

Gases and the Kinetic Molecular Theory

- Importance in atmospheric phenomena, gas phase reactions, combustion engines, etc.

5.1 The Physical States of Matter

- The condensed states – liquid and solid
- The gaseous state
 - Gas volume changes greatly with pressure
 - Gas volume changes greatly with temperature
 - Gases have low viscosity (flow easily)
 - Gases have low density (~1000 times lower than liquids and solids)
 - Gases are miscible in all proportions

- Molecular model of the gaseous state
 - Molecules are in constant, rapid, random motion (explains the absence of definite shape, miscibility, low viscosity)
 - Molecules are widely separated (explains the absence of definite volume, low density, compressibility)

5.2 Pressure

- Gas molecules collide with each other and the walls of the container → molecules exert force on the walls

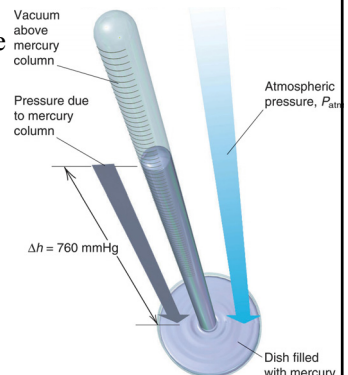
$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

$$P = \frac{F}{A}$$

- **Atmospheric pressure (P_{atm})** – caused by the gravitational pull of the Earth → molecules exert force on all objects

➤ **Barometers** - measure the atmospheric pressure (Torricelli)

- no pressure above the mercury column (vacuum)
- the weight of the Hg column balances P_{atm}
- the height of the Hg column is proportional to P_{atm}



- g - acceleration of free fall (9.81 m/s^2)
- d - density of Hg (13546 kg/m^3)
- V - volume of Hg column
- h - height of Hg column (0.760 m at sea level)
- A - area of Hg column base

$$P_{atm} = P_{Hg} = \frac{F}{A} \quad F = m_{Hg}g$$

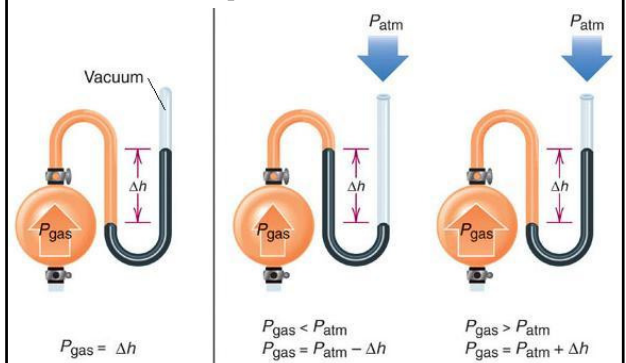
$$m_{Hg} = dV = dhA \quad \Rightarrow \quad F = dhAg$$

$$\Rightarrow P_{atm} = \frac{dhAg}{A} = dhg$$

$$P_{atm} = 13546 \times 0.760 \times 9.81 = 1.01 \times 10^5 \text{ kg} / \text{m} \cdot \text{s}^2$$

➤ **Manometers** – measure the pressure of gases in containers

- **Close-end and open-end manometers**



Units of Pressure

- SI unit → pascal (Pa)

$$1 \text{ Pa} = 1 \text{ N/m}^2 = 1 \text{ kg/m}\cdot\text{s}^2$$

$$P_{\text{atm}} = 1.01 \times 10^5 \text{ Pa} \quad (\text{at sea level})$$

- Conventional units:

$$\text{atm} \rightarrow 1 \text{ atm} = 101325 \text{ Pa} \quad (\text{exactly})$$

$$\text{bar} \rightarrow 1 \text{ bar} = 100000 \text{ Pa} \quad (\text{exactly})$$

$$\text{torr} \rightarrow 760 \text{ Torr} = 1 \text{ atm} \quad (\text{exactly})$$

$$\text{mm Hg} \rightarrow 1 \text{ mmHg} = 1 \text{ Torr}$$

$$\text{lb/in}^2 \rightarrow 14.7 \text{ lb/in}^2 = 1 \text{ atm}$$

Example:

Convert **630.0 Torr** to atmospheres and kilopascals.

