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Ninth
Edition

GENERAL CHEMISTRY

Principles and Modern Applications



Chapter 6: Gases

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Contents

- 6-1 Properties of Gases: Gas Pressure
- 6-2 The Simple Gas Laws
- 6-3 Combining the Gas Laws:
The Ideal Gas Equation and
The General Gas Equation
- 6-4 Applications of the Ideal Gas Equation
- 6-5 Gases in Chemical Reactions
- 6-6 Mixtures of Gases

Contents

- 6-6 Mixtures of Gases
- 6-7 Kinetic—Molecular Theory of Gases
- 6-8 Gas Properties Relating to the
Kinetic—Molecular Theory
- 6-9 Nonideal (Real) Gases

6-1 Properties of Gases: Gas Pressure

- ◆ Four properties determine the physical behavior of a gas: the amount of the gas (in moles) and the volume, temperature, and pressure of the gas.
- ◆ The gaseous states of three halogens.



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- ◆ Most common gases are colorless
 - H_2 , O_2 , N_2 , CO and CO_2

The Concept of Pressure

- ◆ The pressure exerted by a solid.
 - Both cylinders have the same mass
 - They have different areas of contact

$$P \text{ (Pa)} = \frac{\text{Force (N)}}{\text{Area (m}^2\text{)}}$$

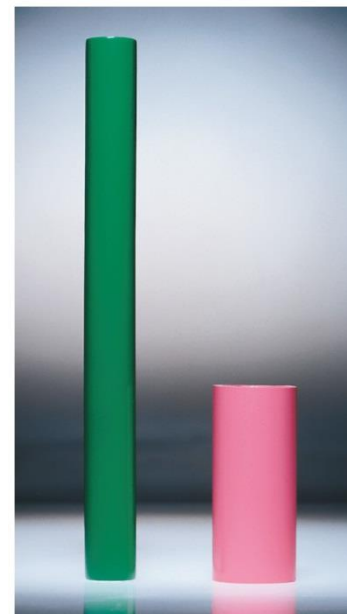


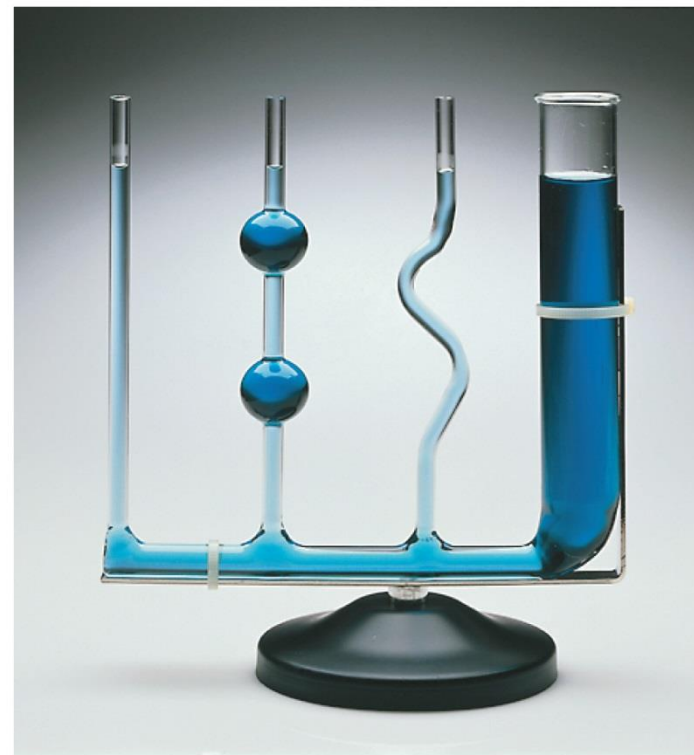
FIGURE 6-2

Illustrating the pressure exerted by a solid

The two cylinders have the same mass and exert the same force on the supporting surface ($F = gxm$). The tall, thin one has a smaller area of contact, however, and exerts a greater pressure ($P = F/A$)

Liquid Pressure

- ◆ The pressure exerted by a liquid depends on:
 - The height of the column of liquid.
 - The density of the column of liquid.

