

Chapter Q

Ideal Gases and Kinetic Theory

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Q.1 - Ideal Gases

Basic Definitions

The assumption behind an ideal gas is that it is a collection of non-interacting point particles. By this we mean that the size of each molecule is small compared to the fraction of the total volume occupied each molecule (the total volume divided by the number of molecules). Also we assume that the forces between the molecules can be neglected.

P = Pressure	SI units = Pa = N/m ²
V = Volume	SI units = m ³
T = Temperature	SI units = K
N = # of molecules	Dimensionless

Pressure is the absolute pressure measured in Pascals, Pa. Temperature is the absolute temperature in K. Our emphasis will be different from that of a chemistry class. In chemistry it is important to keep track of the amount of material; this is related to the number of moles n . In physics our emphasis is relating macroscopic quantities to microscopic ones; the actual number of molecules N is more important in physics.

Ideal Gas Law

There are some basic proportionalities that are satisfied. Keeping N and T constant we get an inverse proportionality between pressure and volume $P \propto 1/V$. With N and V constant we get a proportionality between pressure and temperature $P \propto T$. For the same P and T we get $V \propto N$. The ideal gas law follows from this.

$$P V \propto N T$$

The constant of proportionality is a fundamental constant called Boltzmann's constant k_B

$$P V = N k_B T$$

where Boltzmann's constant has the value

$$k_B = 1.38 \times 10^{-23} \frac{\text{J}}{\text{K}}$$

Note that Boltzmann's constant could be viewed as a conversion between Joules and Kelvins, and temperatures could be measured in Joules. This approach is not standard at this level and will be avoided here.

Example Q.1 - Number of Molecules

How many air molecules are in a room with dimensions, 8 m by 10 m by 3 m? Assume 1 atm of pressure and a temperature of 20 °C.

Solution

This is a straight-forward application of the ideal gas law.

$$V = 8 \text{ m} \times 10 \text{ m} \times 3 \text{ m} = 240 \text{ m}^3, \quad P = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}, \quad T = 20 \text{ °C} = 293 \text{ K}$$

$$P V = N k_B T \implies N = \frac{P V}{k_B T} = 6.01 \times 10^{27}$$

Atomic and Molecular Masses

$$m_{\text{proton}} \approx m_{\text{neutron}} \gg m_{\text{electron}}$$

Atoms consist of protons, neutrons and electrons. The masses of the proton and neutron are approximately equal and both are *much* larger than the mass of an electron.

$$m_{\text{proton}} = 1.6726 \times 10^{-27} \text{ kg}$$

$$m_{\text{neutron}} = 1.6749 \times 10^{-27} \text{ kg}$$

$$m_{\text{electron}} = 9.109 \times 10^{-31} \text{ kg}$$

For atoms the *atomic number* Z is the number of protons in the nucleus, which is the same as the number of electrons in a neutral atom. A , the *atomic mass number*, is the number of nucleons, where protons and neutrons are nucleons.

$$Z = \text{atomic number} = \# \text{ of protons} = \# \text{ of electrons}$$

$$A = \text{atomic mass number} = \# \text{ of nucleons (protons and neutrons)}$$

$$A - Z = \# \text{ of neutrons}$$

One would expect, naively, that the mass of an atom should equal the sum of its constituent parts. This is not the case. It takes energy to break up an atom into its constituent parts. Using the mass-energy equivalence of relativity, $E = mc^2$, it follows that since the constituent parts have more energy, they have more mass.

$$m_{\text{atom}} = Z m_{\text{proton}} + (A - Z) m_{\text{neutron}} + Z m_{\text{electron}} - \left(\frac{\text{Binding Energy}}{c^2} \right)$$

In this expression, the Binding Energy is the amount of energy required to break up the atom into its constituent parts.

