

Chapter 5

Gas Laws

INTRODUCTION

Observations based on physical experimentation often can be synthesized into simple mathematical equations called *laws*. These laws are never perfect and hence are only an approximate representation of reality. There is no universal all-purpose equation of state to describe the PVT (pressure–volume–temperature) behavior of a pure fluid. (An equation of state is an equation that relates pressure, volume, and temperature for any pure fluid.) Since most equations of state deal with gases, this chapter primarily highlights this phase. It should also be noted that liquids and solids exhibit little PVT variation in heat transfer applications; understandably, engineers and scientists are therefore rarely concerned with the PVT behavior of either of these two phases.

The *ideal gas law* (IGL) was derived from experiments in which the effects of pressure and temperature on gaseous volumes were measured over moderate temperature and pressure ranges. This law works well in the pressure and temperature ranges that were used in taking the data; extrapolations outside of the ranges have been found to work well in some cases and poorly in others. As a general rule, this law works best when the molecules of the gas are far apart (i.e., when the pressure is low and the temperature is high). Under these conditions, the gas is said to behave *ideally* and its behavior is a close approximation to the so-called *perfect* or *ideal gas*, a hypothetical entity that obeys the ideal gas law exactly. For engineering calculations, the ideal gas law is almost always assumed to be valid since it generally works well (usually within a few percent of the correct result) up to the highest pressures and down to the lowest temperatures used in most heat transfer applications. Nonetheless, the chapter concludes with comments on non-ideal behavior.

Five sections complement the presentation for this chapter. Topics include:

Boyle's and Charles' Laws

The Ideal Gas Law

Standard Conditions

Partial Pressure and Partial Volume

Non-Ideal Gas Behavior

BOYLE'S AND CHARLES' LAWS

The two precursors of the ideal gas law were *Boyle's* and *Charles's* laws. Boyle found that the volume V of a given mass of gas is inversely proportional to the *absolute* pressure if the temperature is kept constant:

$$P_1 V_1 = P_2 V_2 \quad (5.1)$$

where V_1 = volume of gas at absolute pressure P_1 and temperature T
 V_2 = volume of gas at absolute pressure P_2 and temperature T

Charles found that the volume of a given mass of gas varies directly with the *absolute* temperature at constant pressure:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (5.2)$$

where V_1 = volume of gas at pressure P and absolute temperature T_1
 V_2 = volume of gas at pressure P and absolute temperature T_2

Boyle's and Charles' laws may be combined into a single equation in which neither temperature nor pressure need be held constant:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (5.3)$$

For Equation (5.3) to hold, the mass of gas must be constant as the conditions change from (P_1, T_1) to (P_2, T_2) . This equation indicates that for a given mass of a specific gas, PV/T has a constant value. Since, at the same temperature and pressure, volume and mass must be directly proportional, this statement may be extended to

$$\frac{PV}{mT} = C \quad (5.4)$$

where m = mass of a specific gas
 C = constant that depends on the gas

Note that volume terms may be replaced by volume rate (or volumetric flow rate), q .

ILLUSTRATIVE EXAMPLE 5.1

What is the final (f) volumetric flow rate of a gas that is heated at constant pressure in a heat exchanger from 100 to 300°F if its initial (i) flow is 3500 actual cubic feet per minute (acfm).

SOLUTION: Apply Charles' law on a volume rate basis. See Equation (5.2) and be sure to employ absolute temperature units:

$$\begin{aligned} q_f &= q_i(T_f/T_i) \\ &= 3500[(300 + 460)/(100 + 460)] \\ &= 4750 \text{ acfm} \end{aligned}$$

ILLUSTRATIVE EXAMPLE 5.2

What is the volumetric flow rate of the gas (100°F, 1 atm) in the previous example if it is compressed isothermally (constant temperature) to 3 atm?

SOLUTION: Apply Boyle's law. See Equation (5.1),

$$\begin{aligned} q_f &= q_i(P_i/P_f) \\ &= 3500(1.0/3.0) \\ &= 1167 \text{ acfm} \end{aligned}$$

ILLUSTRATIVE EXAMPLE 5.3

What is the volumetric flow rate of the gas in the previous example if the final temperature is 300°F.