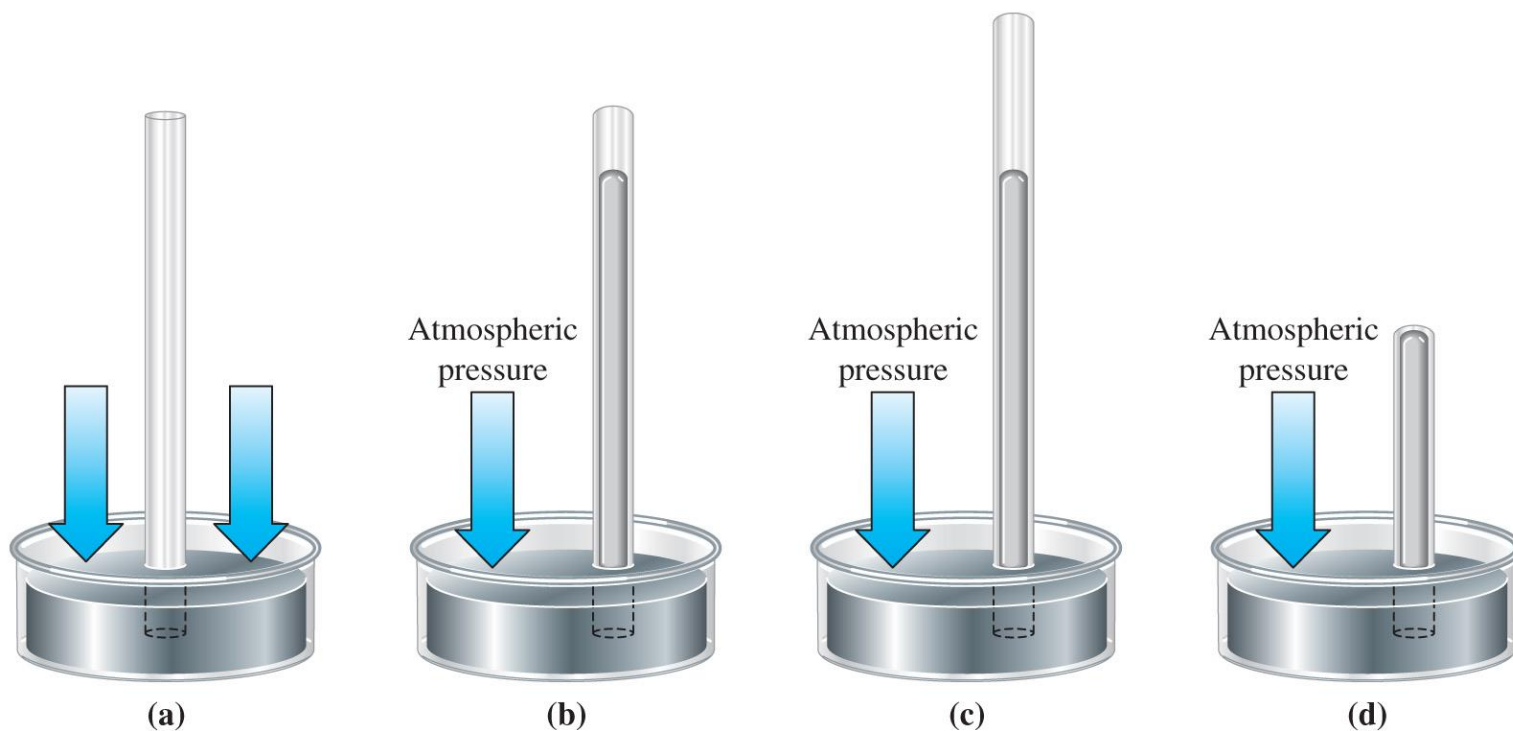


$$P = g \cdot h \cdot d$$

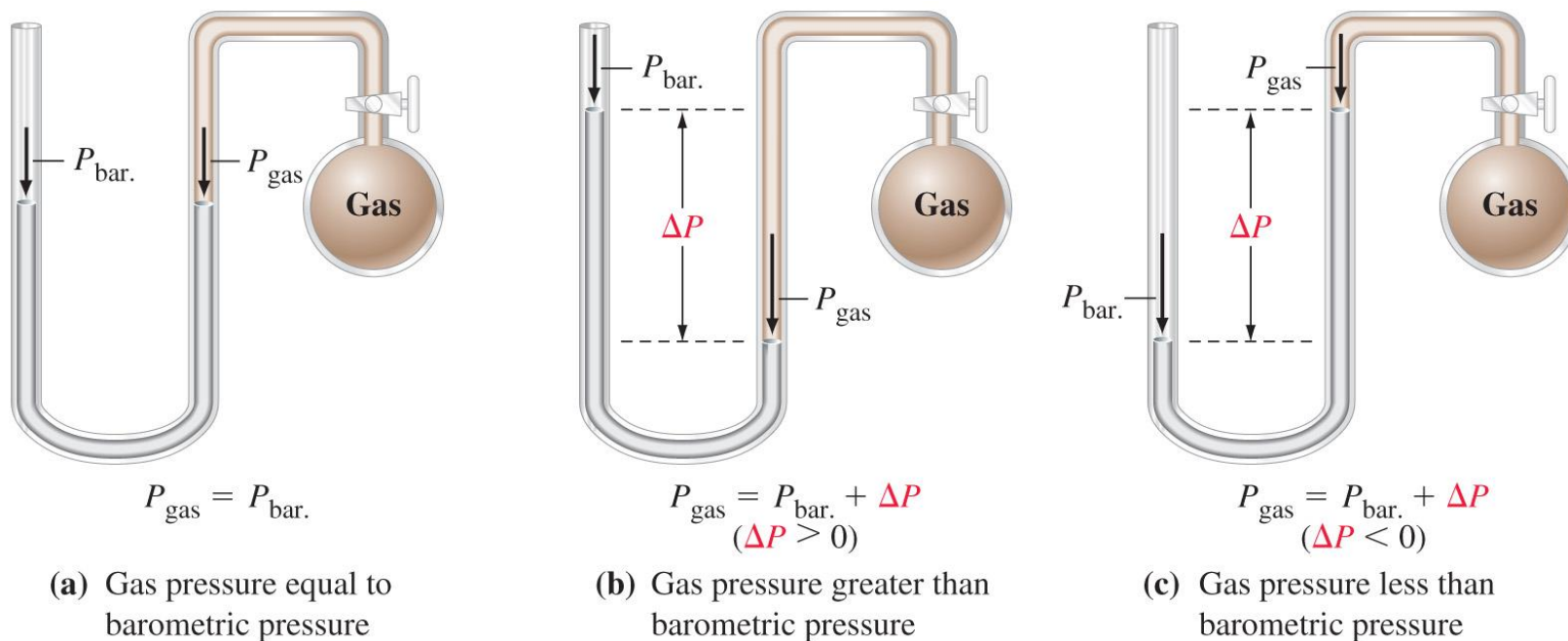
Barometric Pressure

Standard Atmospheric Pressure

1.00 atm, 760 mm Hg, 760 torr, 101.325 kPa, 1.01325 bar



Manometers



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FIGURE 6-5

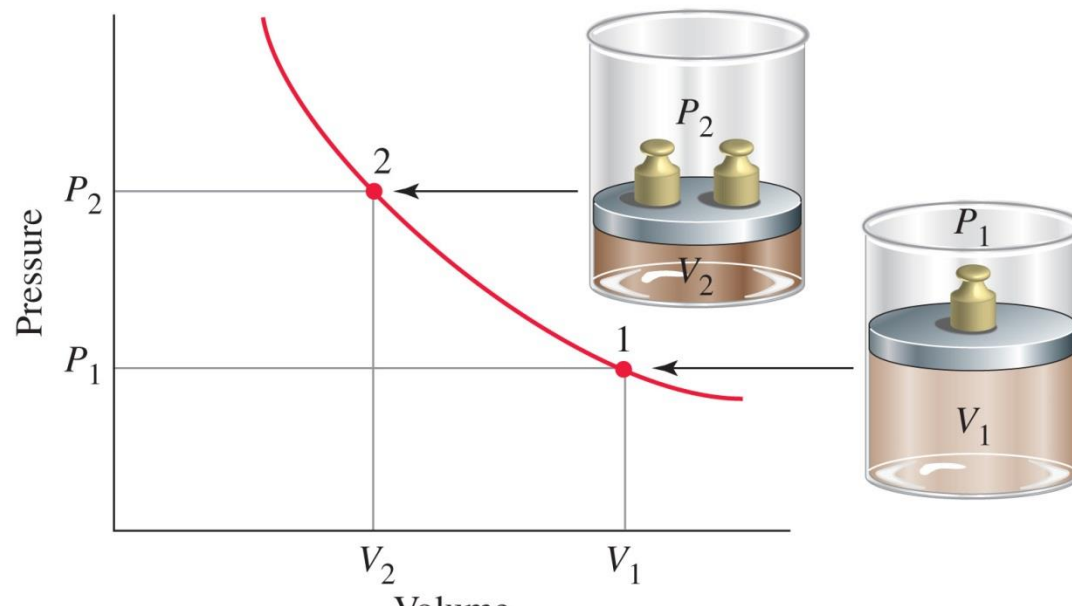
Measurement of gas pressure with an open-end manometer

The possible relationships between barometric pressure and a gas pressure under measurement are pictured here and described in Example 6 2. If P_{gas} and $P_{\text{bar.}}$ are expressed in mmHg, then ΔP is numerically equal to the height h expressed in millimeters.

