tween the molecules was great enough to neglect the effect of the intermolecular forces and the volume of the molecules themselves. Under these conditions a gas came to be termed an **ideal gas.** More properly, an *ideal gas* is an imaginary gas which obeys exactly certain simple laws such as the laws of Boyle, Charles, Dalton, and Amagat. No real gas obeys these laws exactly over all ranges of temperature and pressure, although the "lighter" gases (hydrogen, oxygen, air, etc.) under ordinary circumstances obey the ideal gas laws with but negligible deviations. The properties of the "heavier" gases, such as sulfur dioxide and hydrocarbons, particularly at high pressures and low temperatures, deviate considerably from those predicted by the ideal gas laws. Vapors, under conditions near the boiling point, deviate markedly from the ideal gas laws. However, at low pressures and high temperatures, the behavior of a vapor approaches that of an ideal gas. Thus for many engineering purposes, the ideal gas laws, if properly applied, will give answers that are correct within a few percent or less. But for liquids and solids with the molecules compacted relatively close together, we do not have such general laws.

3.1-1 Calculations Using the Ideal Gas Law

Your objectives in studying this section are to be able to:

1. Write down the ideal gas law, and define all its variables and parameters and their associated dimensions.
2. Calculate the values and units of the ideal gas law constant in any set of units from the standard conditions.
3. Convert gas volumes to moles (and mass), and vice versa.
4. Use ratios of variables in the ideal gas law to calculate p, V, T, or n.

From the work of Boyle and Charles, scientists developed the relationship now called the **ideal gas law** (or sometimes the *perfect gas law*).

$$pV = nRT \tag{3.1}$$

where p = absolute pressure of the gas
V = total volume occupied by the gas
n = number of moles of the gas
R = ideal gas constant in appropriate units
T = absolute temperature of the gas

Sometimes the ideal gas law is written as

$$p\hat{V} = RT \tag{3.1a}$$

where $\hat{V}$ is the specific volume (volume per mole or mass) of the gas. Figure 3.1 illustrates the surface generated by Eq. (3.1a) in terms of the three properties p, $\hat{V}$, and T.

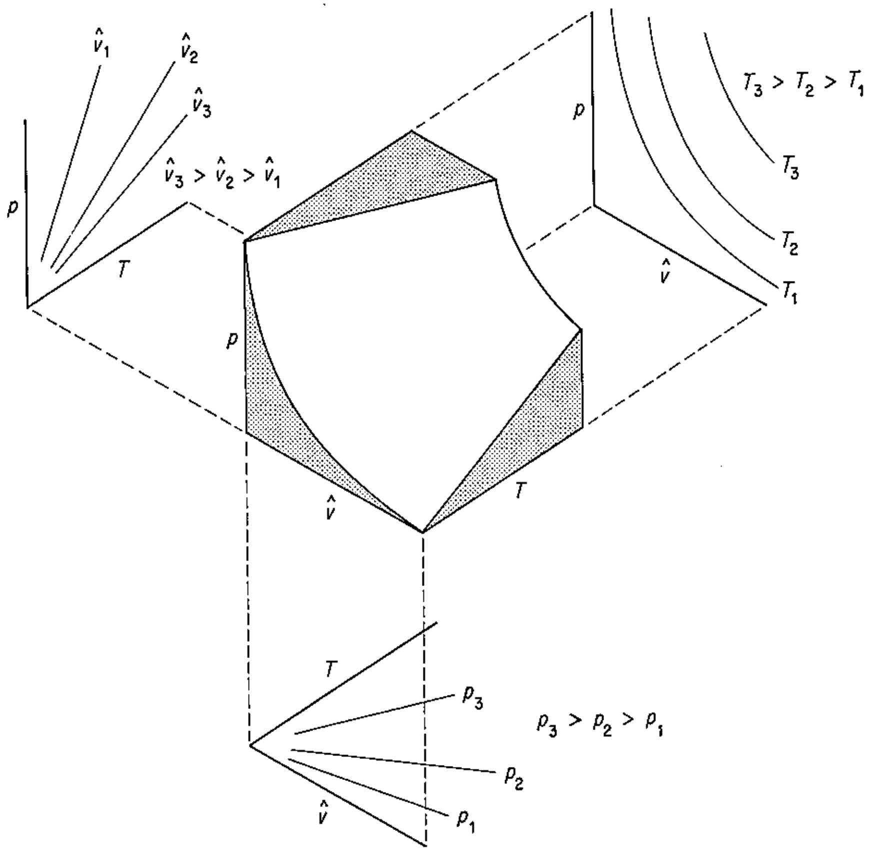

Figure 3.1 Representation of the ideal gas law in three dimensions as a surface.

