PHYSICS 2: FLUID MECHANICS AND THERMODYNAMICS

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CHAPTER 3 THE KINETIC THEORY OF GASES

3.1. Ideal Gases

3.2. Mean Free Path

3.3. The Boltzmann Distribution Law and The Distribution of Molecular Speeds

3.4. The Molar Specific Heats of an Ideal Gas

3.5. The Equipartition of Energy Theorem

3.6. The Adiabatic Expansion of an Ideal Gas

Overview

In this chapter, we consider the physics of gases at the microscopic level:

- A gas consists of atoms that fill their container's volume and the volume is a result of the freedom of the atoms spread throughout the container.
- The temperature is a measure of the kinetic energy of the atoms.
- The pressure exerted by a gas is produced by the collisions of the atoms with the container's wall.

The kinetic theory of gases relates the motion of the atoms to the volume, pressure, and temperature of the gas.

Ideal gases

- A truly ideal gas does NOT exist in nature.
- But all real gases approach the ideal state at low enough densities:
    - Molecules are far enough apart, so they do NOT interact with one another.
    - An ideal gas obeys the ideal gas law.

3.1. Ideal Gases

Avogadro’s law: Equal volumes of gases, at the same temperature and pressure, contain the same number of molecules.

- Useful unit to measure the sizes of our samples is mole.
- One mole is the number of atoms in a 12 g sample of carbon-12

Avogadro’s Number: one mole contains 6.02 x 10^{23} elementary units, i.e. atoms, molecules.

$$N_A = 6.02 \times 10^{23}\,\mathrm{mol}^{-1}$$

Number of moles contained in a sample of any substance:

$$n = \frac{N}{N_A}$$

where N is the number of molecules in the sample

$$n = \frac{M_{sample}}{M} = \frac{M_{sample}}{mN_A}$$

where M_{sample} is the mass of the sample

M is the molar mass or the mass of one mole

m is the mass of one molecule or one atom

Problem 1: Find the mass in kilograms of 7.5×10^{24} atoms of arsenic (As), which has molar mass of 74.9 g/mol.

The number of moles n:

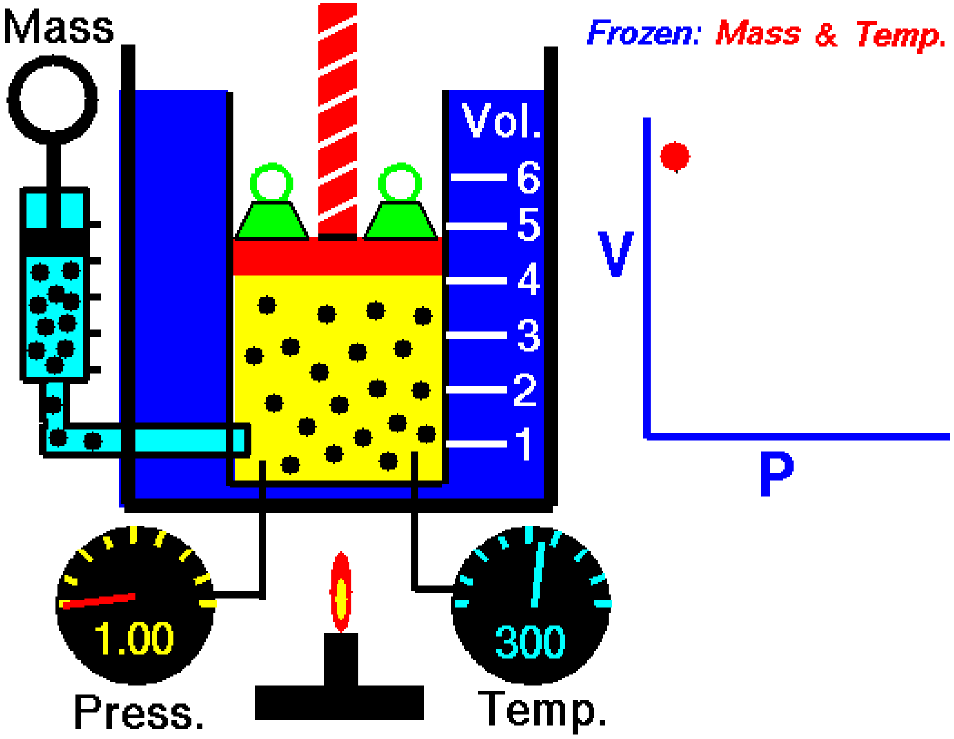
$$n = \frac{M_{arsenic}}{M}$$

$$M_{arsenic} = nM = \frac{N}{N_A} M = \frac{7.5 \times 10^{24}}{6.02 \times 10^{23}} \times 74.9 = 933\,(g)$$

