Chapter 19 – Kinetic Theory of Gases

A gas consists of atoms or molecules which collide with the walls of the container and exert a pressure, P. The gas has temperature T and occupies a volume V. Kinetic theory relates the variables P, V, and T to the motion of the molecules.

Ideal Gas Equation

Gases at low pressures are found to obey the *ideal gas law*:

$$PV = nRT$$

In the gas equation, the following are the symbols in SI units:

P = absolute pressure [Pa = N/m^2]
V = volume [m^3]
T = absolute temperature [K]
n = number of moles [unitless]
R = gas constant = 8.31 J/mole·K

If P is in atmospheres, V in liters, and T in K, then R = 0.0831 L·atm/mole·K

By *absolute* pressure, we mean pressure relative to a vacuum, where P = 0. For example, sometimes *gauge* pressure is given, which means pressure above atmospheric pressure. A tire gauge measures pressure above atmospheric pressure, not absolute pressure. Don't use gauge pressure in the gas equation. Likewise, don't use Celsius or Fahrenheit, since these are not absolute temperature scales. Convert Celsius or Fahrenheit to Kelvin.

Mole

A *mole* of particles (atoms or molecules) is essentially Avogadro's number of particles, where

$$N_A = 6.02 \times 10^{23} \text{ particles/mole}$$

It is also the number of atoms in 12 g of C-12. All elements have an atomic mass number. The atomic mass number is the mass in grams of one mole of the element.

$$n = \frac{mass}{atomic\ mass}$$

The mass of an atom can be calculated from the atomic mass as

$$m_{atom} = \frac{atomic\ mass}{N_A}$$

Thus, the mass of a C-12 atom is

$$m_{C-12} = \frac{12g \, / \, mole}{6.02x10^{23} \, atoms \, / \, mole} = 1.99x10^{-23} \, g \, / \, atom$$

Example:

A 1 liter container is filled with helium at a (gauge) pressure of 2 atm and temperature of 20^oC. How many moles of helium are in the container?

$$P = P_{atm} + P_{guage} = 1 \, atm + 2 \, atm = 3 \, atm = 3x1.013x10^5 \, Pa = 3.039x10^5 \, Pa$$

$$T_K = 20 + 273 = 293K$$

$$V = (1L)(10^{-3} \, m^3 \, / \, L) = 10^{-3} \, m^3$$

$$n = \frac{PV}{RT} = \frac{(3.039x10^5 \, Pa)(10^{-3} \, m^3)}{(8.31 \, J \, / \, mole \cdot K)(293K)} = 0.125 \, mole$$

The mass of the helium is

$$m = (0.125 \, mole)(4g \, / \, mole) = 0.5 \, g$$

Example:

The above container of helium is heated to 100^oC while the volume of the container is reduced to 0.5 liter. What is the resulting pressure? Since the number of moles doesn't change

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$P_2 = \frac{P_1V_1T_2}{V_2T_2} = \frac{(2atm)(1L)(373K)}{(0.5L)(293K)} = 5.09 \, atm$$

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Kinetic Theory

Assume that we have a container of an ideal gas with the following properties:

- Large number of molecules with average spacing between molecules large compared with the size of the molecules.

- Molecules obey Newton's laws of motion.

- Molecules collide elastically with each other and with the walls of the container.

- Forces between molecules are short range – only important during collisions.

- Container consists of only one type of gas (not a mixture).

The pressure exerted by the gas on the walls of the container is a result of collisions by the molecules. Consider a cubical container with dimensions $d \times d \times d$. A molecule with a component of velocity in the x-direction will collide with a wall perpendicular to the *x*-axis and transfer an amount of momentum to the wall given by

$$\Delta p = 2mv_x$$

The average time between collisions with this wall is

$$\Delta t = 2d / v_x$$

The average force exerted on the wall by this collision is

$$F_1 = \frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{2d / v_x} = \frac{mv_x^2}{d}$$

For *N* molecules making collisions, the total average force is

$$F = \frac{Nm\overline{v_x^2}}{d}$$

where $\overline{v_x^2}$ is the average of the square of the velocity in the *x*-direction. However, because of the random motion

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

and

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}, \ or \ \overline{v_x^2} = \frac{1}{3}\overline{v^2}$$

Thus,

$$F = \frac{N\,m\overline{v^2}}{3d}$$

The pressure exerted on the wall is

$$P = \frac{F}{A} = \frac{F}{d^2} = \frac{N\,m\overline{v^2}}{3d^3} = \frac{N\,m\overline{v^2}}{3V}$$

Or,

$$PV = \frac{1}{3}Nm\overline{v^2} = \frac{2}{3}N\frac{1}{2}m\overline{v^2}$$

We compare this with the ideal gas equation, which is

$$PV = nRT = Nk_BT \quad (where \ k_B = nR/N = R/N_A)$$

This means that the average translational kinetic energy is related to the temperature as

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_BT$$

The total translational kinetic energy in the gas is

$$E = N\frac{1}{2}m\overline{v^2} = \frac{3}{2}Nk_BT = \frac{3}{2}nRT$$

From the above we can determine the root-mean-square (rms) speed of the molecules as

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_BT}{m}}$$

We can also write this as

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

where M is the molar mass, since $M = N_A m$ and $N_A k_B = R$.