Several arbitrarily specified standard states (usually known as *standard conditions*, or S.C.) of temperature and pressure have been selected by custom. See Table 3.1 for the most common ones. The fact that a substance cannot exist as a gas at 0°C and 1 atm is immaterial. Thus, as we see later, water vapor at 0°C cannot exist at a pressure greater than its saturation pressure of 0.61 kPa (0.18 in. Hg) without condensation occurring. However, the imaginary volume at standard conditions can be calculated and is just as useful a quantity in the calculation of volume-mole relation-

TABLE 3.1 Common Standard Conditions for the Ideal Gas

System	T	p	$\hat{V}$
SI	273.15K	101.325 kPa	22.415 m^3/kg mol
Universal scientific	0.0°C	760 mm Hg	22.415 liters/g mol
Natural gas industry	60.0°F (15.0°C)	14.696 psia (101.325 kPa)	379.4 ft^3/lb mol
American engineering	32°F	1 atm	359.05 ft^3/lb mol

ships as though it could exist. In the following, the symbol V will stand for total volume and the symbol $\hat{V}$ for volume per mole, or per unit mass.

Because the SI, universal scientific, and American engineering standard conditions are identical, you can use the values in Table 3.1 with their units to change from one system of units to another. Knowing the standard conditions also makes it easy for you to work with mixtures of units from different systems.

The next example illustrates how the standard conditions can be employed to convert mass or moles to volume. Do you see how to convert volume to moles or mass?

EXAMPLE 3.1 Use of Standard Conditions

Calculate the volume, in cubic meters, occupied by 40 kg of CO_2 at standard conditions.

Solution

Basis: 40 kg of CO_2

$$\frac{40\text{ kg }CO_2}{} \left| \frac{1\text{ kg mol }CO_2}{44\text{ kg }CO_2} \right| \frac{22.42\text{ m}^3\ CO_2}{1\text{ kg mol }CO_2} = 20.4\text{ m}^3\ CO_2\text{ at S.C.}$$

Notice in this problem how the information that 22.42 m^3 at S.C. = 1 kg mol is applied to transform a known number of moles into an equivalent number of cubic meters.

Incidentally, whenever you use cubic measure for volume, you must establish the conditions of temperature and pressure at which the cubic measure for volume exists, since the term "m^3" or "ft^3," standing alone, is really not any particular *quantity* of material.

You can apply the ideal gas law, Eq. (3.1), directly by introducing values for three of the four quantities, n, p, T, and V, and solving for the fourth. To do so, you need to look up or calculate R in the proper units. Inside the front cover you will find selected values of R for different combinations of units. Example 3.2 illustrates how to calculate the value of R in any set of units you want from the values of p, T, and $\hat{V}$ at standard conditions.

In many processes going from an initial state to a final state, you can use the ratio of ideal gas law in the respective states and eliminate R as follows (the subscript 1 designates the initial state, and the subscript 2 designates the final state)

$$\frac{p_1 V_1}{p_2 V_2} = \frac{n_1 R T_1}{n_2 R T_2}$$

or

$$\left(\frac{p_1}{p_2}\right)\left(\frac{V_1}{V_2}\right) = \left(\frac{n_1}{n_2}\right)\left(\frac{T_1}{T_2}\right) \tag{3.2}$$

Note how Eq. (3.2) involves ratios of the same variable. This arrangement of the ideal gas law has the convenient feature that the pressures may be expressed in any system of units you choose, such as kPa, in. Hg, mm Hg, atm, and so on, as long as the same units are used for both conditions of pressure (do not forget that the pressure must be *absolute* pressure in both cases). Similarly, the grouping together of the *absolute* temperature and the volume terms gives ratios that are dimensionless. Notice how the ideal gas constant R is eliminated in taking the ratio of the initial to the final state.

Let us see how we can apply the perfect gas law both in the form of Eq. (3.2) and Eq. (3.1) to problems.

EXAMPLE 3.2 Calculation of *R*

Find the value for the universal gas constant R for the following combinations of units:

(a) For 1 lb mol of ideal gas when the pressure is expressed in psia, the volume is in ft³/lb mol, and the temperature is in °R.

(b) For 1 g mol of ideal gas when the pressure is in atm, the volume in cm³, and the temperature in K.

(c) For 1 kg mol of ideal gas when the pressure is in kPa, the volume is in m³/kg mol, and the temperature is in K.

Solution

(a) At standard conditions we will use the approximate values

$$p = 14.7 \text{ psia}$$
$$\hat{V} = 359 \text{ ft}^3/\text{lb mol}$$
$$T = 492°\text{R}$$

Then

$$R = \frac{p\hat{V}}{T} = \frac{14.7 \text{ psia}}{492°\text{R}}\left|\frac{359 \text{ ft}^3}{1 \text{ lb mol}}\right. = 10.73\frac{(\text{psia})(\text{ft}^3)}{(°\text{R})(\text{lb mol})}$$

(b) Similarly, at standard conditions,

$$p = 1 \text{ atm}$$
$$\hat{V} = 22{,}415 \text{ cm}^3/\text{g mol}$$
$$T = 273.15 \text{ K}$$

$$R = \frac{p\hat{V}}{T} = \frac{1 \text{ atm}}{273.15 \text{ K}}\left|\frac{22{,}415 \text{ cm}^3}{1 \text{ g mol}}\right. = 82.06\frac{(\text{cm}^3)(\text{atm})}{(\text{K})(\text{g mol})}$$