$$630.0 \text{ Torr} \times \left(\frac{1 \text{ atm}}{760 \text{ Torr}} \right) = 0.8289 \text{ atm}$$

$$630.0 \text{ Torr} \times \left(\frac{1 \text{ atm}}{760 \text{ Torr}} \right) \times \left(\frac{101325 \text{ Pa}}{1 \text{ atm}} \right) = 8.399 \times 10^4 \text{ Pa} = 83.99 \text{ kPa}$$

5.3 The Gas Laws

- Relate the parameters of the gaseous state – pressure, volume, temperature, and number of moles

Boyle's Law

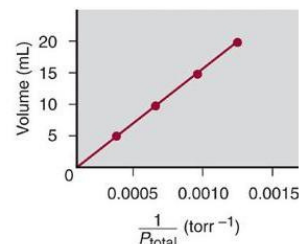
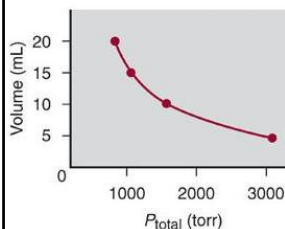
- At constant temperature (T) the pressure (P) of a fixed amount of gas is inversely proportional to its volume (V)

⇒ At constant T and n :

$$P = \frac{k}{V} \quad k \rightarrow \text{constant (depends on } T \text{ and } n)$$

$$PV = k = \text{constant} \quad V \downarrow \Leftrightarrow P \uparrow$$

V (mL)	P (torr)	$\frac{1}{P}$	PV (torr • mL)
20.0	780	0.00128	1.56×10^4
15.0	1038	0.000963	1.56×10^4
10.0	1560	0.000641	1.56×10^4
5.0	3112	0.000321	1.56×10^4



- Assume two states of a gas at constant T

– state 1 → P_1, V_1

– state 2 → P_2, V_2

$$P_1 V_1 = k \quad P_2 V_2 = k$$

$$P_1 V_1 = P_2 V_2$$

Example: A 2.0 L sample of oxygen at 10 atm is transferred to a 15.0 L container at constant temperature. What is the new pressure?

$$V_1 = 2.0 \text{ L} \quad P_1 = 10 \text{ atm} \quad V_2 = 15.0 \text{ L} \quad P_2 = ?$$

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{10 \text{ atm} \times 2.0 \text{ L}}{15.0 \text{ L}} = 1.3 \text{ atm}$$

Charles's Law

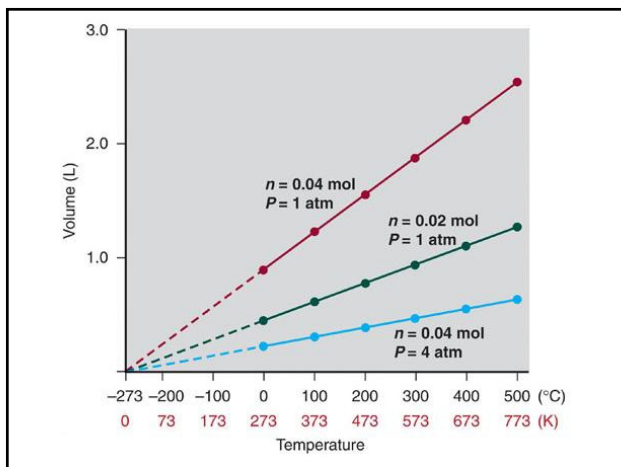
- At constant pressure (P) the volume (V) of a fixed amount of gas is proportional to its absolute temperature (T)

⇒ At constant P and n :

$$V = k' T \quad k' \rightarrow \text{constant (depends on } P \text{ and } n)$$

$$\frac{V}{T} = k' \quad T \uparrow \Leftrightarrow V \uparrow$$

- Charles's law helped devise the absolute temperature scale (Lord Kelvin)



- Assume two states of a gas at constant P

– state 1 $\rightarrow T_1, V_1$

– state 2 $\rightarrow T_2, V_2$

$$\frac{V_1}{T_1} = k' \quad \frac{V_2}{T_2} = k' \quad \Rightarrow \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Example: A balloon is filled with 5.0 L He gas at 15°C. The temperature is changed to 35°C. What is the new volume of the balloon?

$$T_1 = 15^\circ\text{C} = 288 \text{ K} \quad V_1 = 5.0 \text{ L}$$

$$T_2 = 35^\circ\text{C} = 308 \text{ K} \quad V_2 = ?$$

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{5.0 \text{ L} \times 308 \text{ K}}{288 \text{ K}} = 5.3 \text{ L}$$

