

IDEAL GAS LAW

11.1 INTRODUCTION

Observations based on physical experimentation can often be synthesized into simple mathematical equations called *laws*. These laws are never perfect and hence are only an approximate representation of reality. The *ideal gas law* (IGL)^(1,2) 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*, that is, its behavior is a close approximation to the so-called *perfect* or *ideal gas*, a hypothetical entity that obeys the ideal gas law perfectly. For engineering calculations, and specifically for most fluid flow applications, 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 many applications.

11.2 BOYLE'S AND CHARLES' LAWS

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

$$P_1 V_1 = P_2 V_2 \quad (11.1)$$

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:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (11.2)$$

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

11.3 THE IDEAL GAS LAW

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

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (11.3)$$

For Equation (11.3) 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

$$\frac{PV}{mT} = C \quad (11.4)$$

where m = mass of a specific gas

C = constant that depends on the gas

Moreover, experiments with different gases showed that Equation (11.4) 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:

$$\frac{PV}{nT} = R \quad (11.5)$$

where R = universal gas constant.

Equation (11.5) is called the ideal gas law. Numerically, the value of R depends on the units used for P , V , T , and n (see Table 11.1). In this text, all gases are assumed to approximate ideal gas behavior. As is generally the case in engineering practice, the ideal gas law is assumed to be valid for all illustrative and assigned problems. If a case is encountered in practice where the gas behaves in a very nonideal fashion, e.g., a high-molecular-weight gas (such as a chlorinated organic) under high pressure, one of the many *real gas* correlations found in the literature⁽³⁾ should be used.

Illustrative Example 11.1 Explain why the molar volumes of all ideal gases are the same at a given temperature and pressure.

Table 11.1 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

Solution From the ideal gas law

$$\frac{V}{n} = \frac{RT}{P}$$

The proportionality constant, R , is the universal gas constant. The molar volumes of all ideal gases are the same at the same temperature and pressure because R is a universal constant.

Other useful forms of the ideal gas law are shown in Equations (11.6) and (11.7). Equation (11.6) applies to gas flow rather than to gas confined in a container:⁽⁴⁾

$$Pq = \dot{n}RT \quad (11.6)$$

where q = gas volumetric flow rate (ft^3/h)

P = absolute pressure (psia)

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

T = absolute temperature ($^{\circ}\text{R}$)

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

Equation (11.7) combines n and V from Equation (11.5) to express the law in terms of density:

$$P(\text{MW}) = \rho RT \quad (11.7)$$

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

ρ = density of gas (lb/ft^3)

Volumetric flow rates are often given not at the actual conditions of pressure and temperature but 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 unit. 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. Standard conditions most often used are shown in Table 11.2. The reader is cautioned on the incorrect use of acfm and/or scfm. The use of standard conditions is a convenience; when predicting the performance of or designing equipment, the actual conditions must be employed. Designs based on standard conditions can lead to disastrous results, with the unit usually underdesigned. For example, for a flue gas stream at 2140°F, the ratio of acfm to scfm (standard temperature = 60°F) for an incinerator application is 5.0. Equation (11.8), which is a form of Charles’

Table 11.2 Common standard conditions

System	Temperature	Pressure	Molar Volume
SI	273K	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	60°F	1 atm	379 ft ³ /lbmol
Incinerator industry	70°F	1 atm	387 ft ³ /lbmol

law, can be used to correct flow rates from standard to actual conditions:

$$q_a = q_s(T_a/T_s) \quad (11.8)$$

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 11.2 Given the following pressure, temperature, and molecular weight data of an ideal gas, determine its density:

Pressure = 1.0 atm

Temperature = 60°F

Molecular weight of gas = 29

Solution As noted earlier in this chapter, an ideal gas is an imaginary gas that exactly obeys certain simple laws (e.g., Boyle's law, Charles' law, and the ideal gas law). No real gas obeys the ideal gas law exactly, although 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 engineering calculations. The ideal gas law in terms of density, ρ , is (see Eq. 11.7):

$$\begin{aligned} \rho &= m/V = n(\text{MW})/V \\ &= P(\text{MW})/RT \end{aligned}$$

where MW = molecular weight

m = mass of gas

ρ = density of gas

The choice of R is arbitrary, provided consistent units are employed. From Table 11.1 the density of the gas using the appropriate value of R may now be calculated

$$\begin{aligned}\rho &= P(\text{MW})/RT \\ &= (1)(29)/(0.73)(60 + 460) \\ &= 0.0764 \text{ lb/ft}^3\end{aligned}$$

Since the molecular weight of the given gas is 29, this calculated density may be assumed to apply to air.