Because this naive approach doesn't work we introduce the atomic mass unit, u , which is defined to be the approximate contribution to the mass of an atom due to each proton and neutron.

$$u \approx m_{\text{proton}} \approx m_{\text{neutron}}$$

Thus the approximate mass of an atom is Au .

$$m_{\text{atom}} \approx Au$$

We precisely define u in terms of the carbon-12 isotope, ^{12}C . Carbon has $Z = 6$. The 12 refers to the mass number, $A = 12$. u is defined as $1/12^{\text{th}}$ the mass of ^{12}C .

$$u = \frac{1}{12} \text{ mass}(^{12}\text{C}) = 1.6605 \times 10^{-27} \text{ kg} = \frac{1}{6.0221 \times 10^{23}} \text{ g}$$

The mole, abbreviated mol, is an SI base unit related to this. A mole is defined as the number of atoms in 12-grams of carbon-12; this number, known as Avogadro's number, has the approximate value

$$N_A = 6.02 \times 10^{23} / \text{mol}.$$

The number of moles n and the number of molecules N are related by

$$N = n N_A.$$

We can then write the ideal gas law in terms of the number of moles

$$\begin{aligned} PV &= N k_B T \\ &= n N_A k_B T \end{aligned}$$

If we define the ideal gas constant R by

$$R = N_A k_B = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}},$$

then the ideal gas law has the form

$$PV = nRT.$$

The mass of a mole of some molecule can be related to the molecular mass in atomic mass units, u . The value for the molecular mass in u is the same as the molar mass in grams. For example a molecule of CO_2 has molecular mass of 44 u , so its molar mass is 44 g/mol.

$$m_{\text{mol}} = N_A m_{\text{molecule}} = N_A 44 u = 44 \text{ g/mol}, \text{ since } N_A u = \text{g/mol}.$$

The total mass of a gas can then be written as

$$m_{\text{tot}} = N m_{\text{molecule}} = n m_{\text{mol}}$$

Example Q.2 - The Density of Air

(a) Estimate the density of (dry) air at 20 °C and 1 atm, assuming air is composed entirely of nitrogen N_2 .

Solution

$$P = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}, \quad T = 20 \text{ °C} = 293 \text{ K} \quad \text{and} \quad R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

First we need to find the molar mass.

$$m_{\text{molecule}} = m_{N_2} = 2 m_N = 2 \times 14 \text{ u} = 28 \text{ u} \implies m_{\text{mol}} = 28 \text{ g/mol} = 0.028 \text{ kg/mol}$$

We can find an expression for the number of moles n using the ideal gas law and then get an expression for the mass

$$PV = nRT \implies n = \frac{PV}{RT} \quad \text{and} \quad m_{\text{tot}} = n m_{\text{mol}} = m_{\text{mol}} \frac{PV}{RT}$$

Density ρ is mass per volume. The volume V will cancel.

$$\rho = \frac{m_{\text{tot}}}{V} = m_{\text{mol}} \frac{P}{RT} = 1.16 \text{ kg/m}^3$$

(b) The accepted value for the density of dry air at 20 °C is 1.204 kg/m³. Calculate a more accurate result for the density of dry air by taking air to be 78% N_2 , 21% O_2 and 1% Argon, where the atomic mass of argon is: $m_{\text{Ar}} = 40 \text{ u}$.

Solution

$$m_{O_2} = 2 m_O = 2 \times 16 \text{ u} = 32 \text{ u} \implies m_{\text{mol},O_2} = 32 \text{ g/mol} = 0.032 \text{ kg/mol}$$

Also for Argon, which is monatomic, we have

$$m_{\text{Ar}} = 40 \text{ u} \implies m_{\text{mol},\text{Ar}} = 40 \text{ g/mol} = 0.040 \text{ kg/mol}$$

