

8. Ideal Gas Law

More than 300 years ago experimenters found that gases obeyed the following simple empirical laws:

$$(a) \quad P \propto \frac{1}{V} \quad \text{or} \quad PV = \text{constant, at fixed temperature}$$

$$(b) \quad P \propto T \quad \text{or} \quad \frac{P}{T} = \text{constant, for a fixed mass of gas at constant volume.}$$

(a) and (b) are known as Boyle's law and Gay-Lussac's law respectively.

8.1 Ideal gas law

At low densities all real gases are observed to obey

$$PV = nRT \quad \text{ideal gas law}$$

P is pressure in Pa, V is volume in m^3 , n is number of moles of gas

R is called the **gas constant**; $R = 8.31 \text{ J}(\text{mol})^{-1}\text{K}^{-1}$ ‘joules per mole-kelvin’ for **all** gases.

Boltzmann’s constant

Notice that the gas constant R is given in terms of moles. 1 mole of a substance contains **Avogadro’s number** N_A of particles (gas atoms, gas molecules, metal atoms, etc.) *by definition*.

$$N_A = 6.023 \times 10^{23} \text{ particles per mole}$$

Boltzmann’s constant is the gas constant divided by Avogadro’s number:

$$k_B = \frac{R}{N_A}$$

$$k_B = \frac{8.31 \text{ J mol}^{-1} \text{ K}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1}} = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

Using $R = k_B N_A$ and $n = N/N_A$ we have $nR = Nk_B$ and can write
[!! N is the number of gas molecules or atoms !!]

$$PV = NkT \quad \text{ideal gas law}$$

[From now on we will drop the subscript 'B' from Boltzmann's constant and just write k .]

Thus we can write the ideal gas law in two useful forms:

$$\boxed{PV = nRT} \quad \text{or} \quad \boxed{PV = NkT} \quad \text{ideal gas law}$$

8.3 Isothermal Processes

When a gas is compressed or expanded at constant temperature the process is said to be **isothermal**.

We have

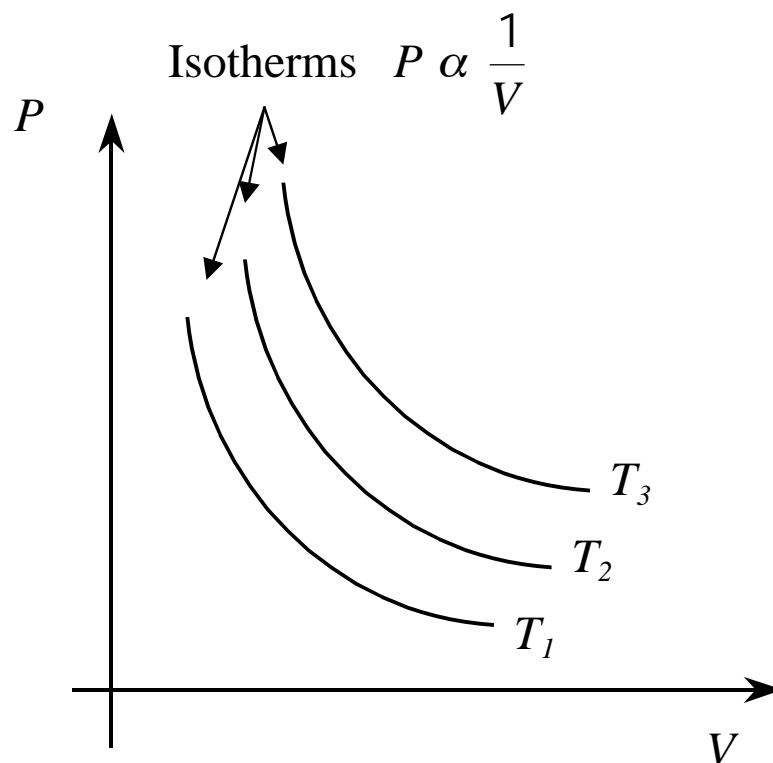
$$PV = nRT \quad \text{or} \quad P = \underbrace{nRT}_{\text{constant}} \cdot \frac{1}{V}$$

for an isothermal process, T is constant, nRT is a constant

so that

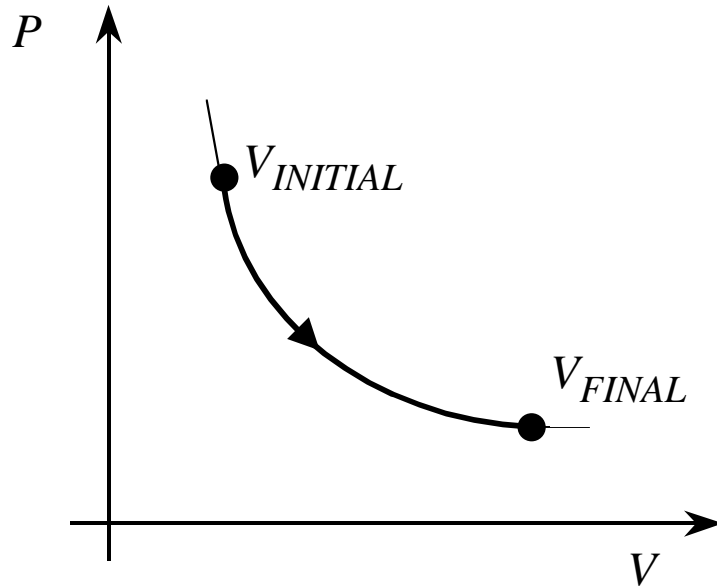
$$P = (\text{const.}) \times \frac{1}{V} \quad \text{or} \quad P \propto \frac{1}{V}$$

