

Chapter 5

Gases



Elements that exist as gases at 25°C and 1 atmosphere

1A																	8A
H	2A											3A	4A	5A	6A	7A	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3B	4B	5B	6B	7B	8B		1B	2B		Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

Ionic compounds can not be gases at 25 °C and 1 atm because of its strong ionic forces.

Molecular compounds at 25 °C and 1 atm varies; some are gases CO, HCl and others are liquid or solid CH₃OH(l)

*No simple rule to help determine if substance is **g** or **l** or **s***

*It depends on magnitude of the **intermolecular forces** among molecules*

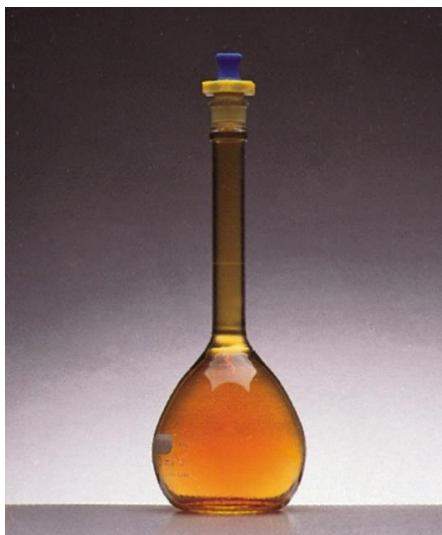
TABLE 5.1 **Some Substances Found as Gases at 1 atm and 25°C**

Elements	Compounds
H ₂ (molecular hydrogen)	HF (hydrogen fluoride)
N ₂ (molecular nitrogen)	HCl (hydrogen chloride)
O ₂ (molecular oxygen)	HBr (hydrogen bromide)
O ₃ (ozone)	HI (hydrogen iodide)
F ₂ (molecular fluorine)	CO (carbon monoxide)
Cl ₂ (molecular chlorine)	CO ₂ (carbon dioxide)
He (helium)	NH ₃ (ammonia)
Ne (neon)	NO (nitric oxide)
Ar (argon)	NO ₂ (nitrogen dioxide)
Kr (krypton)	N ₂ O (nitrous oxide)
Xe (xenon)	SO ₂ (sulfur dioxide)
Rn (radon)	H ₂ S (hydrogen sulfide)
	HCN (hydrogen cyanide)*

*The boiling point of HCN is 26°C, but it is close enough to qualify as a gas at ordinary atmospheric conditions.

Physical Characteristics of Gases

- Gases assume the volume and shape of their containers.
- Gases are the most compressible state of matter.
- Gases have much lower densities than liquids and solids.
- Gases will mix evenly and completely when confined to the same container.



NO_2 gas

Pressure

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

(force = mass x acceleration)

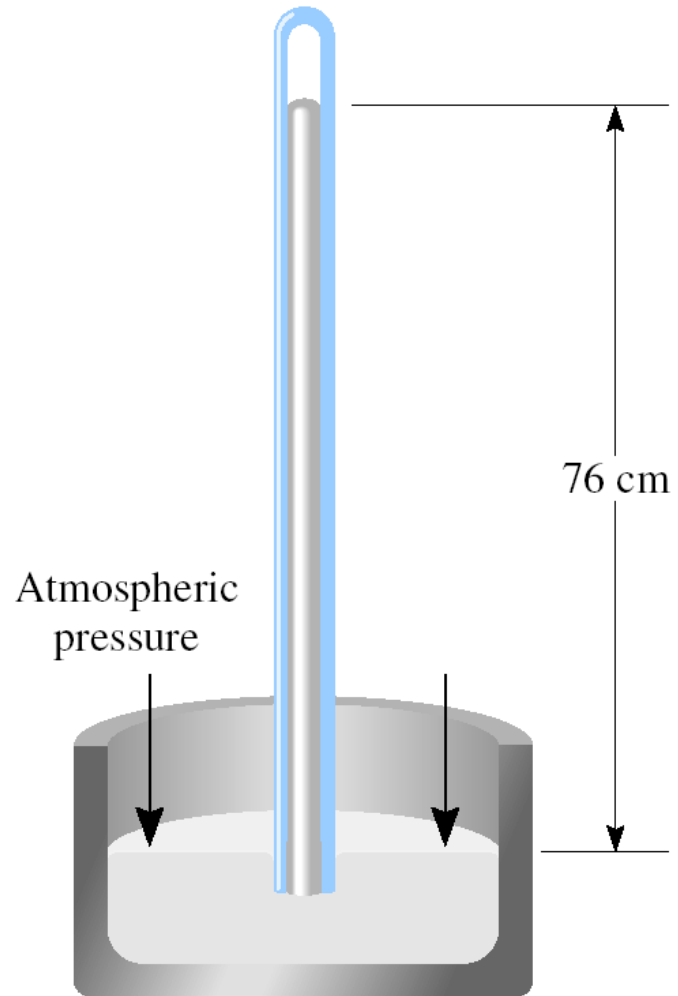
Units of Pressure:

1 pascal (Pa) = 1 N/m²

1 atm = 760 mmHg = 760 torr

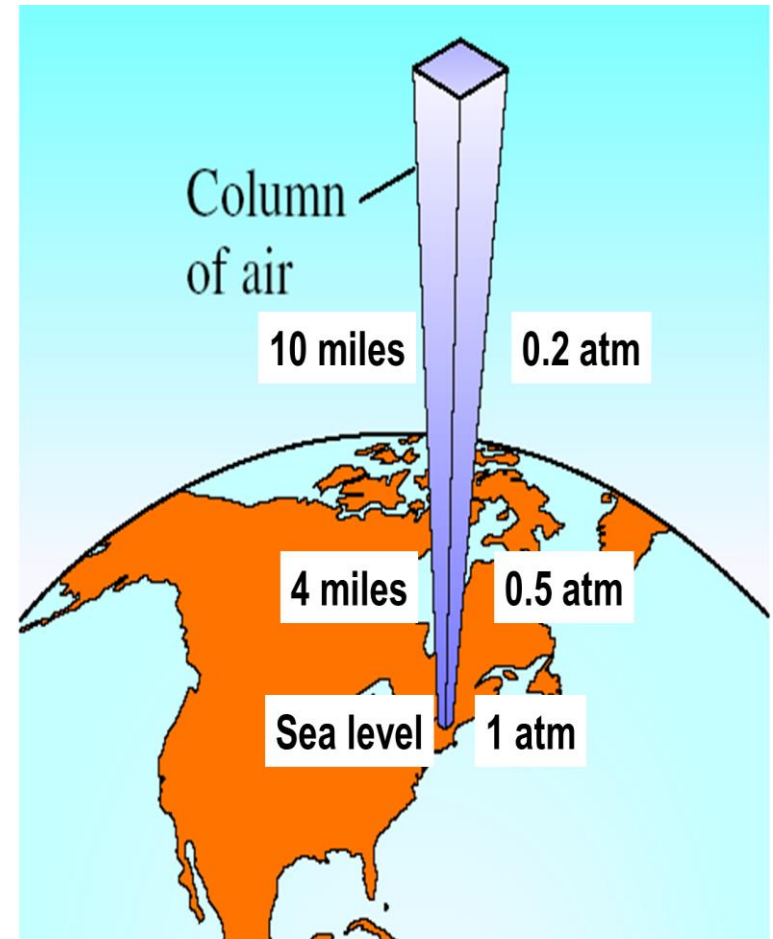
1 atm = 101,325 Pa

SI Units of Pressure is Pascal (Pa)



Standard atmospheric pressure (1 atm) is equal to the pressure that supports a column of mercury exactly **760 mmHg** (or 76 cm) high at **0°C** at **sea level**

- The result of weight of the column of air above it.
- Act on all directions (not down word only)
- Depends on location, T, Weather conditions



EXAMPLE 5.1

The pressure outside a jet plane flying at high altitude falls considerably below standard atmospheric pressure. Therefore, the air inside the cabin must be pressurized to protect the passengers. What is the pressure in atmospheres in the cabin if the barometer reading is 688 mmHg?

Solution The pressure in the cabin is given by

$$\begin{aligned}\text{pressure} &= 688 \cancel{\text{ mmHg}} \times \frac{1 \text{ atm}}{760 \cancel{\text{ mmHg}}} \\ &= 0.905 \text{ atm}\end{aligned}$$

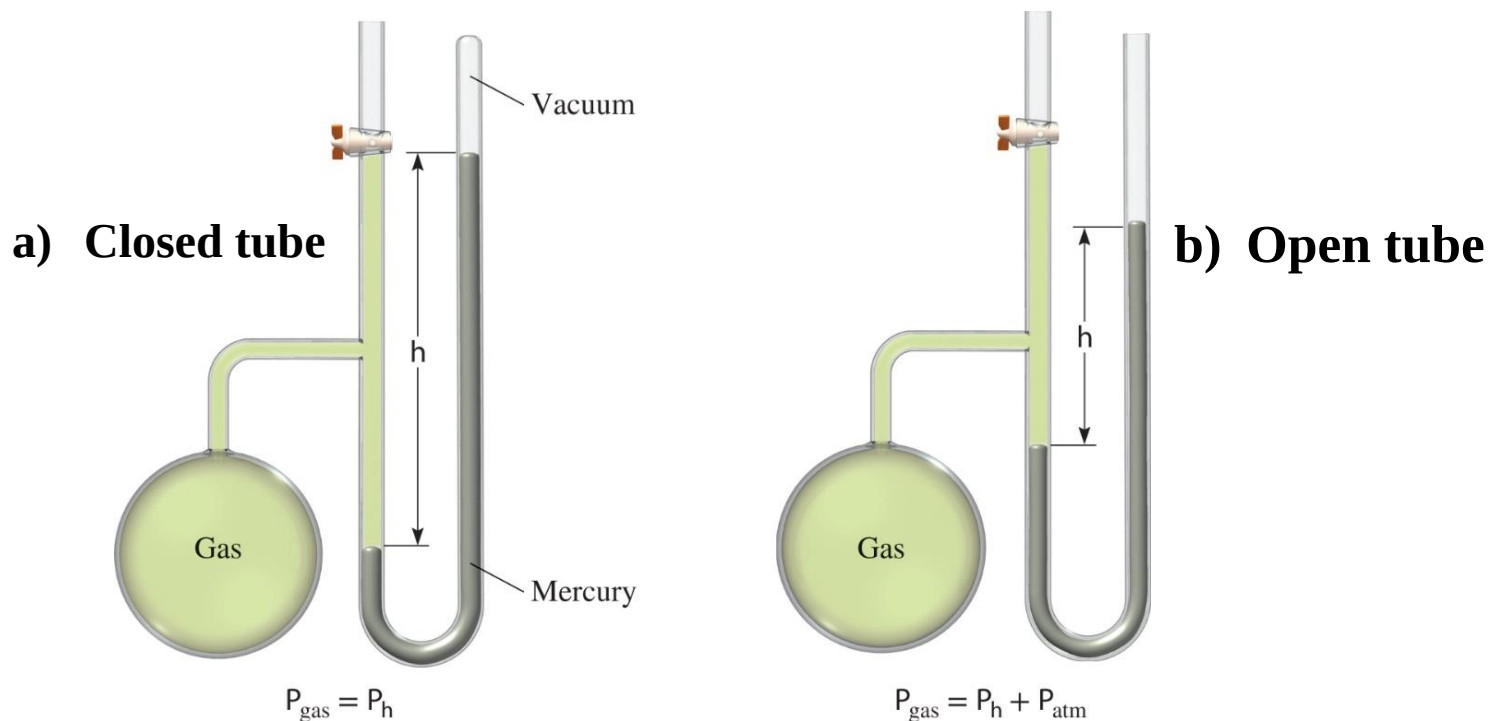
EXAMPLE 5.2

The atmospheric pressure in San Francisco on a certain day was 732 mmHg. What was the pressure in kPa?