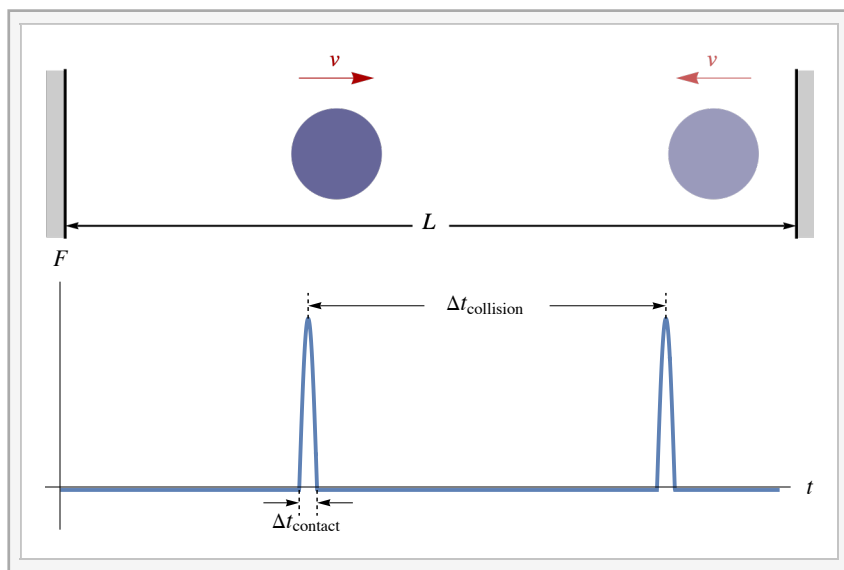
The molar mass of air can be found as a weighted average.

$$m_{\text{mol}} = 0.78 m_{\text{mol},N_2} + 0.21 m_{\text{mol},O_2} + 0.01 m_{\text{mol},\text{Ar}} \implies \rho = \frac{m_{\text{tot}}}{V} = m_{\text{mol}} \frac{P}{RT} = 1.20 \text{ kg/m}^3$$

Q.2 - Kinetic Theory

Temperature and the Microscopic Origin of Pressure

One Particle in a One-Dimensional Box



Interactive Figure - A particle in a one-dimensional box and the impulsive force on a wall.

Consider a particle of mass m moving with speed v in a one-dimensional box between walls separated by L . The particle moves freely, meaning without external force, except for elastic collisions with the walls. With each collision the particle exerts a force on the wall. The impulse-momentum theorem relates the average force on a wall to the change in the particle's momentum.

$$F_{\text{ave}} \Delta t_{\text{collision}} = \Delta p = 2 m v$$

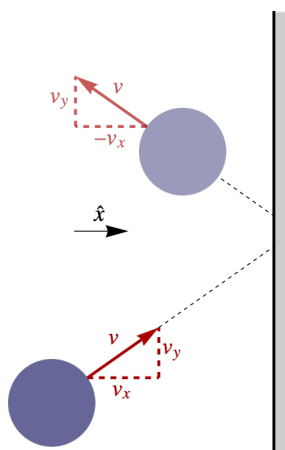
Usually when we use the impulse-momentum theorem, we calculate the very large force during a very brief time of contact of the collision, $\Delta t_{\text{contact}}$; this is not what we are doing here. Now we want the average force over *all time*, so we are using $\Delta t_{\text{collision}}$ as the larger time between collisions with that wall. The time between collisions with one wall is $\Delta t_{\text{collision}} = 2L/v$. This gives an expression for the average force.

$$F_{\text{ave}} \frac{2L}{v} = 2 m v \implies F_{\text{ave}} L = m v^2$$

Our single particle creates far from a steady force on the wall. We will see that when we consider a huge number of particles then we get a very steady average force; this is the microscopic origin of pressure.

One Particle in a Three-Dimensional Box

Now we imagine our particle of mass m moving in a three-dimensional $L_x \times L_y \times L_z$ box and making elastic collisions with the walls. The velocity of the particle is constant until there is a collision. In an elastic collision with a wall parallel to the zy -plane, the y - and z -components of the velocity are unchanged but v_x changes sign.



In an elastic collision with a wall that is parallel to the xy -plane (or perpendicular to the x -axis) the x -component of the velocity changes sign but the y - and z -components of the velocity stay the same.

