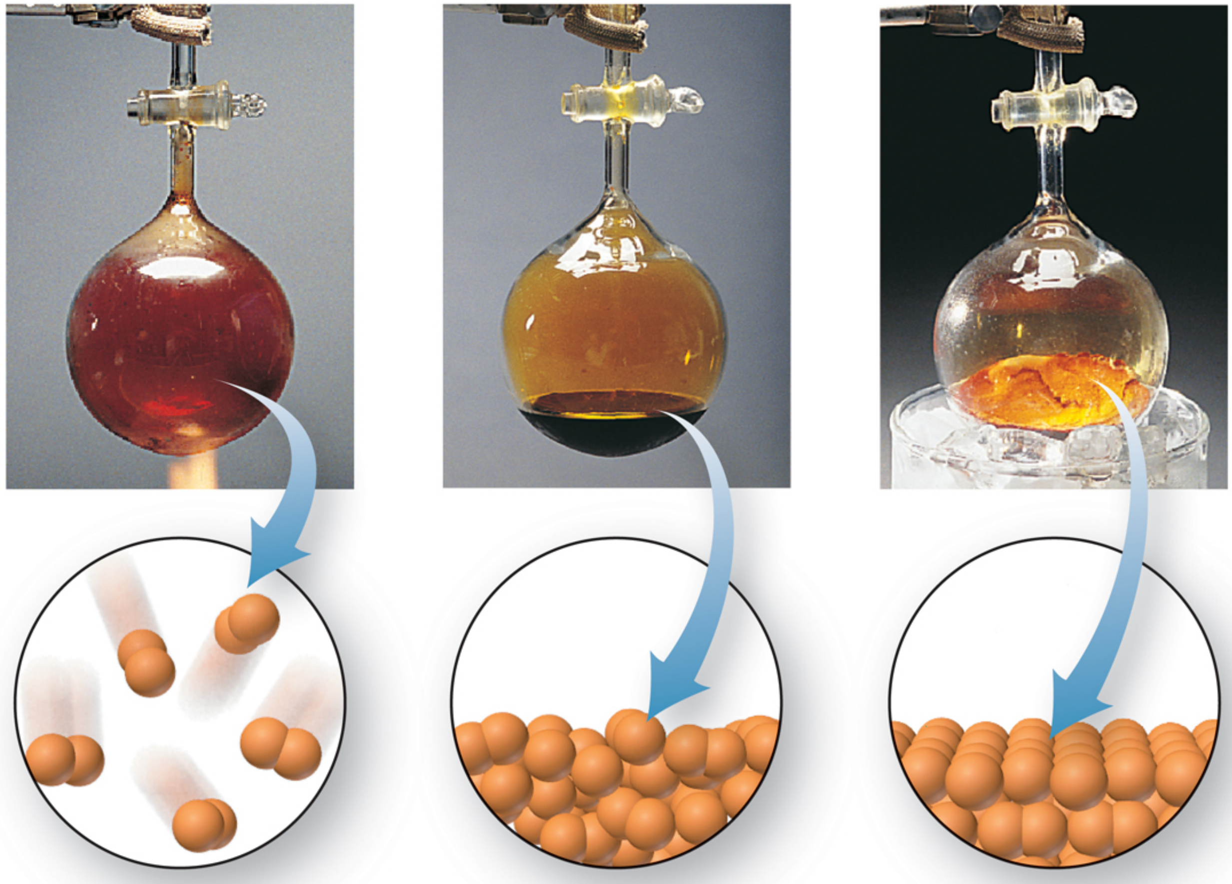
4.1

An Overview of the Physical States of Matter

Distinguishing gases from liquids and solids.

- Gas volume changes significantly with pressure.
  - Solid and liquid volumes are not greatly affected by pressure.
- Gas volume changes significantly with temperature.
  - Gases expand when heated and shrink when cooled.
  - The volume change is 50 to 100 times greater for gases than for liquids and solids.
- Gases flow very freely.
- Gases have relatively low densities.
- Gases form a solution in any proportions.
  - Gases are freely miscible with each other.

Figure 4.1 The three states of matter.



Gas: *Particles are far apart, move freely, and fill the available space.*

Liquid: *Particles are close together but move around one another.*

Solid: *Particles are close together in a regular array and do not move around one another.*

4.2 Gas Pressure and its Measurement

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

Atmospheric pressure arises from the force exerted by atmospheric gases on the earth's surface.

Atmospheric pressure decreases with altitude.

Figure 4.2 Effect of atmospheric pressure on a familiar object.

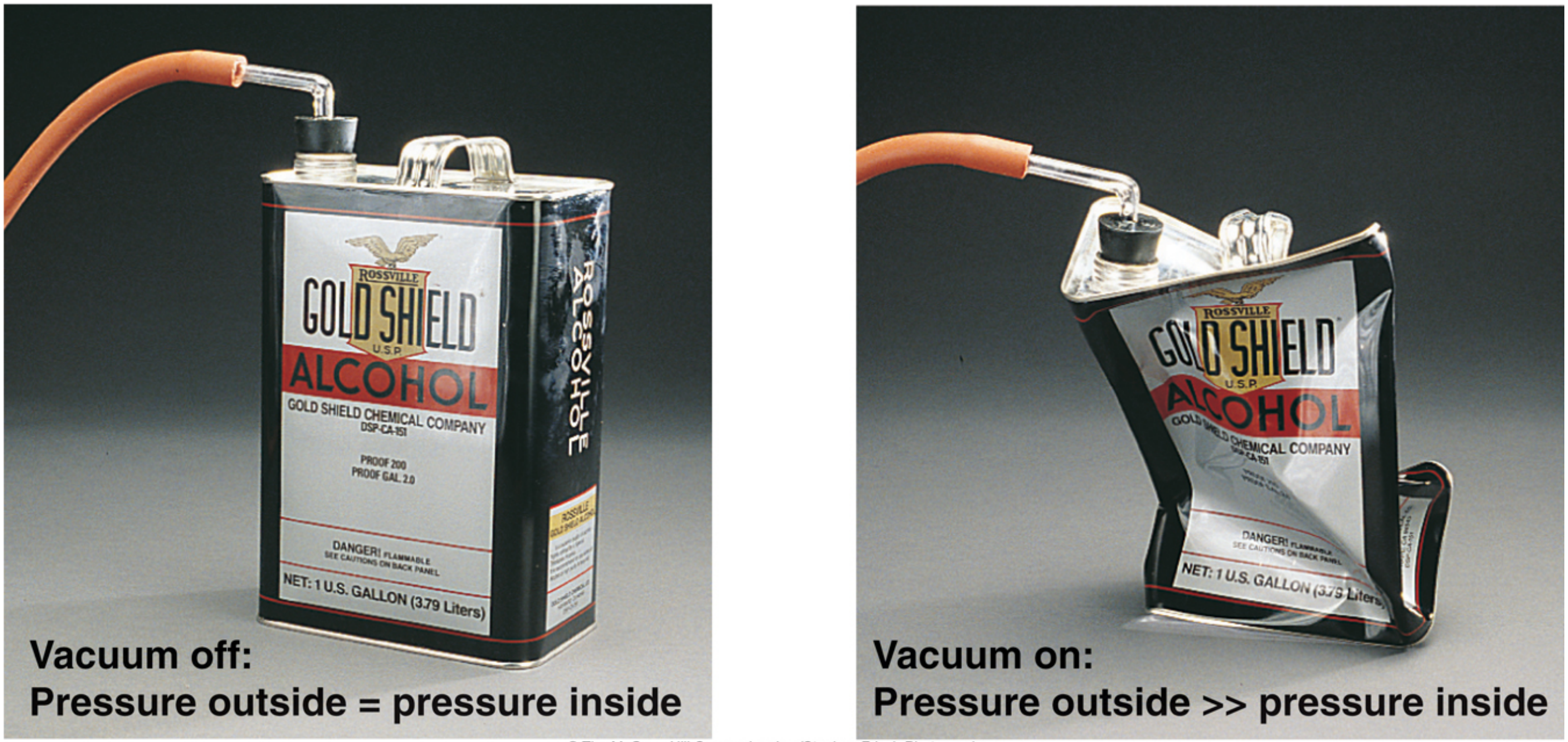


Figure 4.3 A mercury barometer.

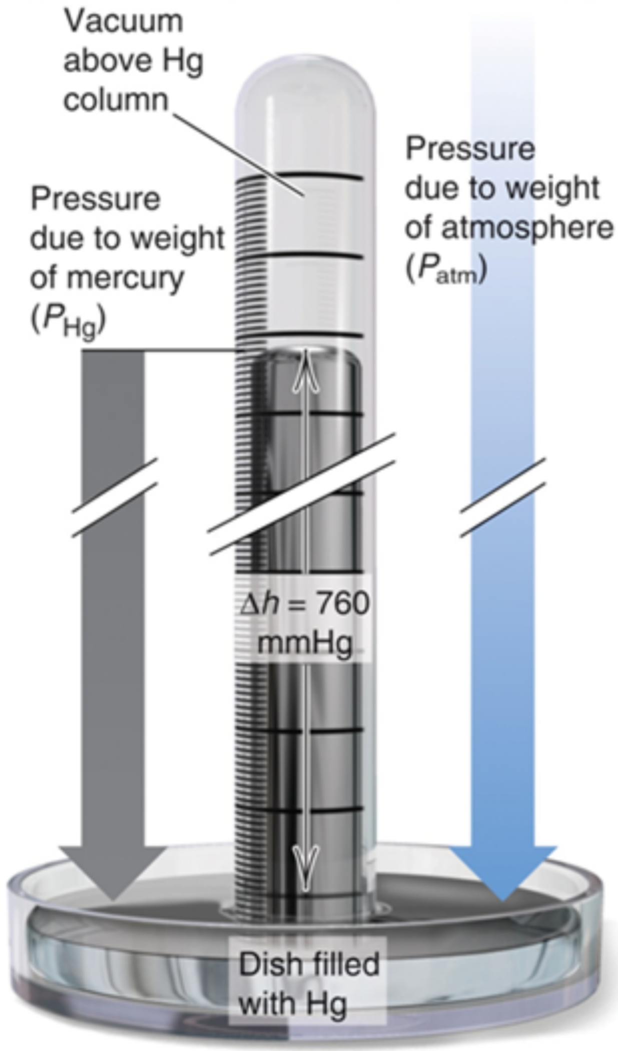
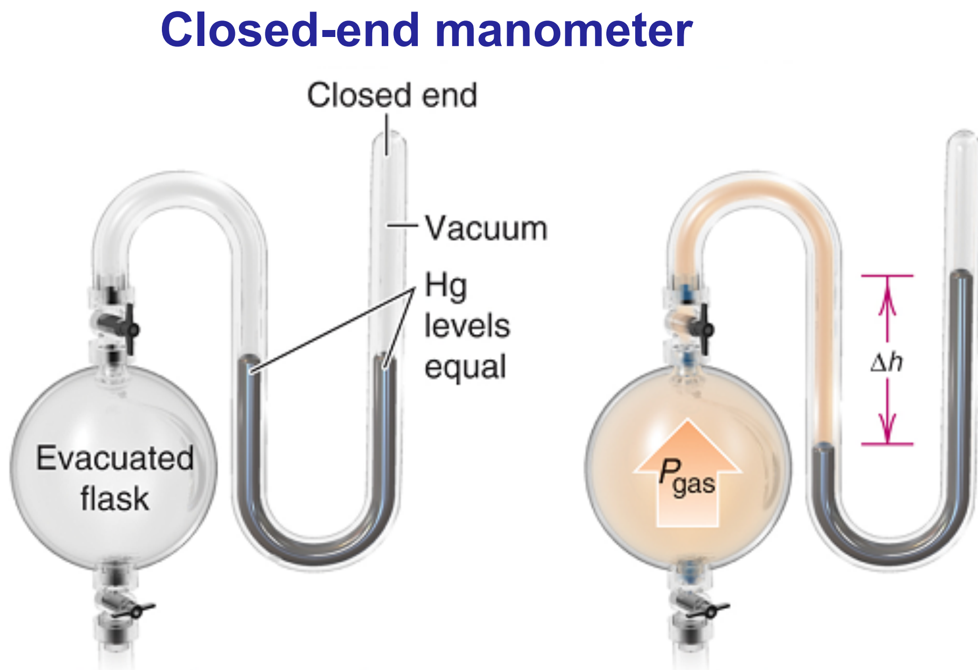