Variations of Charles's law – Amontons's law

- At constant volume (V) the pressure (P) of a fixed amount of gas is proportional to its absolute temperature (T)

\Rightarrow At constant V and n :

$$P = k''T$$

$k'' \rightarrow$ constant (depends on V and n)

$$\frac{P}{T} = k'' \quad T \uparrow \Leftrightarrow P \uparrow$$

- Assume two states of a gas at constant V

– state 1 $\rightarrow T_1, P_1$

– state 2 $\rightarrow T_2, P_2$

$$\frac{P_1}{T_1} = k'' \quad \frac{P_2}{T_2} = k'' \quad \Rightarrow \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Example: A cylinder containing N_2 gas at 15°C and 50 atm is moved to a new location at 35°C. What is the new pressure in the cylinder?

$$T_1 = 15^\circ\text{C} = 288 \text{ K} \quad P_1 = 50 \text{ atm}$$

$$T_2 = 35^\circ\text{C} = 308 \text{ K} \quad P_2 = ?$$

$$P_2 = \frac{P_1 T_2}{T_1} = \frac{50 \text{ atm} \times 308 \text{ K}}{288 \text{ K}} = 53 \text{ atm}$$

Avogadro's Law

- At constant temperature (T) and pressure (P) the volume (V) of a gas is proportional to its amount (n)

– At constant T and P :

$$V = k'''n \quad k''' \rightarrow \text{constant (depends on } T, P)$$

$$\frac{V}{n} = k''' \quad n \uparrow \Leftrightarrow V \uparrow$$

- Molar volume (V_m) – the volume of one mole of a substance

$$V_m = V/n$$

- Avogadro's principle

– At constant T and P equal number of moles of different gases occupy equal volumes

– Molar volumes of gases are very similar ($V/n = \text{constant}$)

- Assume two states of a gas at constant T and P

– state 1 $\rightarrow V_1, n_1$

– state 2 $\rightarrow V_2, n_2$

$$\frac{V_1}{n_1} = k''' \quad \frac{V_2}{n_2} = k''' \quad \Rightarrow \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

The Ideal Gas Law

$$V = k \frac{1}{P} \quad \text{Boyle's Law}$$

$$V = k'T \quad \text{Charles's Law}$$

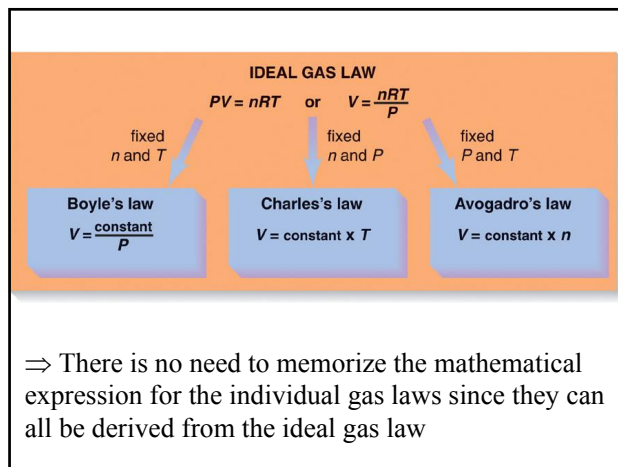
$$V = k''n \quad \text{Avogadro's Law}$$

- Combination of the three laws:

$$V = R \frac{nT}{P} \quad R - \text{proportionality constant}$$

$$PV = nRT \rightarrow \text{ideal gas law}$$

$$R \rightarrow \text{universal gas constant}$$



- **Ideal gas** – obeys the ideal gas law

- **R** is determined experimentally

$$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$$

$$R = 8.314 \text{ J}/\text{mol}\cdot\text{K}$$

- Assume two states of a gas

– state 1 → P_1, V_1, n_1, T_1

– state 2 → P_2, V_2, n_2, T_2

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

Note: T must always be in Kelvin

Example: A 5.0 L gas sample at 1.0 atm and 10°C is moved to a 2.0 L container and heated to 300°C. What is the new pressure?