The curves of $P \propto \frac{1}{V}$ are called **isotherms** and are rectangular hyperbolas.



The **work done by an ideal gas in an isothermal expansion** is found as follows.

Let's select one representative isothermal process:



We know that

$$W = \int dW = \int_{V_I}^{V_F} P dV$$

and using $P = nRT/V$, substitute for P ,

$$W = \int_{V_I}^{V_F} \frac{nRT}{V} dV$$

integrate between initial (V_I)
and final (V_F) volumes

$$W = nRT \int_{V_I}^{V_F} \frac{dV}{V}$$

$$= nRT [\ln V]_{V_I}^{V_F}$$

$$= nRT \ln \frac{V_F}{V_I}$$

$$\begin{aligned} &\ln V_F - \ln V_I \\ &= \ln(V_F/V_I) \end{aligned}$$

for an isothermal process the work done is

$$W = nRT \ln(V_F/V_I)$$

[

Recall the values of $\ln x$ (natural logs):

if $x > 1$	$\ln x$ is +ve
if $x < 1$	$\ln x$ is -ve

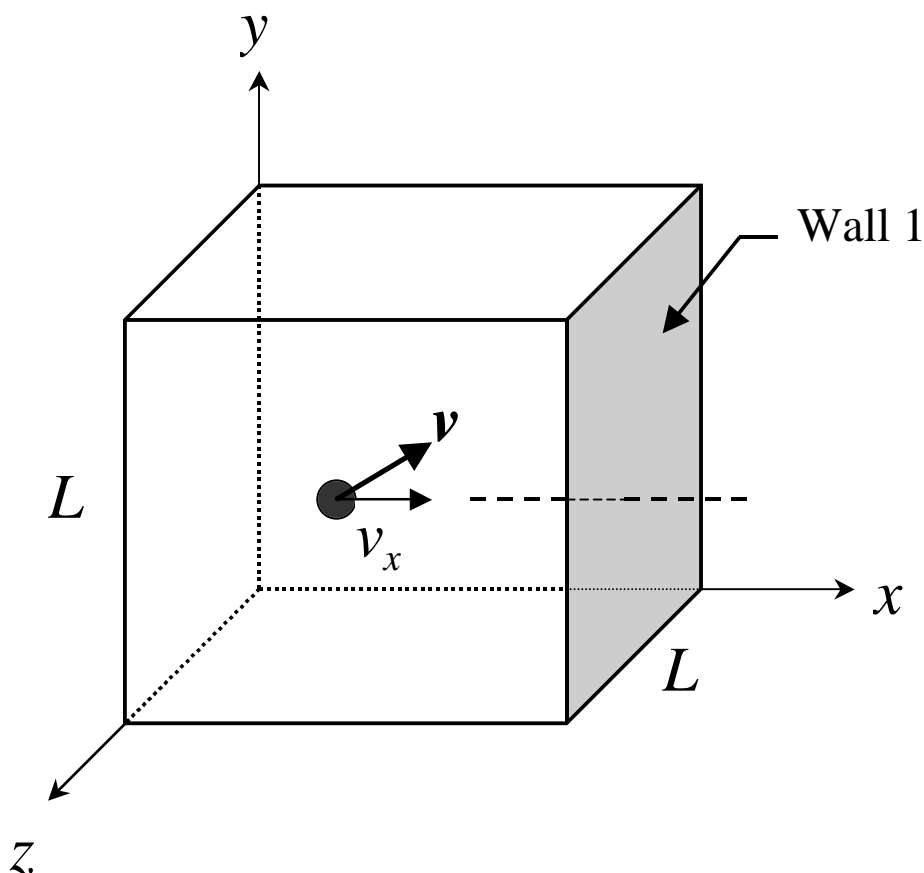
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For an isothermal compression, $V_F < V_I$ so W is negative, the work done by the gas is negative.

For an isothermal expansion, $V_F > V_I$ so W is positive, the work done by the gas is positive.

8.2 Kinetic Theory

We can derive the gas laws beginning with the mechanics of a single molecule and putting in some statistics to take care of the v. large number of molecules involved: this is kinetic theory.



Choose a 'representative' molecule with velocity \mathbf{v} and x-component of velocity v_x .

Molecule collides with Wall 1 and rebounds elastically.

