Lecture 31

- Thermal physics
  - Gases. Absolute temperature
  - Ideal Gas law
  - Kinetic theory
Lightning Review

Last lecture:

1. Thermal physics
   ✓ Temperature. Temperature scales. 0\textsuperscript{th} law of thermodynamics.

**Review Problem:** The coldest temperature ever recorded on Earth is $-89.2\, ^\circ C$, recorded at Vostok Station, Antarctica on July 21, 1983. What is it in degrees Fahrenheit?

Temperature in degrees Fahrenheit = (Temperature in degrees Celsius x 1.8) + 32

Thus, $T_F=-89.2\times1.8+32=-128.6\, ^\circ F$!
The number density of particles

= the number of particles in a unit volume

= $N/V$ where $N$ is the total number of particles contained in a volume $V$.

If a sample contains a single element, the number of particles in the sample is $N = M/m$. $N$ is the total mass of the sample ($M$) divided by the mass per particle ($m$).
Ideal Gas

- Properties of gases
  - A gas does not have a fixed volume or pressure
  - In a container, the gas expands to fill the container

- Ideal gas:
  - Collection of atoms or molecules that move randomly
  - Molecules exert no long-range force on one another
  - Molecules occupy a negligible fraction of the volume of their container

- Most gases at room temperature and pressure behave approximately as an ideal gas
Moles

- It’s convenient to express the amount of gas in a given volume in terms of the number of moles, $n$

\[ n = \frac{mass}{molar\ mass} \]

- One mole is the amount of the substance that contains as many particles as there are atoms in 12 g of carbon-12
Avogadro’s Hypothesis

- Equal volumes of gas at the same temperature and pressure contain the same numbers of molecules

- Corollary: At standard temperature and pressure, one mole quantities of all gases contain the same number of molecules

- This number is called \( N_A \)

- Can also look at the total number of particles: \( N = n \, N_A \)
Avogadro’s Number

• The number of particles in a mole is called *Avogadro’s Number*

  • \( N_A = 6.02 \times 10^{23} \) particles / mole

• The mass of an individual atom can be calculated:

\[
m_{\text{atom}} = \frac{\text{molar mass}}{N_A}
\]
Equation of State for an Ideal Gas

- **Boyle’s Law**
  - At a constant temperature, pressure is inversely proportional to the volume

- **Charles’ Law**
  - At a constant pressure, the temperature is directly proportional to the volume

- **Gay-Lussac’s Law**
  - At a constant volume, the pressure is directly proportional to the temperature
Ideal Gas Law

- Summarizes Boyle’s Law, Charles’ Law, and Guy-Lussac’s Law

\[ PV = n R T \]

- \( R \) is the *Universal Gas Constant*
- \( R = 8.31 \text{ J/mole K} \)
- \( R = 0.0821 \text{ L atm/mole K} \)

\[ PV = N k_B T \]

- \( k_B \) is *Boltzmann’s Constant*
- \( k_B = R / N_A = 1.38 \times 10^{-23} \text{ J/K} \)
An ideal gas is confined to a container with constant volume. The number of moles is constant. By what factor will the pressure change if the absolute temperature triples?

a. 1/9  
b. 1/3  
c. 3.0  
d. 9.0
An ideal gas is confined to a container with adjustable volume. The number of moles and temperature are constant. By what factor will the volume change if pressure triples?

a. 1/9
b. 1/3
c. 3.0
d. 9.0
Example: Incandescent lightbulbs are filled with an inert gas to lengthen the filament life. With the current off (at $T = 20.0^\circ C$), the gas inside a lightbulb has a pressure of 115 kPa. When the bulb is burning, the temperature rises to 70.0$^\circ C$. What is the pressure at the higher temperature?
Example: A cylinder in a car engine takes \( V_i = 4.50 \times 10^{-2} \text{ m}^3 \) of air into the chamber at 30 °C and at atmospheric pressure. The piston then compresses the air to one-ninth of the original volume and to 20.0 times the original pressure. What is the new temperature of the air?

Given: \( V_f = V_i/9 \), \( P_f = 20.0P_i \), and \( T_i = 30 \text{ °C} = 303 \text{ K} \).

\[
\begin{align*}
P_i V_i &= NkT_i \\
P_f V_f &= NkT_f
\end{align*}
\]

The ideal gas law holds for each set of parameters (before compression and after compression).