Figure 4.4 Two types of Manometers



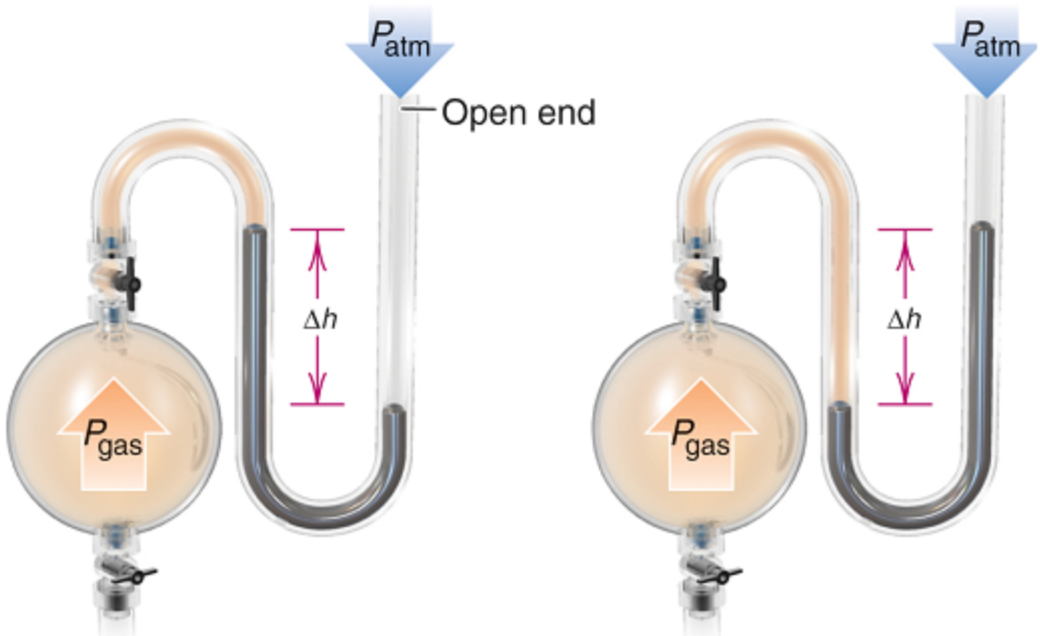
The Hg levels are equal because both arms of the U tube are evacuated.

A gas in the flask pushes the Hg level down in the left arm.

The difference in levels, Δh, equals the gas pressure, P_{gas}.

Figure 4.4

Open-end manometer



When P_{gas} is less than P_{atm}, subtract Δh from P_{atm}.

$P_{gas} < P_{atm}$

$P_{gas} = P_{atm} - \Delta h$

When P_{gas} is greater than P_{atm}, add Δh to P_{atm}.

$P_{gas} > P_{atm}$

$P_{gas} = P_{atm} + \Delta h$

Table 4.1 Common Units of Pressure

Unit	Normal Atmospheric Pressure at Sea Level and 0°C
pascal (Pa); kilopascal (kPa)	$1.013\ 25 \times 10^5$ Pa; 101.325 kPa
atmosphere (atm)	1 atm*
millimetres of mercury (mmHg)	760 mmHg*
torr (Torr)	760 Torr*
bar	1.013 25 bar

*This is an exact quantity.

Sample Problem 4.1 **Converting Units of Pressure**

PROBLEM: A geochemist heats a limestone ($CaCO_3$) sample and collects the CO_2 released in an evacuated flask attached to a closed-end manometer. After the system comes to room temperature, Δh = 291.4 mm Hg. Calculate the CO_2 pressure in units of bars and kilopascals.

PLAN: Construct conversion factors to find the other units of pressure.

SOLUTION:

Converting P_{CO_2} from mm Hg to bar,

$$291.4\ \cancel{\text{mmHg}} \times \frac{1.01325\ \text{bar}}{760\ \cancel{\text{mmHg}}} \quad \boxed{= \mathbf{0.3885\ bar}}$$

Converting from bar to kPa,

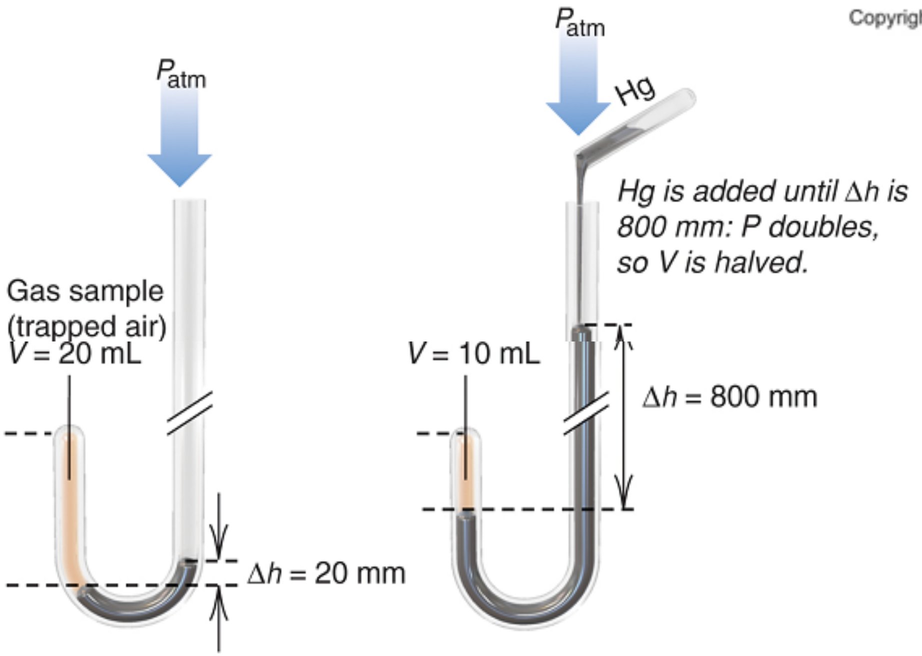
$$0.3885\ \cancel{\text{bar}} \times \frac{100\ \text{kPa}}{1\ \cancel{\text{bar}}} \quad \boxed{= \mathbf{38.85\ kPa}}$$

4.3

The Gas Laws

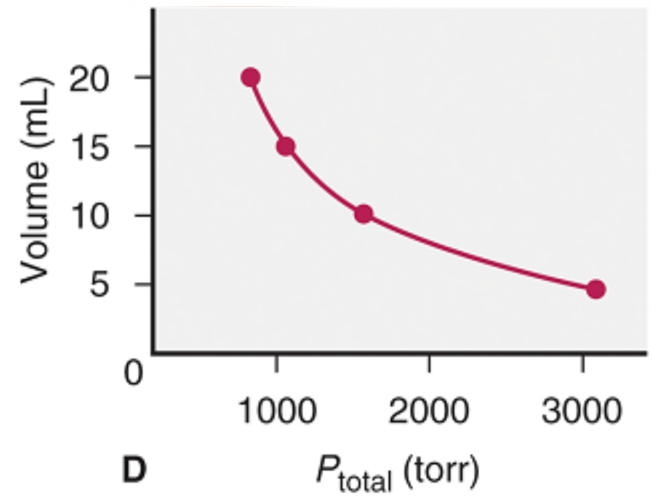
- The gas laws describe the physical behavior of gases in terms of 4 variables:
  - pressure (*P*)
  - temperature (*T*)
  - volume (*V*)
  - amount (number of moles, *n*)
- An ***ideal gas*** is a gas that exhibits linear relationships among these variables.
- ***No ideal gas actually exists***, but most simple gases behave nearly ideally at ordinary temperatures and pressures.

Figure 4.5 Boyle's law, the relationship between the volume and pressure of a gas.



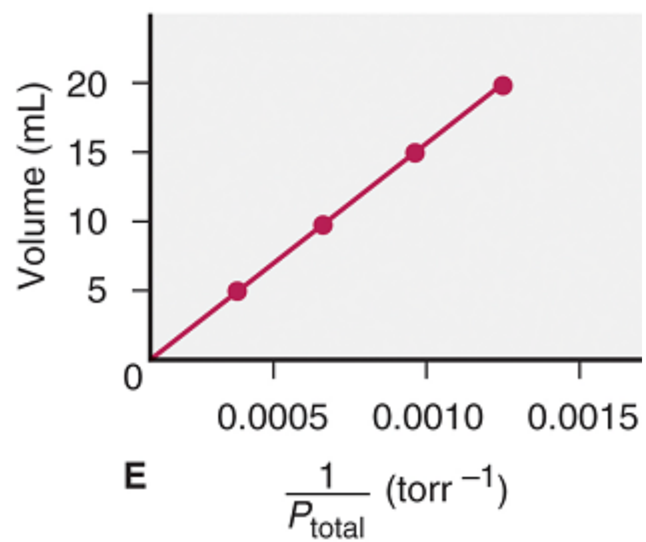
A $P_{total} = P_{atm} + \Delta h$
= 760 torr + 20 torr
= 780 torr

B $P_{total} = P_{atm} + \Delta h$
= 760 torr + 800 torr
= 1560 torr



C

V (mL)	P (torr) Δh +	P_{atm} =	P_{total}	$\frac{1}{P_{total}}$	PV (torr•mL)
20.0	20.0	760	780	0.00128	1.56×10^4
15.0	278	760	1038	0.000963	1.56×10^4
10.0	800	760	1560	0.000641	1.56×10^4
5.0	2352	760	3112	0.000321	1.56×10^4



