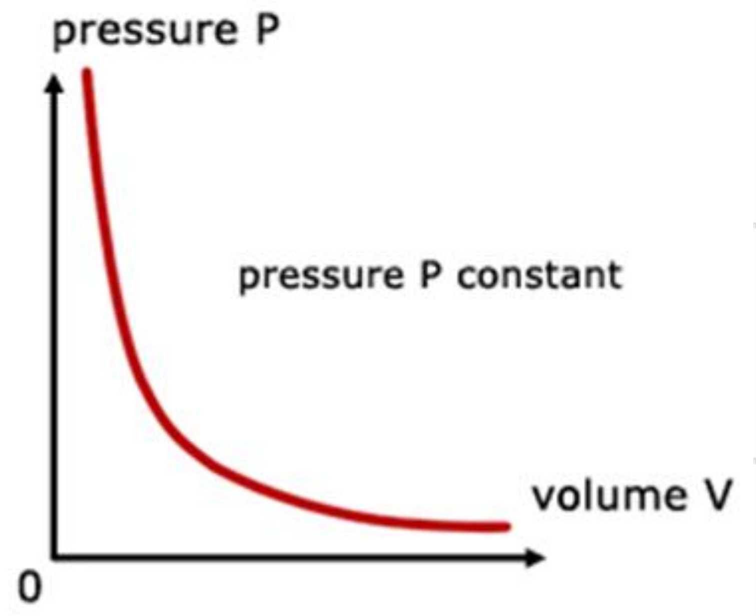
THERMAL PHYSICS
p2

GAS LAWS

Boyle's Law

For a fixed mass of gas at constant temperature and pressure, the pressure is inversely proportional to the volume.



