General Physics II at EPFL

(2018-2019 SS, Wed 17:15-19:00 and Thu 8:15-10:00, Exercise Thu 10:15-12:00)

Thermodynamic (2nd week)

The Laws of Gas

The state of a gas depends on the volume (V), pressure (P), and temperature (T). The relation between the volume, pressure, temperature and mass of the gas is called an equation of state. The equation of state can be applied for a state in equilibrium, i.e. the pressure and temperature are uniform over the volume and do not change with time.
Don't through a left over hair spray into fire.

Gas laws are:

Boyle's law:	PV is constant when T is kept constant, for a given quantity of gas.
Charles's law:	V is proportional to T (in Kelvin) when P is kept constant.
Gay-Lussac's law:	P is proportional to T (in Kelvin) when V is kept constant.
Avogadro's law:	Gasses with identical P, T and V contain the same number of molecules.

The first three laws lead to

$$P \times V \propto T .$$

From the dimensional point of view,

$$P : \left[\mathrm{N/m^2}\right],\ V : \left[\mathrm{m^3}\right],$$

thus

$$P \times V : \left[\mathrm{Nm = Joul}\right]$$

has a dimension of energy. By combining four laws, we introduce the following equation of state for an "ideal" gas:

$$PV = NkT$$

where N is the number of gas molecules and k is called Boltzmann constant given by

$$k = 1.38 \times 10^{-23}\ \mathrm{J \cdot K^{-1}}.$$

Let us recall, the atomic mass unit, where 1 u corresponds the mass of the $^{12}\mathrm{C}$ divided by 12 and

$$1\ \mathrm{u} = 1.6605 \times 10^{-27}\ \mathrm{kg} = 1.6605 \times 10^{-24}\ \mathrm{g}$$

Therefore, in 12 g of $^{12}\mathrm{C}$, there are

$$\frac{12\ \mathrm{g}}{12 \times 1.6605 \times 10^{-24}\ \mathrm{g}} = \frac{1}{1.6605 \times 10^{-24}} = 6.02 \times 10^{23} \equiv N_\mathrm{A}$$

of $^{12}\mathrm{C}$ atoms. This N_A is called Avogadro's number. We introduce a new unit, called Mole, corresponding to N_A particles. We can then rewrite the equation of state for ideal gas to be

$$PV = nRT$$

where,

$$R = N_\mathrm{A} \times k = 8.314\ \mathrm{J/(mol \cdot K)}$$

is called the universal gas constant and

$$n = \frac{N}{N_\mathrm{A}}\ \mathrm{mol}$$

is the number of moles for a given gas. Let us say that the mass of a gas molecule is r u. Then the mass of the gas for one mole can be calculated as

$$r \times N_{\mathrm{A}} = \frac{r \times 1.6605 \times 10^{-24}\ \mathrm{g}}{1.6605 \times 10^{-24}} = r\ \mathrm{g}$$

I.e. one mole is quantity of gas whose mass in gram is numerically equal to the molecular mass of that gas:

Examples; Hydrogen gas (H_2) the atomic mass is 2.0 u (twice the hydrogen atoms), thus 1 mole of H_2 gas corresponds to 2 g. Carbon dioxide (CO_2) the atomic mass is $12.0 + 2 \times 16.0 = 44$, thus 1 mole of CO_2 corresponds to 44g. So, 220 g of CO_2 is 220/44 = 5 moles.

The Ideal Gas law

The standard temperature, $T = 273$ K ($\approx 0^\circ$ C),
and standard pressure, $P = 1.00$ atm $= 1.013 \times 10^5\ \mathrm{N/m^2}$: STP.

Volume of 1.00 mole of any gas at STP, assuming that it behaves like an ideal gas, is given by

$$V = \frac{nRT}{P} = \frac{1\ \mathrm{mol} \times 8.314\ \mathrm{Nm/(mol \cdot K)} \times 273\ \mathrm{K}}{1.013 \times 10^5\ \mathrm{Nm^{-2}}} = 22.4 \times 10^{-3}\ \mathrm{m}^2$$

or 22.4 litters.

The mass of air in a room with a size of $5\ \mathrm{m} \times 3\ \mathrm{m} \times 2.5\ \mathrm{m}$ (high) at STP: the volume of the air in the room is $V = 5\ \mathrm{m} \times 3\ \mathrm{m} \times 2.5\ \mathrm{m} = 37.5\ \mathrm{m}^3$. Since 1 mol of an ideal gas at STP gives 22.4 litters, $37.5\ \mathrm{m}^3$ of an ideal gas at STP corresponds to

$$37.5 / 22.4 \times 10^{-3} = 1674\ \mathrm{mol}.$$

The air is 20% O^2 and 80% N^2. The atomic mass numbers for O and N are 16 and 14, respectively. The molecular mass of air is then given by

$$0.2 \times (2 \times 16) + 0.8 \times (2 \times 14) = 28.8$$

i.e. 1 mole of air is 28.8 g. Therefore 1674 mole of air is 48.2 kg.