$$P_1 = 1.0 \text{ atm} \quad V_1 = 5.0 \text{ L} \quad T_1 = 10^\circ\text{C} = 283 \text{ K}$$

$$P_2 = ? \quad V_2 = 2.0 \text{ L} \quad T_2 = 300^\circ\text{C} = 573 \text{ K}$$

$$n_1 = n_2$$

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2} \quad \Rightarrow \quad P_2 = \frac{P_1 V_1}{n_1 T_1} \times \frac{n_2 T_2}{V_2}$$

$$P_2 = \frac{P_1 V_1 T_2}{T_1 V_2} = \frac{1.0 \text{ atm} \times 5.0 \text{ L} \times 573 \text{ K}}{283 \text{ K} \times 2.0 \text{ L}} = 5.1 \text{ atm}$$

Example: A 3.0 g sample of methane, CH_4 , is placed in a 2.0 L container at 22°C. What is the pressure in the container?

$$PV = nRT$$

$$V = 2.0 \text{ L} \quad T = 22^\circ\text{C} = 295 \text{ K}$$

moles of CH_4 (n):

$$n = 3.0 \text{ g CH}_4 \times \left(\frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4} \right) = 0.19 \text{ mol CH}_4$$

$$P = \frac{nRT}{V} = \frac{0.19 \text{ mol} \times 0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \times 295 \text{ K}}{2.0 \text{ L}} = 2.3 \text{ atm}$$

Standard conditions

- Standard temperature and pressure (STP)

$$P = 1 \text{ atm}; \quad T = 0^\circ\text{C} = 273.15 \text{ K}$$

- The molar volume of the ideal gas at STP

$$V_m = \frac{V}{n} = \frac{nRT/P}{n} = \frac{RT}{P}$$

$$V_m = \frac{RT}{P} = \frac{0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \times 273.15 \text{ K}}{1 \text{ atm}} = 22.41 \frac{\text{L}}{\text{mol}}$$

5.4 Applications of the Ideal Gas Law

The molar mass and density of gasses

$$\text{density} = \frac{\text{mass}}{\text{volume}} \rightarrow d = \frac{m}{V}$$

$$\text{molar mass} = \frac{\text{mass}}{\text{moles}} \rightarrow M = \frac{m}{n} \rightarrow m = nM$$

$$PV = nRT \rightarrow n = \frac{PV}{RT}$$

$$d = \frac{m}{V} = \frac{nM}{V} = \frac{PVM}{RTV} \rightarrow d = \frac{MP}{RT} \rightarrow M = \frac{dRT}{P}$$

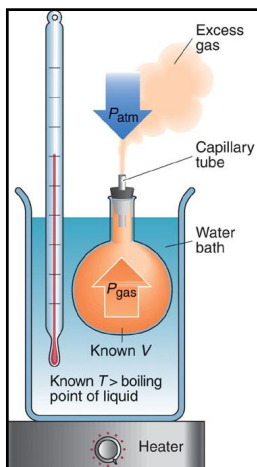
- The density of a gas is proportional to its molar mass and pressure and inversely proportional to its temperature

Example: Calculate the density of O₂ at STP.

$$M = 32.00 \text{ g/mol}$$

$$P = 1 \text{ atm} \quad T = 0^\circ\text{C} = 273.15 \text{ K} \quad (\text{STP})$$

$$d = \frac{MP}{RT} = \frac{32.00 \frac{\text{g}}{\text{mol}} \times 1 \text{ atm}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 273.15 \text{ K}} = 1.428 \frac{\text{g}}{\text{L}}$$



- Finding the molar mass of a volatile liquid

- Weigh a flask with a known volume
- Fill the flask with the vapors of the volatile liquid at a known temperature and pressure
- Cool the flask and let the vapors condense
- Reweigh the flask to get the mass of the vapors

Example: Calculate the molar mass of a liquid if 0.955 g of its vapors occupy 2.50 L at 200°C and 45.0 Torr.

$$d = m/V = 0.955 \text{ g}/2.50 \text{ L} = 0.382 \text{ g/L}$$

$$T = 200^\circ\text{C} = 473 \text{ K}$$

$$P = 45.0 \text{ Torr} \times [1 \text{ atm}/760 \text{ Torr}] = 0.0592 \text{ atm}$$

$$M = \frac{dRT}{P} = \frac{0.382 \frac{\text{g}}{\text{L}} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 473 \text{ K}}{0.0592 \text{ atm}} = 250 \frac{\text{g}}{\text{mol}}$$