Take the ratio:

\[
\frac{P_f V_f}{P_i V_i} = \frac{NkT_f}{NkT_i} = \frac{T_f}{T_i}
\]

The final temperature is

\[
T_f = \left( \frac{P_f}{P_i} \right) \left( \frac{V_f}{V_i} \right) T_i
\]

\[
= \left( \frac{20.0P_i}{P_i} \right) \left( \frac{V_i/9}{V_i} \right) (303 \text{ K}) = 673 \text{ K} = 400 \text{ °C}
\]
Kinetic Theory of the Ideal Gas

An ideal gas is a dilute gas where the particles act as point particles with no interactions except for elastic collisions.

Gas particles have random motions. Each time a particle collides with the walls of its container there is a force exerted on the wall. The force per unit area on the wall is equal to the pressure in the gas.

The pressure will depend on:

- The number of gas particles
- Frequency of collisions with the walls
- Amount of momentum transferred during each collision
The pressure is proportional to the number of molecules per unit volume and to the average translational kinetic energy of a molecule.

\[ P = \frac{2}{3} \frac{N}{V} \langle K_{\text{tr}} \rangle \]

Where \( \langle K_{\text{tr}} \rangle \) is the average translational kinetic energy of the gas particles; it depends on the temperature of the gas.

\[ \langle K_{\text{tr}} \rangle = \frac{3}{2} kT \]
The average kinetic energy also depends on the rms speed of the gas

\[ \langle K_{\text{tr}} \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m v_{\text{rms}}^2 \]

where the rms speed is

\[ \langle K_{\text{tr}} \rangle = \frac{3}{2} kT = \frac{1}{2} m v_{\text{rms}}^2 \]

\[ v_{\text{rms}} = \sqrt{\frac{3kT}{m}} \]
The distribution of speeds in a gas is given by the Maxwell-Boltzmann Distribution.
The distribution of speeds in a gas is given by the Maxwell-Boltzmann Distribution.
Example: What is the temperature of an ideal gas whose molecules have an average translational kinetic energy of $3.20 \times 10^{-20}$ J?

Idea: average translational kinetic energy of the gas particles depends on the temperature of the gas:

$$\langle K_{tr} \rangle = \frac{3}{2} kT$$

$$T = \frac{2\langle K_{tr} \rangle}{3k} = 1550 \text{ K}$$
Temperature and Reaction Rates

For a chemical reaction to proceed, the reactants must have a minimum amount of kinetic energy called activation energy \( (E_a) \).

If \( E_a >> \frac{3}{2} kT \)

then only molecules in the high speed tail of Maxwell-Boltzmann distribution can react. When this is the situation, the reaction rates are an exponential function of \( T \).

\[
\text{reaction rates } \propto e^{-\left(\frac{E_a}{kT}\right)}
\]
Example: The reaction rate for the hydrolysis of benzoyl-l-arginine amide by trypsin at 10.0 °C is 1.878 times faster than at 5.0 °C. Assuming that the reaction rate is exponential, what is the activation energy?

\[ r_1 \propto e^{-\left(\frac{E_a}{kT_1}\right)} \]

where \( T_1 = 10.0 \, ^\circ C = 283 \, K \) and \( T_2 = 5 \, ^\circ C = 278 \, K \); and \( r_1 = 2.878 \, r_2 \).

\[ r_2 \propto e^{-\left(\frac{E_a}{kT_2}\right)} \]

The ratio of the reaction rates is

\[ \frac{r_1}{r_2} = \exp\left(-\frac{E_a}{kT_1} + \frac{E_a}{kT_2}\right) \]

Solving for the activation energy gives:

\[ E_a = \frac{k \ln\left(\frac{r_1}{r_2}\right)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = \left(1.38 \times 10^{-23} \, J/K\right)\ln(1.878) = 1.37 \times 10^{-19} \, J \]
Diffusion

On average, a gas particle will be able to travel a distance

\[ \Lambda = \frac{1}{\sqrt{2\pi d^2 (N/V)}} \]

before colliding with another particle. This is the **mean free path**. The quantity \( \pi d^2 \) is the cross-sectional area of the particle.
After a collision, the molecules involved will have their direction of travel changed. Successive collisions produce a random walk trajectory.
Substances will move from areas of high concentration to areas of lower concentration. This process is called **diffusion**.

In a time $t$, the rms displacement in one direction is:

$$x_{\text{rms}} = \sqrt{2Dt} \quad \text{D is the diffusion constant}$$
Example: Estimate the time it takes a sucrose molecule to move 5.00 mm in one direction by diffusion in water. Assume there is no current in the water.

Recall that

\[ x_{\text{rms}} = \sqrt{2Dt} \]

Solve for \( t \)

\[ t = \frac{x_{\text{rms}}^2}{2D} = \frac{(5.00 \times 10^{-3} \text{ m})^2}{2(5.0 \times 10^{-10} \text{ m}^2/\text{s})} = 25000 \text{ s} \]