Also note that the effect 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 11.3 Given a standard volumetric flowrate, determine the actual volumetric flowrate. Data are provided below:

Standard volumetric flowrate of a gas stream = 2000 scfm

Standard conditions = 60°F and 1 atm

Actual operating conditions = 700°F and 1 atm

Solution As noted earlier, the actual volumetric flowrate, usually in acfm (actual cubic feet per minute), is the volumetric flowrate based on actual operating conditions (temperature and pressure of the system). The standard volumetric flowrate, usually in scfm (standard cubic feet per minute), are 60°F and 1 atm or 32°F and 1 atm.

It should be noted again that Charles' law states that the volume of an ideal gas is directly proportional to the temperature at constant pressure. Boyle's law states that the volume of an ideal gas is inversely proportional to the pressure at constant temperature. One can combine Boyle's law and Charles' law to relate the actual volumetric flowrate to the standard volumetric flowrate:

$$q_a = q_s(T_a/T_s)(P_s/P_a) \quad (11.9)$$

where q_a = actual volumetric flowrate

q_s = standard volumetric flowrate

T_a = actual operating temperature, °R or K

T_s = standard temperature, °R or K

P_s = standard pressure, absolute

P_a = actual operating pressure, absolute

This equation may be used to calculate the actual volumetric flowrate in acfm:

$$\begin{aligned} q_a &= q_s(T_a/T_s) \\ &= 2000(700 + 460)/(60 + 460) \\ &= 4462 \text{ acfm} \end{aligned}$$

If it is desired to convert from acfm to scfm, one can reverse the procedure and use the following equation:

$$q_s = q_a(T_s/T_a)(P_a/P_s) \quad (11.10)$$

Illustrative Example 11.4 Given a mass flowrate, determine the standard volumetric flowrate. Data are provided below:

Mass flowrate of flue gas, $\dot{m} = 50 \text{ lb/min}$

Average molecular weight of flue gas, $MW = 29 \text{ lb/lbmol}$

Standard conditions = 60°F and 1 atm

Solution Another application of the ideal gas law arises when one is interested in converting a mass (or molar) flowrate to a volumetric flowrate (actual or standard), or vice versa. The ideal gas equation is rearranged and solved for one variable in terms of the others. For example, the volume of 1 lbmol of ideal gas is given by

$$\begin{aligned} PV &= nRT \quad R = 0.73 \text{ atm} \cdot \text{ft}^3/(\text{lbmol} \cdot ^\circ\text{R}) \\ V/n &= RT/P \\ &= (0.73)(60 + 460)/1.0 \\ &= 379 \text{ scf/lbmol} \end{aligned}$$

Thus, if the standard conditions are 60°F and 1 atm , there are 379 standard cubic feet of gas per lbmol for any ideal gas (see Table 11.2).

The standard volumetric flowrate, q_s , in scfm is then

$$\begin{aligned} q_s &= (m/MW)(379 \text{ scf/lbmol}) \\ &= (50/29)(379) \\ &= 653 \text{ scfm} \end{aligned}$$

The previous result is an important number to remember in many engineering calculations: 1 lbmol of any ideal gas at 60°F and 1 atm occupies 379 ft^3 ; and, equally

important, 1 lbmol of any ideal gas at 32°F and 1.0 atm occupies 359 ft³. In SI units, 1 gmol of any ideal gas occupies 22.4 liters at 0°C and 1.0 atm.

Illustrative Example 11.5 A certain pure component, one-element ideal gas has a specific volume of 12.084 ft³/lb at 70°F and 14.696 psia. Determine the molecular weight of the gas and state its name.

Solution Rewrite the ideal gas in terms of the specific volume

$$PV = (m/MW)RT$$

$$V/m = RT/(P)(MW); V/m = 12.084 \text{ ft}^3/\text{lb}$$

Since

$$T = 70^\circ\text{F} = 530^\circ\text{R}$$

$$P = 14.7 \text{ psia} = 1 \text{ atm}$$

$$12.084 = (0.73)(530)/(1)(MW)$$

Solving for MW,

$$MW = 32.0$$

Since this is a pure component, one-element gas, the gas is OXYGEN!

11.4 NON-IDEAL GAS BEHAVIOR

As noted earlier, an *ideal* gas is a hypothetical entity that obeys the ideal gas law perfectly. But, in industrial applications, one deals with *real* gases. Although most fluid flow 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⁽³⁻⁵⁾ to account for these deviations.

As noted, deviations from ideality increase at higher pressures and lower temperatures, where the density increases. The aforementioned law does not describe the behavior of ideal 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*.

$$PV = ZnRT \quad (11.11)$$

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

$$Pv = ZRT \quad (11.12)$$

where v is now the *specific* volume (not the total volume or velocity) with units of volume/mole.