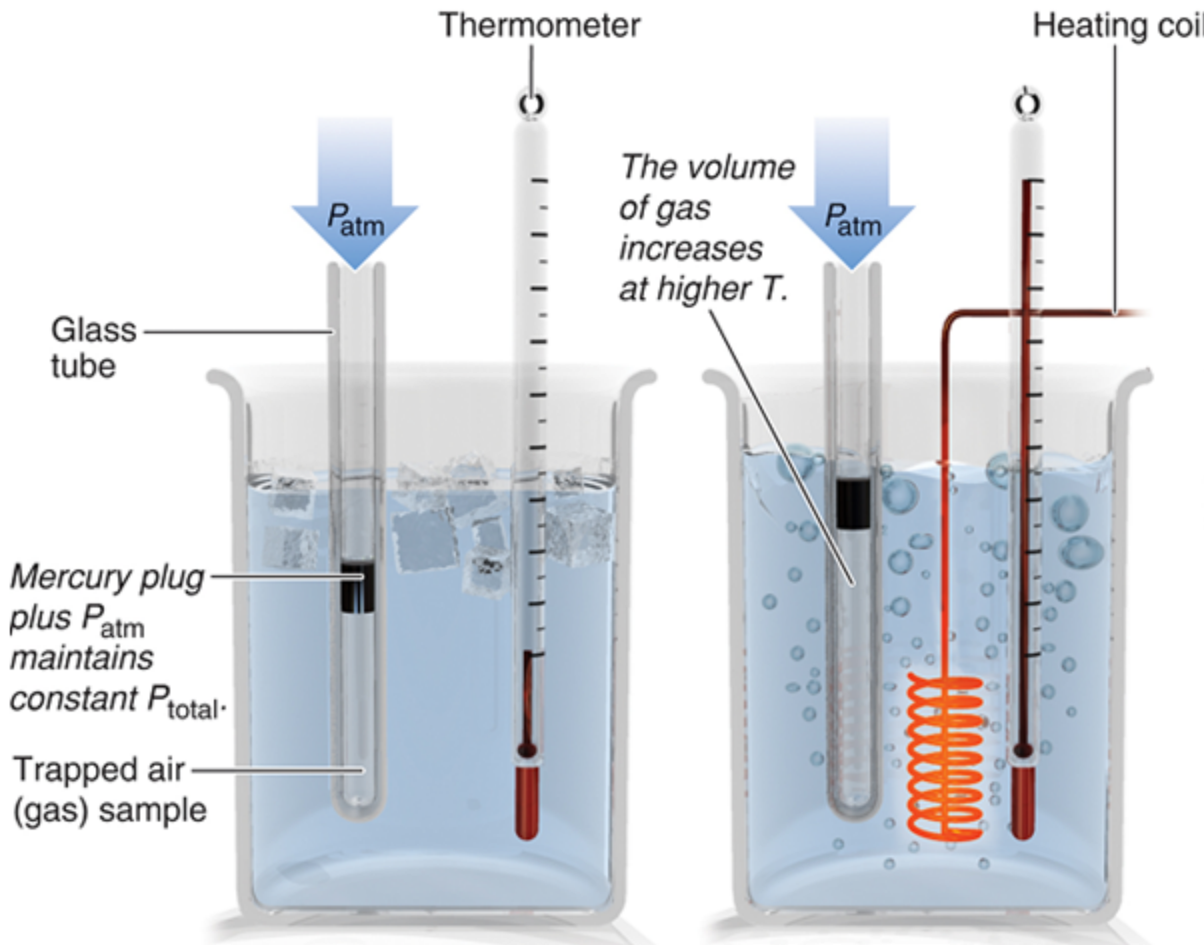
Boyle's Law

At constant temperature, the volume occupied by a fixed amount of gas is ***inversely*** proportional to the external pressure.

$$V \propto \frac{1}{P} \qquad \text{or } PV = \text{constant}$$

At fixed *T* and *n*,
***P* decreases as *V* increases**
***P* increases as *V* decreases**

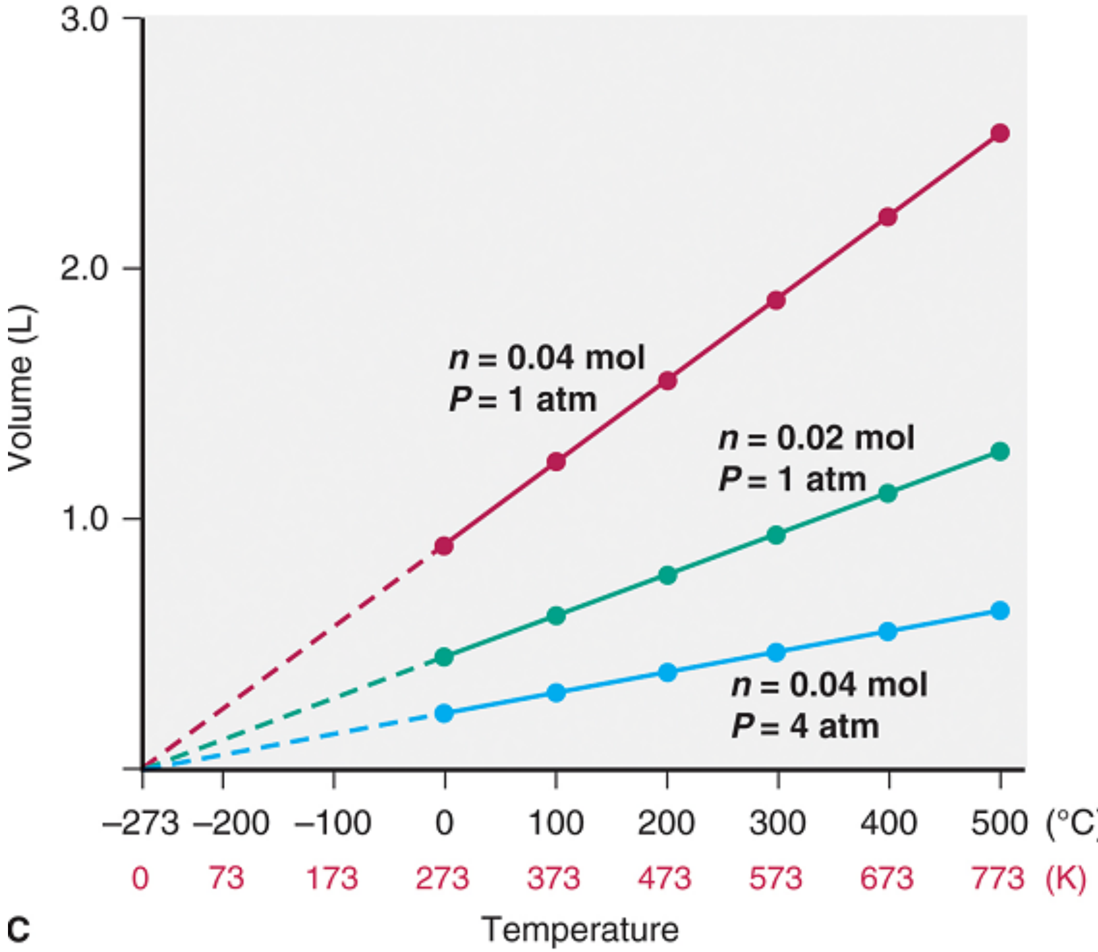
Figure 4.6(A,B) Charles's law, the relationship between the volume and temperature of a gas.



A Ice water bath (0°C, or 273 K)

B Boiling water bath (100°C, or 373 K)

Figure 4.6 C **Charles's law, the relationship between the volume and temperature of a gas.**



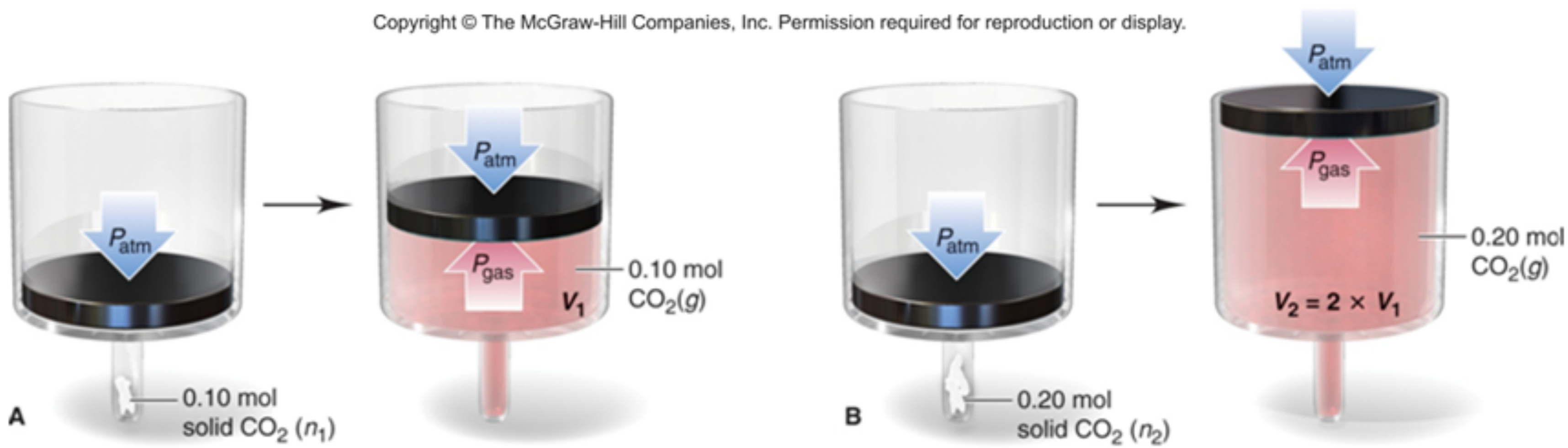
Avogadro's Law

At fixed temperature and pressure, the volume occupied by a gas is directly proportional to the amount of gas. $V \propto n$

$$\frac{V}{n} = \text{constant}$$

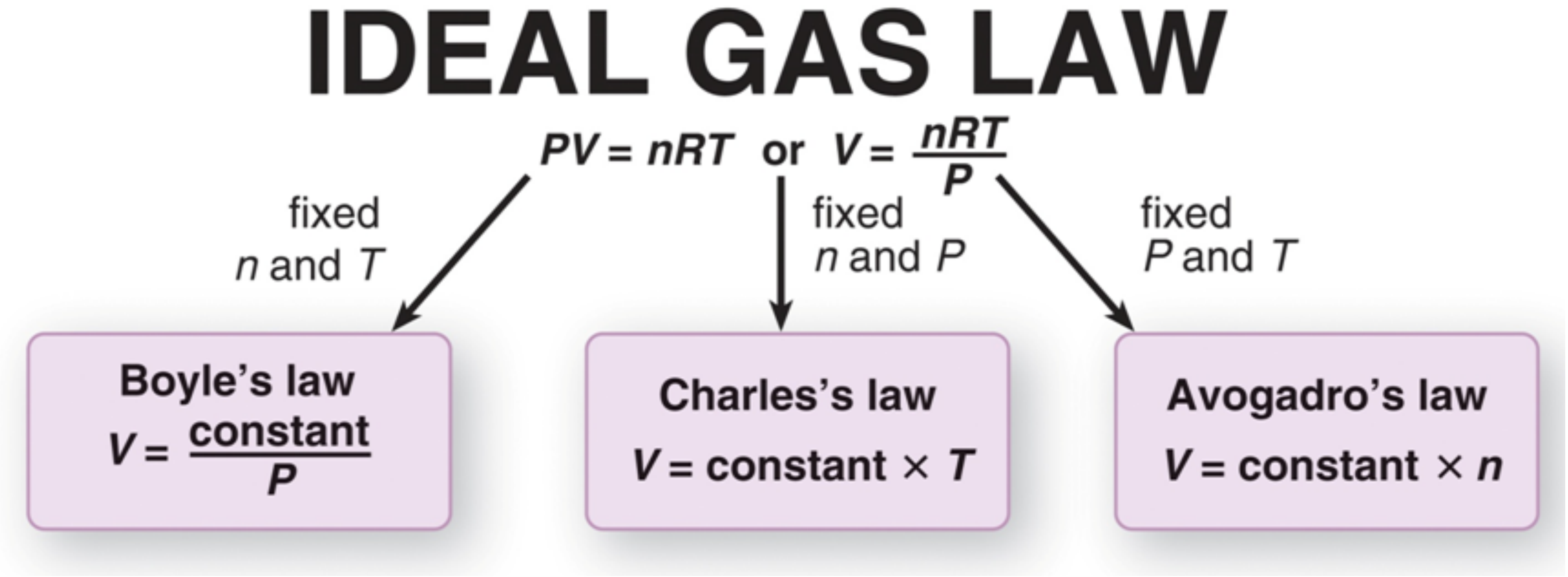
n **increases,** ***V*** **increases** **at fixed** ***P*** **and** ***T***

Figure 4.7 **The relationship between the volume and amount of a gas.**



Avogadro's Law: at fixed temperature and pressure, equal volumes of ***any*** ideal gas contain equal numbers of particles (or moles).

Figure 4.11 The individual gas laws as special cases of the ideal gas law.



