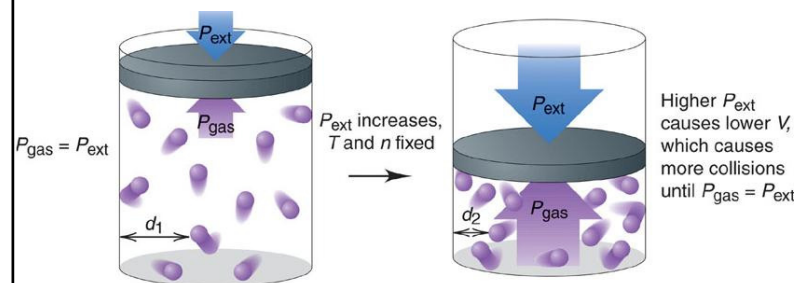


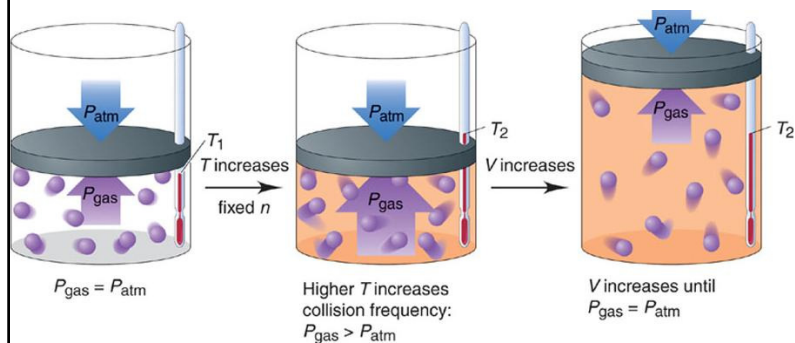
5.5 The Kinetic Molecular Theory

- 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

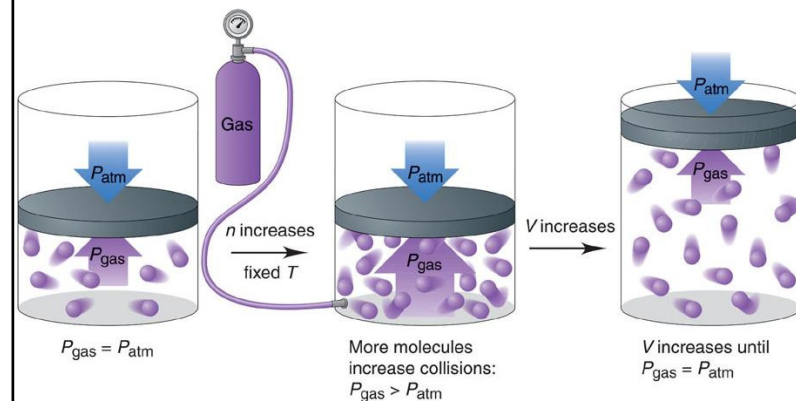
- A molecular view of the gas laws
 - Boyle's law ($V \propto 1/P$)



- 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°C .

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

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

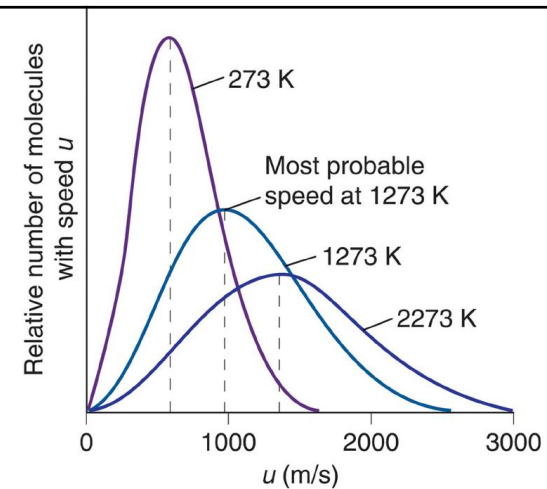
$$R = 8.314 \text{ J/mol}\cdot\text{K}$$

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

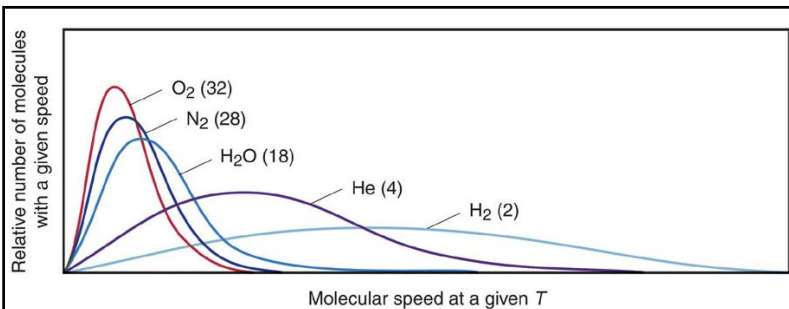
$$515 \sqrt{\frac{\text{kg}\cdot\text{m}^2/\text{s}^2}{\text{kg}}} = 515 \sqrt{\frac{\text{m}^2}{\text{s}^2}} = 515 \frac{\text{m}}{\text{s}}$$

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:

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

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?

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

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

5.6 Real Gases

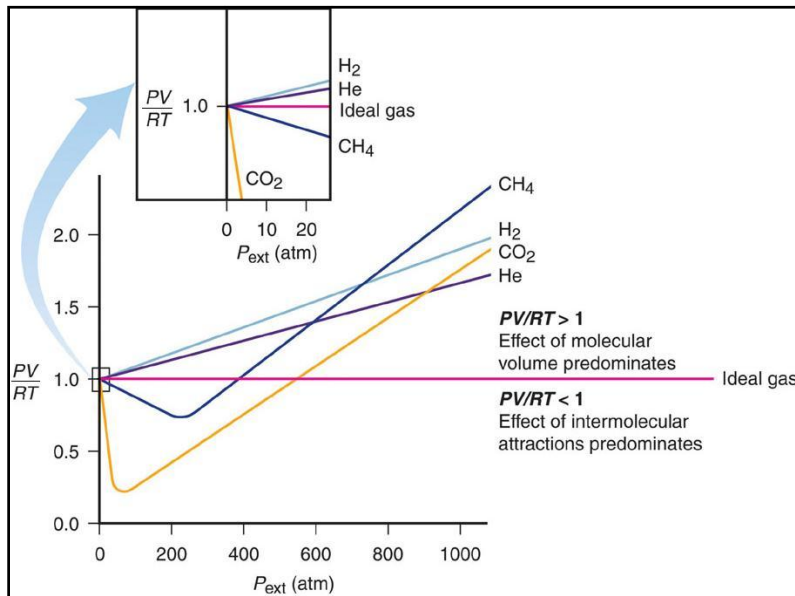
- Real gases deviate from ideal behavior
- Compression factor (Z)

$$Z = PV/nRT$$

- For ideal gases:

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

- 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)