6-2 Simple Gas Laws

◆ Boyle 1662 $P \propto \frac{1}{V}$ $PV = \text{constant}$

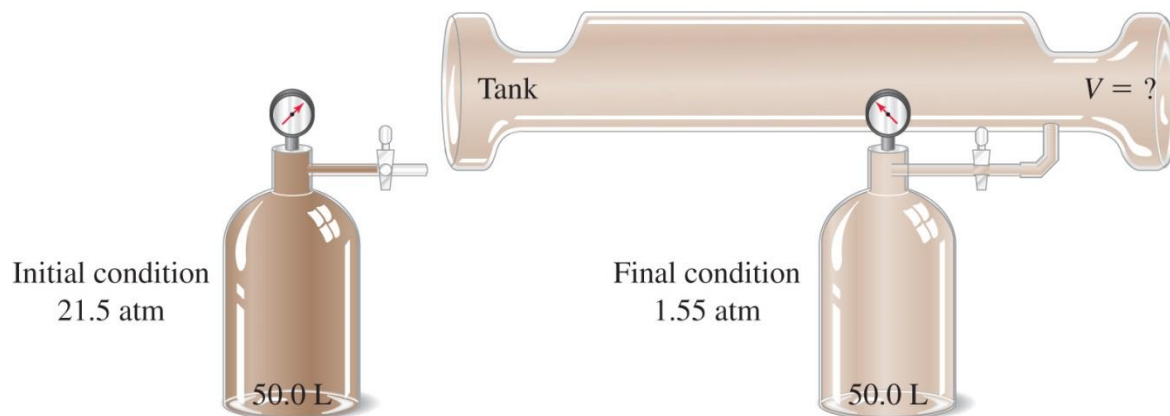
$$P_i V_i = P_f V_f \text{ (n constant, T constant)}$$



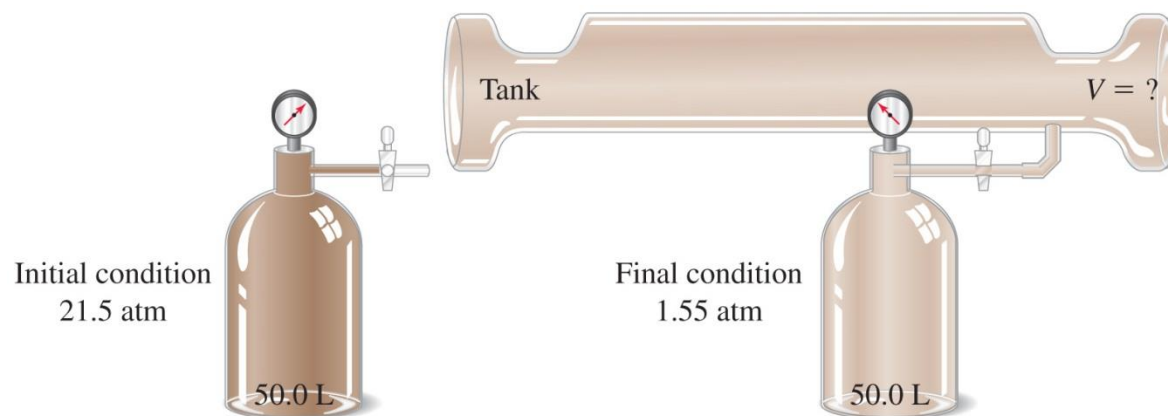
For a fixed amount of gas at a constant temperature, the gas volume is inversely proportional to the gas pressure.

EXAMPLE 6-4

Relating Gas Volume and Pressure – Boyle's Law. The volume of a large irregularly shaped, closed tank can be determined. The tank is first evacuated and then connected to a 50.0 L cylinder of compressed nitrogen gas. The gas pressure in the cylinder, originally at 21.5 atm, falls to 1.55 atm after it is connected to the evacuated tank. What is the volume of the tank?



EXAMPLE 6-4



$$P_1 V_1 = P_2 V_2 \quad V_2 = \frac{P_1 V_1}{P_2} = 694 \text{ L} \quad V_{\text{tank}} = 644 \text{ L}$$