Solution The pressure in kPa is

$$\begin{aligned}\text{pressure} &= 732 \cancel{\text{ mmHg}} \times \frac{1.01325 \times 10^5 \text{ Pa}}{760 \cancel{\text{ mmHg}}} \\ &= 9.76 \times 10^4 \text{ Pa} \\ &= 97.6 \text{ kPa}\end{aligned}$$

Manometers Used to Measure Gas Pressures

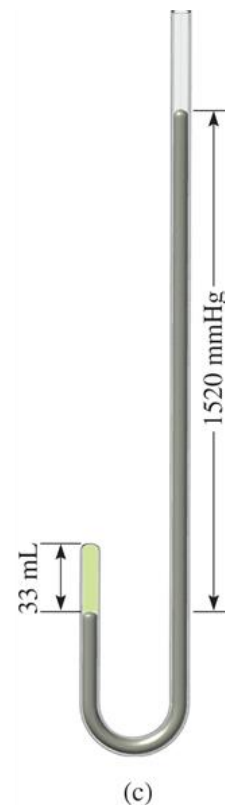
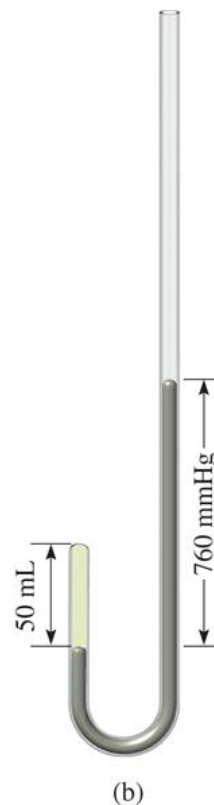
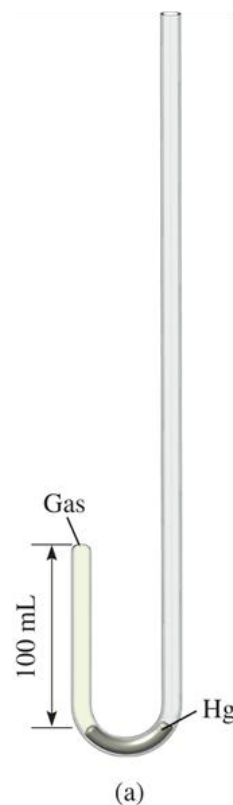


a) The height of the mercury in the tube is equal to the pressure of the gas sample.

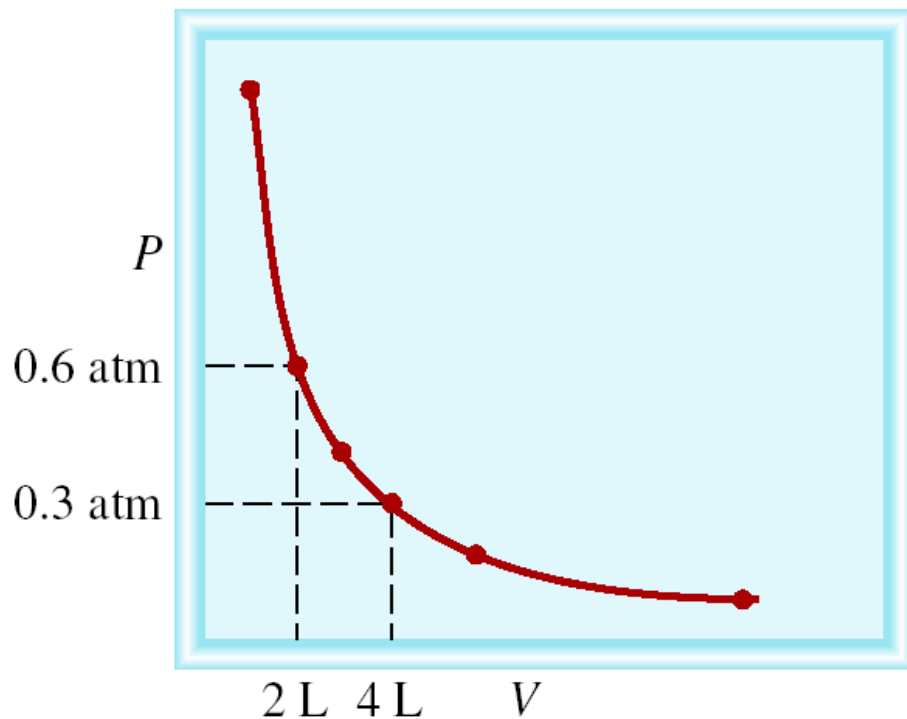
b) The height of the mercury in the tube is equal to the pressure difference between the gas and atmosphere. The gas pressure can be calculated from the atmospheric pressure and this difference.

Apparatus for Studying the Relationship Between Pressure and Volume of a Gas

- A gas sample is placed into a closed-end tube, and mercury is added.
- As more mercury is added to the tube, the **pressure increases**, and the **volume of the gas sample decreases**.
- **Thus, pressure and volume are inversely related.**



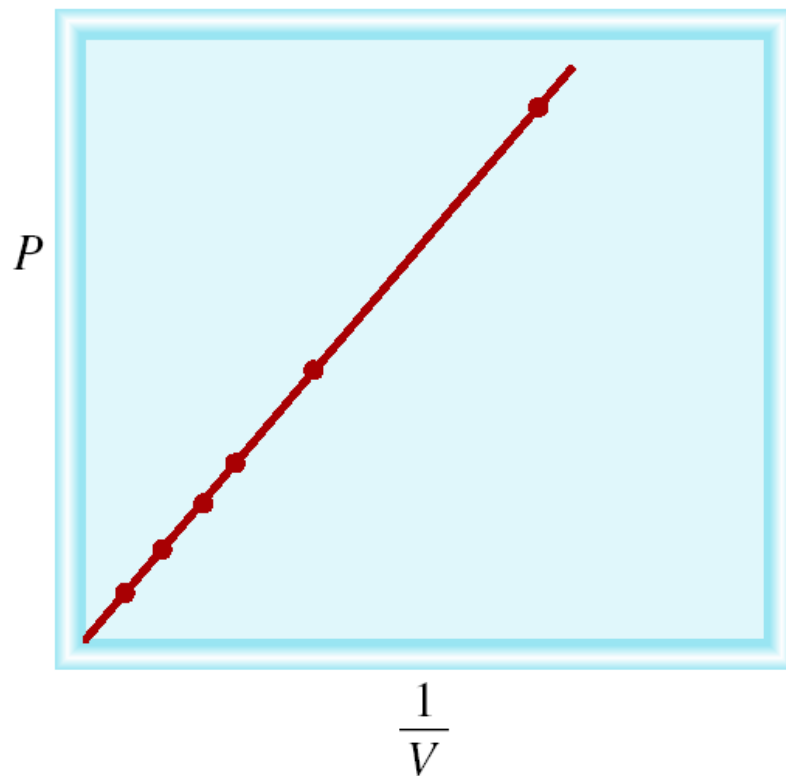
Boyle's Law



$$P \propto 1/V$$

$$P \times V = \text{constant}$$

$$P_1 \times V_1 = P_2 \times V_2$$



Constant temperature
Constant amount of gas

A sample of chlorine gas occupies a volume of 946 mL at a pressure of 726 mmHg. What is the pressure of the gas (in mmHg) if the volume is reduced at constant temperature to 154 mL?

$$P \times V = \text{constant}$$

$$P_1 \times V_1 = P_2 \times V_2$$

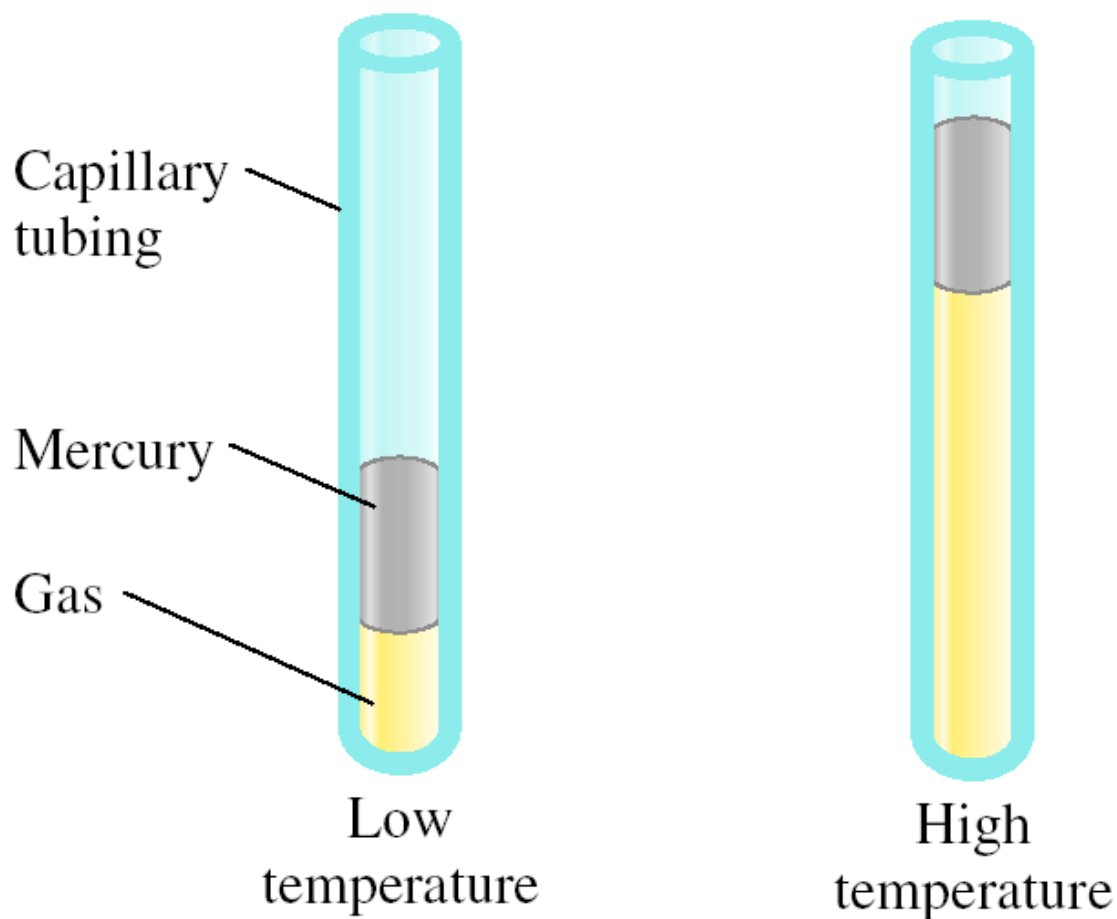
$$P_1 = 726 \text{ mmHg} \qquad P_2 = ?$$

$$V_1 = 946 \text{ mL} \qquad V_2 = 154 \text{ mL}$$

$$P_2 = \frac{P_1 \times V_1}{V_2} = \frac{726 \text{ mmHg} \times 946 \text{ mL}}{154 \text{ mL}} = 4460 \text{ mmHg}$$

