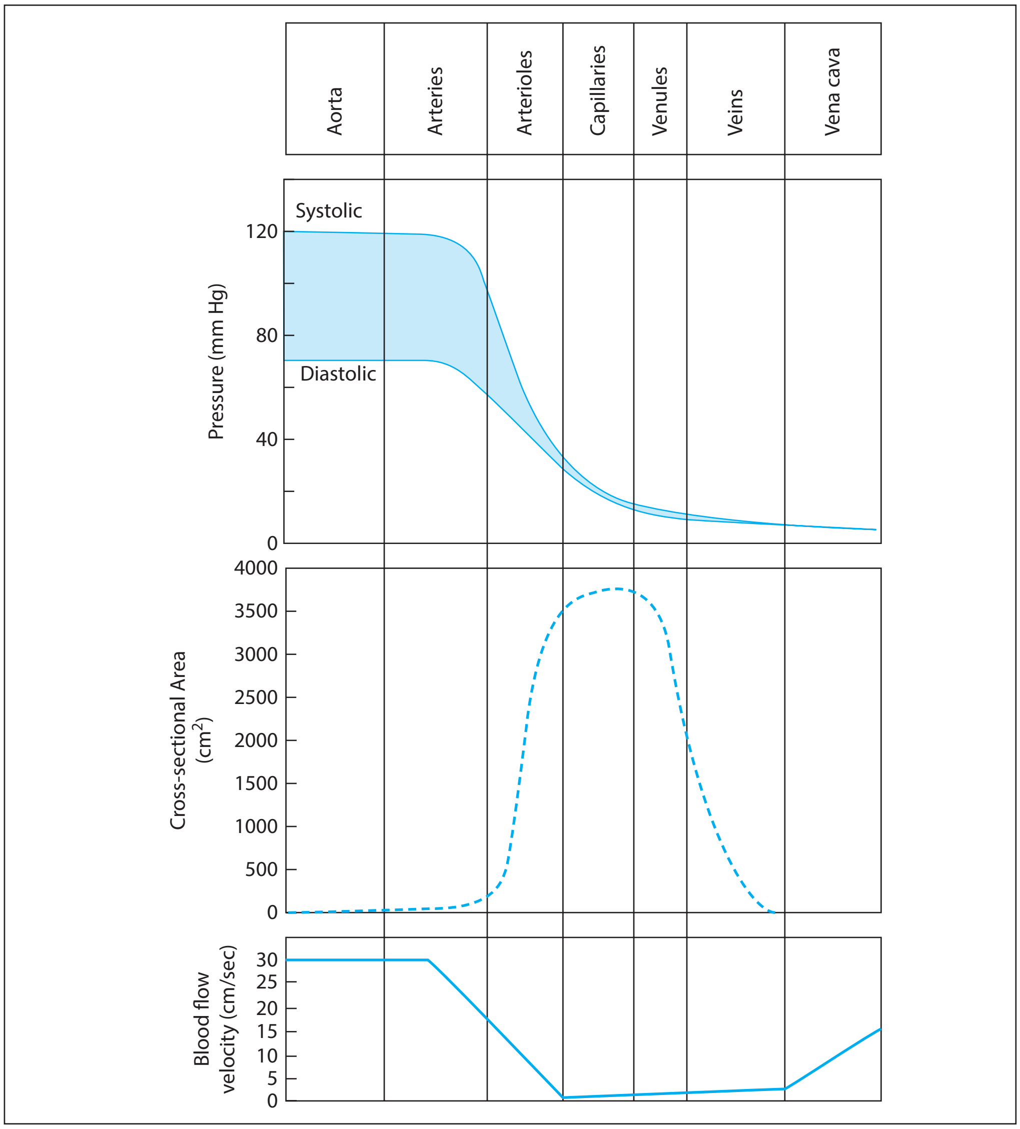

FIGURE 2-6 Pressure and blood flow throughout the human circulatory system.

system, the pressures start to decline steadily. From the aorta, blood flows through the larger arteries at 110 mm Hg, through the medium-sized arteries at 75 mm Hg, and through the smaller arteries or arterioles at 40 mm Hg until it reaches the capillary bed. Blood enters the capillary bed under a pressure of about 30 mm Hg and exits under a pressure of 16 mm Hg. Blood drains from the capillary bed into the smallest veins or venules at 16 mm Hg, continuing into the medium-sized veins under a pressure of 12 mm Hg and into the large veins at 4 mm Hg before returning to the heart.