Charles's Law

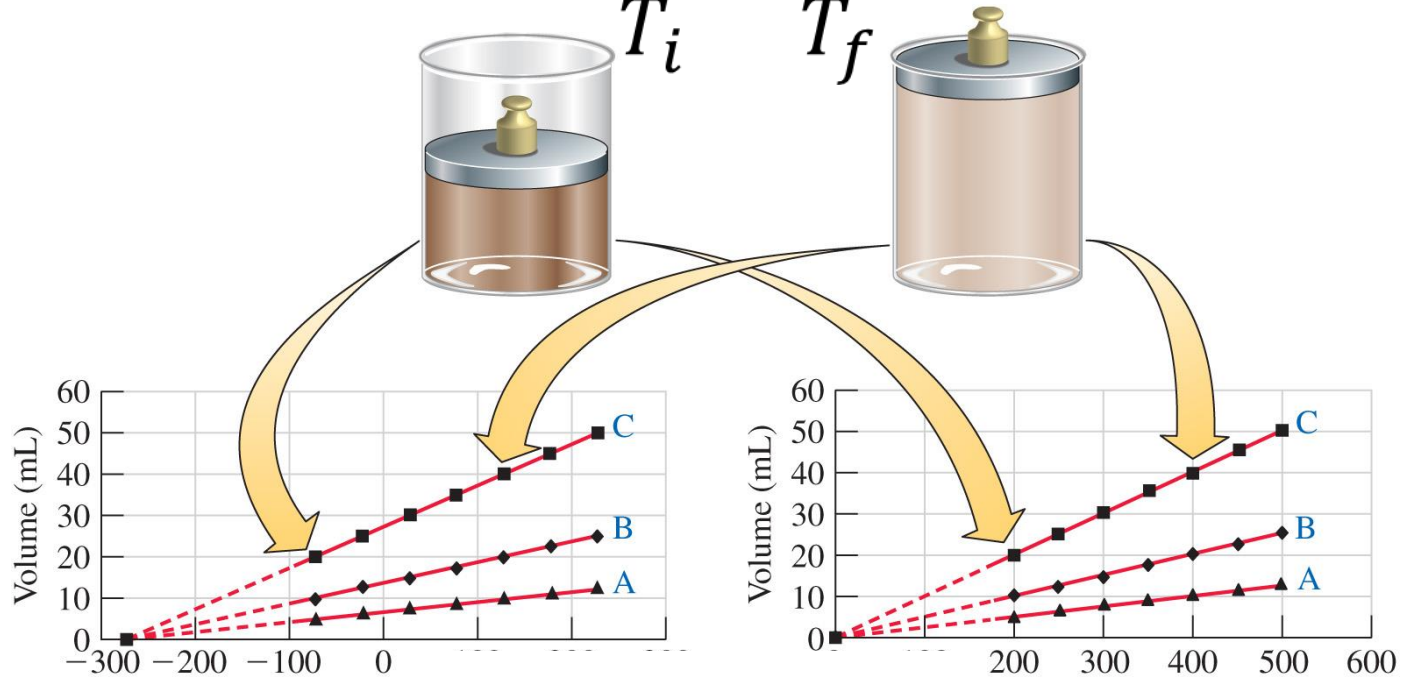
Charles 1787

$$V \propto T$$

$$V = b T$$

Gay-Lussac 1802

$$\frac{V_i}{T_i} = \frac{V_f}{T_f} \quad (n \text{ constant, } P \text{ constant})$$



The volume of a fixed amount of gas at constant pressure is directly proportional to the Kelvin (absolute) temperature.

Standard Temperature and Pressure

- ◆ Gas properties depend on conditions.
- ◆ Define standard conditions of temperature and pressure (STP).

$$P = 1 \text{ atm} = 760 \text{ mm Hg}$$

$$T = 0^{\circ}\text{C} = 273.15 \text{ K}$$

Avogadro's Law

At a fixed temperature and pressure, the volume of a gas is directly proportional to the amount of gas.

$$V \propto n \quad \text{or} \quad V = c n$$

At STP

$$1 \text{ mol gas} = 22.4 \text{ L gas}$$



6-3 Combining the Gas Laws: The Ideal Gas Equation and the General Gas Equation

◆ Boyle's law	$V \propto 1/P$	}	$V \propto \frac{nT}{P}$
◆ Charles's law	$V \propto T$		
◆ Avogadro's law	$V \propto n$		

$$PV = nRT$$

The Gas Constant

$$PV = nRT$$

$$R = \frac{PV}{nT}$$

$$= 0.082057 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 8.3145 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$$

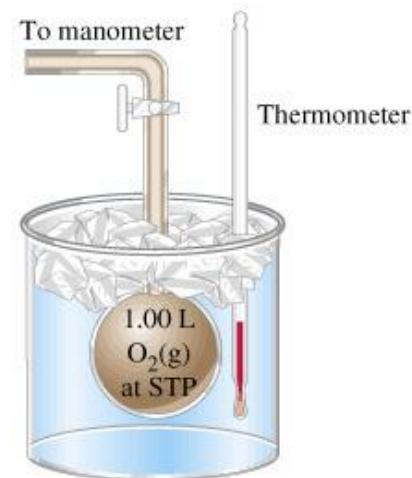
$$= 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$$

The General Gas Equation

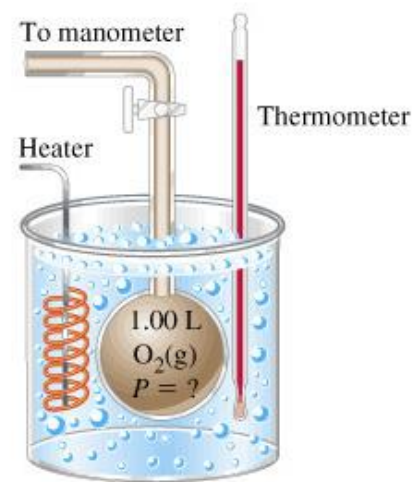
$$R = \frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

If we hold the amount and volume constant:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$



(a) Ice bath



(b) Boiling water

6-4 Applications of the Ideal Gas Equation

Molar Mass Determination

$$PV = nRT \quad \text{and} \quad n = \frac{m}{M}$$

$$PV = \frac{m}{M} RT$$

$$M = \frac{m RT}{PV}$$

EXAMPLE 6-10

Determining a Molar Mass with the Ideal Gas Equation.

Polypropylene is an important commercial chemical. It is used in the synthesis of other organic chemicals and in plastics production. A glass vessel weighs 40.1305 g when clean, dry and evacuated; it weighs 138.2410 when filled with water at 25°C ($\delta_{\text{water}} = 0.9970 \text{ g cm}^{-3}$) and 40.2959 g when filled with propylene gas at 740.3 mm Hg and 24.0°C. What is the molar mass of polypropylene?

Strategy:

Determine V_{flask} . Determine m_{gas} . Use the Gas Equation.

EXAMPLE 6-10

Determine V_{flask} :

$$\begin{aligned} V_{\text{flask}} &= m_{\text{H}_2\text{O}} \div d_{\text{H}_2\text{O}} = (138.2410 \text{ g} - 40.1305 \text{ g}) \div (0.9970 \text{ g cm}^{-3}) \\ &= 98.41 \text{ cm}^3 = 0.09841 \text{ L} \end{aligned}$$

Determine m_{gas} :

$$\begin{aligned} m_{\text{gas}} &= m_{\text{filled}} - m_{\text{empty}} = (40.2959 \text{ g} - 40.1305 \text{ g}) \\ &= 0.1654 \text{ g} \end{aligned}$$

EXAMPLE 5-6

Use the Gas Equation:

$$PV = nRT \quad PV = \frac{m}{M} RT \quad M = \frac{m RT}{PV}$$

$$M = \frac{(0.6145 \text{ g})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(297.2 \text{ K})}{(0.9741 \text{ atm})(0.09841 \text{ L})}$$

$$M = 42.08 \text{ g/mol}$$

Gas Densities

$$PV = nRT \quad \text{and} \quad d = \frac{m}{V}, \quad n = \frac{m}{M}$$

$$P\textcolor{red}{V} = \frac{\textcolor{red}{m}}{M} RT$$

$$\frac{\textcolor{red}{m}}{\textcolor{red}{V}} = d = \frac{MP}{RT}$$

6-5 Gases in Chemical Reactions

- ◆ Stoichiometric factors relate gas quantities to quantities of other reactants or products.
- ◆ Ideal gas equation relates the amount of a gas to volume, temperature and pressure.
- ◆ *Law of combining volumes* can be developed using the gas law.