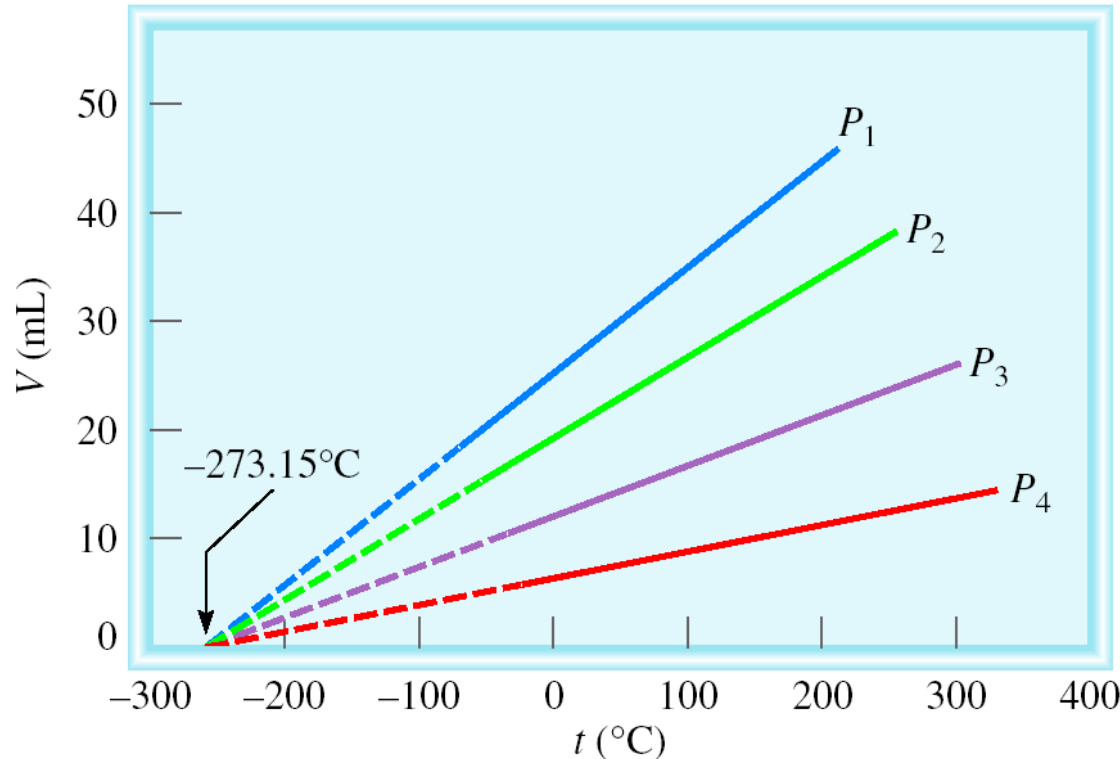
Charles' & Gay-Lussac's Law

Variation in Gas Volume with Temperature at Constant Pressure



As T increases V increases

Variation of Gas Volume with Temperature at Constant Pressure



Charles' &
Gay-Lussac's
Law

$$V \propto T$$

$$V = \text{constant} \times T$$

$$V_1/T_1 = V_2/T_2$$

Temperature **must** be in **Kelvin**

$$T \text{ (K)} = t \text{ (}^\circ\text{C)} + 273.15$$

A sample of carbon monoxide gas occupies 3.20 L at 125 °C. At what temperature will the gas occupy a volume of 1.54 L if the pressure remains constant?

$$V_1/T_1 = V_2/T_2$$

$$V_1 = 3.20 \text{ L}$$

$$V_2 = 1.54 \text{ L}$$

$$T_1 = 398.15 \text{ K}$$

$$T_2 = ?$$

$$T_1 = 125 (^\circ\text{C}) + 273.15 (\text{K}) = 398.15 \text{ K}$$

$$T_2 = \frac{V_2 \times T_1}{V_1} = \frac{1.54 \cancel{\text{ L}} \times 398.15 \text{ K}}{3.20 \cancel{\text{ L}}} = \mathbf{192 \text{ K}}$$

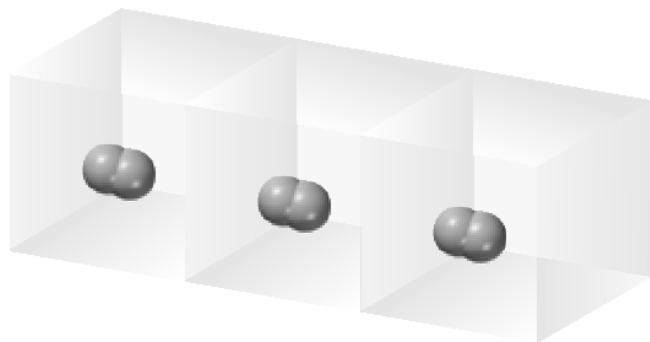
Avogadro's Law

$V \propto$ number of moles (n)

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

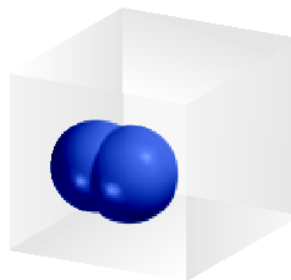
$$V_1 / n_1 = V_2 / n_2$$

Constant temperature
Constant pressure



$3\text{H}_2(\text{g})$
3 molecules
3 moles
3 volumes

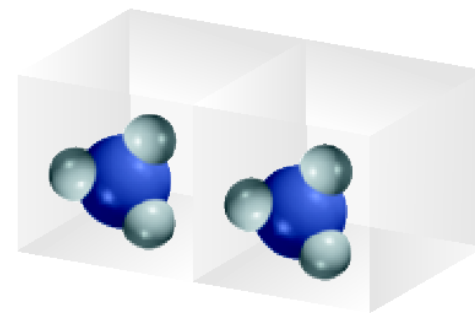
+



+

$\text{N}_2(\text{g})$
1 molecule
1 mole
1 volume

→



→

→

→

→

$2\text{NH}_3(\text{g})$
2 molecules
2 moles
2 volumes

Ammonia burns in oxygen to form nitric oxide (NO) and water vapor. How many volumes of NO are obtained from one volume of ammonia at the same temperature and pressure?