The Virial equation, is another equation of state that can be used to describe gas behavior. (The definition of an equation of state is that it relates pressure, molar or specific volume, and temperature for any pure fluid.) Equations of state can take many forms. The Virial equation is one of the most important of the non-ideal gas modelling correlations because it is the one upon which many other equations of state are based. Its power series representation is:

$$Z = PV/RT = 1 + B/V + C/V^2 + D/V^3 + \dots \quad (11.13)$$

It can also be written as a function of pressure:

$$Z = PV/RT = 1 + B'P + C'P^2 + D'P^3 + \dots \quad (11.14)$$

$$\begin{aligned} \text{where } B' &= B/RT \\ C' &= (C - B^2)/(RT)^2 \end{aligned}$$

In both cases, B and C above are temperature-dependent virial coefficients. Although this power series could be infinitely long, data is generally available only up to the second virial coefficient. However, as one increases the number of terms, the accuracy of the equation improves. The two-term equation can be used up to a pressure of about 15 atmospheres total pressure while with three terms, it can be used up to 50 atmospheres.

Many equations of state for gases have been proposed, but the Redlich–Kwong equation is one of the most widely used for engineering calculations. This is due to the accuracy it provides for many gases. The equation, developed in part from the earlier and less accurate Virial equation, is:

$$P = [RT/(V - b)] - a/[T^{1/2}V(V + b)] \quad (11.15)$$

$$\begin{aligned} \text{where } a &= 0.42748R^2T_c^2/P_c \\ b &= 0.08664RT_c/P_c \end{aligned}$$

and the subscript c refers to a critical property. This equation has been verified from actual experimental PVT data.

Illustrative Example 11.6 The first and second virial coefficients for sulfur dioxide at 400K are specified as:

$$B = -0.159 \text{ m}^3/\text{kgmol}$$

$$C = 0.009 (\text{m}^3/\text{kgmol})^2$$

Calculate the specific volume of SO_2 in L/gmol at 40 atm and 400K.

Solution The Virial equation is

$$Z = PV/RT = 1 + B/V + C/V^2$$

Use

$$R = 0.082 \text{ L} \cdot \text{atm}/\text{gmol} \cdot \text{K} = 82.06 \text{ cm}^3 \cdot \text{atm}/\text{gmol} \cdot \text{K}$$

Insert the appropriate values of the terms and coefficients:

$$(40)(V)/(0.082)(400) = 1 + (-0.159)/V + (0.009)/V^2$$

$$(1.22)(V) = 1 + (-0.159)/V + (0.009)/V^2$$

Solve for V iteratively.

For ideal gas conditions, $V = 1.0/1.22 = 0.820$. Guess $V = 0.820$ L/gmol, substitute into the right-hand side (RHS) of the equation, and calculate the “updated” V from the left-hand side (LHS):

$$\text{For } V_{\text{guess}} = 0.820, V_{\text{new}} = 0.672$$

$$\text{For } V_{\text{guess}} = 0.672, V_{\text{new}} = 0.642$$

$$\text{For } V_{\text{guess}} = 0.642, V_{\text{new}} = 0.635$$

V is approximately 0.635 L/gmol.

Illustrative Example 11.7 Calculate the molar volume of methane gas (ft^3/lbmol) at 373K and 10 atm. Employ the Redlich–Kwong (R–K) equation. The critical temperature and pressure of methane are 190.6K and 45.4 atm, respectively.

Solution Convert the temperature and the critical temperature to $^\circ\text{R}$:

$$T = (373)(1.8)$$

$$= 671^\circ\text{R}$$

$$T_c = 190.6\text{K}$$

$$= 343^\circ\text{R}$$

Calculate the numerical values of the a and b constants

$$\begin{aligned} a &= (0.42748)(0.73)^2(343)^{2.5}/45.4 \\ &= 10,933 \\ b &= (0.08664)(0.73)(343)/45.4 \\ &= 0.478 \end{aligned}$$

Solve iteratively for the molar volume, v , in ft^3/lbmol in the R–K equation.

$$10 = [490/(v - 0.478)] - 10,933/(25.9)(v)(v + 0.478)$$

By trial and error

$$v = 48.8 \text{ ft}^3/\text{lbmol}$$

Illustrative Example 11.8 Briefly discuss Van der Waals' equation.

Solution Van der Waals' equation of state takes the form

$$P = RT/(V - b) - a/V^2$$

The two constants a and b are characteristics of the gas and are called *van der Waals constants*. This equation and many others are loosely based on the previously discussed Virial equation. It is discussed here simply as an academic exercise, i.e., as a bridge between the simplest equation of state (ideal gas law) and the more complicated equations that are available in the literature.

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