Sample Problem 4.2 Applying the Volume-Pressure Relationship

PROBLEM: Boyle's apprentice finds that the air trapped in a J tube occupies 24.8 cm^3 at 1.13 bar. By adding mercury to the tube, he increases the pressure on the trapped air to 2.67 bar. Assuming constant temperature, what is the new volume of air (in litres)?

PLAN: The temperature and amount of gas are fixed, so this problem involves a change in pressure and volume only.

V_1 (cm^3)

↓ **(1 cm^3=1mL,1000mL=1L)**

V_1 (L)

↓ **multiply by P_1/P_2**

V_2 (L)

Sample Problem 4.2

SOLUTION:

$p_1 = 1.13$ bar $p_2 = 2.67$ bar

$V_1 = 24.8$ cm^3 (to L) V_2 = unknown

n and *T* are constant

$$24.8\ \cancel{\text{cm}^3} \times \frac{1\ \cancel{\text{mL}}}{1\ \cancel{\text{cm}^3}} \times \frac{\text{L}}{10^3\ \cancel{\text{mL}}} = 0.0248\ \text{L}$$

$$\frac{p_1V_1}{\cancel{n_1}\cancel{T_1}} = \frac{p_2V_2}{\cancel{n_2}\cancel{T_2}}$$

$$p_1V_1 = p_2V_2$$

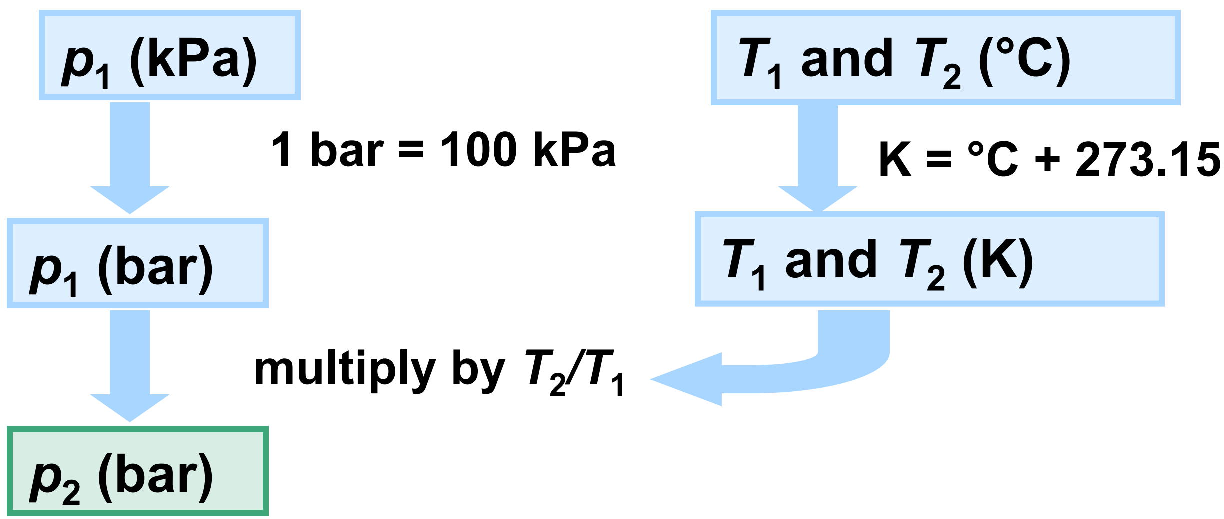
$$V_2 = V_1 \times \frac{p_1}{p_2} = 0.0248\ \text{L} \times \frac{1.13\ \cancel{\text{bar}}}{2.67\ \cancel{\text{bar}}}\ \boxed{= 0.0105\ \text{L}}$$

Sample Problem 4.3

Applying the Pressure-Temperature Relationship

PROBLEM: A steel tank used for fuel delivery is fitted with a safety valve that opens when the internal pressure exceeds 1.33 bar. It is filled with methane at 23°C and 100 kPa and placed in boiling water at exactly 100.°C. Will the safety valve open?

PLAN: We must determine if the pressure will exceed 1.33 bar at the new temperature. Since the gas is in a steel tank, the volume remains constant.



Sample Problem 4.3

SOLUTION:

$p_1 = 100 \text{ kPa}$ $\quad$ $p_2 = \text{unknown}$

$T_1 = 23°\text{C}$ $\quad$ $T_2 = 100.°\text{C}$

n and V are constant

$$100 \cancel{\text{kPa}} \times \frac{1 \text{ bar}}{100 \cancel{\text{kPa}}} = 1 \text{ bar}$$

$T_1 = 23 + 273.15 = 296 \text{ K}$

$T_2 = 100. + 273.15 = 373 \text{ K}$

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

$$p_2 = p_1 \times \frac{T_2}{T_1} = 1 \text{ bar} \times \frac{373 \cancel{\text{K}}}{296 \cancel{\text{K}}} \boxed{= 1.26 \text{ bar}}$$

The safety valve will not open, since p_2 is less than 1.33 bar.

Sample Problem 4.4 **Applying the Volume-Amount Relationship**

PROBLEM: A scale model of a blimp rises when it is filled with helium to a volume of 55.0 dm^3. When 1.10 mol of He is added to the blimp, the volume is 26.2 dm^3. How many more grams of He must be added to make it rise? Assume constant *T* and *P*.

PLAN: The initial amount of helium (n_1) is given, as well as the initial volume (V_1) and the volume needed to make it rise (V_2). We need to calculate n_2 and hence the mass of He to be added.

n_1 (mol) of He

↓ **multiply by V_2/V_1**

n_2 (mol) of He

↓ **subtract n_1**

mol to be added

↓ **multiply by $\mathcal{M}$ (g/mol)**

Mass(g)of He

Sample Problem 4.4

SOLUTION:

$n_1 = 1.10$ mol $\quad n_2 =$ unknown

$V_1 = 26.2\ dm^3 \quad V_2 = 55.0\ dm^3$

T and p are constant

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

$$n_2 = n_1 \times \frac{V_2}{V_1} = 1.10\ \text{mol} \times \frac{55.0\ \cancel{dm^3}}{26.2\ \cancel{dm^3}} = 2.31\ \text{mol He}$$

Additional amount of He needed = 2.31 mol – 1.10 mol = 1.21 mol He

$$1.21\ \cancel{\text{mol He}} \times \frac{4.003\ \text{g He}}{1\ \cancel{\text{mol He}}} \ \boxed{= \mathbf{4.84\ g\ He}}$$

Sample Problem 4.5 **Solving for an Unknown Gas Variable at Fixed Conditions**

PROBLEM: A steel tank has a volume of 438 L and is filled with 0.885 kg of O_2. Calculate the pressure of O_2 at 21^oC.

PLAN: We are given *V*, *T* and mass, which can be converted to moles (*n*). Use the ideal gas law to find *p*.

SOLUTION: V = 438 L T = 21°C = 294 K

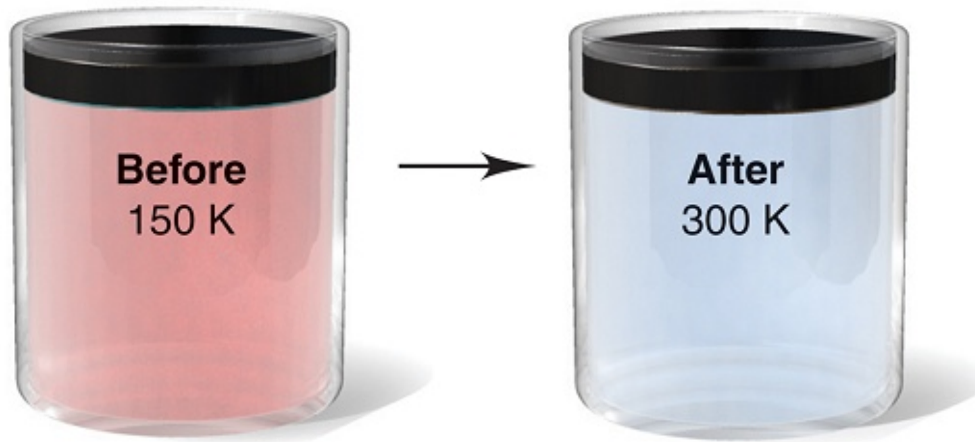
n = 0.885 kg O_2 (convert to mol) p is unknown

$$0.885\ \cancel{kg\ O_2} \times \frac{10^3\ \cancel{g}}{1\ \cancel{kg}} \times \frac{1\ mol\ O_2}{32.00\ \cancel{g}\ O_2} = 27.7\ mol\ O_2$$

$$p = \frac{nRT}{V} = \frac{27.7\ \cancel{mol} \times 8.314\ \frac{Pa.\cancel{m^3}}{\cancel{mol{\cdot}K}} \times 294\ \cancel{K}}{438 \times 10^{-3}\ \cancel{m^3}}\ \boxed{\mathbf{= 1.55{\times}10^5\ Pa}}$$

Sample Problem 4.6 — Using Gas Laws to Determine a Balanced Equation

PROBLEM: The piston-cylinders is depicted before and after a gaseous reaction that is carried out at constant pressure. The temperature is 150 K before the reaction and 300 K after the reaction. (Assume the cylinder is insulated.)



Which of the following balanced equations describes the reaction?

(1) $A_2(g) + B_2(g) \rightarrow 2AB(g)$

(2) $2AB(g) + B_2(g) \rightarrow 2AB_2(g)$

(3) $A(g) + B_2(g) \rightarrow AB_2(g)$

(4) $2AB_2(g) + A_2(g) + 2B_2(g)$

Sample Problem 4.6

PLAN: We are told that P is constant for this system, and the depiction shows that V does not change either. Since T changes, the volume could not remain the same unless the amount of gas in the system also changes.

SOLUTION:

From Gas Law, $\dfrac{P_1 V_1}{n_1 T_1} = \dfrac{P_2 V_2}{n_2 T_2}$ ***So when P and V are constants,***

$$n_1T_1 = n_2T_2 \qquad \frac{n_2}{n_1} = \frac{T_1}{T_2} = \frac{150\text{ K}}{300\text{ K}} = \frac{1}{2}$$

Since T doubles, the total number of moles of gas must halve – i.e., the moles of product must be half the moles of reactant. This relationship is shown by equation (3).

$$\boxed{\mathbf{A}(g) + \mathbf{B_2}(g) \rightarrow \mathbf{AB_2}(g)}$$

Sample Problem 4.8 Finding the Molar Mass of a Volatile Liquid

PROBLEM: An organic chemist isolates a colorless liquid from a petroleum sample. She places the liquid in a preweighed flask and puts the flask in boiling water, causing the liquid to vaporize and fill the flask with gas. She closes the flask and reweighs it. She obtains the following data:

Volume (V) of flask = 213 mL T = 100.0°C p = 1.00 bar

mass of flask + gas = 78.416 g   mass of flask = 77.834 g

Calculate the molar mass of the liquid.

PLAN: The variables V, T and p are given. We find the mass of the gas by subtracting the mass of the flask from the mass of the flask with the gas in it, and use this information to calculate $\mathcal{M}$.