(c) In the SI system of units standard conditions are

$$p = 1.013 \times 10^5 \text{ Pa (or N/m}^2)$$
$$\hat{V} = 22.415 \text{ m}^3/\text{kg mol}$$
$$T = 273.15 \text{ K}$$

$$R = \frac{p\hat{V}}{T} = \frac{1.013 \times 10^5 \text{ Pa}}{273.15 \text{ K}}\left|\frac{22.415 \text{ m}^3}{1 \text{ kg mol}}\right. = 8.313 \times 10^3\frac{(\text{Pa})(\text{m}^3)}{(\text{K})(\text{kg mol})} = 8.313\frac{\text{kJ}}{(\text{K})(\text{kg mol})}$$

To summarize, we want to emphasize that R does not have a universal value even though it is sometimes called the *universal gas constant*. The value of R depends on the units of p, $\hat{V}$, and T.

EXAMPLE 3.3 Application of the Ideal Gas Law

Calculate the volume occupied by 88 lb of CO_2 at a pressure of 32.2 ft of water and at 15°C.

Solution

See Fig. E3.3.

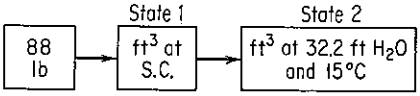

Figure E3.3

Solution 1 [Using Eq. (3.2)]:

At S.C. (state 1)	*At state 2*
$p = 33.91\text{ ft H}_2\text{O}$	$p = 32.2\text{ ft H}_2\text{O}$
$\hat{V} = 359\,\dfrac{\text{ft}^3}{\text{lb mol}}$	$\hat{V} = ?$
$T = 273\text{ K}$	$T = 273 + 15 = 288\text{ K}$

Basis: 88 lb of CO_2

Assume that the pressure is absolute pressure. First, we convert the mass of gas to moles and get the equivalent volume at standard conditions. Finally, we use Eq. (3.2), in which both R and (n_1/n_2) cancel out:

$$V_2 = V_1\left(\frac{p_1}{p_2}\right)\left(\frac{T_2}{T_1}\right)$$

You can say to yourself: The temperature goes up from 0°C at S.C. to 15°C at the final state, hence the volume must increase from S.C., hence the temperature ratio must be greater than unity. Similarly, you can say: The pressure goes down from S.C. to the final state, so that the volume must increase from S.C., hence the pressure ratio must be greater than unity. The calculations are

$$\begin{array}{l|c|c|c|c} 88\text{ lb CO}_2 & & 359\text{ ft}^3 & 288 & 33.91 \\ \hline & \dfrac{44\text{ lb CO}_2}{1\text{ lb mol CO}_2} & 1\text{ lb mol} & 273 & 32.2 \end{array} = \begin{array}{l} 798\text{ ft}^3\text{ CO}_2 \\ \text{at 32.2 ft H}_2\text{O and 15°C} \end{array}$$

Solution 2 [using the gas constant R and the ideal gas law Eq. (3.1)].

First, the value of R must be obtained in the same units as the variables p, $\hat{V}$, and T. For 1 lb mol,

$$R = \frac{p\hat{V}}{T}$$

and at S.C.,

$$p = 33.91 \text{ ft } H_2O$$

$$\hat{V} = 359 \text{ ft}^3/\text{lb mol}$$

$$T = 273 \text{ K}$$

$$R = \frac{33.91}{} \left| \frac{359}{273} \right. = 44.59 \frac{(\text{ft } H_2O)(\text{ft}^3)}{(\text{lb mol})(\text{K})}$$

Now, using Eq. (3.1), insert the given values, and perform the necessary calculations.

Basis: 88 lb of CO_2

$$V = \frac{nRT}{p} = \frac{88 \text{ lb } CO_2}{\frac{44 \text{ lb } CO_2}{\text{lb mol } CO_2}} \left| \frac{44.59 \, (\text{ft } H_2O)(\text{ft}^3)}{(\text{lb mol})(\text{K})} \right| \frac{288 \text{ K}}{32.2 \text{ ft } H_2O}$$

$$= 798 \text{ ft}^3 \; CO_2 \text{ at } 32.2 \text{ ft } H_2O \text{ and } 15°\text{C}$$

If you will inspect both solutions closely, you will observe that in both cases the same numbers appear and that both are identical except that in the second solution using R two steps are used to obtain the solution.

EXAMPLE 3.4 Ideal Gas Law

An oxygen cylinder used as a standby source of oxygen contains O_2 at 70°F. To calibrate the gauge on the O_2 cylinder which has volume of 1.01 ft^3, all of the oxygen, initially at 70°F, is released into an evacuated tank of known volume (15.0 ft^3). At equilibrium, the gas pressure was measured as 4 in. H_2O gauge and the gas temperature in both cylinders was 75°F. See Fig. E3.4. The barometer read 29.99 in. Hg.