Example:

What is the rms speed of nitrogen molecules at 20°C? For N_2, $M = 28$ g/mole = 0.028 kg/mole.

$$v_{rms} = \sqrt{\frac{3(8.31J/mole \cdot K)(293K)}{(0.038kg/mole)}} = \underline{511m/s}$$

What is the total translational kinetic energy in 1 mole of the gas?

$$E = N\frac{1}{2}m\overline{v^2} = N\frac{3}{2}k_B T = \frac{3}{2}nRT = \frac{3}{2}(1mole)(8.31J/mole \cdot K)(293K) = \underline{3.65x10^3 J}$$

Maxwell Speed Distribution

At any instant of time the molecules in a gas have a wide range of speeds both above and below the rms speed. The distribution is described by the *Maxwell speed distribution function*, which gives the probability, *P(v)*, that a molecule will have a given speed, *v*. (*P(v)dv* is the fraction of molecules with speed *v* centered in the interval *dv*.)

$$P(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

M = molecular mass
R = gas constant
T = Kelvin temperature

The distribution is plotted below for two different temperatures. As the temperature increases (or as the molecular mass decreases) the distribution shifts to higher speeds.


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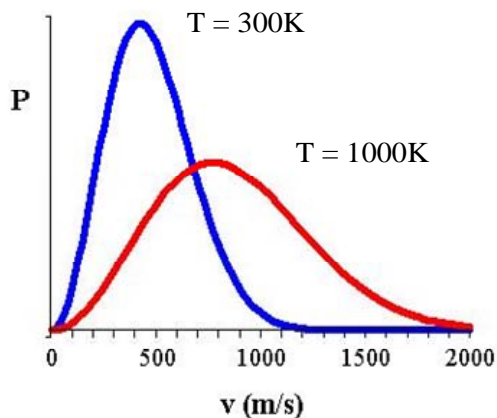
Specific Heat of an Ideal Gas

For gases, it is conventional to refer to the *molar* specific heat, which is the heat absorbed per *mole* per unit temperature rise. The molar specific heat, and thus the heat absorbed for a given temperature rise, depends on whether the pressure or the volume is held constant as the temperature increases.

$$Q = nc_v \Delta T \qquad (\text{constant volume})$$
$$Q = nc_p \Delta T \qquad (\text{constant pressure})$$
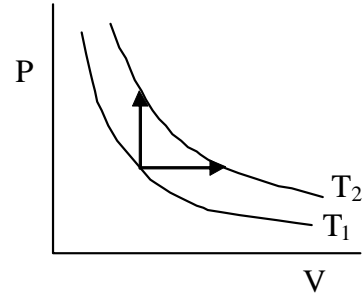
From the 1st law of thermodynamics, no work is done in a constant volume process. Thus,

$$\Delta U = Q \qquad (\text{constant volume})$$

For a *monatomic* gas the internal energy is the total translational kinetic energy. Then

$$U = E = \frac{3}{2}nRT, \ \Delta U = \frac{3}{2}nR\Delta T, \text{ and}$$

$$\frac{3}{2}nR\Delta T = nc_v \Delta T, \text{ or}$$

$$c_v = \frac{3}{2}R$$

For a constant pressure process, $\Delta W = P\Delta V = nR\Delta T$. So,

$$\Delta U = Q - W = Q - P\Delta V = Q - nR\Delta T,$$

or

$$Q = \Delta U + nR\Delta T = \frac{3}{2}nR\Delta T + nR\Delta T = \frac{5}{2}nR\Delta T.$$

Then,

$$c_p = \frac{Q}{n\Delta T} = \frac{5}{2}R$$

and $\quad c_p = c_v + R$

During a constant volume process, no work is done so all the heat absorbed goes into increasing the internal energy and the temperature. During a constant pressure process, the gas expands and reduces the internal energy by doing work. Thus, more heat can be absorbed for a given temperature change.

Specific Heat of Diatomic Gases

Previously, it was shown that

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_BT$$

Since $\frac{1}{2}m\overline{v^2} = \frac{1}{2}m\overline{v_x^2} + \frac{1}{2}m\overline{v_y^2} + \frac{1}{2}m\overline{v_z^2}$, this means that the average kinetic energy is $\frac{1}{2}k_BT$ per term or per degree of freedom. A diatomic molecule is somewhat like two masses connected by a spring. The molecule can rotate about its center of mass and the atoms can vibrate back and forth along the line connecting them. Since the rotational inertia about an axis connecting the atoms is extremely small, there are two energy terms corresponding to rotation about the other two perpendicular axes (two degrees of freedom). The average kinetic energy of each of these terms is $\frac{1}{2}k_BT$ and the total average rotational energy is k_BT .

The vibrational energy of the mass-spring system consists of a kinetic energy and a potential energy term (also two degrees of freedom). Each of these terms has an average of $\frac{1}{2}k_BT$ and the total average vibrational energy is k_BT .

Because of these additional degrees of freedom, the specific heat of a diatomic molecule is greater than that of a monatomic molecule (½ R for each degree of freedom). The rotational and vibrational energies of a molecule are quantized. That is, only certain discrete energies are allowed. In order to excite these rotational and vibrational levels, the gas must be at a sufficiently high temperature. At low temperatures, only translational motions can occur. At higher temperatures, the molecular collisions are sufficient to excite the rotational levels. At still higher temperatures, the vibrational energy levels can be excited. Thus, the specific heat of a diatomic molecule will increase with temperature, giving evidence of the quantum nature of the energies.