The x -component of the force on the wall becomes

$$F_{\text{ave},x} \Delta t_{\text{collision}} = \Delta p_x = 2 m |v_x|$$

The time between collisions with one wall is $\Delta t_{\text{collision}} = 2L_x/|v_x|$. This gives an expression for the average force on the wall.

$$F_{\text{ave},x} \frac{2L_x}{|v_x|} = 2m|v_x| \implies F_{\text{ave},x} L_x = m v_x^2$$

N Non-interacting Particles and Pressure

Now consider N non-interacting particles in the same box. The effect of more particles is more collisions and the right-hand side involves the sum over all N particles, where i labels the i^{th} particle.

$$F_{\text{ave},x} L_x = m \sum_i v_{i,x}^2 = N m (v_x^2)_{\text{ave}},$$

where $(v_x^2)_{\text{ave}}$ is the average of v_x^2 .

$$(v_x^2)_{\text{ave}} = \frac{1}{N} \sum_i v_{i,x}^2 \implies \sum_i v_{i,x}^2 = N (v_x^2)_{\text{ave}}$$

Since pressure is force per area, we can now write this in terms of the pressure on the wall.

$$F_{\text{ave},x} = P \times \text{Area} = P L_y L_z \implies F_{\text{ave},x} L_x = P L_x L_y L_z = P V$$

$$P V = N m (v_x^2)_{\text{ave}},$$

We now want to relate the right-hand side to the average kinetic energy of particles. The average squared-speed can be written as:

$$(v^2)_{\text{ave}} = (v_x^2)_{\text{ave}} + (v_y^2)_{\text{ave}} + (v_z^2)_{\text{ave}}$$

There is nothing distinguishing the x -, y - and z -components so the averages of the squared velocity components must be the same; this allows us to write $(v_x^2)_{\text{ave}}$ in terms of the average of the squared-speed.

$$(v_x^2)_{\text{ave}} = (v_y^2)_{\text{ave}} = (v_z^2)_{\text{ave}} \implies (v_x^2)_{\text{ave}} = \frac{1}{3} \left((v_x^2)_{\text{ave}} + (v_y^2)_{\text{ave}} + (v_z^2)_{\text{ave}} \right) = \frac{1}{3} (v^2)_{\text{ave}}$$

$K_{\text{trans,ave}}$ is the average translational kinetic energy of particles.

$$K_{\text{trans,ave}} = \frac{1}{2} m (v^2)_{\text{ave}}$$

The pressure can now be written in terms of the average translational kinetic energy.

$$P V = N m (v_x^2)_{\text{ave}} = N \frac{m}{3} (v^2)_{\text{ave}} = N \frac{2}{3} K_{\text{trans,ave}}$$

With this we have a microscopic interpretation of pressure. Pressure describes the force per area on walls due to the collisions between gas molecules and the walls. Each molecular collision gives a very small force but with a huge number of molecules we get significant steady forces on walls.

Kinetic Energy, Temperature and Root-mean-squared Speed

Combining the expression above and the ideal gas law

$$P V = N \times \frac{2}{3} K_{\text{trans,ave}} \text{ and } P V = N k_B T$$

we can get an expression relating the average translational kinetic energy of gas molecules to temperature.

$$K_{\text{trans,ave}} = \frac{3}{2} k_B T$$

We have made the assumption that the collisions with the walls are elastic. Let us explore this more deeply. If the walls and the gas are at the same temperature then the collisions are, *on average*, elastic. Suppose instead, that the walls are at a higher temperature than the gas. There is then more random motion in the atoms of the wall than in the molecules of the gas and, on average, the gas molecules gain energy in the collisions with the wall. Similarly, if the gas is at a higher temperature than the collisions tend to give up energy to the wall. This is the mechanism for heat flow between the walls and the gas!

The average velocity of gas molecules is zero, since velocity is a vector and a gas molecule is as likely to move in one direction as any another. A nonzero average velocity would correspond to wind, where \vec{v}_{ave} is the wind velocity. To get a measure of typical speeds of gas molecules we use the root-mean-squared speed, this is the square root of the average (mean) of the speed squared.

$$v_{\text{rms}} = \sqrt{(v^2)_{\text{ave}}} = \sqrt{\frac{1}{N} \sum_i v_i^2} \Rightarrow K_{\text{trans,ave}} = \frac{1}{2} m v_{\text{rms}}^2$$

The rms, or root-mean-squared, speed is a measure of the typical speed of gas molecules. Equating the two expressions for $K_{\text{trans,ave}}$ we get

$$\frac{1}{2} m v_{\text{rms}}^2 = \frac{3}{2} k_B T \quad \text{and} \quad v_{\text{rms}} = \sqrt{\frac{3 k_B T}{m}}$$

In this expression m is the mass of a gas molecule.