What did the pressure gauge on the oxygen tank read in psig if it was a Bourdon gauge?

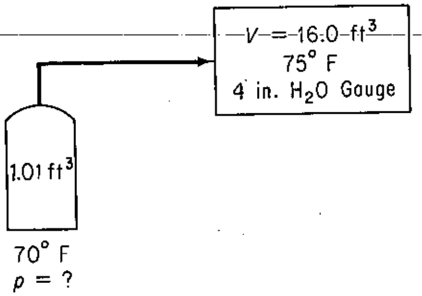

Figure E3.4

Solution

You must first convert the temperatures and pressures into absolute units:

$$460 + 70 = 530°\text{R}$$

$$460 + 75 = 535°\text{R}$$

atmospheric pressure = 29.99 in. Hg = 14.73 psia

$$\text{final pressure} = 29.99 \text{ in. Hg} + \left.\frac{4 \text{ in. H}_2\text{O}}{\dfrac{12 \text{ in. H}_2\text{O}}{\text{ft H}_2\text{O}}}\right|\frac{29.92 \text{ in. Hg}}{33.91 \text{ ft H}_2\text{O}}$$

$$= 29.99 + 0.29 = 30.28 \text{ in. Hg absolute}$$

The simplest way to proceed, now that the data are in good order, is to apply the ideal gas law, Eq. (3.2). Take as a basis, 16.011 ft^3 (do not forget to include the volume of the O_2 tank in your system!) of O_2 at 75°F and 30.28 in. Hg. We want to determine the initial pressure in the O_2 tank alone.

$$p_1 = p_2\left(\frac{V_2}{V_1}\right)\left(\frac{n_1}{n_2}\right)\left(\frac{T_1}{T_2}\right).$$

$$p_1 = 30.28 \text{ in. Hg}\left(\frac{16.01 \text{ ft}^3}{1 \text{ ft}^3}\right)\left(\frac{530°\text{R}}{535°\text{R}}\right) = 480 \text{ in. Hg absolute}$$

In gauge pressure,

$$p_1 = \left.\frac{(480 - 29.99) \text{ in. Hg}}{}\right|\frac{14.696 \text{ psia}}{29.92 \text{ in. Hg}} = 221 \text{ psig}$$

EXAMPLE 3.5 Application of the Ideal Gas Law

One important source of emissions from gasoline-powered automobile engines that causes smog is the nitrogen oxides NO and NO_2. They are formed whether combustion is complete or not as follows. At the high temperatures that occur in an internal combustion engine during the burning process, oxygen and nitrogen combine to form nitric oxide (NO). The higher the peak temperatures and the more oxygen available, the more NO is formed. There is insufficient time for the NO to decompose back to O_2 and N_2 because the burned gases cool too rapidly during the expansion and exhaust cycles in the engine. Although both NO and nitrogen dioxide (NO_2) are significant air pollutants (together termed NO_x), the NO_2 is formed in the atmosphere as NO is oxidized.

Suppose that you collect a sample of a NO-NO_2 mixture (after having removed the other combustion gas products by various separations procedures) in a 100-cm^3 standard cell at 30°C. Certainly some of the NO will have been oxidized to NO_2,

$$2NO + O_2 \longrightarrow 2NO_2$$

during the collection, storage, and processing of the combustion gases, so that measurement of NO alone will be misleading. If the standard cell contains 0.291 g of NO_2 plus NO and the pressure measured in the cell is 170 kPa, what percent of the NO + NO_2 is in the form of NO? See Fig. E3.5.

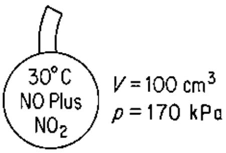

Figure E3.5

Solution

The gas in the cell is composed partly of NO and partly of NO_2. We can use the ideal gas law to calculate the total gram moles present in the cell.

Basis: 100 cm³ of gas at 170 kPa and 30°C

$$R = \frac{101.3\ \text{kPa}}{273\ \text{K}}\left|\frac{22.41\ \text{L}}{1\ \text{g mol}}\right|\frac{1000\ \text{cm}^3}{1\ \text{L}} = 8.316 \times 10^3 \frac{(\text{kPa})(\text{cm}^3)}{(\text{K})(\text{g mol})}$$

$$n = \frac{pV}{RT} = \frac{170\ \text{kPa}}{8.316 \times 10^3 \frac{(\text{kPa})(\text{cm}^3)}{(\text{K})(\text{g mol})}}\left|\frac{100\ \text{cm}^3}{303\ \text{K}}\right. = 0.00675\ \text{g mol}$$

If the mixture is composed of NO (MW = 30) and NO_2 (MW = 46), because we know the total mass in the cell we can compute the fraction of, say, NO. Let x = grams of NO; then $(0.291 - x)$ = g NO_2. In a table format the calculation is

Component	g	Mol. Wt.	g mol
NO	x	30	$\frac{x}{30}$
NO_2	$0.291 - x$	46	$\frac{0.291 - x}{46}$
Total	0.291		0.00675

or

$$\frac{x}{30} + \frac{0.291 - x}{46} = 0.00675$$

$$0.0333x + (0.291 - x)(0.0217) = 0.00675$$

$$x = 0.0366\ \text{g}$$

The weight percent NO is

$$\frac{0.0366}{0.291}(100) = 12.5\%$$

and the mole percent NO is

$$\frac{0.0366\ \text{g NO}}{0.00675\ \text{g mol total}}\left|\frac{1\ \text{g mol NO}}{30\ \text{g NO}}\right.(100) = 18\%$$

Can you let x be the mole fraction NO and obtain the same result? (*Answer:* Yes.) Try the calculation.