SOLUTION: Using the combined gas law provided in Equation (5.3),

$$\begin{aligned} q_f &= q_i(P_i/P_f)(T_f/T_c) \\ &= 3500(1/3)(760/560) = 1167(760/560) \\ &= 1583 \text{ acfm} \end{aligned}$$

THE IDEAL GAS LAW

Experiments with different gases showed that Equation (5.4) could be expressed in a far more generalized form. If the number of moles (n) is used in place of the mass (m), the constant is the same for all gases:

$$\frac{PV}{nT} = R \quad (5.5)$$

where R = universal gas constant.

Equation (5.5) is called the ideal gas law. Numerically, the value of R depends on the units used for P , V , T , and n (see Table 5.1). In this text, heat transfer applications involving gases are generally assumed to approximate ideal gas behavior. As is usually the case in engineering practice, unless otherwise stated the ideal gas law is assumed to

Table 5.1 Values of R in Various Units

R	Temperature scale	Units of V	Units of n	Units of P	Unit of PV (energy)
10.73	°R	ft ³	lbmol	psia	–
0.7302	°R	ft ³	lbmol	atm	–
21.85	°R	ft ³	lbmol	in Hg	–
555.0	°R	ft ³	lbmol	mm Hg	–
297.0	°R	ft ³	lbmol	in H ₂ O	–
0.7398	°R	ft ³	lbmol	bar	–
1545.0	°R	ft ³	lbmol	psfa	–
24.75	°R	ft ³	lbmol	ft H ₂ O	–
1.9872	°R	–	lbmol	–	Btu
0.0007805	°R	–	lbmol	–	hp · h
0.0005819	°R	–	lbmol	–	kW · h
500.7	°R	–	lbmol	–	cal
1.314	K	ft ³	lbmol	atm	–
998.9	K	ft ³	lbmol	mm Hg	–
19.32	K	ft ³	lbmol	psia	–
62.361	K	L	gmol	mm Hg	–
0.08205	K	L	gmol	atm	–
0.08314	K	L	gmol	bar	–
8314	K	L	gmol	Pa	–
8.314	K	m ³	gmol	Pa	–
82.057	K	cm ³	gmol	atm	–
1.9872	K	–	gmol	–	cal
8.3144	K	–	gmol	–	J

be valid for all illustrative examples and assigned problems. If a case is encountered in practice where the gas behaves in a very non-ideal fashion (e.g., a high-molecular-weight gas, such as a chlorinated organic under high pressure), one of the many *real gas* correlations available in the literature should be used.^(1–3)

Other useful forms of the ideal gas law are shown in Equations (5.6) and (5.7). Equation (5.6) applies to a gas volume flow rate rather than to a gas volume confined in a container:⁽⁴⁾

$$Pq = \dot{n}RT \quad (5.6)$$

where q = gas volumetric flow rate (ft³/h)

P = absolute pressure (psia)

\dot{n} = molar flow rate (lbmol/h)

T = absolute temperature (°R)

$R = 10.73 \text{ psia} \cdot \text{ft}^3/\text{lbmol} \cdot \text{°R}$

Equation (5.7) combines n and V from Equation (5.5) to express the law in terms of density:

$$P(MW) = \rho RT \quad (5.7)$$

where MW = molecular weight of gas (lb/lbmol)

ρ = density of gas (lb/ft³)

ILLUSTRATIVE EXAMPLE 5.4

What is the density of air at 75°F and 14.7 psia? The molecular weight of air is approximately 29.

SOLUTION: This example is solved using the ideal gas law:

$$PV = nRT = \left(\frac{m}{MW}\right)RT \quad (5.5)$$

For the density, apply Equation (5.7).

$$\begin{aligned} \rho &= \frac{P(MW)}{RT} = \frac{(14.7 \text{ psia})(29 \text{ lb/lbmol})}{(10.73 \text{ ft}^3 \cdot \text{psi/lbmol} \cdot ^\circ\text{R})(75 + 460)} \\ &= 0.0743 \text{ lb/ft}^3 \end{aligned} \quad \blacksquare$$

ILLUSTRATIVE EXAMPLE 5.5

Calculate the volume (in ft³) of 1.0 lbmol of any ideal gas at 60°F and 14.7 psia.

SOLUTION: Solve the ideal gas law for V and calculate the volume:

$$\begin{aligned} V &= \frac{nRT}{P} = \frac{(1)(10.73)(60 + 460)}{14.7} \\ &= 379 \text{ ft}^3 \end{aligned}$$

This result is an important number to remember in many heat transfer calculations—1 lbmol of any (ideal) gas at 60°F and 1 atm occupies 379 ft³. ■

ILLUSTRATIVE EXAMPLE 5.6

Calculate the density of a gas ($MW = 29$) in g/cm³ at 20°C and 1.2 atm using the ideal gas law.