EXAMPLE 6-12

Using the Ideal gas Equation in Reaction Stoichiometry Calculations. The decomposition of sodium azide, NaN_3 , at high temperatures produces $\text{N}_2(\text{g})$. Together with the necessary devices to initiate the reaction and trap the sodium metal formed, this reaction is used in **air-bag safety systems**. What volume of $\text{N}_2(\text{g})$, measured at 735 mm Hg and 26°C , is produced when 70.0 g NaN_3 is decomposed? $\text{NaN}_3 = 65.01 \text{ g/mol}$



EXAMPLE 6-12

Determine moles of N_2 :

$$n_{N_2} = 70 \text{ g } \cancel{\text{NaN}_3} \times \frac{1 \cancel{\text{ mol NaN}_3}}{65.01 \text{ g } \cancel{\text{NaN}_3}} \times \frac{3 \text{ mol } N_2}{2 \cancel{\text{ mol NaN}_3}} = 1.62 \text{ mol } N_2$$

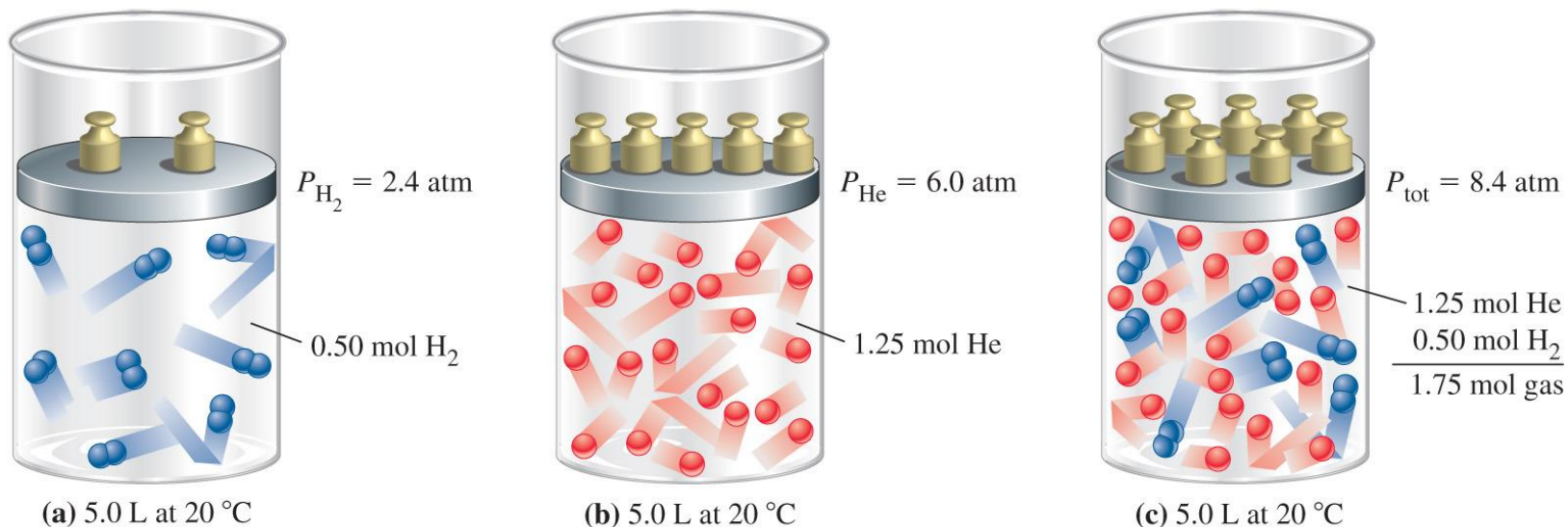
Determine volume of N_2 :

$$V = \frac{nRT}{P} = \frac{(1.62 \cancel{\text{ mol}})(0.08206 \text{ L } \cancel{\text{ atm mol}^{-1} \text{ K}^{-1}})(299 \cancel{\text{ K}})}{\left\{ (735 \cancel{\text{ mm Hg}}) \times \frac{1.00 \cancel{\text{ atm}}}{760 \cancel{\text{ mm Hg}}} \right\}} = 41.1 \text{ L}$$

6-6 Mixtures of Gases

- ◆ Gas laws apply to *mixtures* of gases.
- ◆ Simplest approach is to use n_{total} , but....
- ◆ Partial pressure
 - Each component of a gas mixture exerts a pressure that it would exert if it were in the container alone.

Dalton's Law of Partial Pressure



The total pressure of a mixture of gases is the sum of the partial pressures of the components of the mixture.