Velocity of blood flow as blood exits the heart is approximately 30 cm/s and drops to 0.07 cm/s as it moves through the capillary vessels. In the large veins, blood flow maintains a speed of about 10 cm/s. The variation of pressure and blood flow velocity throughout the entire circulatory system is described in Figure 2-6.

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GASES

The volume, pressure, and temperature of gases are all related. These relationships for ideal gases, in which there is no intermolecular interaction, have been described through a series of laws—Boyle's law, Charles's law, and Avogadro's law—that make up the Ideal Gas Law. That law and Dalton's law concerning partial pressures in a mixture of gases provide a model for the behavior of ideal gases—the kinetic molecular theory of gases. The van der Waals constants allow for the correction for real gas behavior from that of ideal gases.

Temperature

Temperature is a physical property of a body that reflects its warmth or coldness. Temperature is a scalar quantity that is measured with a thermometer and is expressed in units that are dependent on the temperature measurement scale used. Three common scales of temperature measurement are Fahrenheit (°F), Celsius (°C), and Kelvin (K). (The SI unit for temperature is degrees Celsius.) They are defined according to absolute zero as well as the freezing point and boiling point of water:

TABLE 2-1

	Fahrenheit (°F)	Celsius (°C)	Kelvin (K)
Absolute zero	−460	−273	0
Freezing point of water	32	0	273
Boiling point of water	212	100	373

Absolute zero is the lowest possible threshold of temperature and is defined as 0 K. The temperature scales described in this table are related according to the following equations:

Fahrenheit ⇔ Celsius: $T_F = \frac{9}{5}T_C + 32^\circ$ $\quad T_C = \frac{5}{9}(T_F - 32^\circ)$

Celsius ⇔ Kelvin: $T_C = T_K - 273^\circ$ $\quad T_K = T_C + 273^\circ$

EXAMPLE: Normal body temperature is 98.6 °F. Convert this temperature to degrees Celsius.

SOLUTION: To convert degrees Fahrenheit to degrees Celsius, begin with the equation

$$T_C = \frac{5}{9}(T_F - 32^\circ)$$

Solving for T_C yields

$$T_C = \frac{5}{9}(98.6^\circ - 32^\circ) = 37\,^\circ\text{C}$$

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EXAMPLE: Derive a relationship between the Fahrenheit and Kelvin temperature scales.

SOLUTION: The Fahrenheit and Celsius temperature scales and the Celsius and Kelvin temperature scales are related by the equations given previously.

Substituting the first Celsius ⇔ Kelvin equation into the first Fahrenheit ⇔ Celsius equation yields

$$T_F = \frac{9}{5}\left(T_K - 273^\circ\right) + 32^\circ = \frac{9}{5}T_K - \frac{9}{5}\left(273^\circ\right) + 32^\circ$$
$$= \frac{9}{5}T_K - 491.4^\circ + 32^\circ = \frac{9}{5}T_K - 460^\circ$$

So the desired equation is

$$T_F = \frac{9}{5}T_K - 460^\circ$$

Pressure

A gas exerts pressure on the walls of its container. The pressure within a container is measured using a **manometer**. The atmosphere exerts pressure onto the Earth due to gravity. Atmospheric pressure is measured using a mercury **barometer**.

A barometer consists of an evacuated tube in a dish of mercury. The atmospheric pressure pushes the mercury into the tube. At sea level, the mercury rises 760 millimeters (mm). Thus the conversion equation is 1 atmosphere (atm) = 760 mm Hg.

Pressure is a force per unit area. It has various units, including pounds per square inch (psi), Pascal (Pa), or torr.

Ideal Gases

Ideal gases are those in which there is no intermolecular interaction between the molecules. The molecules are many times farther apart than their diameter. Boyle's law, Charles's law, and Avogadro's law describe the relationship between pressure, volume, and temperature in these gases, respectively.

BOYLE'S LAW

Boyle's law derives from experiments done in the 1660s. Robert Boyle determined that the pressure is inversely related to the volume of a gas at constant temperature. In other words, the pressure times the volume equals a constant for a given amount of gas at a constant temperature:

$$PV = \text{constant}$$

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CHARLES'S LAW

Charles's law derives from experiments done in the early 1800s. Jacques Charles determined that the volume of a gas is directly related to temperature. The Kelvin scale, with 0 K as the lowest possible temperature, must be used with Charles's law. To obtain a temperature in K, simply add 273.15 to the temperature in degrees Celsius (°C). Charles's law states that the volume divided by the temperature equals a constant for a given amount of gas at a constant pressure:

$$V/T = \text{constant}$$

AVOGADRO'S LAW

Amedeo Avogadro determined that 1 mole (6.022×10^{23} particles) of any gas occupies the same volume at a given temperature and pressure. The use of moles (mol) allows for the counting of particles, thus ignoring the masses of the particles. Moles, with the symbol n, are part of the constant in Boyle's law and Charles's law.