SOLUTION: Calculate the density of the gas again using the ideal gas law:

$$\begin{aligned}
 PV &= nRT = \left(\frac{m}{MW}\right)RT & (5.5) \\
 \frac{m}{V} &= \rho = \frac{P(MW)}{RT} \frac{(1.2)(29)}{(82.06)(20 + 273)} \\
 &= 0.00145 \text{ g/cm}^3
 \end{aligned}$$

The effects of pressure, temperature, and molecular weight on density can be obtained directly from the ideal gas law equation. Increasing the pressure and molecular weight increases the density; increasing the temperature decreases the density. ■

ILLUSTRATIVE EXAMPLE 5.7

A certain pure-component two-element ideal gas has a specific volume v of 10.58 ft³/lb at 70°F and 14.7 psia. Determine the molecular weight of the gas and state its name. (*Hint:* The gas is acidic and soluble in water.)

SOLUTION: Rewrite the ideal gas law equation in terms of MW ,

$$MW = \left(\frac{m}{V}\right) \frac{RT}{P} = \frac{RT}{vP}; \quad v = \text{specific volume, volume/mass} \quad (5.7)$$

Substituting,

$$\begin{aligned}
 MW &= \frac{(10.73)(460 + 70)}{(10.58)(14.7)} \\
 &= 36.56 \text{ lb/lbmol}
 \end{aligned}$$

It appears that the gas is HCl (i.e., hydrogen chloride). ■

STANDARD CONDITIONS

Volumetric flow rates are often not given at the actual conditions of pressure and temperature but rather at arbitrarily chosen standard conditions (*STP, standard temperature and pressure*). To distinguish between flow rates based on the two conditions, the letters a and s are often used as part of the units. The units acfm and scfm stand for actual cubic feet per minute and standard cubic feet per minute, respectively. The ideal gas law can be used to convert from *standard* to *actual* conditions, but since there are many standard conditions in use, the STP being used must be known or specified. Standard conditions most often used are shown in Table 5.2. The reader is cautioned on the incorrect use of acfm and/or scfm. The use of standard conditions is a convenience; actual conditions *must* be employed when predicting the performance of or designing heat transfer equipment. Designs based on standard conditions can lead to disastrous results, with the unit usually underdesigned. For example, for

Table 5.2 Common Standard Conditions

System	Temperature	Pressure	Molar volume
SI	273 K	101.3 kPa	22.4 m ³ /kmol
Universal scientific	0°C	760 mm Hg	22.4 L/gmol
Natural gas industry	60°F	14.7 psia	379 ft ³ /lbmol
American engineering	32°F	1 atm	359 ft ³ /lbmol
Hazardous waste incineration industry	60°F	1 atm	379 ft ³ /lbmol
	70°F	1 atm	387 ft ³ /lbmol

a flue gas stream at 2140°F, the ratio of acfm to scfm (standard temperature = 60°F) for a thermal application is 5.0.

Equation (5.8), which is a form of Charles' law, can be used to convert flow rates from standard to actual conditions:

$$q_a = q_s \left(\frac{T_a}{T_s} \right) \quad (5.8)$$

where q_a = volumetric flow rate at actual conditions (ft³/h)

q_s = volumetric flow rate at standard conditions (ft³/h)

T_a = actual absolute temperature (°R)

T_s = standard absolute temperature (°R)

The reader is again reminded that absolute temperatures and pressures must be employed in all ideal gas law calculations.

ILLUSTRATIVE EXAMPLE 5.8

Data from a heat exchanger indicate a volumetric flow rate of 30,000 scfm (60°F, 1 atm). If the operating temperature and pressure of the unit are 1100°F and 1 atm, respectively, calculate the flow rate in actual cubic feet per minute (acfm).

SOLUTION: Since the pressure remains constant, the standard cubic feet per minute using Charles' law is calculated as:

$$q_a = q_s \left(\frac{T_a}{T_s} \right) \quad (5.8)$$

Substituting,

$$\begin{aligned} q_a &= 30,000 \left(\frac{1100 + 460}{60 + 460} \right) \\ &= 90,000 \text{ acfm} \end{aligned}$$

The reader is again cautioned on the use of acfm and/or scfm. Predicting the performance of and designing heat exchangers should always be based on *actual* conditions. ■

ILLUSTRATIVE EXAMPLE 5.9

The exhaust gas flow rate from a condenser is 1000 scfm. All of the gas is vented through a small stack that has an inlet area of 2.0 ft^2 . The exhaust gas temperature is 300°F . What is the velocity of the gas through the stack inlet in feet per second? Assume standard conditions to be 70°F and 1.0 atm . Neglect the pressure drop across the stack.