Partial Pressure

$$P_{\text{tot}} = P_a + P_b + \dots$$

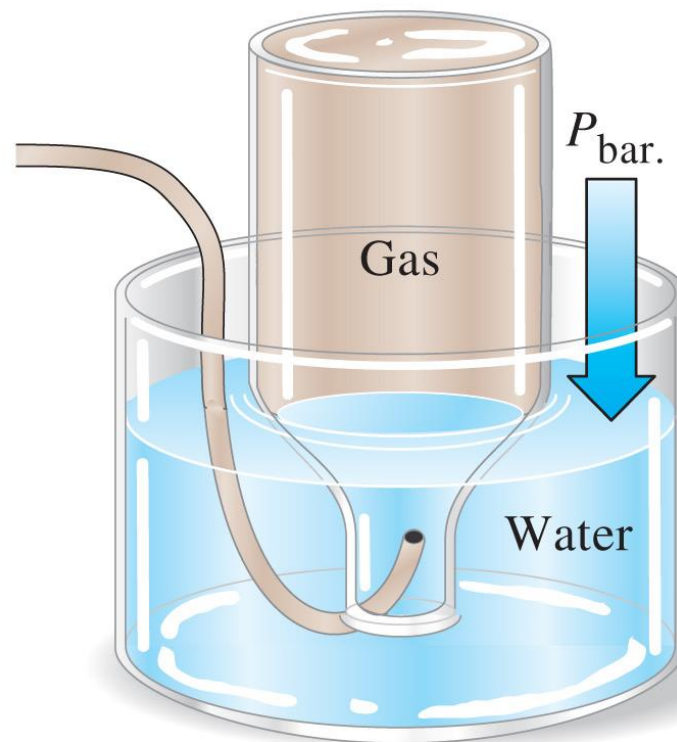
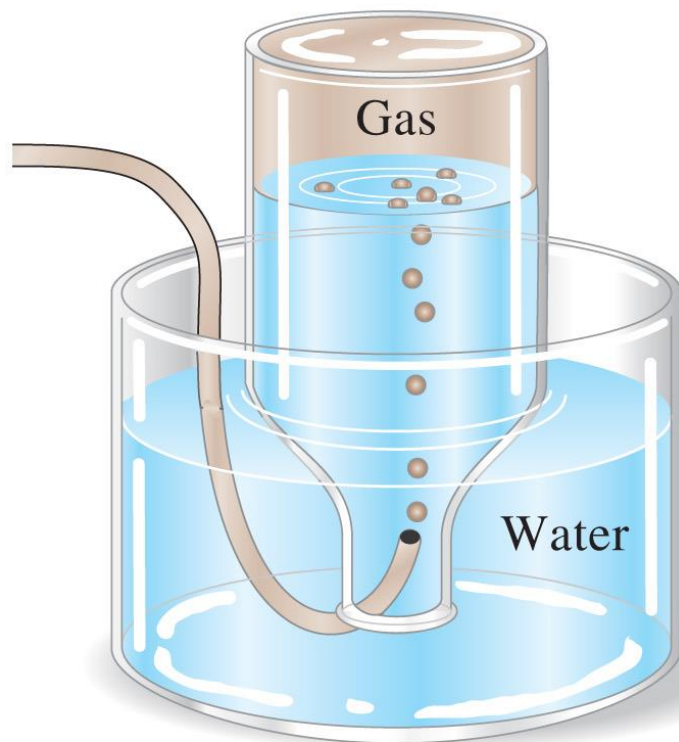
$$V_a = n_a RT / P_{\text{tot}} \quad \text{and} \quad V_{\text{tot}} = V_a + V_b + \dots$$

$$\frac{V_a}{V_{\text{tot}}} = \frac{n_a RT / P_{\text{tot}}}{n_{\text{tot}} RT / P_{\text{tot}}} = \frac{n_a}{n_{\text{tot}}}$$

$$\text{Recall} \quad \frac{n_a}{n_{\text{tot}}} = \chi_a$$

$$\frac{P_a}{P_{\text{tot}}} = \frac{n_a RT / V_{\text{tot}}}{n_{\text{tot}} RT / V_{\text{tot}}} = \frac{n_a}{n_{\text{tot}}}$$

Pneumatic Trough



$$P_{\text{tot}} = P_{\text{bar}} = P_{\text{gas}} + P_{\text{H}_2\text{O}}$$

6-7 Kinetic Molecular Theory

- ◆ A gas is composed of a very large number of extremely small particles (molecules or, in some cases, atoms) in constant, random, straight-line motion.
- ◆ Particles are separated by great distances.
- ◆ Molecules collide only fleetingly with one another and with the walls of their container, and most of the time molecules are not colliding.
- ◆ There are assumed to be no forces between molecules except very briefly during collisions. That is, each molecule acts independently of all the others and is unaffected by their presence, except during collisions.
- ◆ Individual molecules may gain or lose energy as a result of collisions. In a collection of molecules at constant temperature, however, *the total energy remains constant*



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FIGURE 6-14

Visualizing molecular motion

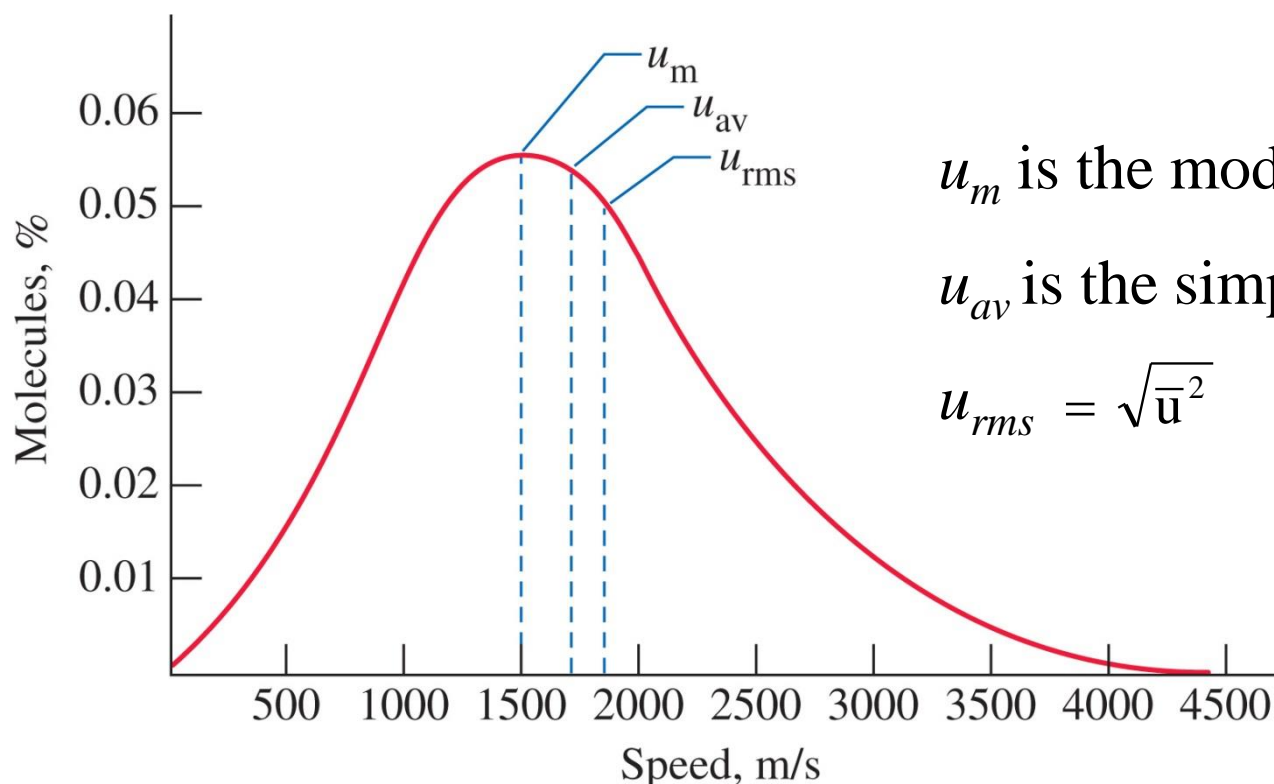
Molecules of a gas are in constant motion and collide with one another and with the container wall.