\Rightarrow molecule's x-momentum change is

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

\Rightarrow momentum imparted to Wall 1 is

$$\Delta p_{x,wall} = 2mv_x$$

Molecule travels at velocity v_x . It will collide with Wall 1 again after a time $\Delta t = 2L/v_x$ (the time for a 'round trip' to the opposite wall).

The rate at which momentum is transferred to Wall 1 is the force on wall 1 ($F = dp/dt$, Newton's 2nd law) and is

$$F_x = \frac{\Delta p_{x,wall}}{\Delta t} = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L} \quad \text{force on Wall 1 due to a single molecule}$$

Now, consider all molecules from 1 up to N with x-velocities

$$v_{x1}, v_{x2}, \dots, v_{xN}.$$

Recalling that $P = F/A = F/L^2$ (where $A = L^2$ the wall area),

We have

$$P = \frac{F_x}{L^2} = \frac{mv_{x1}^2 + mv_{x2}^2 + \dots + mv_{xN}^2}{L^2} \quad \left[F_x = \frac{mv_x}{L} \right]$$

pressure=force/area

$$= \left(\frac{m}{L^3} \right) (v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2) \quad (*)$$

Now $n = N/N_A$ so $N = nN_A$. This means there is a total of $N = nN_A$ terms in the second bracket and we can write

$$\left(\frac{m}{L^3} \right) (v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2) = \left(\frac{m}{L^3} \right) nN_A (v_x^2)_{av}$$

We have set $(v_{x1}^2 + v_{x2}^2 + \dots v_{xN}^2) = nN_A(v_x^2)_{av}$ and averaged over all molecules with x-components of velocity:

$(v_x^2)_{av}$ is the average value of the x-components of all the molecular speeds.

Equation (*) above is then

$$P = \frac{nmN_A}{L^3}(v_x^2)_{av}$$

If we note further that

$$mN_A = \text{mass of one mole of gas} = M$$

and

$$L^3 = V$$

we have

$$P = \frac{nM}{V}(v_x^2)_{av}$$

For any of these molecules we have $v^2 = v_x^2 + v_y^2 + v_z^2$

Now the gas contains $\sim N_A = 10^{23}$ molecules, a very large number, moving at random. We can therefore set

$$v_x^2 = \frac{1}{3}v^2$$

We further note that

$$\sqrt{(v^2)_{av}} = v_{rms}$$

where v_{rms} is the root-mean-square molecular speed, so that

$$P = \frac{1}{3} \frac{nMv_{rms}^2}{V}$$

Kinetic theory

8.4 Temperature and kinetic theory

Using the kinetic theory result $P = \frac{1}{3} \frac{nMv_{rms}^2}{V}$ and putting $nM = Nm$,

we have,

$$PV = \frac{1}{3} Nm v_{rms}^2$$

The ideal gas law is

$$PV = NkT.$$

Combining these,

$$NkT = \frac{1}{3}Nmv_{rms}^2$$

and

$$T = \frac{m}{3k}v_{rms}^2 \quad (*)$$

A single molecule or atom of gas has an average (translational – it could also rotate or vibrate) kinetic energy

$$KE_{av} = \frac{1}{2}mv_{rms}^2$$

so that we can write

$$T = \frac{2}{3k}KE_{av}$$

or

$$KE_{av} = \frac{3}{2}kT$$

The connection between absolute temperature T and the average kinetic energy of a molecule

When we measure the temperature of a gas we are measuring the average translational kinetic energy of any particle (atom, molecule) of the gas!

8.5 Root-mean-square (rms) molecular speed

Using the expression $T = \frac{m}{3k} v_{rms}^2$ {eqn (*) from above} we can see that

$$v_{rms} = \sqrt{\frac{3kT}{m}} \quad \text{root-mean-square speed of gas molecules.}$$

This can also be written in useful alternative forms:

Recalling that $k = R/N_A$, we have

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

We also had previously

$$\begin{array}{ccc} & M = mN_A & \\ \swarrow & \uparrow & \searrow \\ \left\{ \begin{array}{l} \text{molar mass} \\ \text{i.e. mass of} \\ \text{one mole} \end{array} \right\} & \left\{ \begin{array}{l} \text{mass of one} \\ \text{molecule} \end{array} \right\} & \left\{ \begin{array}{l} \text{Avogadro's} \\ \text{number} \end{array} \right\} \end{array}$$

and we can write

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

rms molecular speed in terms of the mass of one mole of gas

What is the rms speed of gas molecules in the air?

Let's consider the oxygen, molecular mass $M = 32 \times 10^{-3} \text{ kg mol}^{-1}$ and take the air temperature to be $27^\circ\text{C} = 300\text{K}$.

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.31 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K})}{32 \times 10^{-3} \text{ kg}}} = 483 \text{ ms}^{-1}$$

We find values of the same order for N_2 , CO_2 and water vapour.

For the lighter gases, $v_{rms, \text{He}} = 1370 \text{ ms}^{-1}$ and $v_{rms, \text{H}_2} = 1920 \text{ ms}^{-1}$ both at 300K.