Sample Problem 4.8

SOLUTION: m of gas = (78.416 - 77.834) = 0.582 g

$$V = 213\ \cancel{\text{mL}} \times \frac{1\ \cancel{\text{L}}}{10^3\ \cancel{\text{mL}}} \times \frac{1\ \text{m}^3}{10^3\ \cancel{\text{L}}} = 2.13 \times 10^{-4}\ \text{m}^3$$

T = 100.0°C + 273.15 = 373.2 K

$$p = 1.00\ \cancel{\text{bar}} \times \frac{10^5\ \text{Pa}}{1\ \cancel{\text{bar}}} = 1.00 \times 10^5\ \text{Pa}$$

m= 78.416g-77.834 g = *0.582 g*

$$\mathcal{M} = \frac{mRT}{pV} = \frac{0.582\ \text{g} \times 8.314\ \dfrac{\cancel{\text{Pa}}.\ \cancel{\text{m}^3}}{\text{mol}\cdot\cancel{\text{K}}} \times 373.2\ \cancel{\text{K}}}{1.00 \times 10^5\ \cancel{\text{Pa}} \times 2.13 \times 10^{-4}\ \cancel{\text{m}^3}}$$

$$\boxed{= 84.8\ \text{g/mol}}$$

Mixtures of Gases

- Gases mix homogeneously in any proportions.
  - Each gas in a mixture behaves as if it were the only gas present.
- The pressure exerted by each gas in a mixture is called its ***partial pressure***.
- ***Dalton's Law of partial pressures*** states that the total pressure in a mixture is the sum of the partial pressures of the component gases.
- The partial pressure of a gas is proportional to its mole fraction:

$$p_A = X_A \times p_{total} \qquad X_A = \frac{n_A}{n_{total}}$$

Sample Problem 4.9 **Applying Dalton's Law of Partial Pressures**

PROBLEM: In a study of O_2 uptake by muscle at high altitude, a physiologist prepares an atmosphere consisting of 79 mole % N_2, 17 mole % $^{16}O_2$, and 4.0 mole % $^{18}O_2$. (The isotope ^{18}O will be measured to determine the O_2 uptake.) The pressure of the mixture is 0.76 bar to simulate high altitude. Calculate the mole fraction and partial pressure of $^{18}O_2$ in the mixture.

PLAN: Find $X_{^{18}O_2}$ and $p_{^{18}O_2}$ from p_{total} and mol % $^{18}O_2$.

mole % $^{18}O_2$

↓ **divide by 100**

mole fraction, $X_{^{18}O_2}$

↓ **multiply by p_{total}**

partial pressure $p_{^{18}O_2}$

Sample Problem 4.9

SOLUTION:

$$X_{^{18}O_2} = \frac{4.0 \text{ mol \% } ^{18}O_2}{100} = 0.040$$

$$p_{^{18}O_2} = X_{^{18}O_2} \times P_{\text{total}} = 0.040 \times 0.76 \text{ bar} \quad \boxed{\mathbf{= 0.030\ bar}}$$

TABLE 4.2 Vapour Pressure of Water (p_{H_2O}) at Different *T*

T (°C)	p_{H_2O} (kPa)	*T* (°C)	p_{H_2O} (kPa)
0	0.611 15	29	4.0092
5	0.872 58	30	4.247
10	1.2282	35	5.629
15	1.7058	40	7.3849
16	1.8188	45	9.595
17	1.9384	50	12.352
18	2.0647	55	15.762
19	2.1983	60	19.946
20	2.3393	65	25.042
21	2.4882	70	31.201
22	2.6453	75	38.595
23	2.8111	80	47.414
24	2.9858	85	57.867
25	3.1699	90	70.182
26	3.3639	95	84.608
27	3.5681	100	101.33
28	3.7831	105	120.8

Sample Problem 4.10 **Calculating the Amount of Gas Collected over Water**

PROBLEM: Acetylene (C_2H_2) is produced in the laboratory when calcium carbide (CaC_2) reacts with water:

$$CaC_2(s) + 2H_2O(l) \longrightarrow C_2H_2(g) + Ca(OH)_2(aq)$$

A collected sample of acetylene has a total gas pressure of 0.984 bar and a volume of 523 mL. At the temperature of the gas (23^{o}C), the vapor pressure of water is 2.8×10^3 Pa. How many grams of acetylene are collected?

PLAN: The difference in pressures will give *P* for the C_2H_2. The number of moles (*n*) is calculated from the ideal gas law and converted to mass using the molar mass.

Sample Problem 4.10

SOLUTION:

PLAN:

p_{total}

subtract p for H_2O

p of C_2H_2

use ideal gas law

n of C_2H_2

multiply by $\mathcal{M}(mol/L)$

Mass(g) of C_2H_2

p_{total} =0.984× 10^5 Pa, p_{H_2O} = 2.8 × 10^3 Pa

$$p_{C_2H_2} = (p_{total} - p_{H_2O}) = 9.56 \times 10^4 \text{ Pa}$$

$$T = 23°C + 273.15 \text{ K} = 296 \text{ K}$$

$$V = 523 \cancel{\text{mL}} \times \frac{1 \cancel{\text{L}}}{10^3 \cancel{\text{mL}}} \times \frac{1 \text{ m}^3}{10^3 \cancel{\text{L}}} = 5.23 \times 10^{-4} \text{ m}^3$$

Sample Problem 4.10

SOLUTION:

$$n_{C_2H_2} = \frac{pV}{RT} = \frac{9.56\times10^4\ \cancel{Pa} \times 5.23\times10^{-4}\ \cancel{m^3}}{8.314\ \dfrac{\cancel{Pa}\cdot\cancel{m^3}}{mol\cdot\cancel{K}} \times 296\ \cancel{K}} \quad \boxed{\mathbf{= 0.0203\ mol}}$$

$$0.0203\ \cancel{mol} \times \frac{26.04\ g\ C_2H_2}{1\ \cancel{mol}\ C_2H_2} \quad \boxed{\mathbf{= 0.529\ g\ C_2H_2}}$$

The Ideal Gas Law and Stoichiometry

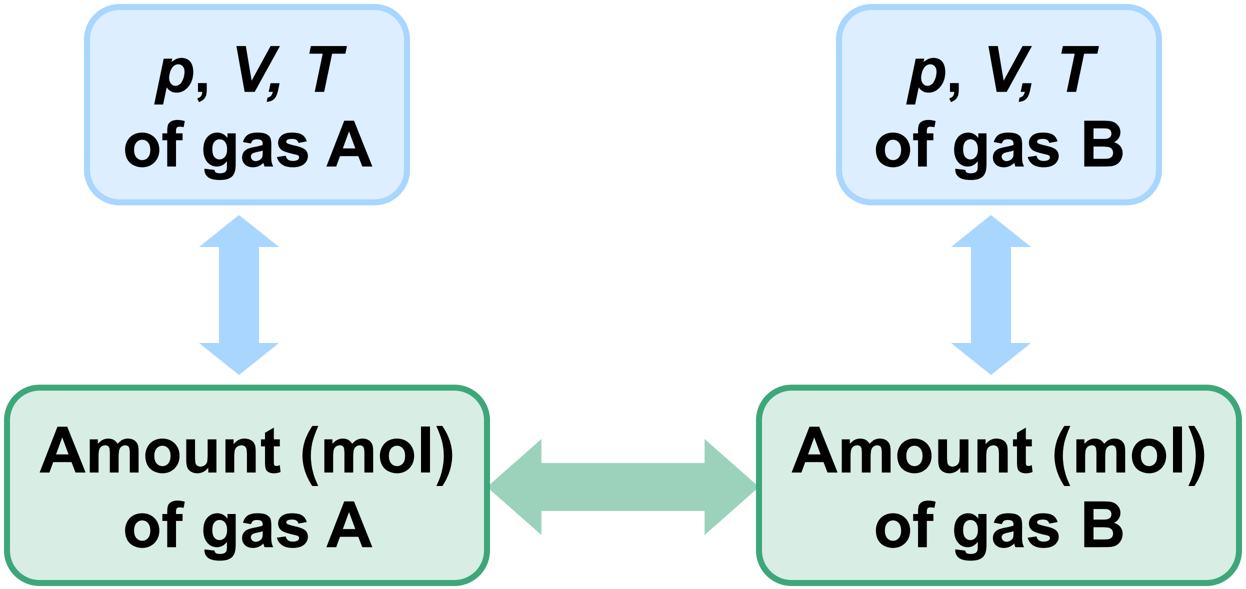


Figure 4.13

The relationships among the amount (mol, *n*) of gaseous reactant (or product) and the gas pressure (*p*), volume (*V*), and temperature (*T*).

Sample Problem 4.11

Using Gas Variables to Find Amounts of Reactants and Products I

PROBLEM: Engineers use copper in absorbent beds to react with and remove oxygen impurities in the ethylene used to make polythene.The beds are regenerated when hot H_2 reduces the copper (II) oxide forming pure metal and water. On a laboratory scale what volume of H_2 gas at 1.02 bar and 225°C is needed to reduce 35.5 g of copper(II) oxide to form pure copper and water?

PLAN: Write a balanced equation. Convert the mass of copper (II) oxide to moles and find the moles of H_2, using the mole ratio from the balanced equation. Calculate the corresponding volume of H_2 using the ideal gas law.

mass (g) of CuO

↓ **divide by** $\mathcal{M}$ *(g/mol)*

mol CuO

↓ **use mole ratio**

mol H_2 → **ideal gas law** → **volume of** H_2

Sample Problem 4.11

SOLUTION: $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$

$$35.5\ \cancel{\text{g CuO}} \times \frac{1\ \cancel{\text{mol CuO}}}{79.55\ \cancel{\text{g CuO}}} \times \frac{1\ \text{mol } H_2}{1\ \cancel{\text{mol CuO}}} = 0.446\ \text{mol } H_2$$

$$p = 1.02\ \cancel{\text{bar}} \times \frac{10^5\ \text{Pa}}{1\ \cancel{\text{bar}}} = 1.02\times10^5\ \text{Pa}, \quad T = 225°\text{C} + 273.15\ \text{K} = 498\ \text{K}$$

$$V = \frac{nRT}{p} = \frac{0.446\ \cancel{\text{mol}}\ H_2 \times 8.314\ \dfrac{\cancel{\text{Pa}}\cdot \text{m}^3}{\cancel{\text{mol}}\cdot\cancel{\text{K}}} \times 498\ \cancel{\text{K}}}{1.02\times10^5\ \cancel{\text{Pa}}}$$

$$= 18.1 \times 10^{-3}\ \text{m}^3 \quad \boxed{\mathbf{= 18.1\ L\ H_2}}$$

Sample Problem 4.12

Using Gas Variables to Find Amounts of Reactants and Products II

PROBLEM: The alkali metals(Group I) react with halogens(Group 17) to form ionic metal halides. What mass of potassium chloride forms when 5.25 L of chlorine gas at 0.963 bar and 293 K reacts with 17.0 g of potassium metal?

PLAN: First we must write a balanced equation. Since the quantities of both reactants are given, we must next determine which reactant is limiting. We will use the ideal gas law to calculate the moles of Cl_2 present.

SOLUTION: The balanced equation is:

$$Cl_2(g) + 2K(s) \rightarrow 2KCl(s)$$

For Cl_2:

$p = 9.63\times 10^4$ Pa $V = 5.25 \times 10^{-3}$ m^3

$T = 293$ K n = unknown

Sample Problem 4.12

$$n_{Cl_2} = \frac{pV}{RT} = \frac{9.63\times 10^4\ \cancel{Pa} \times 5.25\times 10^{-3}\ \cancel{m^3}}{8.314\ \frac{\cancel{Pa\ m^3}}{mol\cdot \cancel{K}} \times 293\ \cancel{K}} = 0.207\ mol\ Cl_2$$

If Cl_2 is limiting: $0.207\ \cancel{mol\ Cl_2} \times \frac{2\ mol\ KCl}{1\ \cancel{mol\ Cl_2}} = 0.414\ mol\ KCl$

If K is limiting: $17.0\ \cancel{g\ K} \times \frac{1\ \cancel{mol\ K}}{39.10\ \cancel{g\ K}} \times \frac{2\ mol\ KCl}{2\ \cancel{mol\ K}} = 0.435\ mol\ KCl$

Cl_2 is the limiting reactant.

$$0.414\ \cancel{mol\ KCl} \times \frac{74.55\ g\ KCl}{1\ \cancel{mol\ KCl}} \boxed{= \mathbf{30.9\ g\ KCl}}$$

4.5 The Kinetic-Molecular Theory: A Model for Gas Behavior

Postulate 1:

Gas particles are tiny with large spaces between them. The volume of each particle is so small compared to the total volume of the gas that it is assumed to be zero.