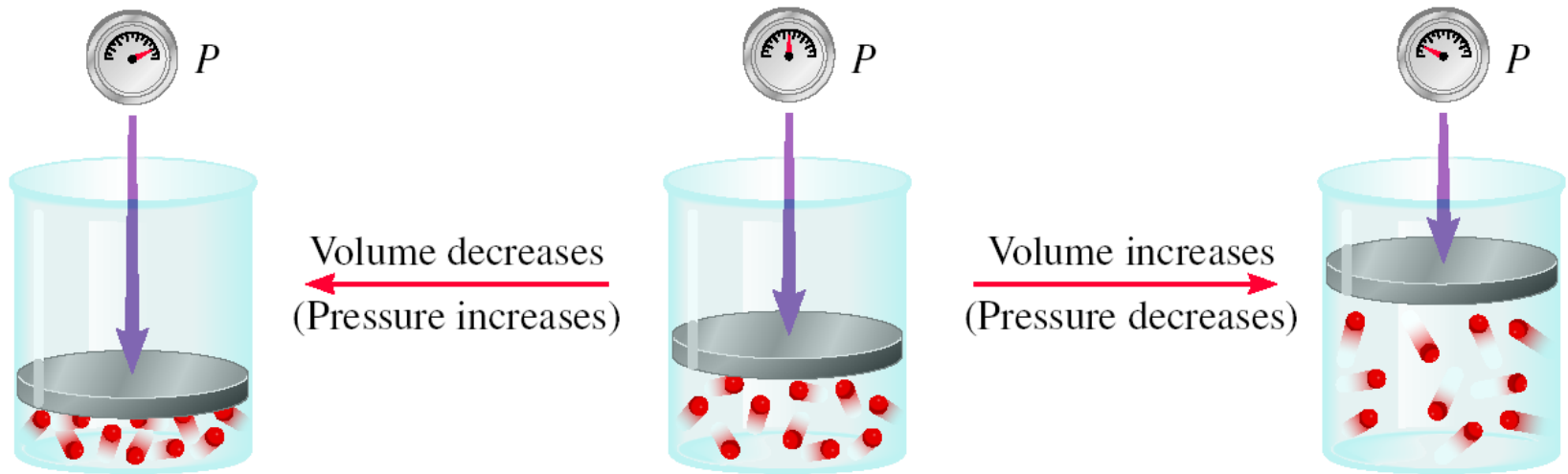
At constant T and P



Summary of Gas Laws

Boyle's Law

Increasing or decreasing the volume of a gas at a constant temperature

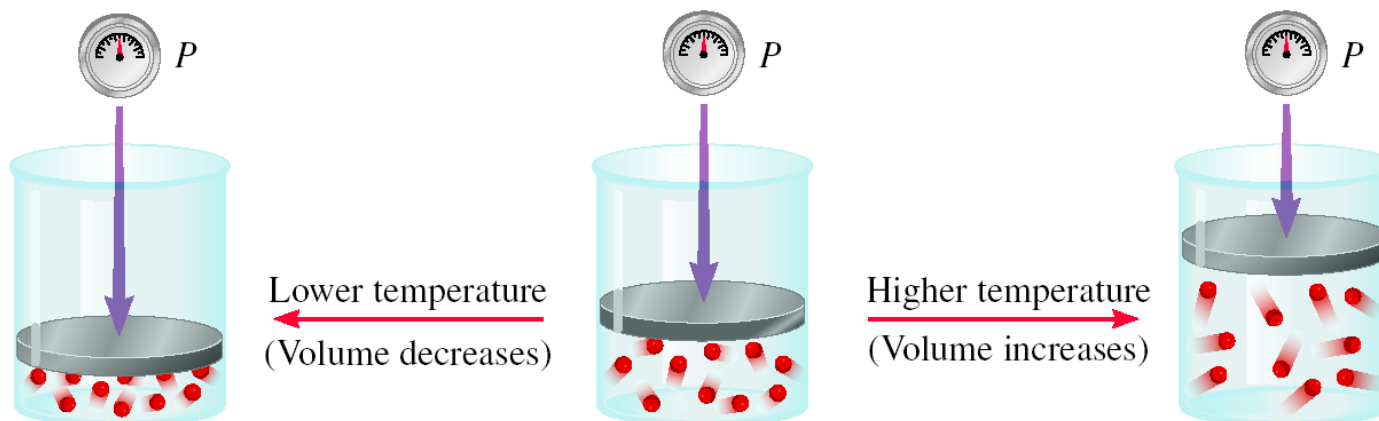


Boyle's Law

$$P = (nRT) \frac{1}{V} \quad nRT \text{ is constant}$$

Charles Law

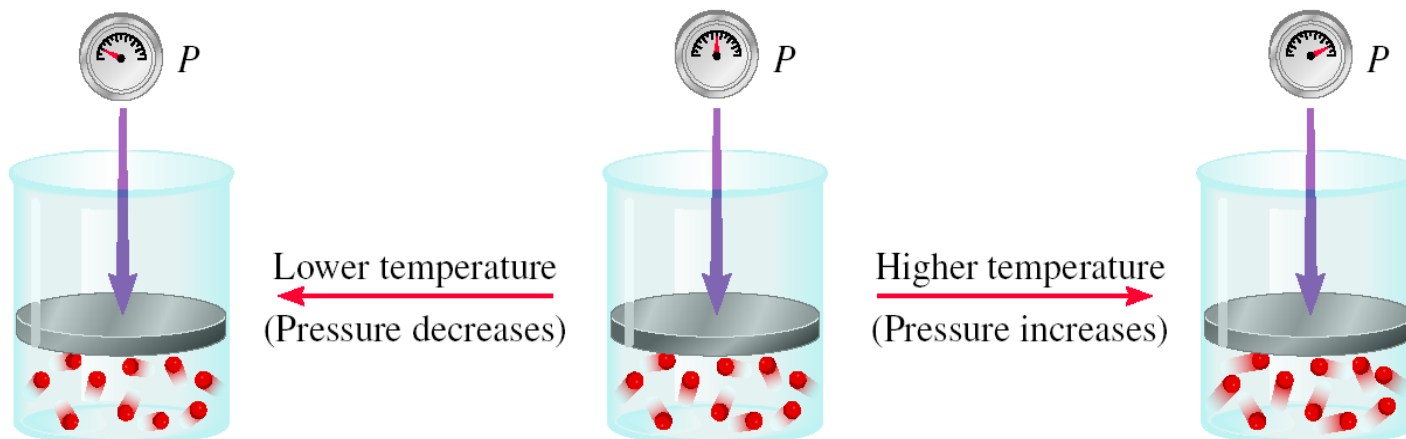
Heating or cooling a gas at constant pressure



Charles's Law

$$V = \left(\frac{nR}{P}\right) T \quad \frac{nR}{P} \text{ is constant}$$

Heating or cooling a gas at constant volume

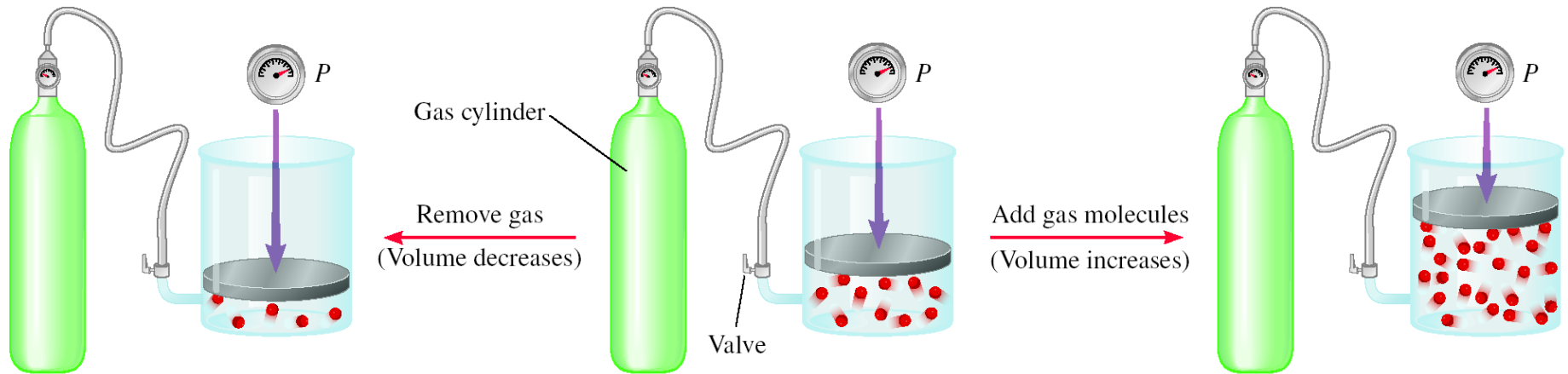


Charles's Law

$$P = \left(\frac{nR}{V}\right) T \quad \frac{nR}{V} \text{ is constant}$$

Avogadro's Law

Dependence of volume on amount
of gas at constant temperature and pressure



Avogadro's Law

$$V = \left(\frac{RT}{P}\right)n \quad \frac{RT}{P} \text{ is constant}$$

Ideal Gas Equation

Boyle's law: $P \propto \frac{1}{V}$ (at constant n and T)

Charles' law: $V \propto T$ (at constant n and P)

Avogadro's law: $V \propto n$ (at constant P and T)

$$V \propto \frac{nT}{P}$$

$$V = \text{constant} \times \frac{nT}{P} = R \frac{nT}{P} \quad R \text{ is the } \mathbf{gas\ constant}$$

$$PV = nRT$$

Standard Temperature and Pressure

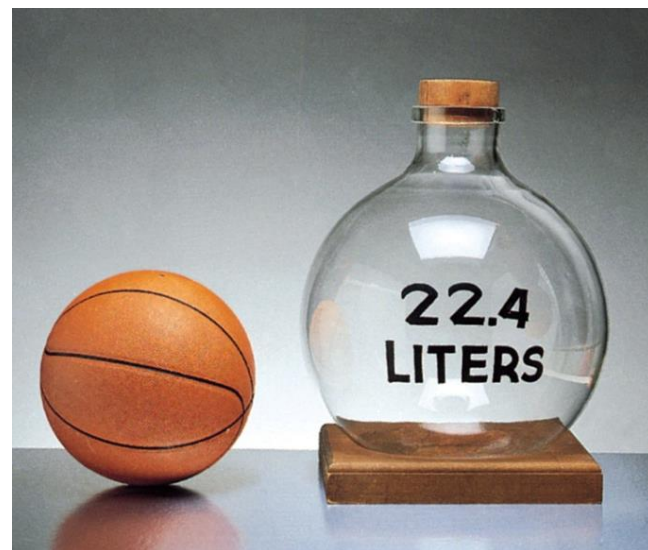
The conditions 0 °C and 1 atm are called **standard temperature and pressure (STP)**.

Experiments show that at STP, 1 mole of an ideal gas occupies 22.414 L.

$$PV = nRT$$

$$R = \frac{PV}{nT} = \frac{(1 \text{ atm})(22.414 \text{ L})}{(1 \text{ mol})(273.15 \text{ K})}$$

$$R = 0.082057 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K}$$



It is a hypothetical gas which follows ideal gas equation

Ideal gas:

- ❑ don't attract or repel one another
- ❑ Its volume is negligible compare to the volume of the container

If all variables change, we use:

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2} \quad \text{In general, } n_1 = n_2 \text{ thus } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

What is the volume (in liters) occupied by 49.8 g of HCl at STP?

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

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

$$PV = nRT$$

$$n = 49.8\text{ g} \times \frac{1\text{ mol HCl}}{36.45\text{ g HCl}} = 1.37\text{ mol}$$

$$V = \frac{nRT}{P}$$

$$V = \frac{1.37\text{ mol} \times 0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \times 273.15\text{ K}}{1\text{ atm}}$$

$$V = 30.7\text{ L}$$

Argon is an inert gas used in lightbulbs to retard the vaporization of the filament. A certain lightbulb containing argon at 1.20 atm and 18 °C is heated to 85 °C at constant volume. What is the final pressure of argon in the lightbulb (in atm)?

$$PV = nRT \quad n, V \text{ and } R \text{ are constant}$$

$$\frac{nR}{V} = \frac{P}{T} = \text{constant}$$

$$P_1 = 1.20 \text{ atm} \quad P_2 = ?$$

$$T_1 = 291 \text{ K} \quad T_2 = 358 \text{ K}$$

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

$$P_2 = P_1 \times \frac{T_2}{T_1} = 1.20 \text{ atm} \times \frac{358 \text{ K}}{291 \text{ K}} = \mathbf{1.48 \text{ atm}}$$



EXAMPLE 5.3

Sulfur hexafluoride (SF_6) is a colorless, odorless, very unreactive gas. Calculate the pressure (in atm) exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 L at 69.5°C .

Strategy The problem gives the amount of the gas and its volume and temperature. Is the gas undergoing a change in any of its properties? What equation should we use to solve for the pressure? What temperature unit should we use?

Solution Because no changes in gas properties occur, we can use the ideal gas equation to calculate the pressure. Rearranging Equation (5.8), we write

$$\begin{aligned} P &= \frac{nRT}{V} \\ &= \frac{(1.82 \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(69.5 + 273) \text{ K}}{5.43 \text{ L}} \\ &= 9.42 \text{ atm} \end{aligned}$$

EXAMPLE 5.4

Calculate the volume (in liters) occupied by 7.40 g of NH_3 at STP.

Strategy What is the volume of one mole of an ideal gas at STP? How many moles are there in 7.40 g of NH_3 ?

Solution Recognizing that 1 mole of an ideal gas occupies 22.41 L at STP and using the molar mass of NH_3 (17.03 g), we write the sequence of conversions as

grams of NH_3 $\longrightarrow$ moles of NH_3 $\longrightarrow$ liters of NH_3 at STP

so the volume of NH_3 is given by

$$\begin{aligned} V &= 7.40 \text{ g } \cancel{\text{NH}_3} \times \frac{1 \cancel{\text{ mol NH}_3}}{17.03 \text{ g } \cancel{\text{NH}_3}} \times \frac{22.41 \text{ L}}{1 \cancel{\text{ mol NH}_3}} \\ &= 9.74 \text{ L} \end{aligned}$$

It is often true in chemistry, particularly in gas-law calculations, that a problem can be solved in more than one way. Here the problem can also be solved by first converting 7.40 g of NH_3 to number of moles of NH_3 , and then applying the ideal gas equation ($V = nRT/P$). Try it.