Self-Assessment Test

1. Write down the ideal gas law.
2. What are the dimensions of T, p, V, n, and R?
3. List the standard conditions for a gas in the SI, universal scientific, and American engineering systems of units.

4. Calculate the volume in ft^3 of 10 lb mol of an ideal gas at 68°F and 30 psia.
5. A steel cylinder of volume 2 m^3 contains methane gas (CH_4) at 50°C and 250 kPa absolute. How many kilograms of methane are in the cylinder?
6. What is the value of the ideal gas constant R to use if the pressure is to be expressed in atm, the temperature in kelvin, the volume in cubic feet, and the quantity of material in pound moles?
7. Twenty-two kilograms per hour of CH_4 are flowing in a gas pipeline at 30°C and 920 mm Hg. What is the volumetric flow rate of the CH_4 in m^3 per hour?

Thought Problems

1. A candle is placed vertically in a soup plate, and the soup plate filled with water. Then the candle is lit. An inverted water glass is carefully placed over the candle. The candle soon goes out, and the water rises inside the glass. It is often said that this shows how much oxygen in the air has been used up. Is this conclusion correct?
2. A scientific supply house markets aerosol-type cans containing compressed helium for filling balloons, doing demonstrations, and the like. On the label there appears the notice: "Because the can contains helium, it quite naturally feels empty. It is actually lighter full than empty."

   Is this statement correct? If so, why? If not, why not?

3.1-2 Gas Density and Specific Gravity

Your objectives in studying this section are to be able to:

1. Define gas density and specific gravity.
2. Calculate the specific gravity of a gas even if the reference condition is not clearly specified.
3. Calculate the density of a gas given its specific gravity.

The **density of a gas** is defined as the mass per unit volume and can be expressed in kilograms per cubic meter, pounds per cubic foot, grams per liter, or other units. Inasmuch as the mass contained in a unit volume varies with the temperature and pressure, as we have previously mentioned, you should always be careful to specify these two conditions. If not otherwise specified, the densities are presumed to be at S.C. Density can be calculated by selecting a unit volume as the basis and calculating the mass of the contained gas.

EXAMPLE 3.6 Calculation of Gas Density

What is the density of N_2 at 27°C and 100 kPa expressed in:

(a) SI units?

(b) American engineering units?

Solution

(a)

Basis: 1 m^3 of N_2 at 27°C and 100 kPa

$$\begin{array}{l|l|l|l|l}
1\ \text{m}^3 & 273\ \text{K} & 100\ \text{kPa} & 1\ \text{kg mol} & 28\ \text{kg} \\ \hline
 & 300\ \text{K} & 101.3\ \text{kPa} & 22.4\ \text{m}^3 & 1\ \text{kg mol}
\end{array} = 1.123\ \text{kg}$$

density = 1.123 kg/m^3 of N_2 at 27°C (300 K) and 100 kPa

(b)

Basis: 1 ft^3 of N_2 at 27°C and 100 kPa

$$\begin{array}{l|l|l|l|l}
1\ \text{ft}^3 & 273\ \text{K} & 100\ \text{kPa} & 1\ \text{lb mol} & 28\ \text{lb} \\ \hline
 & 300\ \text{K} & 101.3\ \text{kPa} & 359\ \text{ft}^3 & 1\ \text{lb mol}
\end{array} = 0.0701\ \text{lb}$$

density = 0.0701 lb/ft^3 of N_2 at 27°C (80°F) and 100 kPa (14.5 psia)

The **specific gravity of a gas** is usually defined as the ratio of the density of the gas at a desired temperature and pressure to that of air (or any specified reference gas) at a certain temperature and pressure. The use of specific gravity occasionally may be confusing because of the manner in which the values of specific gravity are reported in the literature. You must be very careful in using literature values of specific gravity to ascertain that the conditions of temperature and pressure are known both for the gas in question and for the reference gas. Among the examples below, several represent inadequate methods of expressing specific gravity.