Postulate 2:

Gas particles are in constant, random, straight-line motion except when they collide with each other or with the container walls.

Postulate 3:

Collisions are elastic, meaning that colliding particles exchange energy but do not lose any energy due to friction. Their *total kinetic energy is constant*. Between collisions the particles do not influence each other by attractive or repulsive forces.

Figure 4.14 Distribution of molecular speeds for N_2 at three temperatures.

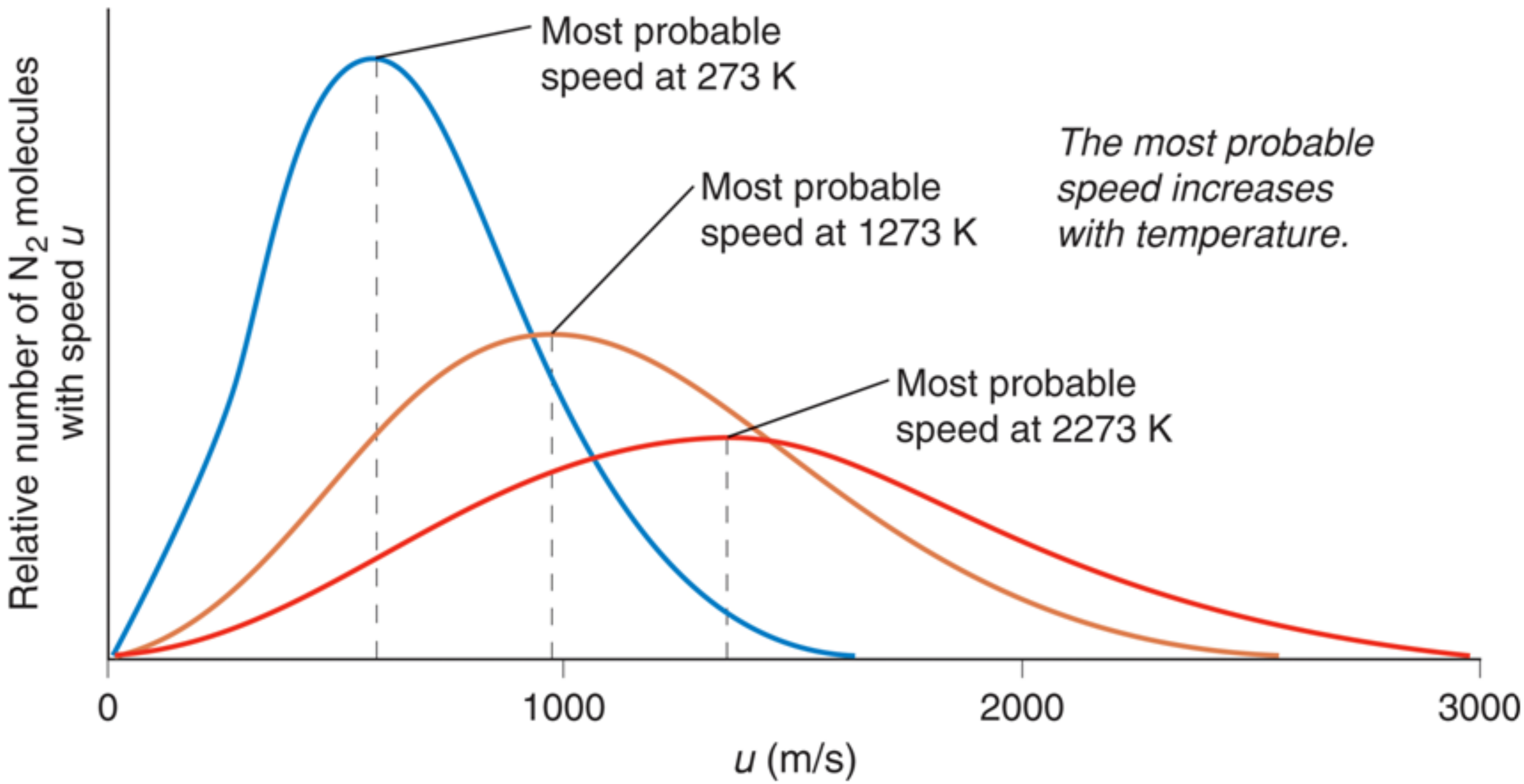


Figure 4.15 **Pressure arise from countless collisions between gas particles and walls.**

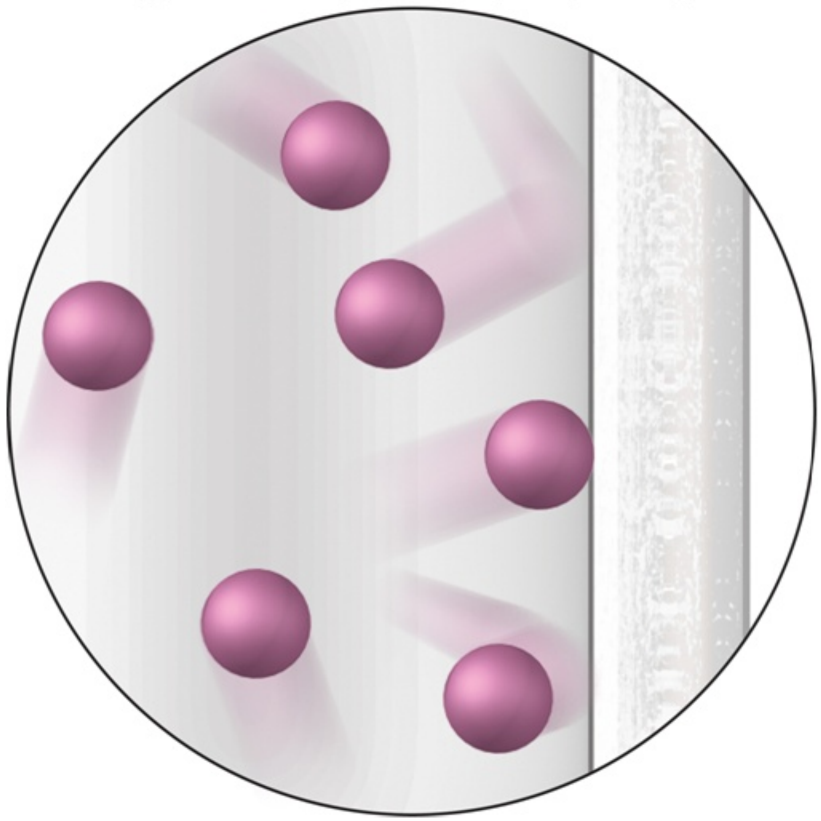


Figure 4.16 A molecular view of Boyle's law.