Let us assume that a system of ideal gas is in an equilibrium state with, (V_1, P_1, T_1), where

$$\frac{P_1 V_1}{T_1} = nR.$$

We then change the same gas to a different equilibrium state (V_2, P_2, T_2). Since it is the identical gas to what was in the state of (V_1, P_1, T_1), nR remains constant. Thus

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}.$$

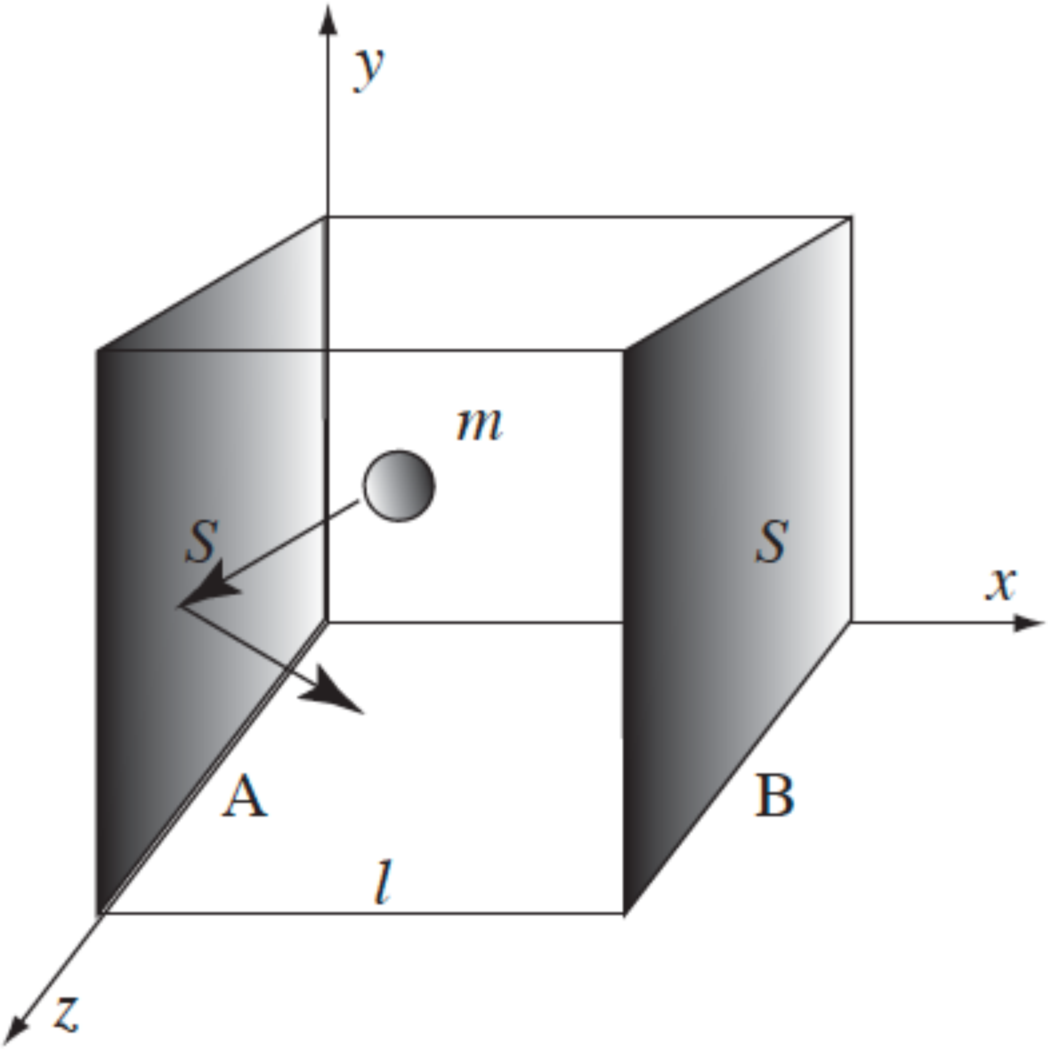
Kinetic Theory of Gasses

We try to describe the equation of the state from the microscopic view, i.e. as an ensemble of particles with an identical mass moving in random directions isotropically. There is no interaction between the particle and the wall of the container, containing the gas, nor between the particles themselves. When the particle collides with the wall or with other particles, it makes an elastic scattering.

The gas is in a cubic container, as shown in the figure. The pressure, P, of the gas acting on the container wall is caused by the elastic scattering of the gas molecules with the wall. Let us consider first that there is one gas molecule in the container. The force acting on the wall A by the molecule through the elastic scattering can be given by

$$\frac{\Delta p}{\Delta t}$$

where Δp is the momentum change of the molecule within the time interval Δt. In the scattering process, only the x-component of the velocity changes from v_x to $-v_x$ and the time interval to have one scattering corresponding to the time needed to traverse for the molecule from A to B and back to A.