IDEAL GAS CONSTANT

Combining the three laws, one gets

$$PV = n\,\text{constant}\;T$$

The constant is called the **ideal gas constant**. It is given the symbol R and has the value 0.08206 L atm/mol K.

Avogadro used this ideal gas law to determine that 1 mole of any ideal gas would occupy 22.4 L at 0 °C and 1 atm pressure.

APPLICATIONS OF THE IDEAL GAS LAW

There are two major ways to use the ideal gas law. The first method involves changing conditions. If there are initial conditions that are changed, one can solve for any unknown final condition. The mole amount, n, and the gas constant, R, are constant, thus:

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

If five of the six variables are given, the sixth variable can be solved for. If any value remains constant, it falls out of the equation.

EXAMPLE: A sample of gas has volume 3.14 L at 512 mm Hg and 45.6 °C. Calculate the volume at 675 mm Hg and 18.2 °C.

SOLUTION:

1. Change all temperatures to Kelvin

$$45.6\ °\text{C} = 318.8\ \text{K} \qquad 18.2\ °\text{C} = 291.4\ \text{K}$$

2. Rearrange the equation and solve for V_f

$$V_f = \frac{P_i V_i T_f}{T_i P_f} = \frac{(512 \text{ mm Hg})\ (3.14 \text{ L})\ (291.4 \text{ K})}{(318.8 \text{ K})\ (675 \text{ mm Hg})} = 2.18 \text{ L}$$

The second way to use the ideal gas law is under a set of conditions. There are four variables (P, V, T, and n). If three of them are given, the fourth can be solved by using $PV = nRT$.

EXAMPLE: Calculate the molar mass of a gas if a 12.8-gram (g) sample occupies 9.73 L at 21.0 °C and 754 mm Hg.

SOLUTION:

1. Change the temperature to Kelvin and the pressure to atm

$$21.0\ ^\circ\text{C} = 294.2 \text{ K}$$

$$P = 752 \text{ mm Hg}/760 \text{ mm Hg}/\text{atm} = 0.989 \text{ atm}$$

2. Solve for n

$$n = \frac{PV}{RT} = \frac{(0.989 \text{ atm})\ (9.73 \text{ L})}{(0.08206 \text{ L atm}/\text{mol K})\ (294.2 \text{ K})} = 0.399 \text{ mole}$$

3. Calculate the molar mass

$$\text{mass}/\text{mole} = 12.8 \text{ g}/0.399 \text{ mole} = 32.0 \text{ g}/\text{mole}$$

The Kinetic Molecular Theory of Gases

The **kinetic molecular theory of gases** is a model for gas behavior. It consists of five assumptions concerning ideal gases and explains Boyle's, Charles's, and Avogadro's laws. The five assumptions are:

- A gas consists of very small particles that move randomly.
- The volume of each gas particle is negligible compared to the spaces between particles.
- There are no intermolecular attractive forces between the gas particles.
- When gas particles collide with each other or with the walls of the container, there is no net gain or loss of kinetic energy.
- The average kinetic energy of each gas particle is proportional to the temperature.

These assumptions are related to Boyle's law, $P \propto 1/V$. Because the pressure is related to the collisions each particle has, the more crowded the particles, the more collisions there are, and the higher the pressure. So as the volume is decreased, crowding and collisions increase, and the pressure increases.

These assumptions are also related to Charles's law, $V \propto T$. Because the particles move faster when the temperature is increased, it follows that there are more collisions when the particles are moving faster. Thus the higher the temperature, the greater the volume required to keep the pressure constant.

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The assumptions also relate to Avogadro's law, $V \propto n$. As the number of particles increases, the number of collisions increases (pressure and temperature are constant). Thus the volume must increase to contain the particles.

The kinetic energy of a gas particle is defined by E_k

$$E_k = {}^1\!/_2 mv^2$$

where v is the velocity and m is the mass, and v can be shown to be equal to

$$v = (3RT/M)^{1/2}$$

where R is the gas constant 8.314 J/mole K, M is the molar mass, and T is the temperature in K.

The heavier the gas particle, the slower it moves.