3.1.1. Experimental Laws and the Equation of State

Boyle's Law: For a given mass, at constant temperature (isothermal), the pressure times the volume is a constant for an ideal gas.

$$pV = \text{constant}$$



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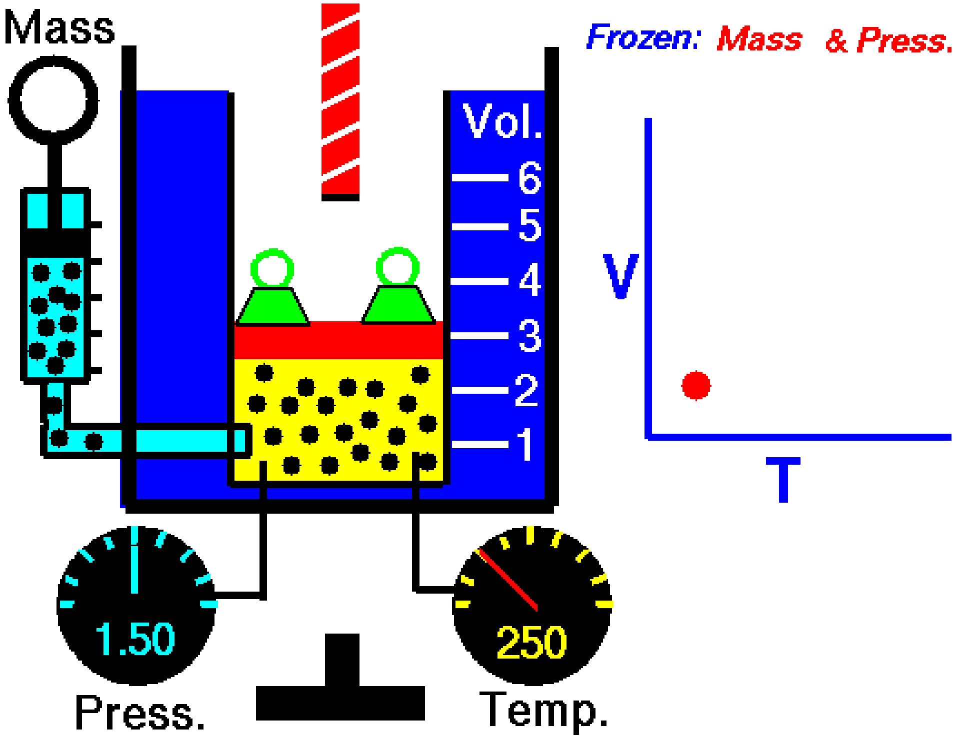
Charles's Law: For a given mass, at constant pressure (isobaric), the volume is directly proportional to the temperature.