It follows that

$$\Delta p = -mv_x - mv_x = -2mv_x,\ \Delta t = \frac{2l}{v_x}$$

leading to

$$\frac{\Delta p}{\Delta t} = \frac{-2mv_x}{2l/v_x} = -\frac{mv_x^2}{l}$$

The force onto the wall is then

$$F = \frac{mv_x^2}{l}.$$

Now we consider the case where there are a large number of N molecules. The force then becomes

$$F = \frac{m\sum_{i=1}^{N} v_x^{i\,2}}{l}$$

By introducing the average of v_x^2, given by

$$\left\langle v_x^2 \right\rangle = \frac{\sum_{i=1}^{N} v_x^{i\,2}}{N}$$

the force can be given by

$$F = \frac{Nm\left\langle v_x^2 \right\rangle}{l}$$

Recalling $v^2 = v_x^2 + v_y^2 + v_z^2$, it follows that

$$\left\langle v^2 \right\rangle = \frac{1}{N}\sum_{i=1}^{N}\left(v_x^{i\,2} + v_y^{i\,2} + v_z^{i\,2}\right) = \frac{1}{N}\left(\sum_{i=1}^{N} v_x^{i\,2} + \sum_{i=1}^{N} v_y^{i\,2} + \sum_{i=1}^{N} v_z^{i\,2}\right) = \left\langle v_x^2 \right\rangle + \left\langle v_y^2 \right\rangle + \left\langle v_z^2 \right\rangle$$

If the movement of the gas molecules are random and isotropic, $\left\langle v_x^2 \right\rangle = \left\langle v_y^2 \right\rangle = \left\langle v_z^2 \right\rangle$, thus

$$\left\langle v_x^2 \right\rangle = \frac{\left\langle v^2 \right\rangle}{3}$$

and

$$F = \frac{Nm\left\langle v^2 \right\rangle}{3l}$$

By denoting the area of the wall A to be S, the pressure is given by

$$P = \frac{F}{S} = \frac{Nm\left\langle v^2 \right\rangle}{3lS} = \frac{Nm\left\langle v^2 \right\rangle}{3V}$$

where V is the volume of the container. It follows that

$$PV = \frac{2}{3}N\left(\frac{m}{2}\left\langle v^2 \right\rangle\right) = \frac{2}{3}N\langle K \rangle$$

where $\langle K \rangle = m\left\langle v^2 \right\rangle / 2$ is the average of the kinetic energy of the gas molecule. By comparing this to the equation of the state for the ideal gas,

$$PV = NkT$$

we can conclude

$$\langle K \rangle = \frac{3}{2}kT$$

i.e. the average kinetic energy of the molecule of an ideal gas is directly proportional to the absolute temperature. What is the average kinetic energy of an ideal gas molecule at 37° C? Noting that 37° C is 310 K and we obtain

$$\langle K \rangle = \frac{3}{2}kT = \frac{3}{2}\cdot 1.38 \times 10^{-23}\ \mathrm{J}/K \cdot 310\ \mathrm{K} = 6.42 \times 10^{-21}\ \mathrm{J}$$

For one mole of molecules, the kinetic energy becomes

$$N_\mathrm{A}\langle K \rangle = 6.02 \times 10^{23} \cdot 6.42 \times 10^{-21}\ \mathrm{J} = 3860\ \mathrm{J} \approx 1\ \mathrm{kcal}.$$

The root-mean-squared velocity of an ideal gas molecule at an absolute temperature T is then given by

$$v_{\mathrm{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{2\langle K \rangle}{m}} = \sqrt{\frac{3kT}{m}}$$

The root-mean-squared velocity of O_2 (molecular mass 32 u) and N_2 (molecular mass 28 u) at 37° C can be calculated using the above equation. Since 1 u corresponds to 1.66×10^{-27} kg, the masses of one molecule for them are given by

$$m\left(\mathrm{O}^2\right) = 32 \cdot 1.66 \times 10^{-27}\ \mathrm{kg} = 5.3 \times 10^{-26}\ \mathrm{kg}$$

$$m\left(\mathrm{N}^2\right) = 28 \cdot 1.66 \times 10^{-27}\ \mathrm{kg} = 4.6 \times 10^{-26}\ \mathrm{kg}$$

and

$$v_{\mathrm{rms}}\left(\mathrm{O}_2\right) = \sqrt{\frac{3kT}{m\left(\mathrm{O}_2\right)}} = \sqrt{\frac{3 \cdot 1.38 \times 10^{-23}\ \mathrm{J/K} \cdot 293\mathrm{K}}{5.3 \times 10^{-26}\mathrm{kg}}} = 480\ \mathrm{m/s}$$

$$v_{\mathrm{rms}}\left(\mathrm{N}_2\right) = \sqrt{\frac{3kT}{m\left(\mathrm{N}_2\right)}} = \sqrt{\frac{3 \cdot 1.38 \times 10^{-23}\ \mathrm{J/K} \cdot 293\mathrm{K}}{4.6 \times 10^{-26}\mathrm{kg}}} = 510\ \mathrm{m/s}$$

Note that the lighter gas molecule moves faster at a same temperature.