Mixtures of Gasses

- Mixtures are treated just like pure gases – same gas laws apply
- Partial pressure** of a gas in a mixture – the pressure the gas would exert if it occupied the container alone
- Dalton's **law of partial pressures** – the total pressure (P) of a gaseous mixture is the sum of the partial pressures (P_i) of its components

$$P = P_A + P_B + \dots \quad \text{or} \quad P = \sum P_i$$

- Mole fraction** (χ_i) of a gas in a mixture – a fraction of the total number of moles that belongs to that gas

$$\chi_i = \frac{n_i}{\sum n_i} = \frac{n_i}{n} \quad \sum n_i = n \quad \sum \chi_i = 1$$

- The sum of all mol fractions is equal to one
- The ideal gas law can be written for each gas in a mixture in terms of partial pressures

$$P_i V = n_i RT \quad PV = nRT$$

$$\frac{P_i V}{P V} = \frac{n_i R T}{n R T} \quad \frac{P_i}{P} = \frac{n_i}{n} = \chi_i$$

$$P_i = \chi_i P$$

⇒ The partial pressure of a gas is proportional to its mol fraction

Example: Calculate the total pressure and the partial pressures of He and Ne in a 2.0 L mixture containing 1.0 g He and 2.0 g Ne at 20°C.

grams of He and Ne → moles of He and Ne → mole fractions of He and Ne

total pressure → partial pressures

$$1.0 \text{ g He} \times \left(\frac{1 \text{ mol He}}{4.00 \text{ g He}} \right) = 0.25 \text{ mol He}$$

$$2.0 \text{ g Ne} \times \left(\frac{1 \text{ mol Ne}}{20.18 \text{ g Ne}} \right) = 0.099 \text{ mol Ne}$$

$$\chi_{\text{He}} = \frac{n_{\text{He}}}{n_{\text{He}} + n_{\text{Ne}}} = \frac{0.25}{0.25 + 0.099} = 0.72$$

$$\chi_{\text{Ne}} = \frac{n_{\text{Ne}}}{n_{\text{He}} + n_{\text{Ne}}} = \frac{0.099}{0.25 + 0.099} = 0.28$$

$$n = 0.25 + 0.099 = 0.35 \text{ mol}$$

$$P V = n R T \quad \rightarrow \quad P = \frac{n R T}{V}$$

$$P = \frac{n R T}{V} =$$

$$= \frac{0.35 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 293 \text{ K}}{2.0 \text{ L}} =$$

$$= 4.2 \text{ atm}$$

$$P_{\text{He}} = \chi_{\text{He}} P = 0.72 \times 4.2 \text{ atm} = 3.0 \text{ atm}$$

$$P_{\text{Ne}} = \chi_{\text{Ne}} P = 0.28 \times 4.2 \text{ atm} = 1.2 \text{ atm}$$

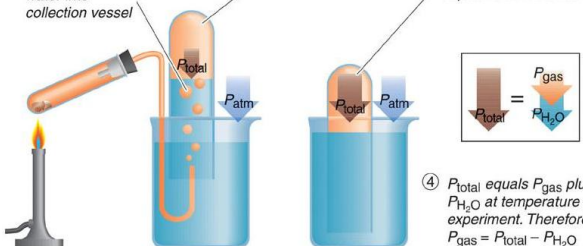
• Collecting a gas over water

$$P_{\text{total}} = P_{\text{gas}} + P_{\text{water}}$$

$$P_{\text{total}} = P_{\text{atm}}$$

P_{water} (vapor pressure of water) → given in tables

- Water-insoluble gaseous product bubbles through water into collection vessel
- P_{gas} adds to vapor pressure of water ($P_{\text{H}_2\text{O}}$) to give P_{total} . As shown $P_{\text{total}} < P_{\text{atm}}$
- P_{total} is made equal to P_{atm} by adjusting height of vessel until water level equals that in beaker



- P_{total} equals P_{gas} plus $P_{\text{H}_2\text{O}}$ at temperature of experiment. Therefore, $P_{\text{gas}} = P_{\text{total}} - P_{\text{H}_2\text{O}}$

Example: A 2.5 L sample of O_2 gas was collected over water at 26°C and 745 torr atmospheric pressure. What is the mass of O_2 in the sample? (The vapor pressure of water at 26°C is 25 torr.)