(a) *What is the specific gravity of methane?* Actually, this question may have the same answer as the question: How many grapes are in a bunch? Unfortunately, occasionally one may see this question and the best possible answer is

$$\text{sp gr} = \frac{\text{density of methane at S.C.}}{\text{density of air at S.C.}}$$

(b) *What is the specific gravity of methane* (H_2 = 1.00)? Again a poor question. The notation of (H_2 = 1.00) means that H_2 at S.C. is used as the reference gas, but the question does not tell what the conditions of temperature and pressure of the methane are. Therefore, the best interpretation is

$$\text{sp gr} = \frac{\text{density of methane at S.C.}}{\text{density of } H_2 \text{ at S.C.}}$$

(c) *What is the specific gravity of ethane* (air = 1.00)? Same as question (b) except that in the petroleum industry the following is used:

$$\text{sp gr} = \frac{\text{density of ethane at 60°F and 760 mm Hg}}{\text{density of air at S.C. (60°F, 760 mm Hg)}}$$

(d) *What is the specific gravity of butane at* 50°C *and* 90 kPa? No reference gas nor state of reference gas is mentioned. However, when no reference gas is mentioned, it is taken for granted that air is the reference gas. In the case at hand the best thing to do is to assume that the reference gas and the desired gas are under the same conditions of temperature and pressure:

$$\text{sp gr} = \frac{\text{density of butane at } 50^\circ\text{C and 90 kPa}}{\text{density of air at } 50^\circ\text{C and 90 kPa}}$$

(e) *What is the specific gravity of* CO_2 *at* 60°F *and* 740 mm Hg (air = 1.00)?

$$\text{sp gr} = \frac{\text{density of } CO_2 \text{ at } 60^\circ\text{F and 740 mm Hg}}{\text{density of air at S.C.}}$$

(f) *What is the specific gravity of* CO_2 *at* 60°F *and* 740 mm Hg (ref. air at S.C.)?

$$\text{sp gr} = \text{same as question (e)}$$

EXAMPLE 3.7 Specific Gravity of a Gas

What is the specific gravity of N_2 at 80°F and 745 mm Hg compared to

(a) Air at S.C. (32°F and 760 mm Hg)?
(b) Air at 80°F and 745 mm Hg?

Solution

First you must obtain the density of the N_2 and the air at their respective conditions of temperature and pressure, and then calculate the specific gravity by taking a ratio of their densities. Example 3.6 covers the calculation of the density of a gas, and therefore, to save space, no units will appear in the intermediate calculations:

(a)

Basis: 1 ft^3 of N_2 at 80°F and 745 mm Hg

$$\begin{array}{c|c|c|c|c} 1 & 492 & 745 & & 28 \\ \hline & 540 & 760 & 359 & \end{array} = 0.0697\ \text{lb } N_2/\text{ft}^3 \text{ at } 80^\circ\text{F, 745 mm Hg}$$

Basis: 1 ft^3 of air at 32°F and 760 mm Hg

$$\begin{array}{c|c|c|c|c} 1 & 492 & 760 & & 29 \\ \hline & 492 & 760 & 359 & \end{array} = 0.0808\ \text{lb air/ft}^3 \text{ at } 32^\circ\text{F, 760 mm Hg}$$

Therefore,

$$\text{sp.gr.} = \frac{0.0697}{0.0808} = 0.862 \frac{\text{lb } N_2/\text{ft}^3\ N_2 \text{ at } 80^\circ\text{F, 745 mm Hg}}{\text{lb air/ft}^3 \text{ air at S.C.}}$$

Note: Specific gravity is not a dimensionless number.

(b)

Basis: 1 ft^3 of air at 80°F and 745 mm Hg

$$\begin{array}{c|c|c|c|c} 1 & 492 & 745 & & 29 \\ \hline & 540 & 760 & 359 & \end{array} = 0.0721\ \text{lb/ft}^3 \text{ at } 80^\circ\text{F and 745 mm Hg}$$

$$(\text{sp. gr.})_{N_2} = \frac{0.0697}{0.0721} = 0.967 \frac{\text{lb } N_2/\text{ft}^3\ N_2 \text{ at } 80^\circ\text{F, 745 mm Hg}}{\text{lb air/ft}^3 \text{ air at } 80^\circ\text{F, 745 mm Hg}}$$

$$= 0.967 \text{ lb } N_2/\text{lb air}$$

Note that you can also obtain the specific gravity of a gas directly by taking the ratio of the ideal gas law densities of each gas. Thus (the gases are denoted by the respective subscripts A and B)

$$pV = \frac{mRT}{\text{mol. wt.}}$$

where m is the mass of gas. The gas density is

$$\rho = \frac{m}{V} = \frac{p(\text{mol. wt.})}{RT}$$

and the ratio of gas densities is

$$\text{sp gr} = \frac{\rho_A}{\rho_B} = \left(\frac{p_A}{p_B}\right)\left(\frac{\text{mol. wt.}_A}{\text{mol. wt.}_B}\right)\left(\frac{T_B}{T_A}\right) \tag{3.3}$$

For gases at the *same* temperature and pressure, the specific gravity is just the ratio of the respective molecular weights.

Self-Assessment Test

1. What is the density of a gas that has a molecular weight of 0.123 kg/kg mol at 300 K and 1000 kPa?
2. What is the specific gravity of CH_4 at 70°F and 2 atm compared to air at S.C.?