SOLUTION: The actual flow rate, in acfm, using Charles' law is calculated as:

$$q_a = q_s \left(\frac{T_a}{T_s} \right) \quad (5.8)$$

Substituting,

$$\begin{aligned} &= 1000 \left(\frac{460 + 300}{460 + 70} \right) \\ &= 1434 \text{ acfm} \end{aligned}$$

Note that since the gas from the condenser is vented through the stack to the atmosphere, the pressure is 1.0 atm . The velocity v of the gas is calculated as follows:

$$\begin{aligned} v &= \frac{q_a}{A} = \frac{1434}{2.0} \\ &= 717 \text{ ft/min} = 12 \text{ ft/s} \end{aligned} \quad \blacksquare$$

ILLUSTRATIVE EXAMPLE 5.10

$\text{C}_6\text{H}_5\text{Cl}$ is fed into a thermal oxidizer at a rate of 5000 scfm (60°F , 1 atm) and is combusted in the presence of air fed at a rate of 3000 scfm (60°F , 1 atm). Both streams enter the oxidizer at 70°F . The products are then cooled from 2000°F and exit the cooler at 180°F . At what rate (lb/h) do the products exit the cooler? The molecular weight of $\text{C}_6\text{H}_5\text{Cl}$ is 112.5; the molecular weight of air is 29.

SOLUTION: First convert the scfm feed to acfm using Charles' law:

$$\begin{aligned} 5000 \text{ scfm} \left(\frac{460 + 70}{460 + 60} \right) &= 5096 \text{ acfm of } \text{C}_6\text{H}_5\text{Cl} \\ 3000 \text{ scfm} \left(\frac{460 + 70}{460 + 60} \right) &= 3058 \text{ acfm of air} \end{aligned}$$

One lbmol of any ideal gas occupies 387 ft^3 at 70°F and 1 atm (see Table 5.2). Therefore, the molar flow rate (\dot{n}) may be calculated by dividing these results by 387:

$$\begin{aligned} \dot{n}(\text{C}_6\text{H}_5\text{Cl}) &= \frac{5096}{387} \\ &= 13.17 \text{ lbmol/min} \\ \dot{n}(\text{air}) &= \frac{3058}{387} \\ &= 7.90 \text{ lbmol/min} \end{aligned}$$

The mass flow rate is obtained by multiplying these results by the molecular weight

$$\begin{aligned}\dot{m}(\text{C}_6\text{H}_5\text{Cl}) &= (13.17)(112.5)(60) \\ &= 88,898 \text{ lb/h} \\ \dot{m}(\text{air}) &= (7.90)(29)(60) \\ &= 13,746 \text{ lb/h}\end{aligned}$$

Since mass is conserved, \dot{m}_{in} is equal to \dot{m}_{out} :

$$\dot{m}_{\text{out, total}} = \dot{m}_{\text{in, total}} = 88,898 + 13,746 = 102,644 \text{ lb/h} \quad \blacksquare$$

PARTIAL PRESSURE AND PARTIAL VOLUME

Mixtures of gases are more often encountered than single or pure gases in engineering practice. The ideal gas law is based on the *number* of molecules present in the gas volume; the *kind* of molecules is not a significant factor, only the number. This law applies equally well to mixtures and pure gases alike. Dalton and Amagat both applied the ideal gas law to mixtures of gases. Since pressure is caused by gas molecules colliding with the walls of the container, it seems reasonable that the total pressure of a gas mixture is made up of pressure contributions due to each of the component gases. These pressure contributions are called *partial pressures*.

Dalton defined the partial pressure of a component as the pressure that would be exerted if the same mass of the component gas occupied the same total volume *alone* at the same temperature as the mixture. The sum of these partial pressures would then equal the total pressure:

$$P = p_A + p_B + p_C + \cdots + p_n = \sum_{i=1}^n p_i \quad (5.9)$$

where P = total pressure

n = number of components

p_i = partial pressure of component i .