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



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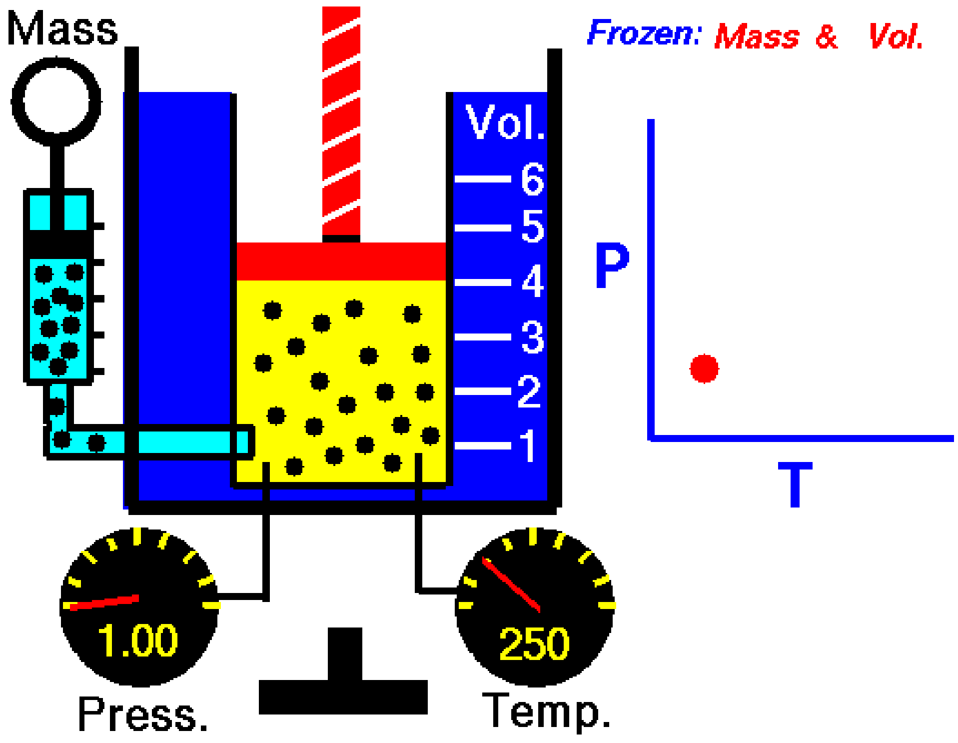
Gay-Lussac's Law: For a given mass, at constant volume (isochoric), the pressure is directly proportional to the temperature.

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



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Equation of State:

Boyle's Law: $pV = \text{constant}$

Charles's Law: $V = \text{constant} \times T$

Gay-Lussac's Law: $p = \text{constant} \times T$

The gas laws of Boyle, Charles and Gay-Lussac can be combined into a single equation of state (Ideal gas law):

$$\boxed{pV = nRT}$$

where p is the absolute pressure

n is the number of moles of gas

T is the temperature (in K)

R is a constant, called the gas constant

$$R = 8.31\ \text{J mol}^{-1}\text{K}^{-1}$$

The Boltzmann constant k is:

$$k = \frac{R}{N_A} = \frac{8.31 \mathrm{J\,mol^{-1}\,K^{-1}}}{6.02 \times 10^{23} \mathrm{mol^{-1}}} = 1.38 \times 10^{-23} \mathrm{J\,K^{-1}}$$

$$nR = \frac{N}{N_A} k N_A = kN$$

Where N is the number of molecules

$$\boxed{pV = NkT}$$

Sample Problem: A cylinder contains 12 L of oxygen at 20^0C and 15 atm. The temperature is raised to 35^0C, and the volume is reduced to 8.5 L. What is the final pressure of the gas in atmospheres? Assume that the gas is ideal.

Key equation: $$pV = nRT$$

At the initial state i: $$p_i V_i = nRT_i$$

At the final state f: $$p_f V_f = nRT_f$$

$$\rightarrow \quad \frac{p_f V_f}{p_i V_i} = \frac{T_f}{T_i} \rightarrow p_f = \frac{p_i V_i T_f}{T_i V_f}$$

Note: We must convert temperatures T_i and T_f in C^0 to that in K.

$$\rightarrow \quad p_f = \frac{(15\ \text{atm})(308\ \text{K})(12\ \text{L})}{(293\ \text{K})(8.5\ \text{L})} \approx 22.3\ \text{atm}$$

Problem 5: The best laboratory vacuum has a pressure of about 10^{-18} atm, or 1.01×10^{-13} Pa. How many gas molecules are there per cubic centimeter in such a vacuum at 293 K?