Thought Problem

1. Sea breezes provide welcome relief from the summer heat for residents who live close to the shore. No matter what part of the world—the coast of California, Australia where sea breezes can be very strong, even along the shores of the Great Lakes—the daily pattern in summertime is the same. The sea breeze, a wind blowing from sea to land, begins to develop three or four hours after sunrise and reaches its peak intensity by mid-afternoon. It may penetrate inland as much as 60 or 70 km. The sea breeze dies out in the evening and three or four hours after sunset may be replaced by a land breeze, blowing from land to sea. The land breeze, much weaker than the sea breeze, reaches its peak intensity just before sunrise.

   What causes these breezes?
2. A distillation column reboiler in a room, as shown in the figure, had been cleaned, but the

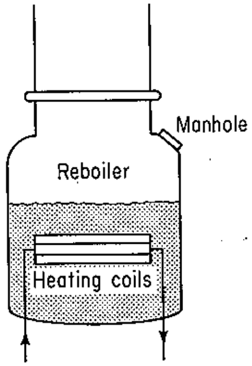

Figure TP3.2

manhole cover was not securely fastened on startup again. As a result benzene vapor escaped from the manhole and one operator died by asphyxiation. How could this occur?

3.1-3 Ideal Gas Mixtures

Your objectives in studying this section are to be able to:

1. Write down and apply Dalton's law and Amagat's law.
2. Define and use partial pressure in gas calculations.
3. Show that under certain assumptions the volume fraction equals the mole fraction in a gas.

Frequently, as an engineer, you will want to make calculations for mixtures of gases instead of individual gases. You can use the ideal gas law (under the proper assumptions of course) for a mixture of gases by interpreting p as the total pressure of the mixture, V as the volume occupied by the mixture, n as the total number of moles of all components in the mixture, and T as the temperature of the mixture. Is it possible to calculate a pressure or volume for the individual components? The answer is yes in a certain sense. Two classical definitions exist:

(a) The **partial pressure** of Dalton, p_i, namely the pressure that would be exerted by a single component in a gaseous mixture if it existed by itself in the *same volume* as occupied by the mixture and at the *same temperature* of the mixture

$$p_i V_{\text{total}} = n_i R T_{\text{total}} \tag{3.4}$$

where p_i is the partial pressure of component i. If you divide Eq. (3.4) by Eq. (3.1), you find that

$$\frac{p_i V_{\text{total}}}{p_{\text{total}} V_{\text{total}}} = \frac{n_i R T_{\text{total}}}{n_{\text{total}} R T_{\text{total}}}$$

or

$$p_i = p_t \frac{n_i}{n_t} = p_t y_i \tag{3.5}$$

where y_i is the mole fraction of component i. Can you show that Dalton's law of the summation of partial pressures is true?

$$p_1 + p_2 + \cdots + p_n = p_t \tag{3.6}$$

(b) The **partial volume** of Amagat, V_i, namely the volume that would be occupied by a single component of the mixture if the component were at the *same temperature and total pressure* as the mixture

$$p_{\text{total}} V_i = n_i R T_{\text{total}} \tag{3.7}$$

Division by Eq. (3.1) yields

$$\frac{p_t V_i}{p_t V_t} = \frac{n_i R T_t}{n_t R T_t}$$

or

$$V_i = V_t\left(\frac{n_i}{n_t}\right) = V_t y_i \tag{3.8}$$

Can you show that Amagat's law of the summation of partial volumes is true?

$$V_1 + V_2 + \cdots + V_n = V_t \tag{3.9}$$

To illustrate the significance of Eq. (3.4) and the meaning of partial pressure, suppose that you carried out the following experiment with ideal gases. Two tanks of 1.50 m^3 volume, one containing gas A at 300 mm Hg and the other gas B at 400 mm of Hg (both gases being at the same temperature of 20°C), are connected together. All the gas in B is forced into tank A isothermally. Now you have a 1.50-m^3 tank of $A + B$ at 700 mm of Hg. For this mixture (in the 1.50-m^3 tank at 20°C and a total pressure of 700 mm Hg) you could say that gas A exerts a partial pressure of 300 mm and gas B exerts a partial pressure of 400 mm. Of course you cannot put a pressure gauge on the tank and check this conclusion because the pressure gauge will read only the total pressure. These partial pressures are hypothetical pressures that the individual gases would exert and are equivalent to the pressures they actually would have if they were put into the same volume at the same temperature all by themselves. If the total pressure of the gaseous mixture is known as well as the mole fraction of a component, the partial pressure of the component can be calculated via Eq. (3.5):

$$p_A = 700\left(\frac{3}{7}\right) = 300 \text{ mm Hg}$$

An analogous explanation can be made for the partial volume of A in the mixture using Eq. (3.8):

$$V_A = 1.50\left(\frac{3}{7}\right) = 0.64 \text{ m}^3 \text{ at 700 mm Hg and } 20°\text{C}$$

Finally, Eq. (3.8) leads to the principle, stated earlier in Chap. 1, that

$$\text{volume fraction} = \text{mole fraction} = y_i \tag{3.10}$$

for an ideal gas.