Equation (5.9) is known as *Dalton's law*. Applying the ideal gas law to one component (A) only,

$$p_A V = n_A R T \quad (5.10)$$

where n_A = number of moles of component A .

Eliminating R , T , and V between Equation (5.5) and (5.10) yields

$$\frac{p_A}{P} = \frac{n_A}{n} = y_A$$

or

$$p_A = y_A P \quad (5.11)$$

where y_A = mole fraction of component A .

Amagat's law is similar to Dalton's. Instead of considering the total pressure to be made up of partial pressures, where each component occupies the total container volume, Amagat considered the total volume to be made up of partial volumes in which each component is at the total pressure. The definition of the *partial volume* is therefore the volume occupied by a component gas alone at the same temperature and pressure as the mixture. For this case:

$$V = V_A + V_B + V_C + \cdots + V_n = \sum_{i=1}^n V_i \quad (5.12)$$

Applying Equation (5.5), as before,

$$\frac{V_A}{V} = \frac{n_A}{n} = y_A \quad (5.13)$$

where V_A = partial volume of component A.

It is common in heat exchanger applications to describe low concentrations of corrosive components in gaseous mixtures in parts per million (ppm) by volume. Since partial volumes are proportional to mole fractions, it is only necessary to multiply the mole fraction of the component by 1 million (10^6) to obtain the concentration in parts per million. [For liquids and solids, parts per million (ppm) is also used to express concentration, although it is usually on a *mass* basis rather than a *volume* basis. The terms ppmv and ppmw are sometimes used to distinguish between the volume and mass bases, respectively.]

ILLUSTRATIVE EXAMPLE 5.11

The exhaust to the atmosphere from a thermal device has a SO_3 concentration expressed as 0.15 mm Hg partial pressure. Calculate the parts per million of SO_3 in the exhaust.

SOLUTION: First calculate the mole fraction (y). By definition,

$$y_{\text{SO}_3} = p_{\text{SO}_3}/P \quad (5.11)$$

(Strictly speaking, this equation only applies to ideal gas mixtures.) Since the exhaust is discharged into the atmosphere, the atmospheric pressure (760 mm Hg) is the total pressure (P). Thus,

$$y_{\text{SO}_3} = (0.15)/(760) = 1.97 \times 10^{-4}$$

As noted above, partial pressures may be converted to ppm (parts per million) by multiplying by 10^6 :

$$\begin{aligned} \text{ppm} &= (y_{\text{SO}_3})(10^6) = (1.97 \times 10^{-4})(10^6) \\ &= 197 \text{ ppm} \end{aligned}$$

Note: Since the concentration of a *gas* is involved, it is understood (unless otherwise specified) that ppm is on a volume basis. ■

NON-IDEAL GAS BEHAVIOR

As noted earlier, an *ideal* gas is a hypothetical entity that obeys the ideal gas law perfectly. But, in heat transfer applications, one almost always deals with *real* gases. Although most heat exchanger applications involving gases occur at conditions approaching ideal gas behavior, there are rare occasions when the deviation from ideality is significant. Detailed calculation procedures are available^(1,2,5) to account for these deviations.

Although no real gas obeys the ideal gas law exactly, the “lighter” gases (hydrogen, oxygen, air, and so on) at ambient conditions approach ideal gas law behavior. The “heavier” gases such as sulfur dioxide and hydrocarbons, particularly at high pressures and low temperatures, deviate considerably from the ideal gas law. Despite these deviations, the ideal gas law is routinely used in not only heat transfer but also engineering calculations.

As noted earlier, deviations from ideality increase at higher pressures and lower temperatures, where the density increases. The aforementioned law does not describe the behavior of real gases in some cases because the fluid molecules themselves occupy a finite volume, and they exert forces of attraction and repulsion on each other.

Numerous attempts have been made to develop an all-purpose gas law. Although it is beyond the scope of this book to review these theories in any great detail, a brief outline and discussion is presented below.

One (and perhaps the most popular) approach to account for deviations from ideality is to include a “correction factor,” Z , which is defined as the *compressibility coefficient* or *factor*,

$$PV = ZnRT \quad (5.13)$$

Note that Z approaches 1.0 as P approaches a vacuum. For an ideal gas, Z is exactly unity. This equation may also be written as

$$Pv = ZRT \quad (5.14)$$

where v is now the *specific* volume (not the total volume or velocity) with units of volume/mole. Details on calculating Z are available in the literature.^(1,2,5)

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