Examples

1) 20.8 g of CH_4 gas was confined in 5.200 L vessel at 50°C . Calculate the pressure exerted by the gas?

$$\mathcal{M}_{\text{CH}_4} = 16.04 \text{ g mol}^{-1}$$

6.529 atm

2) 1.05 L balloon at 25°C , Calculate its volume in a summer day at 50°C ?

1.138 L

3) Gas volume is 2.31 L at 1 atm, Calculate its pressure in mmHg when its volume becomes 7.32 L?

239.8 mmHg

Density (d) Calculations

$$d = \frac{m}{V} = \frac{P\mathcal{M}}{RT}$$

m is the mass of the gas in g
 $\mathcal{M}$ is the molar mass of the gas

Molar Mass ($\mathcal{M}$) of a Gaseous Substance

$$\mathcal{M} = \frac{dRT}{P}$$

d is the density of the gas in g/L

A 2.10-L vessel contains 4.65 g of a gas at 1.00 atm and 27.0 °C. What is the molar mass of the gas?

$$\mathcal{M} = \frac{dRT}{P}$$

$$d = \frac{m}{V} = \frac{4.65 \text{ g}}{2.10 \text{ L}} = 2.21 \frac{\text{g}}{\text{L}}$$

$$\mathcal{M} = \frac{2.21 \frac{\text{g}}{\text{L}} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 300.15 \text{ K}}{1 \text{ atm}}$$

$$\mathcal{M} = 54.5 \text{ g/mol}$$

EXAMPLE 5.9

A chemist has synthesized a greenish-yellow gaseous compound of chlorine and oxygen and finds that its density is 7.71 g/L at 36°C and 2.88 atm. Calculate the molar mass of the compound and determine its molecular formula.

Strategy Because Equations (5.11) and (5.12) are rearrangements of each other, we can calculate the molar mass of a gas if we know its density, temperature, and pressure. The molecular formula of the compound must be consistent with its molar mass. What temperature unit should we use?

Solution From Equation (5.12)

$$\begin{aligned}\mathcal{M} &= \frac{dRT}{P} \\ &= \frac{(7.71 \text{ g/L})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(36 + 273) \text{ K}}{2.88 \text{ atm}} \\ &= 67.9 \text{ g/mol}\end{aligned}$$

(Continued)

Alternatively, we can solve for the molar mass by writing

$$\text{molar mass of compound} = \frac{\text{mass of compound}}{\text{moles of compound}}$$

From the given density we know there are 7.71 g of the gas in 1 L. The number of moles of the gas in this volume can be obtained from the ideal gas equation

$$\begin{aligned} n &= \frac{PV}{RT} \\ &= \frac{(2.88 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(309 \text{ K})} \\ &= 0.1135 \text{ mol} \end{aligned}$$

Therefore, the molar mass is given by

$$\mathcal{M} = \frac{\text{mass}}{\text{number of moles}} = \frac{7.71 \text{ g}}{0.1135 \text{ mol}} = 67.9 \text{ g/mol}$$

We can determine the molecular formula of the compound by trial and error, using only the knowledge of the molar masses of chlorine (35.45 g) and oxygen (16.00 g). We know that a compound containing one Cl atom and one O atom would have a molar mass of 51.45 g, which is too low, while the molar mass of a compound made up of two Cl atoms and one O atom is 86.90 g, which is too high. Thus, the compound must contain one Cl atom and two O atoms and have the formula ClO_2 , which has a molar mass of 67.45 g.

EXAMPLE 5.10

Chemical analysis of a gaseous compound showed that it contained 33.0 percent silicon (Si) and 67.0 percent fluorine (F) by mass. At 35°C, 0.210 L of the compound exerted a pressure of 1.70 atm. If the mass of 0.210 L of the compound was 2.38 g, calculate the molecular formula of the compound.

Strategy This problem can be divided into two parts. First, it asks for the empirical formula of the compound from the percent by mass of Si and F. Second, the information provided enables us to calculate the molar mass of the compound and hence determine its molecular formula. What is the relationship between empirical molar mass and molar mass calculated from the molecular formula?

Solution We follow the procedure in Example 3.9 (p. 90) to calculate the empirical formula by assuming that we have 100 g of the compound, so the percentages are converted to grams. The number of moles of Si and F are given by

$$n_{\text{Si}} = 33.0 \text{ g Si} \times \frac{1 \text{ mol Si}}{28.09 \text{ g Si}} = 1.17 \text{ mol Si}$$
$$n_{\text{F}} = 67.0 \text{ g F} \times \frac{1 \text{ mol F}}{19.00 \text{ g F}} = 3.53 \text{ mol F}$$

(Continued)

Therefore, the empirical formula is $\text{Si}_{1.17}\text{F}_{3.53}$, or, dividing by the smaller subscript (1.17), we obtain SiF_3 .

To calculate the molar mass of the compound, we need first to calculate the number of moles contained in 2.38 g of the compound. From the ideal gas equation

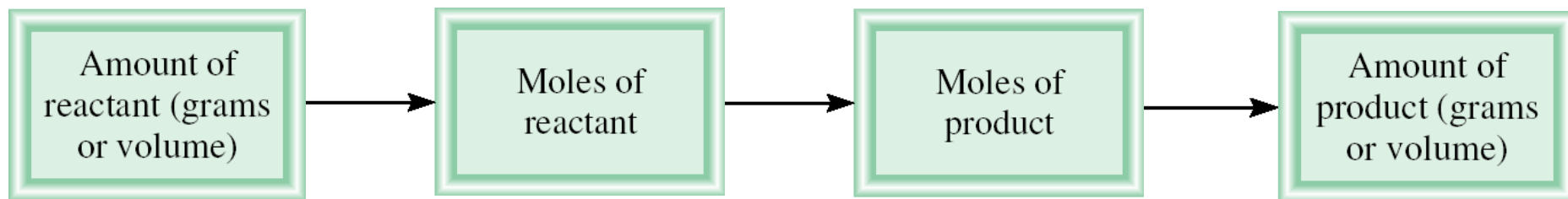
$$\begin{aligned} n &= \frac{PV}{RT} \\ &= \frac{(1.70 \text{ atm})(0.210 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(308 \text{ K})} = 0.0141 \text{ mol} \end{aligned}$$

Because there are 2.38 g in 0.0141 mole of the compound, the mass in 1 mole, or the molar mass, is given by

$$\mathcal{M} = \frac{2.38 \text{ g}}{0.0141 \text{ mol}} = 169 \text{ g/mol}$$

The molar mass of the empirical formula SiF_3 is 85.09 g. Recall that the ratio (molar mass/empirical molar mass) is always an integer ($169/85.09 \approx 2$). Therefore, the molecular formula of the compound must be $(\text{SiF}_3)_2$ or Si_2F_6 .

Gas Stoichiometry



What is the volume of CO_2 produced at 37°C and 1.00 atm when 5.60 g of glucose are used up in the reaction:

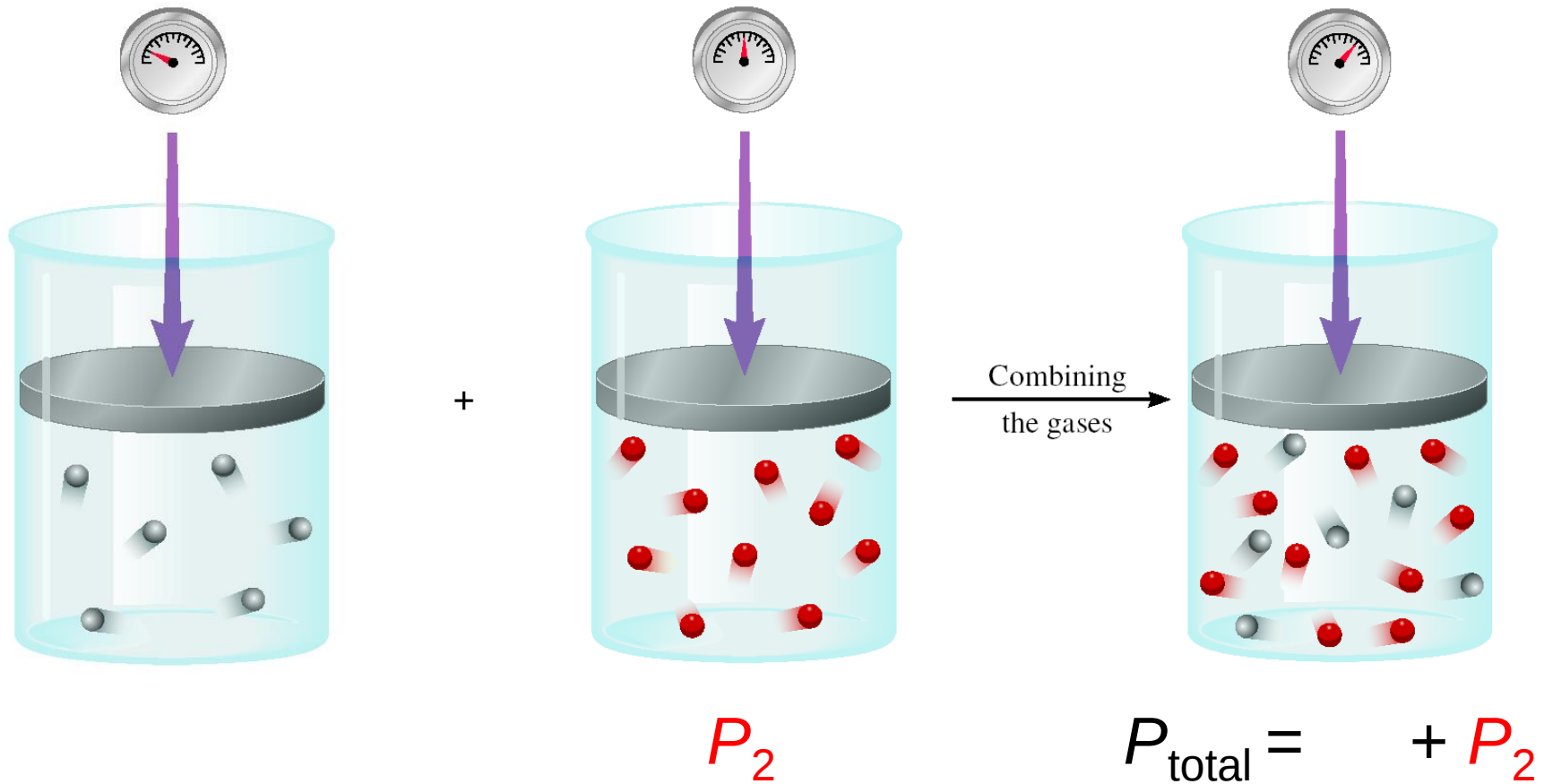


$$5.60 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6} \times \frac{1 \text{ mol } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}}{180 \text{ g } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}} \times \frac{6 \text{ mol CO}_2}{1 \text{ mol } \cancel{\text{C}_6\text{H}_{12}\text{O}_6}} = 0.187 \text{ mol CO}_2$$

$$V = \frac{nRT}{P} = \frac{0.187 \text{ mol} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 310.15 \text{ K}}{1.00 \text{ atm}} = 4.76 \text{ L}$$