HEAT CAPACITY AT CONSTANT VOLUME AND AT CONSTANT PRESSURE

Heat capacity, a quantity unique to a substance, is a measure of the amount of heat energy required (measured in units of joules) to raise the temperature, ΔT, of 1 gram of a substance by 1 degree Celsius. In equation form, the heat energy, Q, generated or released by a change in temperature is given as:

$$Q = mC\Delta T$$

where C is the heat capacity. However, when applied to gases, the heat capacity is different, depending on whether the gas is under constant volume or under constant pressure.

When a gas is under constant volume, the applied heat to the gas cannot result in an expansion of the volume of the gas, so the heat energy is transferred to the internal energy, ΔU, of the gas and the equation noted previously can be rewritten as:

$$\Delta U = mC_V\Delta T$$

where C_V is the heat capacity of a gas at constant volume.

When a gas is under constant pressure, the flow of heat, known as **enthalpy**, H, can be determined by:

$$Q = \Delta H = mC_p\Delta T$$

where C_p is the heat capacity of a gas at constant pressure.

BOLTZMANN'S CONSTANT

The ideal gas law describes the behavior of the pressure (p), volume (V), and temperature (T) of an ideal gas and is typically expressed as:

$$pV = nRT$$

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where n is the number of moles and R is a gas constant (= 8.3145 J/mol K). However, the ideal gas law can be rewritten to describe a gas in terms of the number of particles of the gas, N, instead of the number of moles by the inclusion of a different constant, k:

$$pV = NkT$$

The constant k, equal numerically to 1.38×10^{-23} J/K, is known as **Boltzmann's constant**.

Real Gases

A real gas deviates somewhat in its behavior from the ideal gas, because the basic assumptions about an ideal gas are not always strictly true.

For example, under conditions of high pressure and/or small volume, gas particles can get close enough to exhibit intermolecular attractive forces. Thus at certain pressures, the actual volume is somewhat smaller than predicted by the ideal gas law.

When pressures get even higher, repulsive forces between particles become important, and the actual volume becomes somewhat larger than predicted by the ideal gas law.

The **van der Waals constants** a and b, which are characteristic for each type of gas, allow for the correction for real gas behavior as follows.

The correction for pressure is $(P + an^2/V^2)$, and the correction for volume is $(V - nb)$. So the van der Waals equation for real gases becomes:

$$(P + an^2/V^2)\,(V - nb) = nRT$$

Partial Pressure of Gases—Dalton's Law

Dalton's law of partial pressures concerns mixtures of gases. It states that each gas in a mixture exerts its own pressure, and the total of each gas's partial pressure equals the total pressure in the container.

At constant V and T, $P_A + P_B + P_C = P_{total}$ for gases A, B, and C in the mixture. Thus $P_{total} = n_{total}RT/V$. Each gas consists of a fraction of the entire amount, n_{total}. Each mole fraction is calculated:

$$X_A = n_A/n_{total} \qquad X_B = n_B/n_{total} \qquad X_C = n_C/n_{total}$$

And each partial pressure is:

$$P_A = X_A P_{total} \qquad P_B = X_B P_{total} \qquad P_C = X_C P_{total}$$

EXAMPLE: Calculate the partial pressure of each gas in a balloon that contains 50.97 g nitrogen, 23.8 g helium, and 19.5 g argon at a total pressure of 2.67 atm.

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SOLUTION:

1. Calculate the moles of each gas

$$(50.97 \text{ g } N_2)\ (1 \text{ mole } N_2/28.020 \text{ g}) = 1.819 \text{ mole } N_2$$

$$(23.80 \text{ g He})\ (1 \text{ mole He}/4.003 \text{ g}) = 5.945 \text{ mole He}$$

$$(19.59 \text{ g Ar})\ (1 \text{ mole Ar}/39.950 \text{ g}) = 0.488 \text{ mole Ar}$$

2. Sum the moles

$$\text{Sum} = 8.25 \text{ mole total}$$

3. Determine the mole fraction X of each gas

$$X_{N_2} = 1.819 \text{ mole}/8.25 \text{ mole} = 0.2200$$

$$X_{He} = 5.945 \text{ mole}/8.25 \text{ mole} = 0.7200$$

$$X_{Ar} = 0.488 \text{ mole}/8.25 \text{ mole} = 0.0591$$

4. Multiply each mole fraction by the total pressure in the balloon

$$P_{N_2} = 0.2200 \times 2.67 \text{ atm} = 0.587 \text{ atm } N_2$$

$$P_{He} = 0.7200 \times 2.67 \text{ atm} = 1.92 \text{ atm He}$$

$$P_{Ar} = 0.0591 \times 2.67 \text{ atm} = 0.158 \text{ atm Ar}$$