$$P_{\text{oxygen}} = P_{\text{total}} - P_{\text{water}} = 745 - 25 = 720 \text{ torr}$$

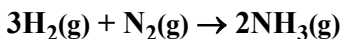
$$T = 26 + 273.15 = 299 \text{ K}$$

$$n_{\text{O}_2} = \frac{P_{\text{O}_2} V}{R T} = \frac{720 \text{ torr} \times \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \times 2.5 \text{ L}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 299 \text{ K}} = 0.097 \text{ mol}$$

$$0.097 \text{ mol O}_2 \times \left(\frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2} \right) = 3.1 \text{ g O}_2$$

Stoichiometry and the Ideal Gas Law

- The volume ratios of gases in reactions are the same as their mole ratios (follows from Avogadro's principle)



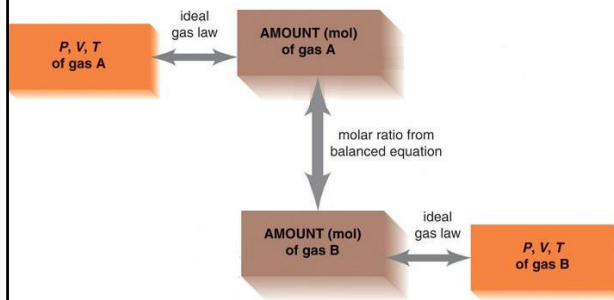
$\Rightarrow 3 \text{ mol H}_2$ react with 1 mol N_2

$\Rightarrow 3 \text{ L H}_2$ react with 1 L N_2

Example: How many liters of N_2 are needed to react completely with 5.0 L H_2 ?

$$5.0 \text{ L H}_2 \times [1 \text{ L N}_2 / 3 \text{ L H}_2] = 1.7 \text{ L N}_2$$

- The ideal gas law can be used to convert between the number of moles of gaseous reactants (or products) and their volumes at certain T and P



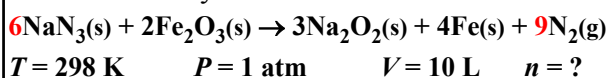
Example: Calculate the volume of CO_2 produced by the decomposition of 2.0 g CaCO_3 at 25°C and 1.0 atm .



$$2.0 \text{ g CaCO}_3 \times \left(\frac{1 \text{ mol CaCO}_3}{100.1 \text{ g CaCO}_3} \right) \times \left(\frac{1 \text{ mol CO}_2}{1 \text{ mol CaCO}_3} \right) = 0.020 \text{ mol CO}_2$$

$$V = \frac{nRT}{P} = \frac{0.020 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K}}{1.0 \text{ atm}} = 0.49 \text{ L}$$

Example: Calculate the mass of NaN_3 needed to produce 10 L of N_2 in an air bag at 25°C and 1.0 atm by the reaction:



$$T = 298 \text{ K} \quad P = 1 \text{ atm} \quad V = 10 \text{ L} \quad n = ?$$

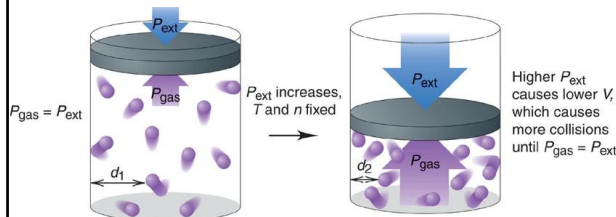
$$n = \frac{PV}{RT} = \frac{1 \text{ atm} \times 10 \text{ L}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K}} = 0.41 \text{ mol}$$

$$0.41 \text{ mol N}_2 \left(\frac{6 \text{ mol NaN}_3}{9 \text{ mol N}_2} \right) \left(\frac{65.02 \text{ g NaN}_3}{1 \text{ mol NaN}_3} \right) = 18 \text{ g NaN}_3$$