Example Q.3 - v_{rms} for N_2

What is the root-mean-squared speed of nitrogen molecules N_2 at room temperature 20°C ?

Solution

We will need to find the mass of nitrogen in kg. The atomic mass of nitrogen is 14 u; from this we can find the molecular mass in kg.

$$u = 1.6605 \times 10^{-27} \text{ kg} \Rightarrow m_{N_2} = 2 \times m_N = 2 \times 14 \text{ u} = 28 \text{ u} = 4.649 \times 10^{-27} \text{ kg}$$

Using the listed value for Boltzmann's constant and the temperature in K, we can now solve for v_{rms} .

$$k_B = 1.38 \times 10^{-23} \frac{\text{J}}{\text{K}}, \quad 20^\circ\text{C} = 293 \text{ K} \quad \text{and} \quad \frac{1}{2} m v_{\text{rms}}^2 = \frac{3}{2} k_B T \Rightarrow v_{\text{rms}} = \sqrt{\frac{3 k_B T}{m}} = 511 \frac{\text{m}}{\text{s}}$$

Internal Energy of a Monatomic Ideal Gas

From the perspective of kinetic theory, the internal energy of a system is the sum of the kinetic and potential energies of all the particles. Since an ideal gas consists of non-interacting particles there is no potential energy between the particles. There could be gravitational potential energy but in we will neglect that. A particle has only translational kinetic energy, where by a particle we mean a point. Single atoms behave like particles, so monatomic gases only have translational kinetic energy. We saw that rigid bodies also have rotational kinetic energy, so diatomic and polyatomic gases will have rotational kinetic energies. Here we will only consider only the monatomic case. The most common examples of monatomic gases are the noble gases; these are the elements on the far right of the periodic table. These atoms have all filled shells of electrons and are averse to forming molecules. The noble gases consists of: helium, neon, argon, krypton, xenon and radon.

For a monatomic gas, since there is only translational kinetic energy, the average kinetic energy is the average translational kinetic energy $K_{\text{ave}} = K_{\text{trans,ave}}$. The total energy of the gas, its internal energy U , is given by $U = N K_{\text{ave}}$, where N is the number of molecules (or atoms in this case) in the gas.

$$U = N K_{\text{ave}} = N K_{\text{trans,ave}} = N \frac{3}{2} k_B T$$

This also allows us to write the internal energy of a monatomic ideal gas in term of both the number of molecules N or the number of moles n .

$$U = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

Example Q.4 - Internal Energy of Helium Gas

A pressurized tank used for filling balloons contains 0.260 kg of helium gas at 20°C . What is the internal energy of the gas? (Helium is a monatomic gas with atoms consisting of two protons with two neutrons. Its atomic mass number is $A = 4$, so its atomic mass is 4 u.

Solution

We are given the temperature, which must be converted to kelvins. Also we are given the mass which will allow us to find the number of moles. We saw in the discussion of ideal gases that the atomic or molecular mass in atomic mass units u is the same as the molar mass in g/mol.

$$m_{\text{atom}} = 4 \text{ u} \Rightarrow m_{\text{mol}} = 4 \text{ g/mol} = 0.004 \text{ kg/mol}$$

Since we know the total mass of helium, we can find the number of moles.

$$m_{\text{tot}} = 0.260 \text{ kg and } m_{\text{tot}} = n m_{\text{mol}} \implies n = \frac{m_{\text{tot}}}{m_{\text{mol}}} = 65 \text{ mol}$$

Using this and the temperature we can find the internal energy.

$$R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \text{ and } T = 20 \text{ }^\circ\text{C} = 293 \text{ K} \implies U = \frac{3}{2} n R T = 238\,000 \text{ J}$$