Pressure – Assessing Collision Forces

- ◆ Translational kinetic energy, $e_k = \frac{1}{2} mu^2$
- ◆ Frequency of collisions, $\nu = u \frac{N}{V}$
- ◆ Impulse or momentum transfer, $I = mu$
- ◆ Pressure proportional to impulse times frequency $P \propto \frac{N}{V} mu^2$

Pressure and Molecular Speed

- ◆ Three dimensional systems lead to: $P = \frac{1}{3} \frac{N}{V} m \bar{u}^2$



u_m is the modal speed

u_{av} is the simple average

$$u_{rms} = \sqrt{\bar{u}^2}$$

Pressure

Assume one mole:

$$PV = \frac{1}{3} N_A m \bar{u}^2$$

$PV=RT$ so:

$$3RT = N_A m \bar{u}^2$$

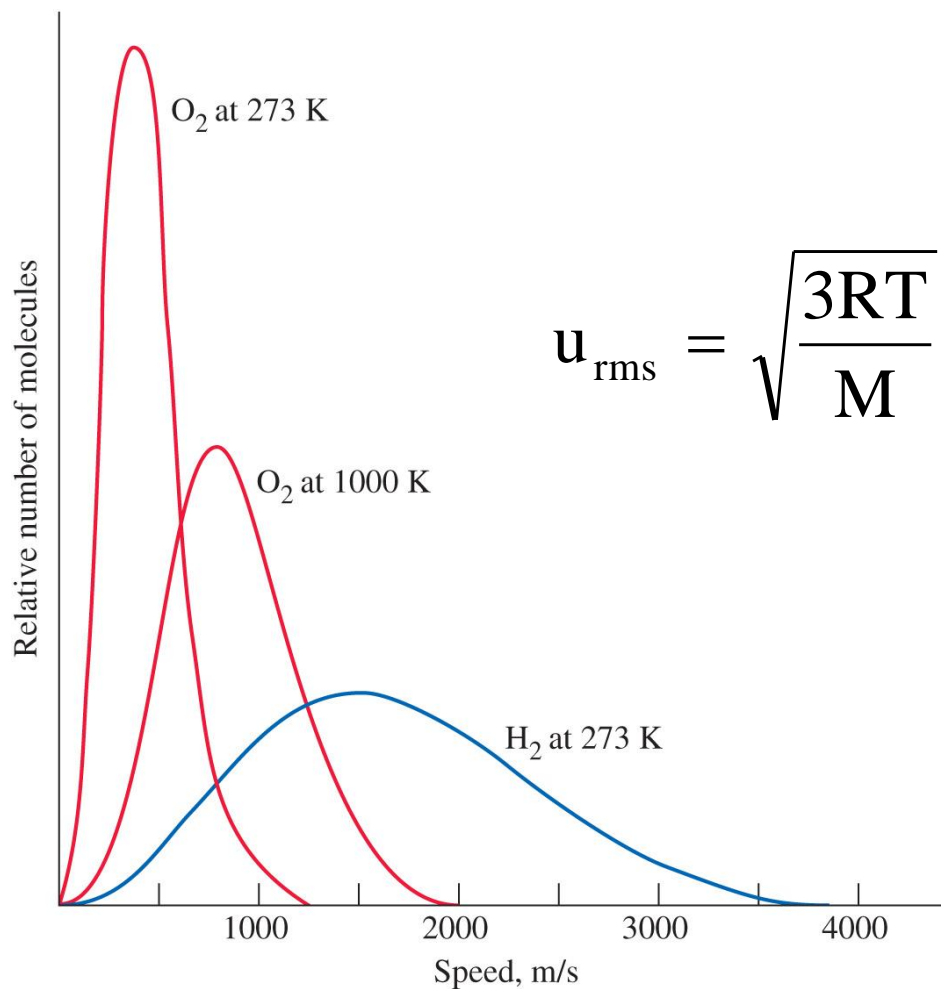
$N_A m = M$:

$$3RT = M \bar{u}^2$$

Rearrange:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Distribution of Molecular Speeds



Temperature

Modify: $PV = \frac{1}{3} N_A m \bar{u}^2 = \frac{2}{3} N_A \left(\frac{1}{2} m \bar{u}^2 \right)$

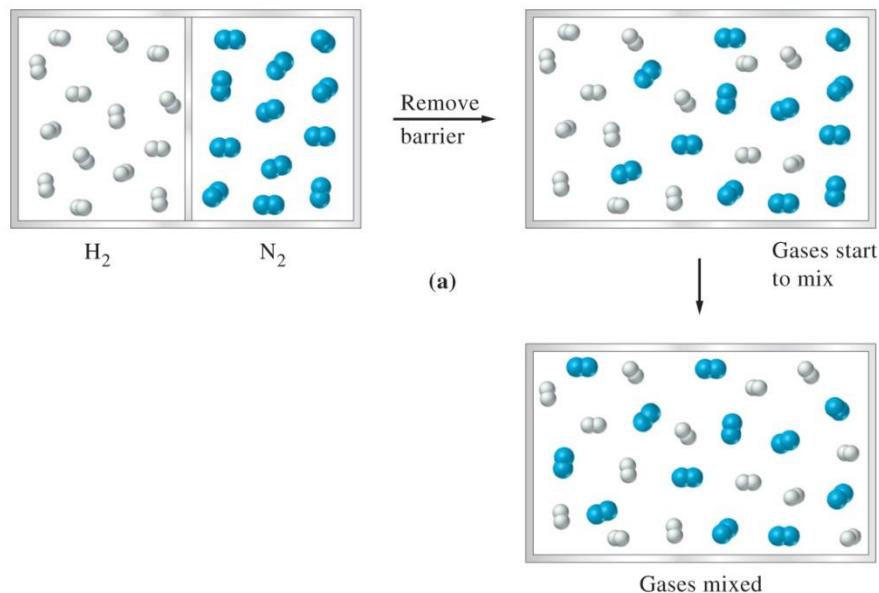
PV=RT so: $RT = \frac{2}{3} N_A \bar{e}_k$

Solve for \bar{e}_k : $\bar{e}_k = \frac{3}{2} \frac{R}{N_A} (T)$

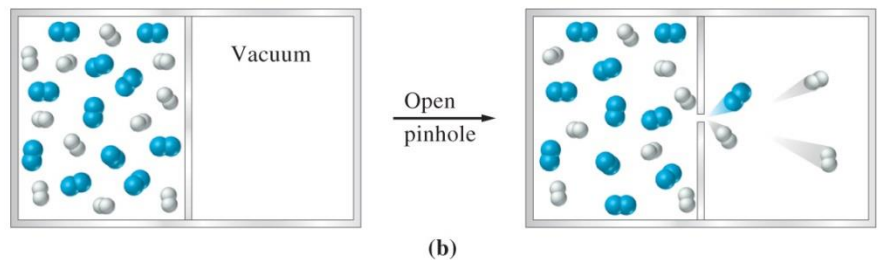
Average kinetic energy is directly proportional to temperature!