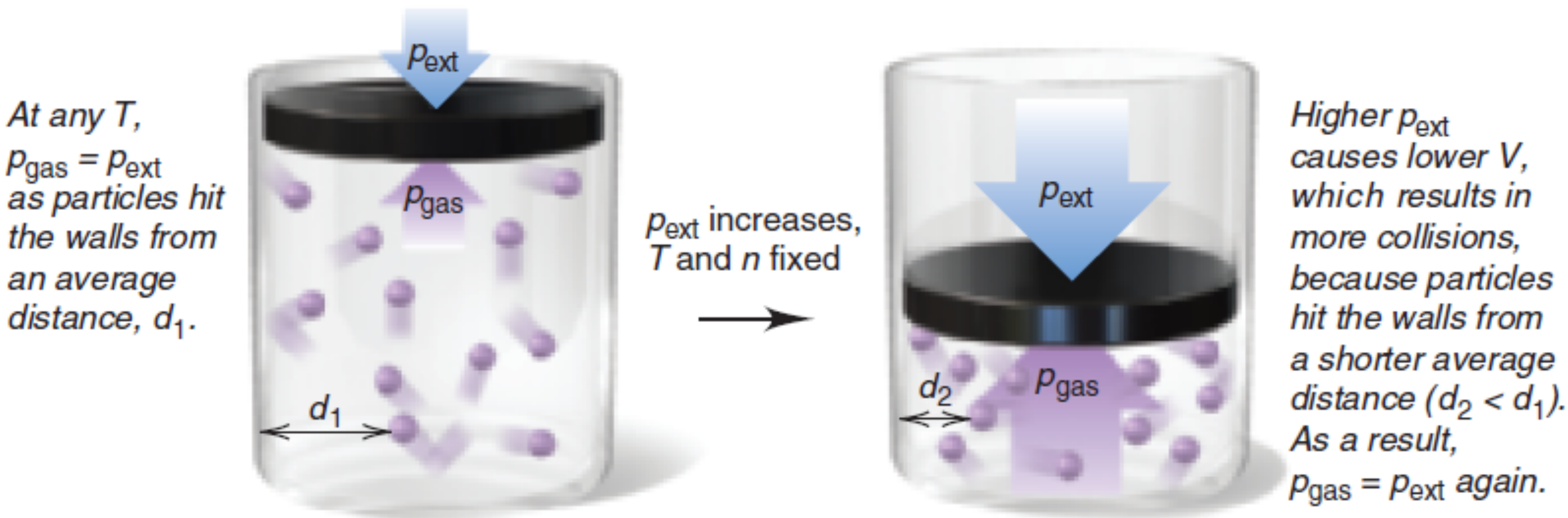


Figure 4.17 A molecular view of Dalton's law

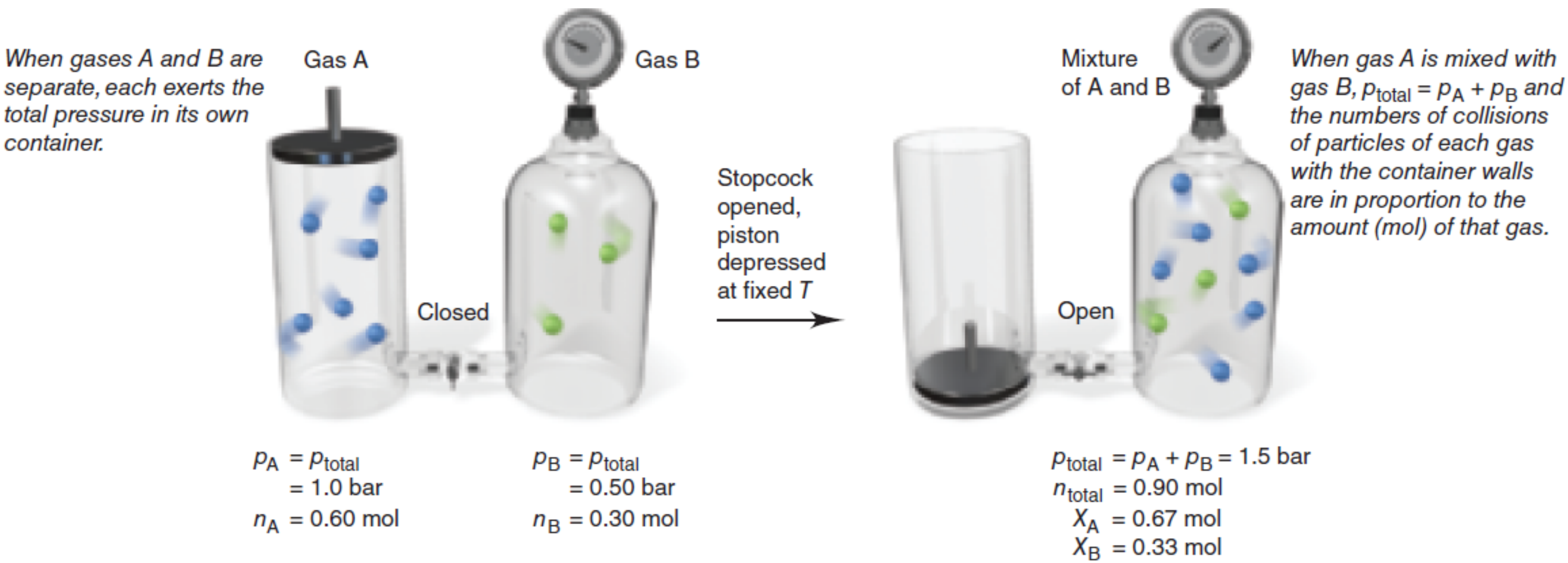
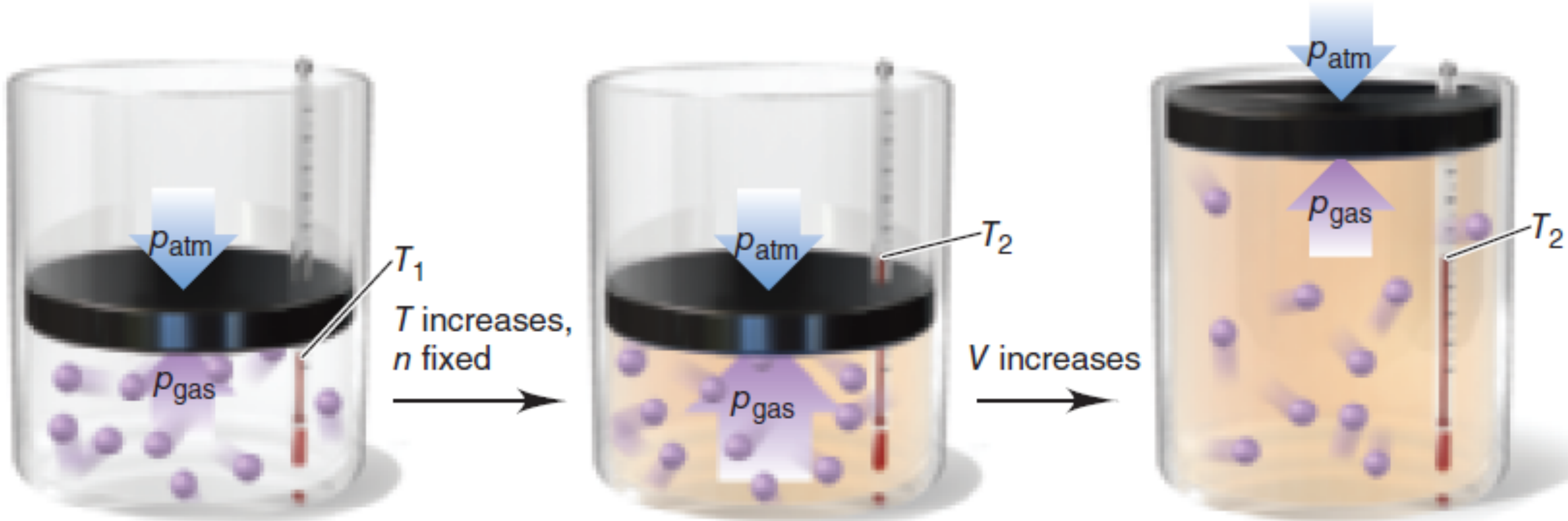


Figure 4.18 A molecular view of Charles's law

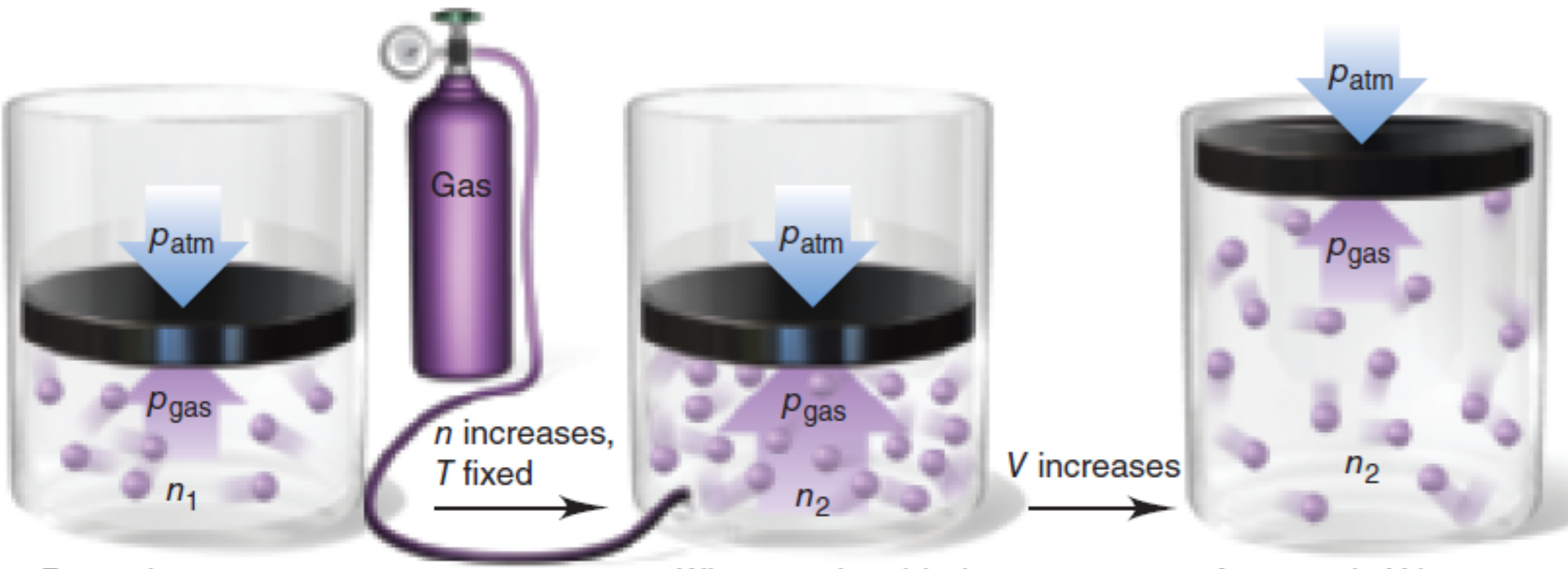


At T_1, $p_{gas} = p_{atm}$.

Higher T increases collision frequency, so $p_{gas} > p_{atm}$.

Thus, V increases until $p_{gas} = p_{atm}$ at T_2.

Figure 4.19 A molecular view of Avogadro's law



For a given amount, n_1, of gas, $p_{gas} = p_{atm}$.

When gas is added to reach n_2, the collision frequency of the particles increases, so $p_{gas} > p_{atm}$.

As a result, V increases until $p_{gas} = p_{atm}$ again.

Kinetic Energy and Gas Behavior

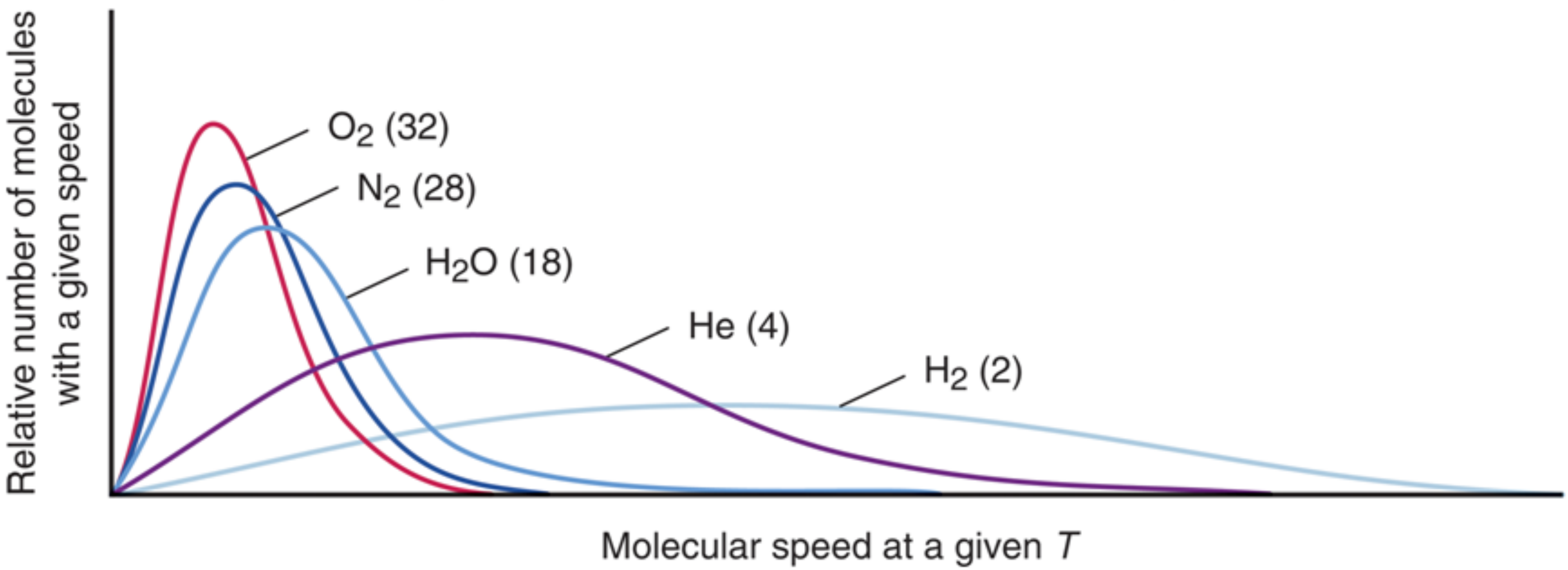
At a given T, all gases in a sample have the same average kinetic energy.

$$\boxed{E_k = \frac{1}{2}\text{ mass x speed}^2}$$

Kinetic energy depends on both the mass and the speed of a particle.

At the same T, a heavier gas particle moves more slowly than a lighter one.

Figure 4.20 The relationship between molar mass and molecular speed.



Graham's Law of Effusion

Effusion is the process by which a gas escapes through a small hole in its container into an evacuated space.

Graham's law of effusion states that the rate of effusion of a gas is inversely proportional to the square root of its molar mass.

A lighter gas moves more quickly and therefore has a higher rate of effusion than a heavier gas at the same *T*.

$$\boxed{\text{Rate of effusion} \propto \frac{1}{\sqrt{\mathcal{M}}}}$$

Sample Problem 4.13 **Applying Graham's Law of Effusion**

PROBLEM: A mixture of helium (He) and methane (CH_4) is placed in an effusion apparatus. Calculate the ratio of their effusion rates.

PLAN: The effusion rate is inversely proportional $\sqrt{\mathcal{M}}$ for each gas, so we find the molar mass for each substance using its formula and take the square root. The ratio of the effusion rates is the inverse of the ratio of these square roots.

SOLUTION: $\mathcal{M}$ of CH_4 = 16.04 g/mol $\mathcal{M}$ of He = 4.003 g/mol

$$\frac{\text{rate}_{\text{He}}}{\text{rate}_{CH_4}} = \sqrt{\frac{16.04}{4.003}} \boxed{= 2.002}$$

4.6 Non-Ideal Gases: Deviations from Ideal Behavior

- The kinetic-molecular model describes the behavior of ideal gases. Real gases(non-ideal gases) deviate from this behavior.
- Non-ideal gases have real volume.
  - Gas particles are **not** points of mass, but have volumes determined by the sizes of their atoms and the bonds between them.
- Non-ideal gases do experience attractive and repulsive forces between their particles.
- Non-ideal gases deviate most from ideal behavior at ***low temperature*** and ***high pressure***.