Key equation: $$pV = nRT$$

The number of moles: $$n = \frac{pV}{RT}; \qquad R = 8.31\ \mathrm{J\,mol^{-1}K^{-1}}$$

$$p = 1.01 \times 10^{-13}\ \mathrm{Pa};\ V = 1\ \mathrm{cm^3} = 10^{-6}\ \mathrm{m^3};\ T = 293\ \mathrm{K}$$

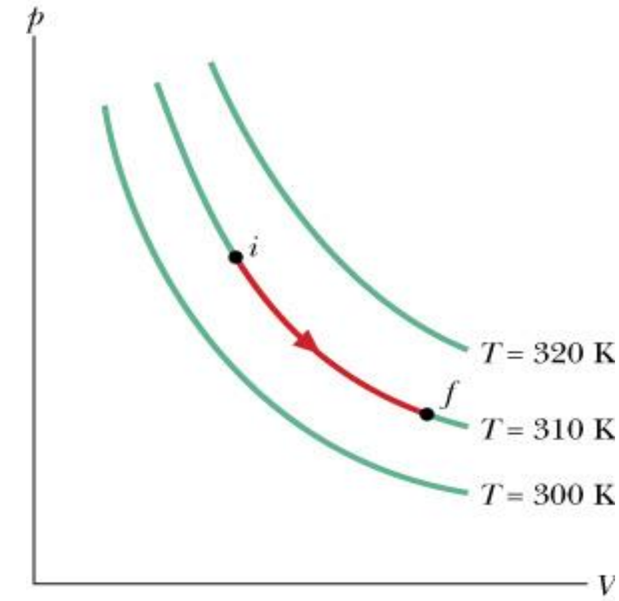
The number of molecules: $$N = n \times N_A$$

$$\rightarrow N = \frac{1.01 \times 10^{-13} \times 10^{-6}}{8.31 \times 293} \times 6.02 \times 10^{23} \approx 25\ (\text{molecules})$$

Work Done by an Ideal Gas at Constant Temperature

A process at constant temperature is called an isothermal expansion/compression.
The equation of state for n moles:

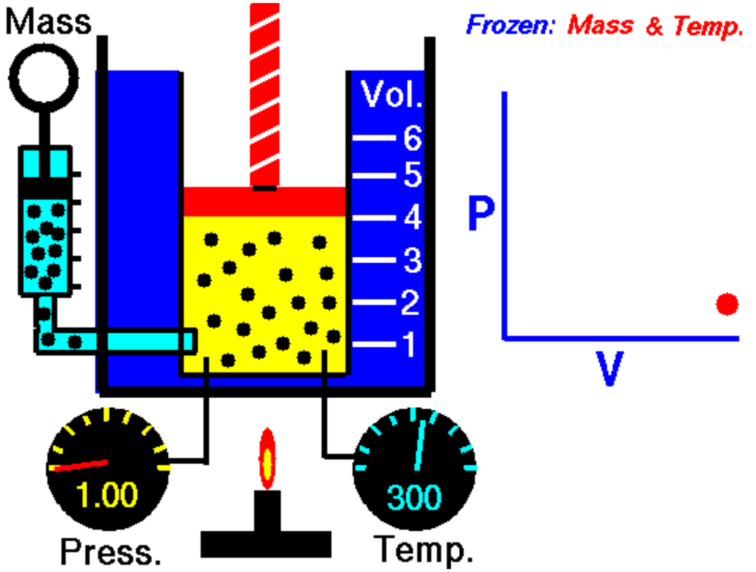
$$p = nRT\,\frac{1}{V} = \text{constant} \times \frac{1}{V}$$



The work done during an isothermal process:

$$W = \int_{V_i}^{V_f} p\,dV = \int_{V_i}^{V_f} \frac{nRT}{V}\,dV = nRT\,\left[\ln V\right]_{V_i}^{V_f}$$

$$W = nRT \ln \frac{V_f}{V_i}$$



Summary

The equations below allows us to calculate work done by the gas for three special cases:

$$W = \int_{V_i}^{V_f} p\,dV$$

1) If V = constant (isochoric), $W = 0$

2) If p = constant (isobaric), $W = p(V_f - V_i) = p\Delta V$

3) If T = constant (isothermal), $W = nRT \ln \frac{V_f}{V_i}$

Checkpoint: An ideal gas has an initial pressure of 3 pressure units and an initial volume of 4 volume units. The table gives the final pressure and volume of the gas (in those same units) in 5 processes. Which processes start and end on the same isothermal?

	a	b	c	d	e
p	12	6	5	4	1
V	1	2	7	3	12

3.1.2. Molecular Model for an Ideal Gas

In this model:

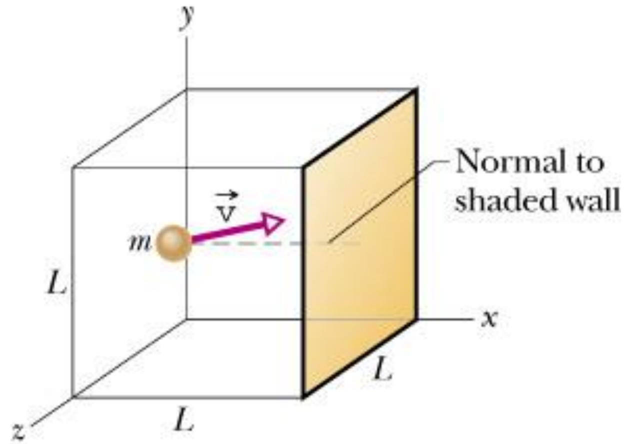
1. The molecules obey Newton's laws of motion.
2. The molecules move in all direction with equal probability.
3. There is no interactions between molecules (no collisions between molecules).
4. The molecules undergo elastic collisions with the walls.

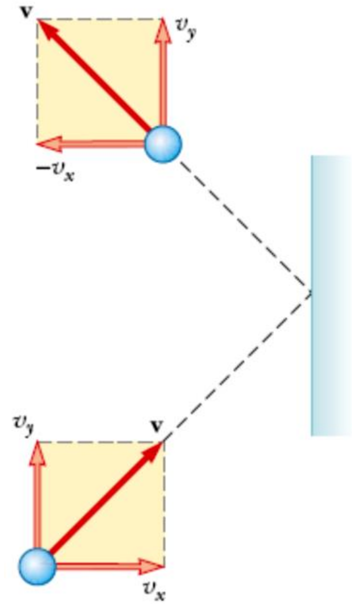
a. Pressure, Temperature, and RMS Speed

Problem: Let n moles of an ideal gas be confined in a cubical box of volume V, (see the figure below). The walls of the box are held at temperature T.

Key question: What is the connection between the pressure p exerted by the gas and the speed of the molecules?

First, we consider a cubical box of edge length L, containing n moles of an ideal gas. A molecule of mass m and velocity v is about to collide with the shaded wall.





For an elastic collision, the particle's momentum (=m.v) along the x axis is reserved and change with an amount:

$$\Delta p_x = (-mv_x) - (mv_x) = -2mv_x$$

The average rate at which momentum is delivered to the shaded wall by this molecule:

$$\frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}$$

Recall: $\vec{F} = m\vec{a} = m\frac{d\vec{v}}{dt} = \frac{d(m\vec{v})}{dt} = \frac{d\vec{p}}{dt}$

$$F_{x,1} = \frac{mv_x^2}{L}$$

The pressure exerted on the wall by this single molecule:

$$p_1 = \frac{F_{x,1}}{L^2}$$

For N molecules, the total pressure p:

$$p = \frac{F_x}{L^2} = \frac{mv_{x,1}^2/L + mv_{x,2}^2/L + \ldots + mv_{x,N}^2/L}{L^2}$$

$$p = \left(\frac{m}{L^3}\right)(v_{x,1}^2 + v_{x,2}^2 + \ldots + v_{x,N}^2)$$

The average value of the square of the x components of all the molecular speeds:

$$\overline{v_x^2} = \frac{v_{x,1}^2 + v_{x,2}^2 + \ldots + v_{x,N}^2}{N}$$

$$p = \frac{nmN_A}{L^3}\overline{v_x^2}$$

Since, the molar mass of the gas: $M = mN_A$ and $V = L^3$

$$p = \frac{nM}{V}\overline{v_x^2}$$

For any molecule: $v^2 = v_x^2 + v_y^2 + v_z^2$

As all molecules move in random directions: $v_x^2 = \frac{1}{3}v^2$

$$p = \frac{nM}{3V}\overline{v^2}$$

The square root of $\overline{v^2}$ is called the root-mean-square speed:

$$\sqrt{\overline{v^2}} = v_{rms}$$

$$p = \frac{nM v_{rms}^2}{3V}$$

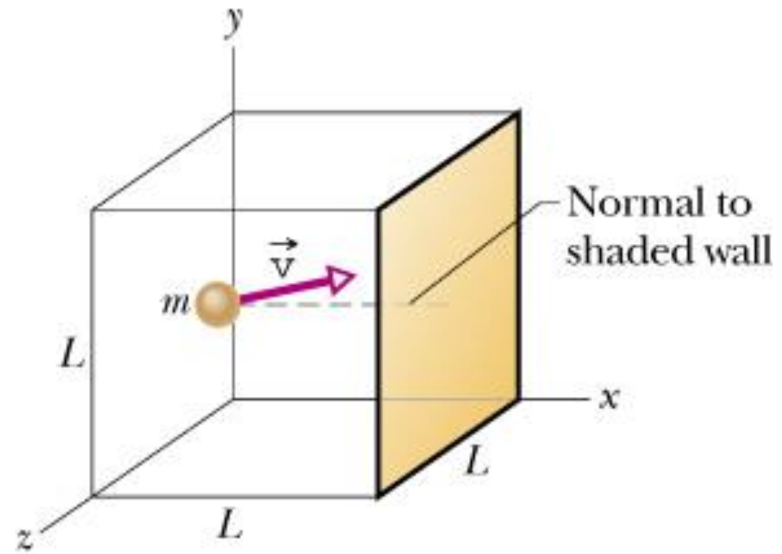
This relationship shows us how the pressure of the gas (a macroscopic quantity) depends on the speed of the molecules (a microscopic quantity).

Combining with the equation of state: $pV = nRT$

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

b. Translational Kinetic Energy

Consider a single molecule of an ideal gas moving around in the box (see Section a) .



$$\overline{K} = \overline{\frac{1}{2} m v^2} = \frac{1}{2} m \overline{v^2} = \frac{1}{2} m v_{rms}^2$$

$$\overline{K} = \left(\frac{1}{2} m\right) \frac{3RT}{M} = \frac{1}{2} \frac{3RT}{M/m}$$

$$\overline{K} = \frac{3RT}{2N_A}$$

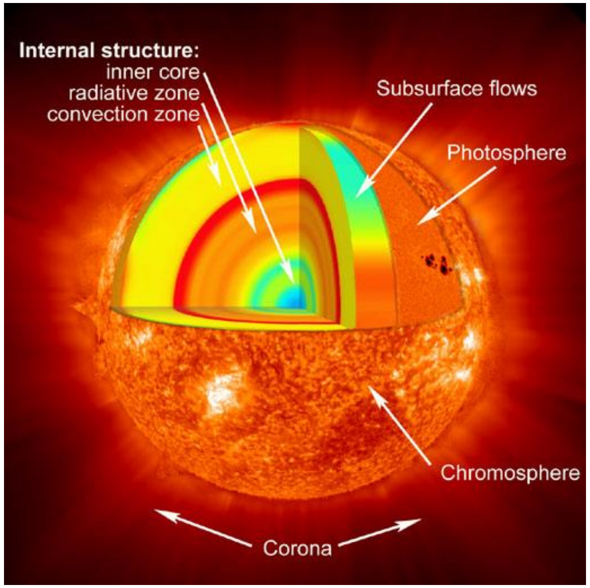
Recall: The Boltzmann constant: $k = \frac{R}{N_A}$

$$\overline{K} = \frac{3}{2} kT$$

→ $\overline{K}$ does NOT depend on the mass of the molecule

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3} \overline{v^2} \quad \rightarrow \frac{1}{2} m \overline{v_x^2} = \frac{1}{2} m \overline{v_y^2} = \frac{1}{2} m \overline{v_z^2} = \frac{1}{2} kT$$

Problem 18. The temperature and pressure in the Sun's atmosphere are 2.00×10^6 K and 0.0300 Pa. Calculate the rms speed of free electrons (mass 9.11×10^{-31} kg) there, assuming they are an ideal gas.



$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3RT}{mN_A}}$$

$$v_{rms} = \sqrt{\frac{3 \times 8.31 \times 2 \times 10^6}{9.11 \times 10^{-31} \times 6.023 \times 10^{23}}} = 9.5 \times 10^6 \text{ (m/s)}$$

Homework:

Problems 4, 13, 14, 20, 24 in Chapter 19 Textbook