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.

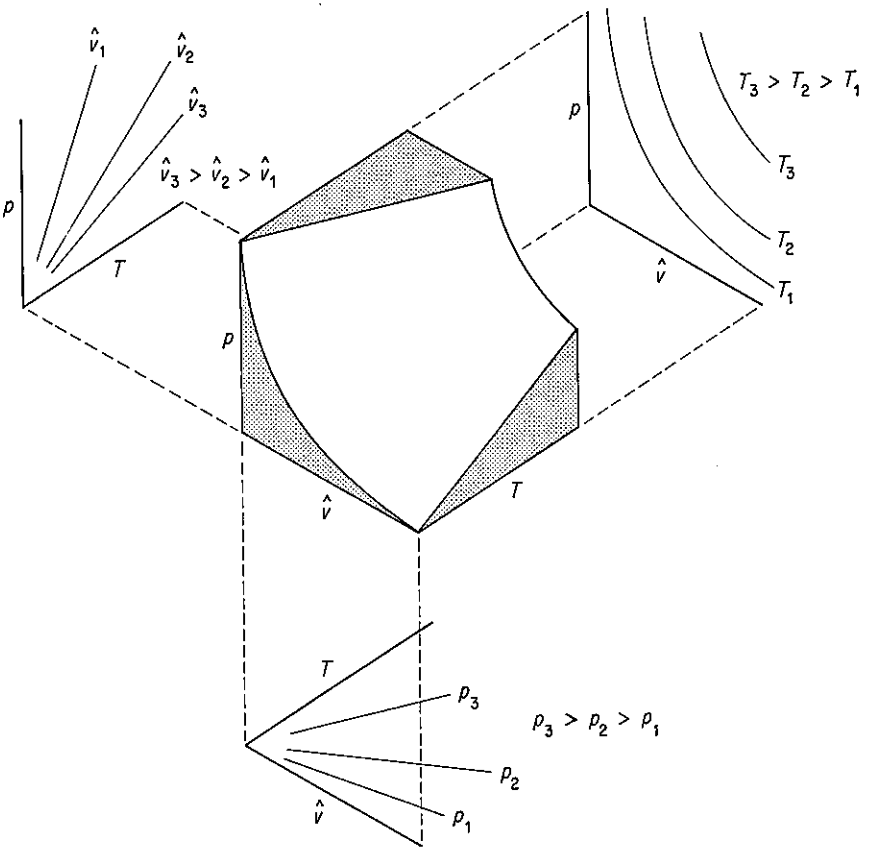

Figure 3.1 Representation of the ideal gas law in three dimensions as a surface.

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

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

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

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

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

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.

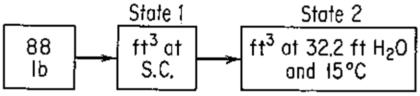

Figure E3.3

Solution 1 [Using Eq. (3.2)]:

At S.C. (state 1)	*At state 2*
$p = 33.91$ ft H_2O	$p = 32.2$ ft H_2O
$\hat{V} = 359 \dfrac{\text{ft}^3}{\text{lb mol}}$	$\hat{V} = ?$
$T = 273$ K	$T = 273 + 15 = 288$ 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

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

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.,

$$p = 33.91 \text{ ft H}_2\text{O}$$

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

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

$$R = \frac{33.91}{} \left| \frac{359}{273} \right. = 44.59 \frac{(\text{ft H}_2\text{O})(\text{ft}^3)}{(\text{lb mol})(\text{K})}$$

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

Basis: 88 lb of CO_2

$$V = \frac{nRT}{p} = \begin{array}{c|c|c} 88 \text{ lb CO}_2 & 44.59 \text{ (ft H}_2\text{O)(ft}^3) & 288 \text{ K} \\ \hline \frac{44 \text{ lb CO}_2}{\text{lb mol CO}_2} & (\text{lb mol})(\text{K}) & 32.2 \text{ ft H}_2\text{O} \end{array}$$

$$= 798 \text{ ft}^3 \text{ CO}_2 \text{ at } 32.2 \text{ ft H}_2\text{O and } 15°\text{C}$$

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?

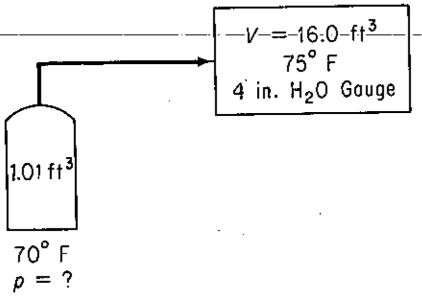

Figure E3.4

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

$$\text{final pressure} = 29.99 \text{ in. Hg} + \begin{array}{c|c} 4 \text{ in. } H_2O & 29.92 \text{ in. Hg} \\ \hline \dfrac{12 \text{ in. } H_2O}{\text{ft } H_2O} & 33.91 \text{ ft } H_2O \end{array}$$

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

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,

$$p_1 = \begin{array}{c|c} (480 - 29.99) \text{ in. Hg} & 14.696 \text{ psia} \\ \hline & 29.92 \text{ in. Hg} \end{array} = 221 \text{ psig}$$

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.

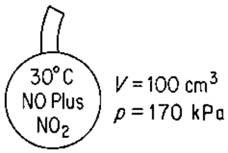

Figure E3.5

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 cm^3 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.