Dalton's Law of Partial Pressures

V and T are constant



Partial Pressures

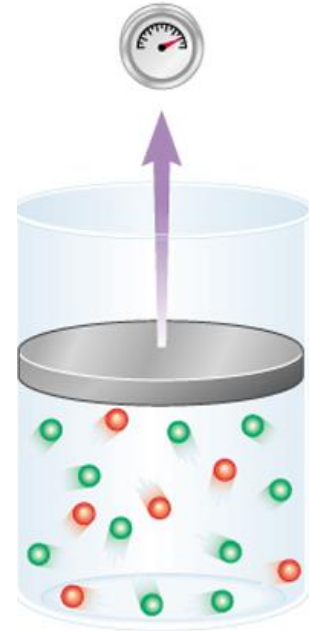
Consider a case in which two gases **A** and **B**, are in a container of volume V .

$$P_A = \frac{n_A RT}{V}$$

n_A is the number of moles of **A**

$$P_B = \frac{n_B RT}{V}$$

n_B is the number of moles of **B**



Partial Pressures

$$P_T = P_A + P_B$$

$$X_A = \frac{n_A}{n_A + n_B}$$

$$X_B = \frac{n_B}{n_A + n_B}$$

$$P_A = X_A P_T$$

$$P_B = X_B P_T$$

$$P_i = X_i P_T$$

$$\text{mole fraction } (X_i) = \frac{n_i}{n_T}$$

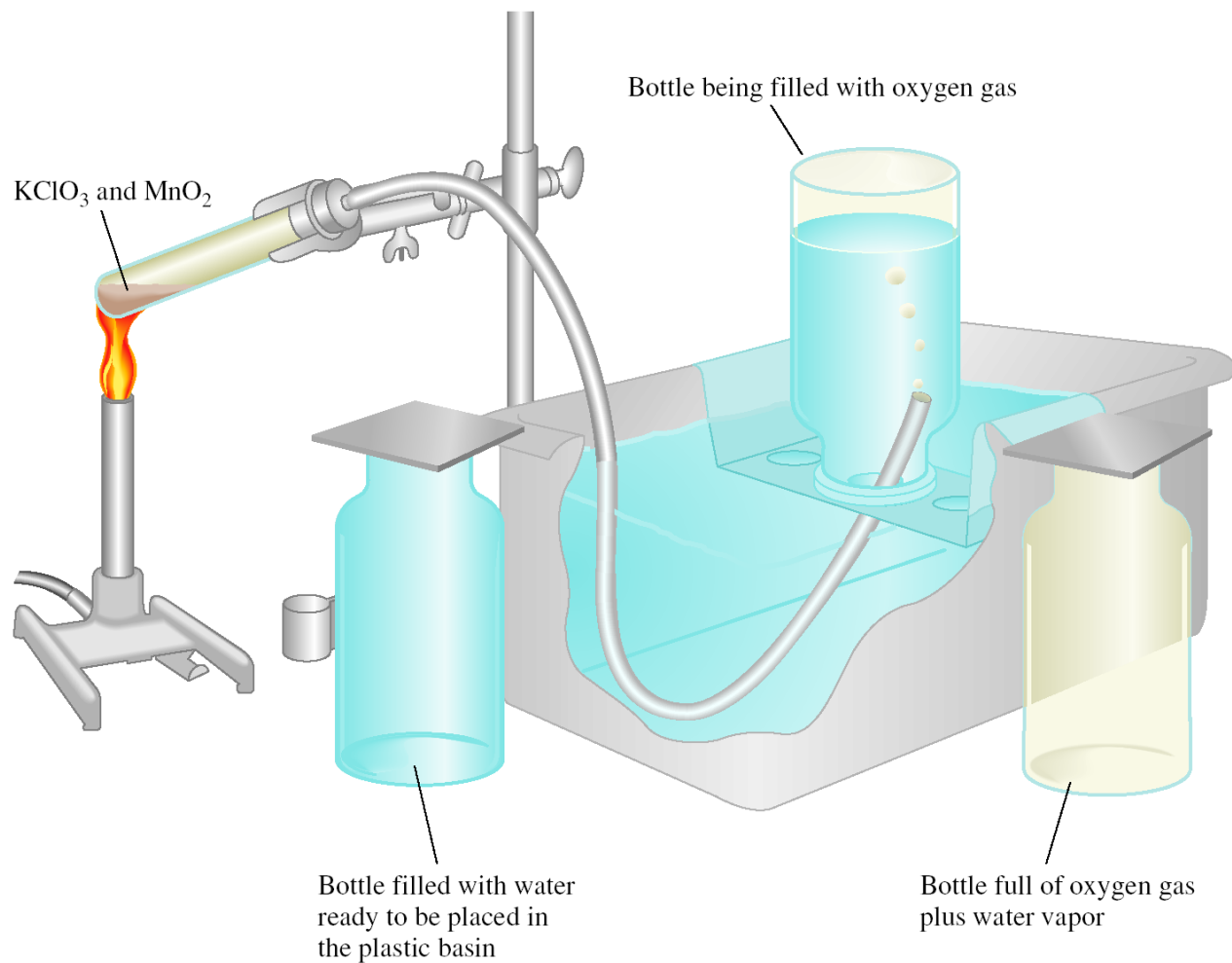
A sample of natural gas contains 8.24 moles of CH_4 , 0.421 moles of C_2H_6 , and 0.116 moles of C_3H_8 . If the total pressure of the gases is 1.37 atm, what is the partial pressure of propane (C_3H_8)?

$$P_i = X_i P_T \quad P_T = 1.37 \text{ atm}$$

$$X_{\text{propane}} = \frac{0.116}{8.24 + 0.421 + 0.116} = 0.0132$$

$$P_{\text{propane}} = 0.0132 \times 1.37 \text{ atm} = \mathbf{0.0181 \text{ atm}}$$

Collecting a Gas over Water



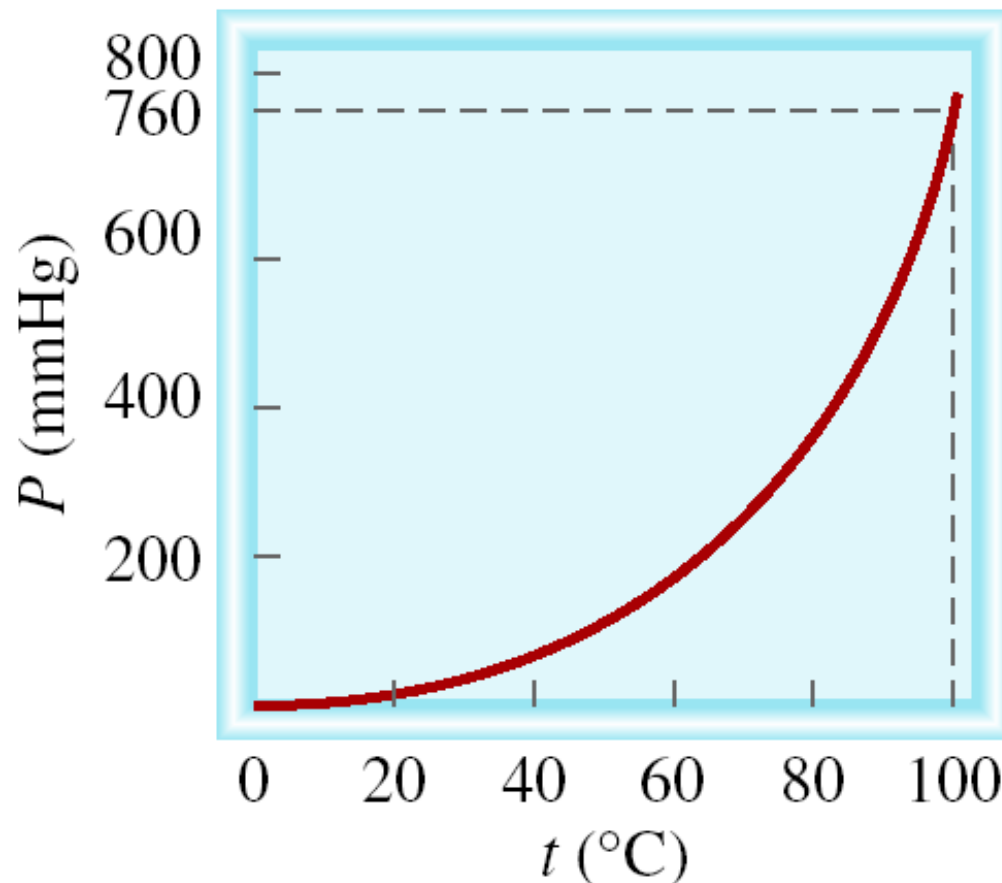
$$P_{\text{T}} = P_{\text{O}_2} + P_{\text{H}_2\text{O}}$$

Vapor of Water and Temperature

TABLE 5.3

Pressure of Water Vapor
at Various Temperatures

Temperature (°C)	Water Vapor Pressure (mmHg)
0	4.58
5	6.54
10	9.21
15	12.79
20	17.54
25	23.76
30	31.82
35	42.18
40	55.32
45	71.88
50	92.51
55	118.04
60	149.38
65	187.54
70	233.7
75	289.1
80	355.1
85	433.6
90	525.76
95	633.90
100	760.00



EXAMPLE 5.15

Oxygen gas generated by the decomposition of potassium chlorate is collected as shown in Figure 5.15. The volume of oxygen collected at 24°C and atmospheric pressure of 762 mmHg is 128 mL. Calculate the mass (in grams) of oxygen gas obtained. The pressure of the water vapor at 24°C is 22.4 mmHg.