Table 4.3 Molar Volume of Some Common Gases at 0°C and 1 bar.

Gas	Molar Volume (L/mol)	Boiling Point (^oC)
He	22.732	-268.9
H_2	22.729	-252.8
Ne	22.719	-246.1
Ideal gas	**22.711**	–
Ar	22.694	-185.9
N_2	22.693	-195.8
O_2	22.687	-183.0
CO	22.685	-191.5
Cl_2	22.478	-34.0
NH_3	22.372	-33.4

Figure 4.23 Deviations from ideal behavior with increasing external pressure

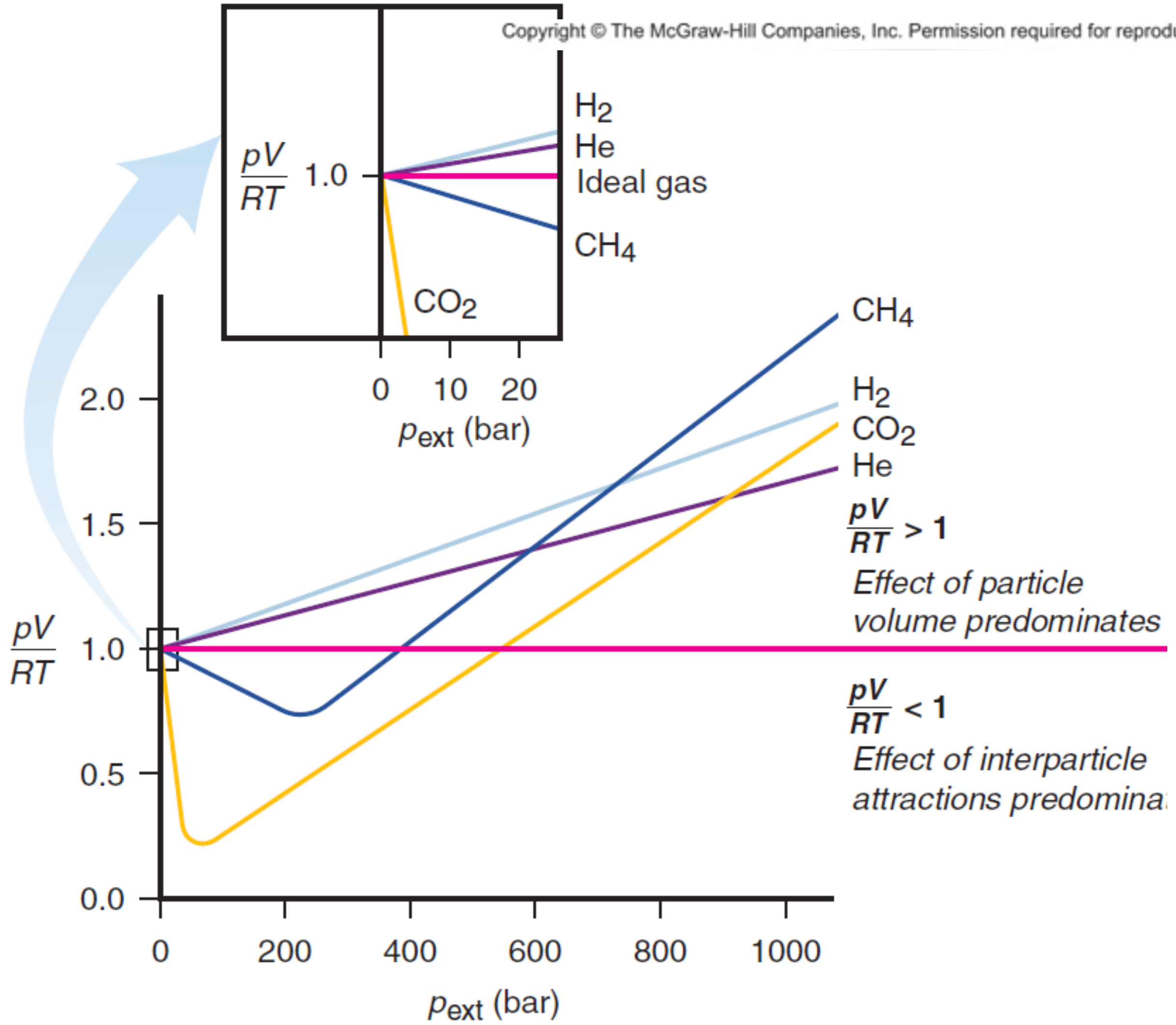


Figure 4.24 The effect of interparticle attractions on measured gas pressure.

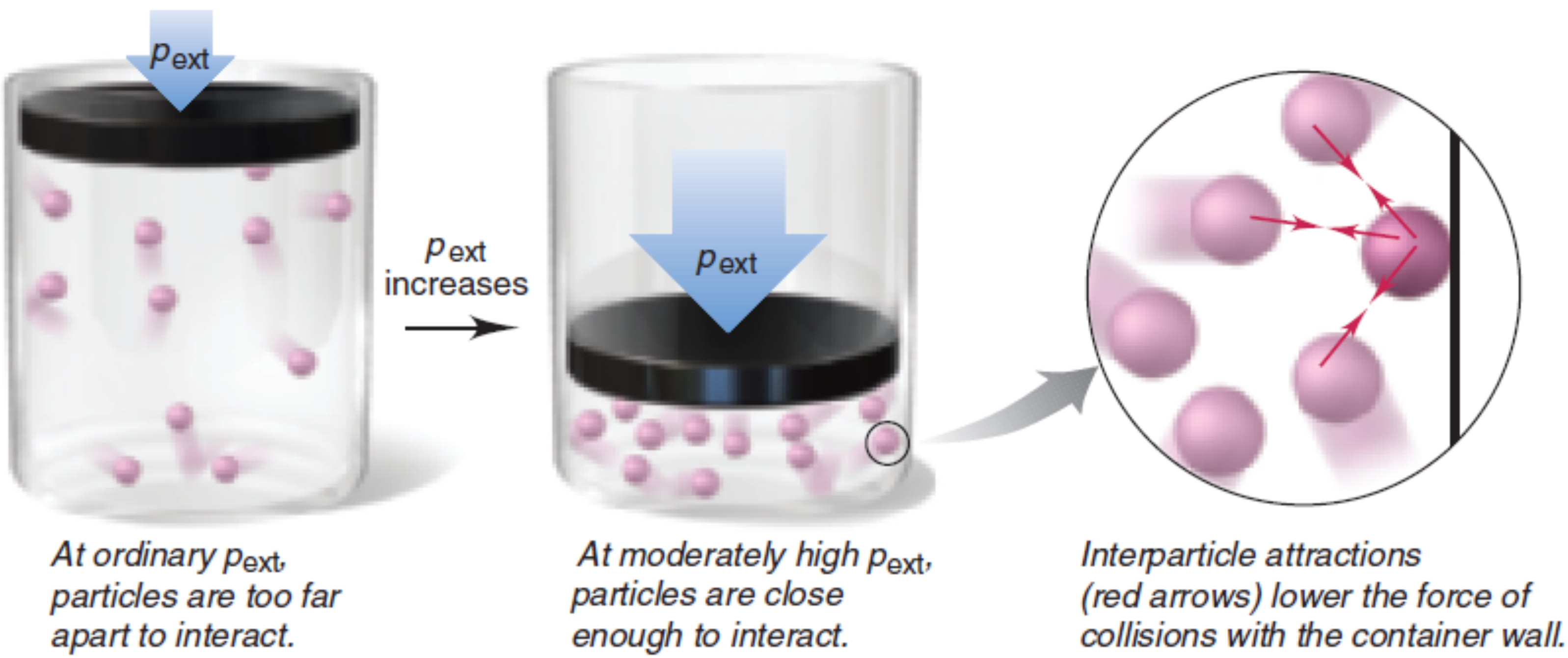
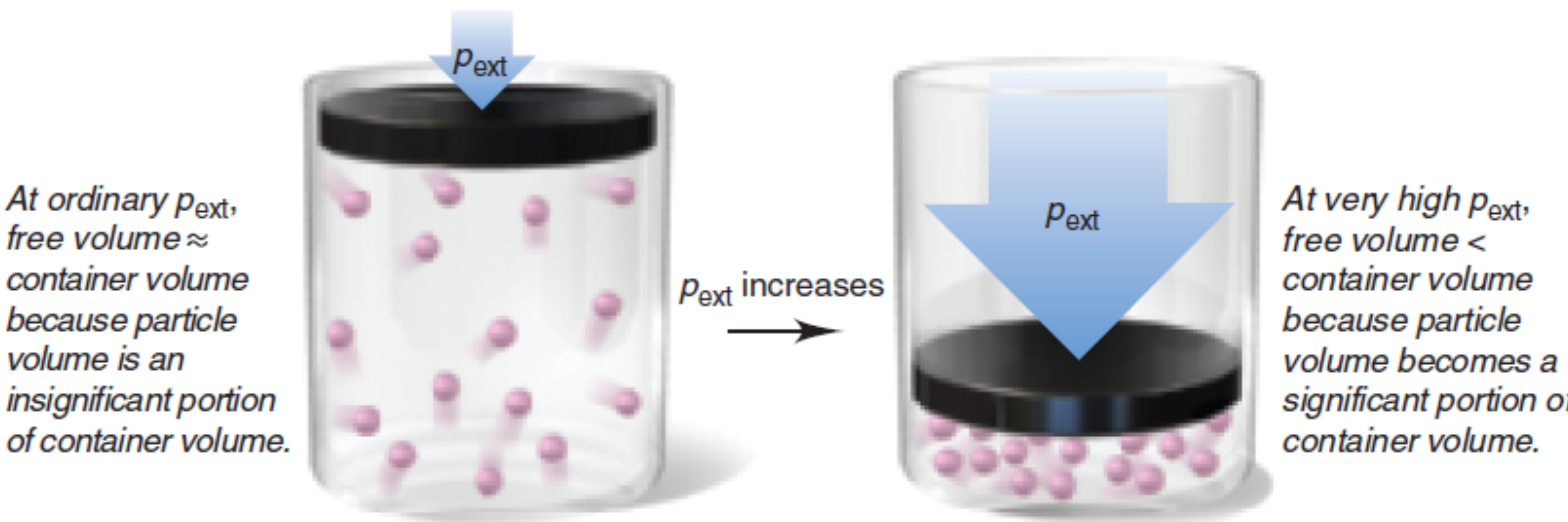


Figure 4.25 The effect of particle volume on measured gas volume.



The van der Waals equation

- The van der Waals equation adjusts the ideal gas law to take into account
  - the real volume of the gas particles and
  - the effect of interparticle attractions.

Van der Waals equation for *n* moles of a real gas

$$\underbrace{\left(p + \frac{n^2 a}{V^2}\right)}_{\text{adjusts } p \text{ up}} \underbrace{(V - nb)}_{\text{adjusts } V \text{ down}} = nRT$$

The constant *a* relates to factors that influence the attraction between particles.

The constant *b* relates to particle volume.

Table 4.4 Van der Waals Constants for Some Common Gases

Gas	$a \left(\frac{\text{bar·L}^2}{\text{mol}^2}\right)$	$b \left(\frac{\text{L}}{\text{mol}}\right)$
He	0.0346	0.0238
Ne	0.208	0.01672
Ar	1.355	0.03201
Kr	2.325	0.0396
Xe	4.192	0.05156
H_2	0.2453	0.02651
N_2	1.370	0.0387
O_2	1.382	0.03186
Cl_2	6.343	0.05422
CH_4	2.300	0.04301
CO	1.472	0.03948
CO_2	3.658	0.04286
NH_3	4.225	0.03713
H_2O	5.357	0.03049