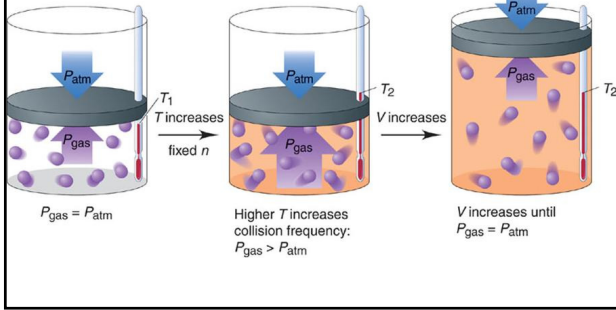
5.5 The Kinetic Molecular Theory

- Postulates of the Kinetic Molecular Theory
 - The gas particles are negligibly small (their volume can be neglected)
 - The gas particles are in constant, random motion and move in straight lines until they collide
 - The gas particles do not interact except during collisions. The collisions are elastic so there is no loss of energy due to friction
 - The average kinetic energy of gas particles, \bar{E}_k , is proportional to the absolute temperature, T

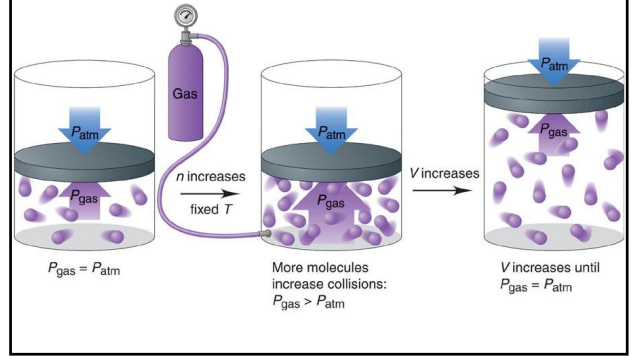
- A molecular view of the gas laws
 - Boyle's law ($V \propto 1/P$)



- A molecular view of the gas laws
 - Charles's law ($V \propto T$)



- A molecular view of the gas laws
 - Avogadro's law ($V \propto n$)



- Average kinetic energy of the gas particles

$$\bar{E}_k \propto T \quad \bar{E}_k = \frac{1}{2} m \bar{u}^2$$

$$\Rightarrow \bar{u}^2 \propto T \quad \sqrt{\bar{u}^2} \propto \sqrt{T}$$

m – mass of particles

\bar{u}^2 – average square speed

- Root-mean-square speed of the gas particles

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

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

Example: Calculate the root-mean-square speed of N_2 at $25^\circ C$.

$$T = 25^\circ C = 298 \text{ K}$$

$$M = 28.02 \text{ g/mol} = 0.02802 \text{ kg/mol}$$

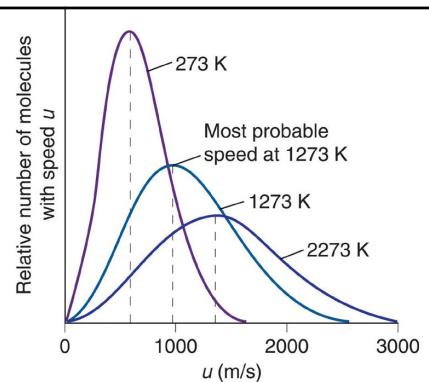
$$R = 8.314 \text{ J/mol}\cdot\text{K}$$

$$u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \times 298 \text{ K}}{0.02802 \frac{\text{kg}}{\text{mol}}}} = 515 \sqrt{\frac{\text{J}}{\text{kg}}}$$

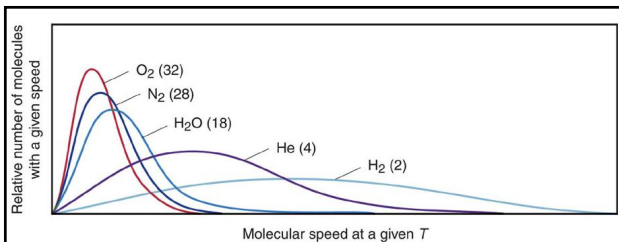
$$515 \sqrt{\frac{\text{kg}\cdot\text{m}^2/\text{s}^2}{\text{kg}}} = 515 \sqrt{\frac{\text{m}^2}{\text{s}^2}} = 515 \frac{\text{m}}{\text{s}}$$

The Maxwell Distribution of Speeds

- Gives the fraction of particles moving at each particle speed
- Gas molecules travel with a wide range of speeds with a bell-shaped distribution
- The most probable speed, the average speed and the root-mean-square speed are very close in magnitude



- The range of speeds widens and u_{rms} increases with increasing the temperature