Solution From Dalton's law of partial pressures we know that

$$P_T = P_{O_2} + P_{H_2O}$$

Therefore,

$$\begin{aligned}P_{O_2} &= P_T - P_{H_2O} \\&= 762 \text{ mmHg} - 22.4 \text{ mmHg} \\&= 740 \text{ mmHg}\end{aligned}$$

From the ideal gas equation we write

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

where m and $\mathcal{M}$ are the mass of O_2 collected and the molar mass of O_2 , respectively. Rearranging the equation we obtain

$$\begin{aligned}m &= \frac{PV\mathcal{M}}{RT} = \frac{(740/760)\text{atm}(0.128 \text{ L})(32.00 \text{ g/mol})}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(273 + 24) \text{ K}} \\&= 0.164 \text{ g}\end{aligned}$$

Calculate the mass of $\text{Zn}_{(s)}$ used to produce $\text{H}_{2(g)}$ over water at 25.0°C in a 7.80 L vessel and pressure 0.980 atm knowing that $p_{\text{H}_2\text{O}} = 23.8\text{ mmHg}$ according to the following equation:



$$m_{\text{Zn}} = 19.8\text{ g}$$

Kinetic Molecular Theory of Gases

1. A gas is composed of molecules that are separated from each other by **distances** far greater than their own dimensions. The molecules can be considered to be **points**; that is, they possess mass but have **negligible volume**.
2. Gas molecules are in constant motion in **random directions**, and they frequently collide with one another. **Collisions** among molecules are perfectly elastic.
3. Gas molecules exert **neither attractive nor repulsive** forces on one another.
4. The average kinetic energy of the molecules is proportional to the temperature of the gas in kelvins. **Any two gases at the same temperature will have the same average kinetic energy**

$$\overline{\text{KE}} = \frac{1}{2} m \overline{u^2}$$

Kinetic theory of gases

- Compressibility of Gases
- Boyle's Law

$P \propto$ collision rate with wall

Collision rate $\propto$ number density

Number density $\propto 1/V$

$P \propto 1/V$

- Charles' Law

$P \propto$ collision rate with wall

Collision rate $\propto$ average kinetic energy of gas molecules

Average kinetic energy $\propto T$

$P \propto T$

Kinetic theory of gases

- Avogadro's Law

$P \propto$ collision rate with wall

Collision rate $\propto$ number density

Number density $\propto n$

$$P \propto n$$

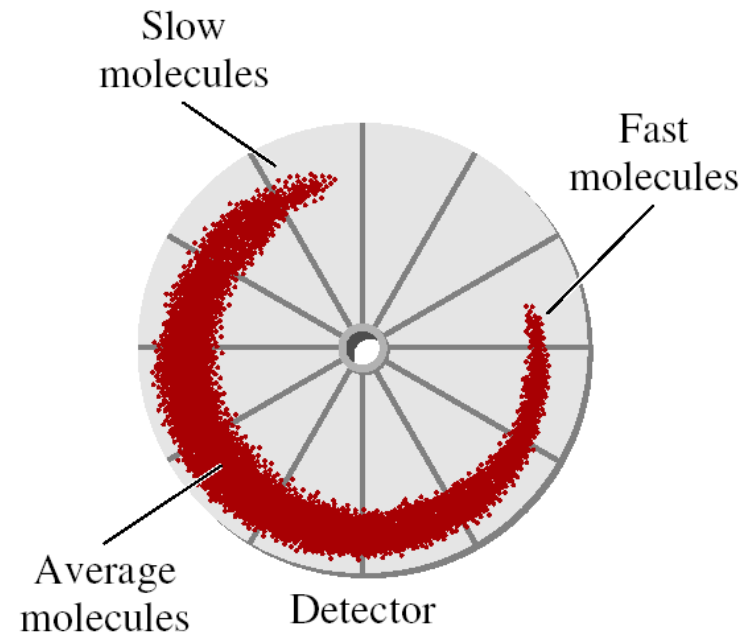
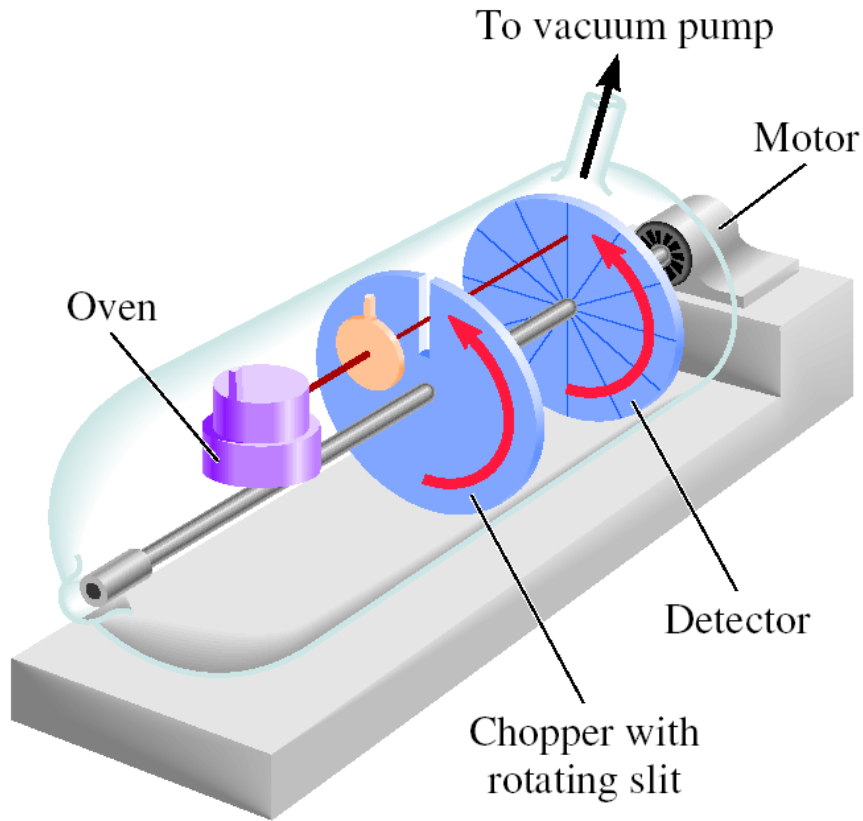
- Dalton's Law of Partial Pressures

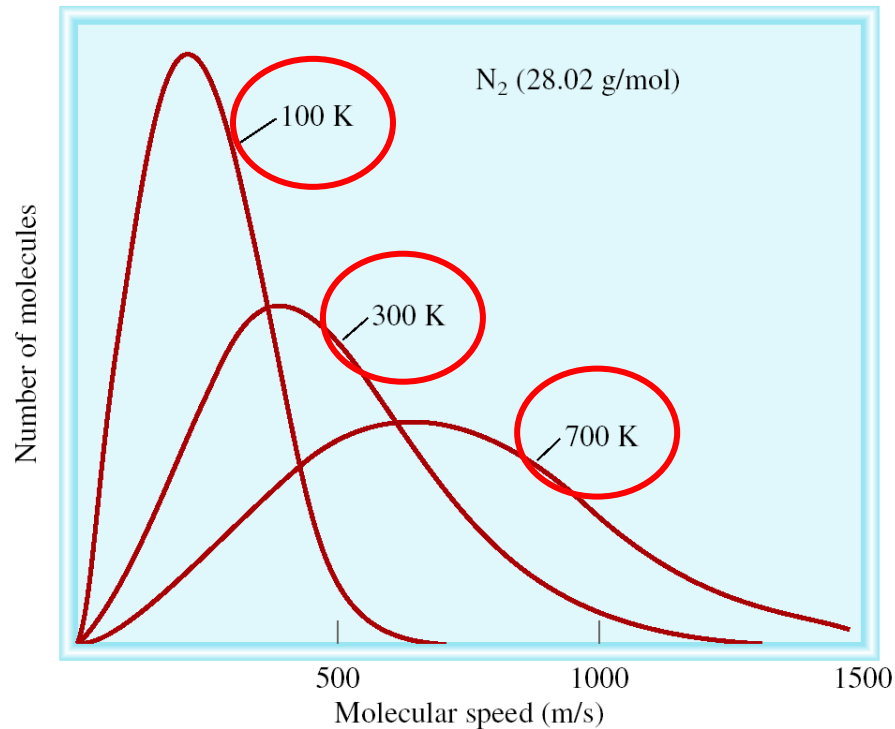
Molecules do not attract or repel one another

P exerted by one type of molecule is unaffected by the presence of another gas

$$P_{\text{total}} = \sum P_i$$

Apparatus for Studying Molecular Speed Distribution



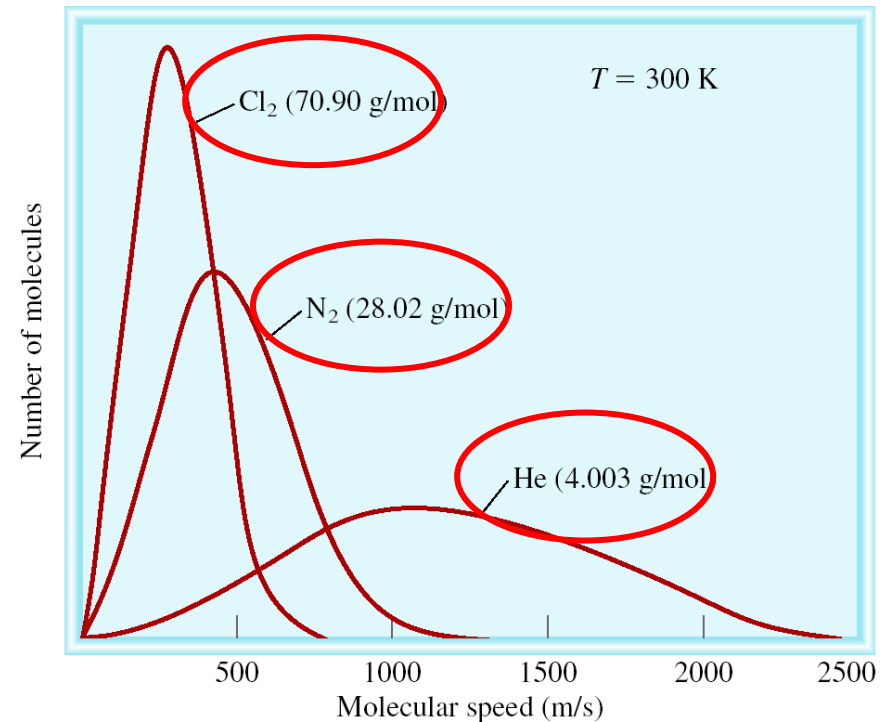


The distribution of speeds for nitrogen gas molecules at three **different temperatures**

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

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

The distribution of speeds of three **different gases** at the same temperature



EXAMPLE 5.16

Calculate the root-mean-square speeds of helium atoms and nitrogen molecules in m/s at 25°C.

Strategy To calculate the root-mean-square speed we need Equation (5.16). What units should we use for R and $\mathcal{M}$ so that u_{rms} will be expressed in m/s?

Solution To calculate u_{rms} , the units of R should be $8.314 \text{ J/K} \cdot \text{mol}$ and, because $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$, the molar mass must be in kg/mol . The molar mass of He is 4.003 g/mol , or $4.003 \times 10^{-3} \text{ kg/mol}$. From Equation (5.16),

$$\begin{aligned} u_{\text{rms}} &= \sqrt{\frac{3RT}{\mathcal{M}}} \\ &= \sqrt{\frac{3(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K})}{4.003 \times 10^{-3} \text{ kg/mol}}} \\ &= \sqrt{1.86 \times 10^6 \text{ J/kg}} \end{aligned}$$

Using the conversion factor $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$ we get

$$\begin{aligned} u_{\text{rms}} &= \sqrt{1.86 \times 10^6 \text{ kg m}^2/\text{kg} \cdot \text{s}^2} \\ &= \sqrt{1.86 \times 10^6 \text{ m}^2/\text{s}^2} \\ &= 1.36 \times 10^3 \text{ m/s} \end{aligned}$$

Continue ..