6-8 Gas Properties Relating to the Kinetic-Molecular Theory

- ◆ **Diffusion** is the migration of molecules as a result of random molecular motion.



- ◆ **Effusion** is the escape of gas molecules from their container through a tiny pinhole.



Graham's Law

$$\frac{\text{rate of effusion of } A}{\text{rate of effusion of } B} = \frac{(u_{\text{rms}})_A}{(u_{\text{rms}})_B} = \sqrt{\frac{3RT/M_A}{3RT/M_B}} = \sqrt{\frac{M_B}{M_A}}$$

The rate of effusion of a gas is inversely proportional to the square root of its molar mass.

- ◆ Only for gases at **low** pressure (natural escape, not a jet).
- ◆ Tiny orifice (no collisions)
- ◆ Does not apply to diffusion.

- ◆ Ratio used can be:
 - Rate of effusion (as above)
 - Molecular speeds
 - Effusion times
 - Distances traveled by molecules
 - Amounts of gas effused.

6-9 Nonideal (Real) Gases

The behavior of real gases can be explained as follows. According to Boyle's law, at very high pressures the gas volume is very small and approaches zero. However, in real gases, the molecules themselves have a volume, and this volume cannot be suppressed. In addition, real gases have intermolecular forces of attraction. It shows that the force of collision of gas molecules with the walls of the container due to intermolecular attraction forces is less than expected from ideal gas.

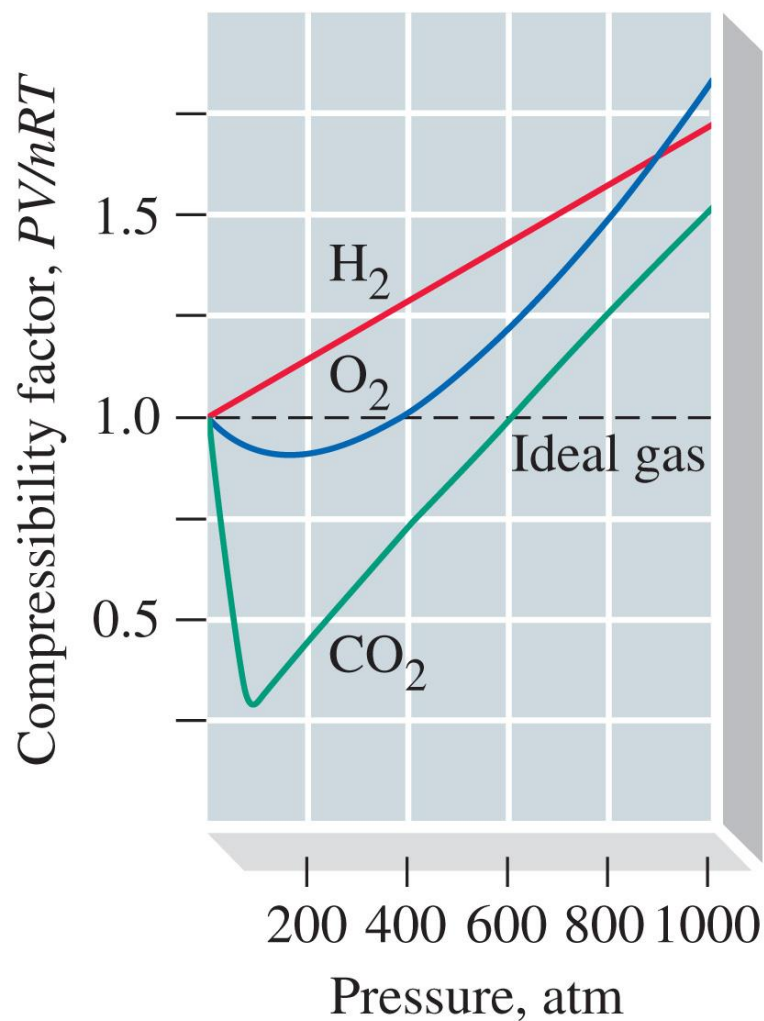
- Gases tend to behave *ideally at high temperatures and low pressures.*
- Gases tend to behave *nonideally at low temperatures and high pressures.*

TABLE 6.5 van der Waals Constants and Compressibility Factors (at 10 bar and 300 K) for Various Gases

Gas	van der Waals Constants		Compressibility Factor
	$a, \text{bar L}^2 \text{mol}^{-2}$	$b, \text{L mol}^{-1}$	
H ₂	0.2452	0.0265	1.006
He	0.0346	0.0238	1.005
Ideal gas	0	0	1
N ₂	1.370	0.0387	0.998
CO	1.472	0.0395	0.997
O ₂	1.382	0.0319	0.994
CH ₄	2.303	0.0431	0.983
NF ₃	3.58	0.0545	0.965
CO ₂	3.658	0.0429	0.950
N ₂ O	3.852	0.0444	0.945
C ₂ H ₆	5.580	0.0651	0.922
NH ₃	4.225	0.0371	0.887
SF ₆	5.580	0.0651	0.880
C ₃ H ₈	9.39	0.0905	a
SO ₂	7.857	0.0879	a

- ◆ Compressibility factor $PV/nRT = 1$
- ◆ Deviations occur for real gases.
 - $PV/nRT > 1$ - molecular volume is significant.
 - $PV/nRT < 1$ – intermolecular forces of attraction.

Real Gases



van der Waals Equation

A number of equations can be used for real gases. They carry correction terms that depend on the volumes of the molecules and the intermolecular forces. The van der Waals equation is one of them:

$$PV = nRT \longrightarrow \left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

Correction for
molecular attraction

Correction for
volume of molecules

V=the volume of n moles of gas,

n^2a/V^2 = relates to the intermolecular force of attraction,

The values of a and b vary from gas to gas. It depends more or less on temperature and pressure.