- The range of speeds widens and u_{rms} increases with decreasing the molar mass of the gas
 - Lighter gases have higher molecular speeds

- The meaning of temperature

$$\bar{E}_k = \frac{1}{2} m \overline{u^2} = \frac{1}{2} m u_{rms}^2 = \frac{1}{2} m \left(\frac{3RT}{M} \right) = \frac{m3RT}{2mN_A}$$

$$\bar{E}_k = \frac{3RT}{2N_A}$$

and

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

- ⇒ u_{rms} depends on T and M
- ⇒ \bar{E}_k depends only on T
- ⇒ T is a measure of the average kinetic energy of the molecular motion

Diffusion and Effusion

- **Diffusion** – gradual dispersal of one substance through another
 - gases diffuse from places with high to places with low concentration
- **Effusion** – escape of a substance through a small hole into vacuum
 - effusion through porous materials, pin holes, cracks, etc.

- **Graham's Law** – the effusion rate (ER) of a gas is inversely proportional to the square root of its molar mass (same relation is valid in general for the diffusion rate)

$$ER \propto \sqrt{\frac{1}{M}}$$

– Can be explained with $u_{rms} = \sqrt{3RT/M}$

- The time of effusion (t_{eff}) is inversely proportional to ER

$$t_{eff} \propto \frac{1}{ER} \Rightarrow t_{eff} \propto \sqrt{M}$$

For two gases, A and B:

$$\frac{ER(A)}{ER(B)} = \sqrt{\frac{M_B}{M_A}} \quad t_{eff}(A) = \sqrt{\frac{M_A}{M_B}} \times t_{eff}(B)$$

Example: If it takes a certain amount of H₂ 15 s to effuse through a small hole, how long does it take for the same amount of O₂?

$$\frac{t_{eff}(O_2)}{t_{eff}(H_2)} = \sqrt{\frac{M_{O_2}}{M_{H_2}}} \quad t_{eff}(O_2) = \sqrt{\frac{M_{O_2}}{M_{H_2}}} \times t_{eff}(H_2)$$

$$t_{eff}(O_2) = \sqrt{\frac{32.00 \text{ g/mol}}{2.02 \text{ g/mol}}} \times 15 \text{ s} = 60 \text{ s}$$

5.6 Real Gases

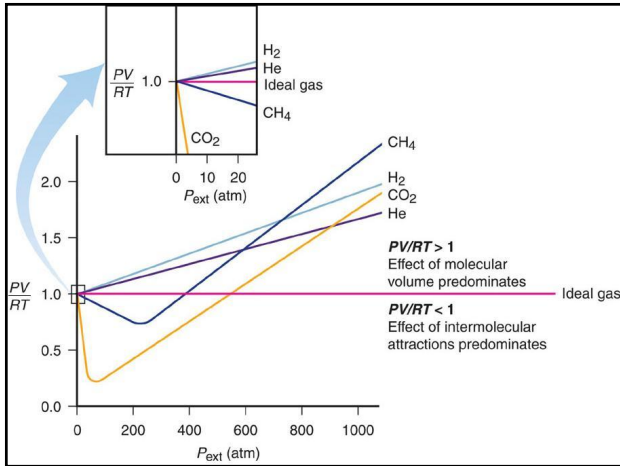
- Real gases deviate from ideal behavior
- Compression factor (Z)

$$Z = PV/nRT$$

- For ideal gases:

$$PV = nRT \Rightarrow Z = PV/nRT = 1$$

- A plot of Z versus P gives a straight line for ideal gases, but not for real gases



- **Negative deviations** – important at moderately high pressures ($PV/nRT < 1$)
 - Due to attractive forces between the molecules
 - The molecules attract each other and impact the walls with a weaker force (P and Z decrease)
- **Positive deviations** – important at very high pressures ($PV/nRT > 1$)
 - Due to the actual volume of the molecules
 - The physical volume of the molecules reduces the free volume in the container, but we still use the volume of the entire container, V , which is larger than the free volume (Z increases)

- Van der Waals equation:

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

a, b - van der Waals constants (zero for ideal gases)

an^2/V^2 - pressure correction (a depends on the attractive forces between molecules)

nb - volume correction (b is a measure for the actual volume of the gas molecules)

- Real gases approach ideal behavior at low pressures and high temperatures (away from conditions of condensation)