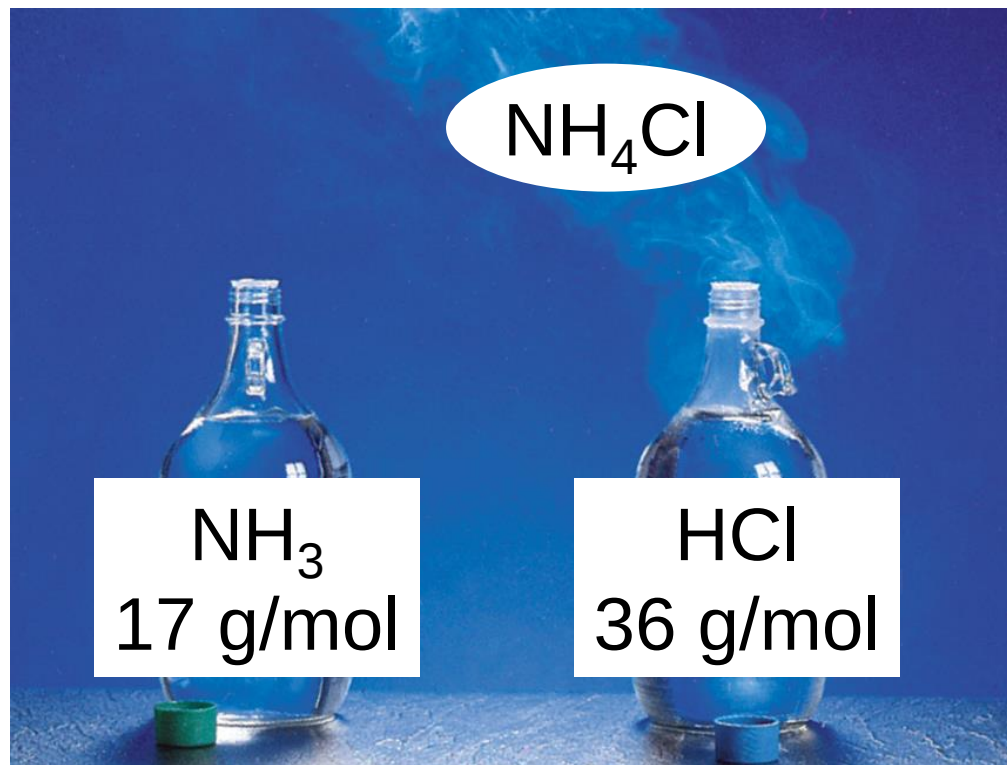
The procedure is the same for N₂, the molar mass of which is 28.02 g/mol, or 2.802×10^{-2} kg/mol so that we write

$$\begin{aligned} u_{\text{rms}} &= \sqrt{\frac{3(8.314 \text{ J/K} \cdot \text{mole})(298 \text{ K})}{2.802 \times 10^{-2} \text{ kg/mol}}} \\ &= \sqrt{2.65 \times 10^5 \text{ m}^2/\text{s}^2} \\ &= 515 \text{ m/s} \end{aligned}$$

Gas diffusion is the gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic properties.



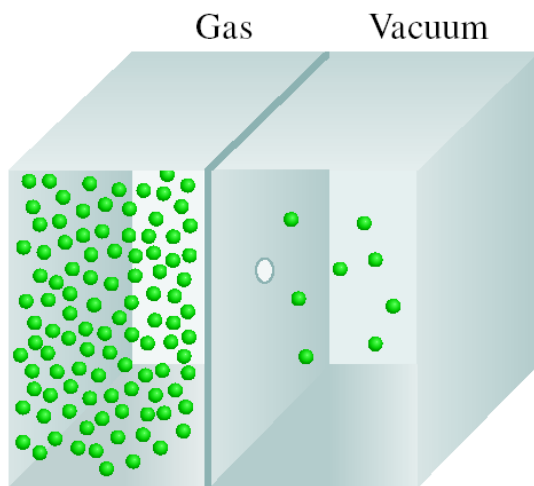
molecular path



Graham's law of diffusion under the same conditions of T and P, rates of diffusion for gases are inversely proportional to the square roots of their molar masses.

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

Gas effusion is the process by which gas under pressure escapes from one compartment of a container to another by passing through a small opening.



$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

Nickel forms a gaseous compound of the formula $\text{Ni}(\text{CO})_x$
 What is the value of x given that under the same conditions methane (CH_4) effuses 3.3 times faster than the compound?

$$r_1 = 3.3 \times r_2 \quad \mathcal{M}_2 = \left(\frac{r_1}{r_2}\right)^2 \times \mathcal{M}_1 \quad 58.7 + (x \cdot 28) = 174.2$$

$$\mathcal{M}_1 = 16 \text{ g/mol} \quad = (3.3)^2 \times 16 = 174.2 \quad x = 4.1 \sim 4$$

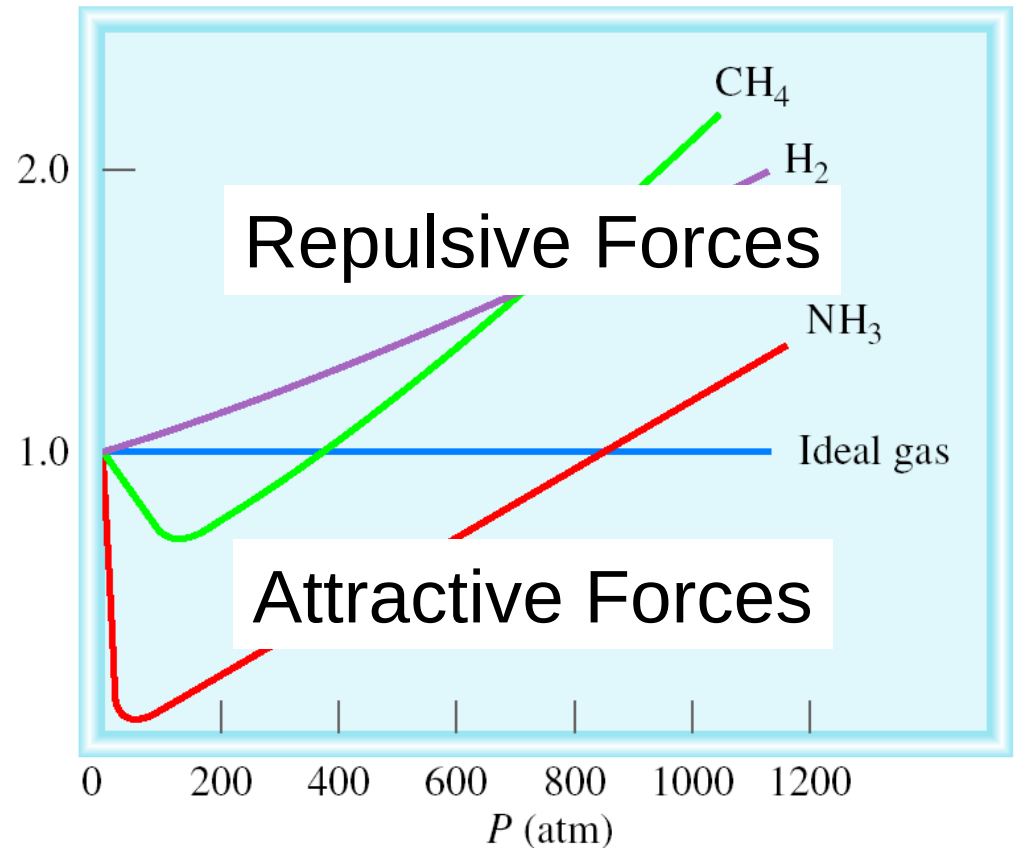
Deviations from Ideal Behavior

1 mole of ideal gas

$$PV = nRT$$

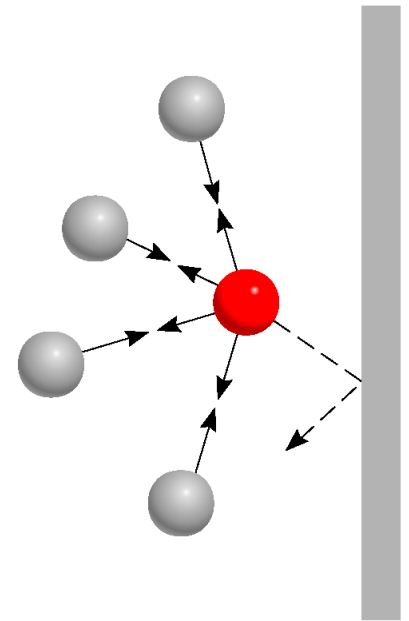
$$n = \frac{PV}{RT} = 1.0$$

$$\frac{PV}{RT}$$



Effect of intermolecular forces on the pressure exerted by a gas

- When a gas particle experiences attractive forces from other gas particles, its behavior changes.
- When it approaches the wall of a container, the particle is "pulled back" by the attractive forces present.
- These attractive forces prevent the particle from imparting its full force on the wall of a container, **decreasing the pressure** within the container.
- The speed of a molecule that is moving toward the container wall (red sphere) is reduced by the attractive forces exerted by its neighbors (gray spheres). **behaved non-ideally.**



Van der Waals equation nonideal gas

$$\underbrace{\left(P + \frac{an^2}{V^2}\right)}_{\text{corrected pressure}} \underbrace{(V - nb)}_{\text{corrected volume}} = nRT$$

TABLE 5.4

van der Waals Constants
of Some Common Gases

Gas	a $\left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}\right)$	b $\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0266
H ₂	0.244	0.0266
N ₂	1.39	0.0391
O ₂	1.36	0.0318
Cl ₂	6.49	0.0562
CO ₂	3.59	0.0427
CH ₄	2.25	0.0428
CCl ₄	20.4	0.138
NH ₃	4.17	0.0371
H ₂ O	5.46	0.0305

Given that 3.50 moles of NH_3 occupy 5.20 L at 47°C , calculate the pressure of the gas (in atm) using:
a) the ideal gas equation
b) the van der Waals equation.

$$\text{a) } P = \frac{nRT}{V} = \frac{(3.50 \text{ mol})(0.0821 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol})(320 \text{ K})}{5.20 \text{ L}} = \mathbf{17.7 \text{ atm}}$$

$$\text{b) } \frac{an^2}{V^2} = \frac{(4.17 \text{ atm}\cdot\text{L}^2/\text{mol}^2)(3.50 \text{ mol})^2}{(5.20 \text{ L})^2} = 1.89 \text{ atm}$$

$$nb = (3.50 \text{ mol})(0.0371 \text{ L/mol}) = 0.130 \text{ L}$$

$$(P + 1.89 \text{ atm})(5.20 \text{ L} - 0.130 \text{ L}) = (3.50 \text{ mol})(0.0821 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol})(320 \text{ K})$$

$$\mathbf{P = 16.2 \text{ atm}}$$