EXAMPLE 3.8 Partial Pressures and Volumes

A gas-tight room has a volume of 1000 m^3. This room contains air (considered to be 21% O_2 and 79% N_2) at 20°C and a total pressure of 1 atm.

(a) What is the partial volume of O_2 in the room?

(b) What is the partial volume of N_2 in the room?

(c) What is the partial pressure of O_2 in the room?

(d) What is the partial pressure of N_2 in the room?

(e) If all of the O_2 were removed from the room by some method, what would be the subsequent total pressure in the room?

Solution

See Fig. E3.8

Basis: 1000 m^3 of air at 20°C and 1 atm

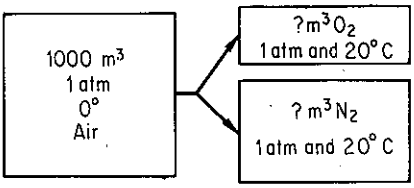

Figure E3.8

Partial volumes can be calculated by multiplying the total volume by the respective component mole fractions [Eq. (3.8)]:

$$\begin{aligned}
&\textbf{(a)}\ V_{O_2} = (0.21)(1000) = && 210\ \text{m}^3\ \text{O}_2\ \text{at } 20°\text{C, 1 atm}\\
&\textbf{(b)}\ V_{N_2} = (0.79)(1000) = && \underline{790\ \text{m}^3\ \text{N}_2\ \text{at } 20°\text{C, 1 atm}}\\
&\qquad\qquad \text{total volume} = && 1000\ \text{m}^3\ \text{air at } 20°\text{C, 1 atm}
\end{aligned}$$

Note how the temperature and pressure have to be specified for the partial volumes to make them meaningful.

Partial pressures can be calculated by multiplying the total pressure by the respective component mole fractions [Eq. (3.5)]; the basis is still the same:

$$\begin{aligned}
&\textbf{(c)}\ p_{O_2} = (0.21)(1\ \text{atm}) = && 0.21\ \text{atm when } V = 1000\ \text{m}^3 \text{ at } 20°\text{C}\\
&\textbf{(d)}\ p_{N_2} = (0.79)(1\ \text{atm}) = && \underline{0.79\ \text{atm when } V = 1000\ \text{m}^3 \text{ at } 20°\text{C}}\\
&\qquad\qquad \text{total pressure} = && 1.00\ \text{atm when } V = 1000\ \text{m}^3 \text{ at } 20°\text{C}
\end{aligned}$$

(e) If a tight room held dry air at 1 atm and all the oxygen were removed from the air by a chemical reaction, the pressure reading would fall to 0.79 atm.

For use in our subsequent calculations you should clearly understand now that the original room contained:

(1) 790 m^3 dry N_2 at 1 atm and 20°C
(2) $\underline{210}$ m^3 dry O_2 at 1 atm and 20°C
(3) 1000 m^3 dry air at 1 atm and 20°C (add 1 and 2)

or

(1) 1000 m^3 dry O_2 at 0.21 atm and 20°C
(2) 1000 m^3 dry N_2 at $\underline{0.79}$ atm and 20°C
(3) 1000 m^3 dry air at 1.00 atm and 20°C (add 1 and 2)

EXAMPLE 3.9 Calculation of Partial Pressures from Gas Analysis

A flue gas analyzes 14.0% CO_2, 6.0% O_2, and 80.0% N_2. It is at 400°F and 765.0 mm Hg pressure. Calculate the partial pressure of each component.

Solution

Use Eq. (3.5).

Basis: 1.00 kg (or lb) mol flue gas

Component	*kg (or lb) mol*	*p (mm Hg)*
CO_2	0.140	107.1
O_2	0.060	45.9
N_2	0.800	612.0
Total	1.000	765.0

On the basis of 1.00 mole of flue gas, the mole fraction y of each component, when multiplied by the total pressure, gives the partial pressure of that component.

Self-Assessment Test

1. Write down Dalton's law and Amagat's law.
2. A gas has the following composition at 120°F and 13.8 psia.

Component	Mol %
N_2	2
CH_4	79
C_2H_6	19

(a) What is the partial pressure of each component?
(b) What is the partial volume of each component if the total volume of the container is 2 ft^3?
(c) What is the volume fraction of each component?

3. (a) If the C_2H_6 were removed from the gas in problem 2, what would be the subsequent pressure in the vessel?
(b) What would be the subsequent partial pressure of the N_2?

3.1-4 Material Balances Involving Gases

Now that you have had a chance to practice applying the ideal gas law to simple transformations, we turn our attention back to material balances. The only difference between the subject matter of Chapter 2 and this section is that here the amount of material flow can be specified in terms of p, V, and T rather than solely mass or moles. For example, the basis for a problem, or the quantity to be solved for, might be a volume of gas at a given temperature and pressure rather than a mass of gas. The next two examples illustrate two of the same types of the problems you have encountered before.