$$p \propto \frac{1}{V}$$

making the proportionality into an equality,

$$pV = k$$

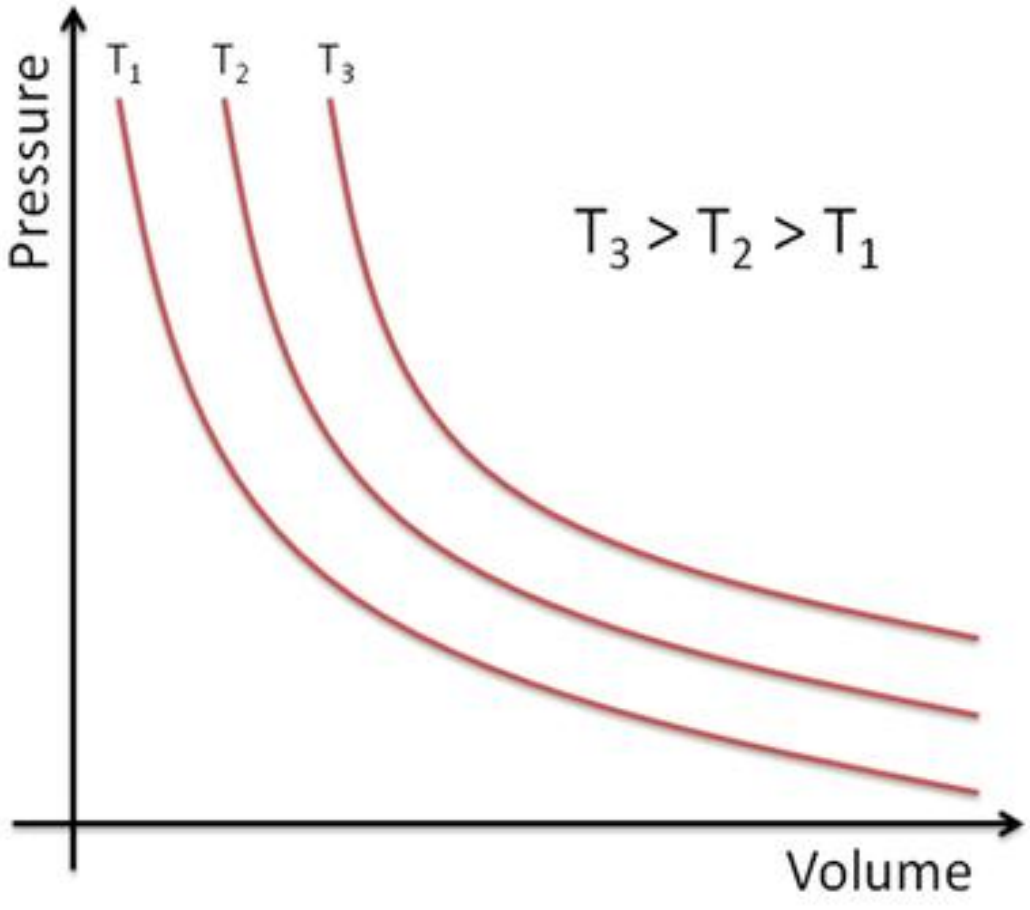
where ***k*** is a constant

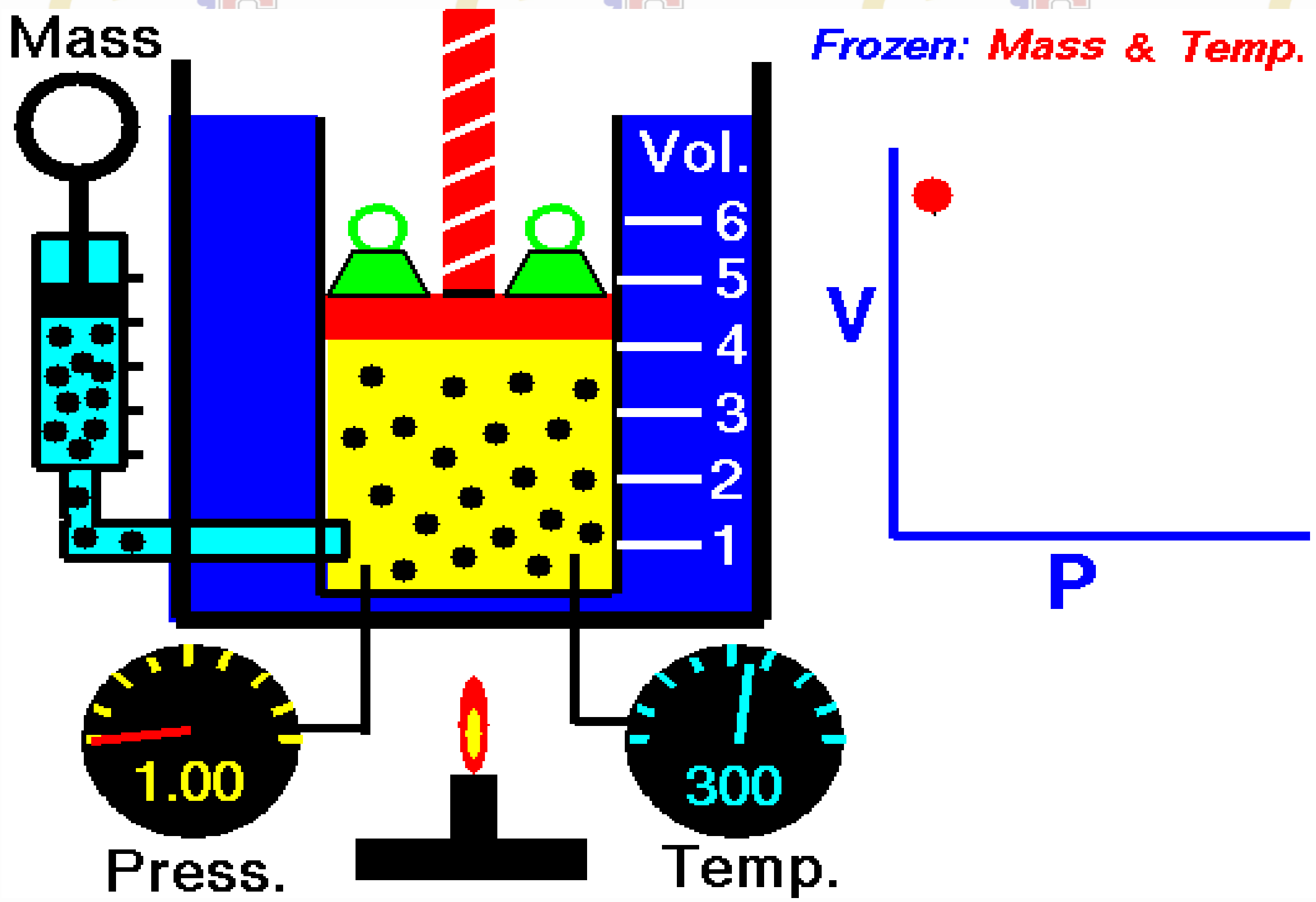
Now, consider a fixed mass of gas at one temperature at different pressures and volumes,

$$p_1V_1 = k \qquad p_2V_2 = k$$

elimenating the constant ***k***

$$p_1V_1 = p_2V_2$$

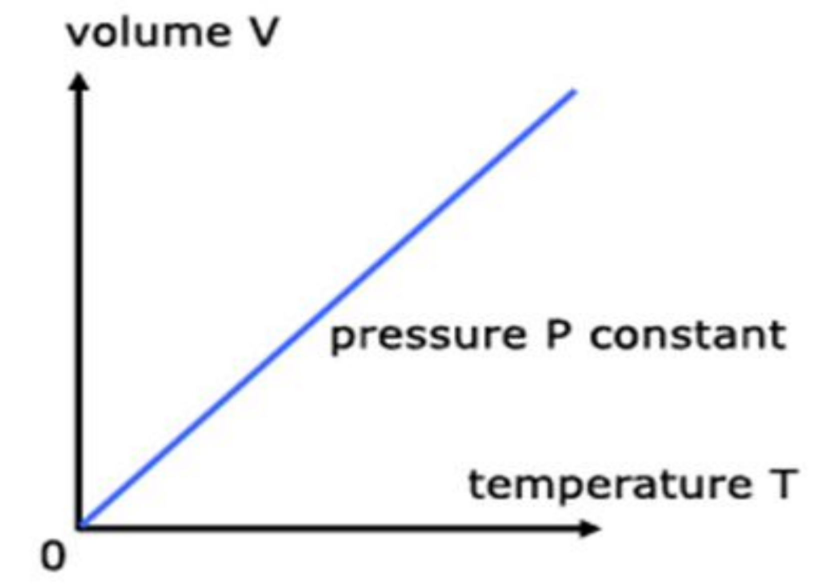




The pressure of a gas at constant temperature is increased by reducing its volume because gas molecules travel less distance between impacts at the walls due to the reduced volume. This means there are more impacts per second, so the pressure is greater.

Charles' Law

For a fixed mass of gas at constant temperature and pressure, the volume is directly proportional to the temperature(K).



$$V \propto T$$

making the proportionality into an equality,

$$V = mT$$

where ***m*** is a constant

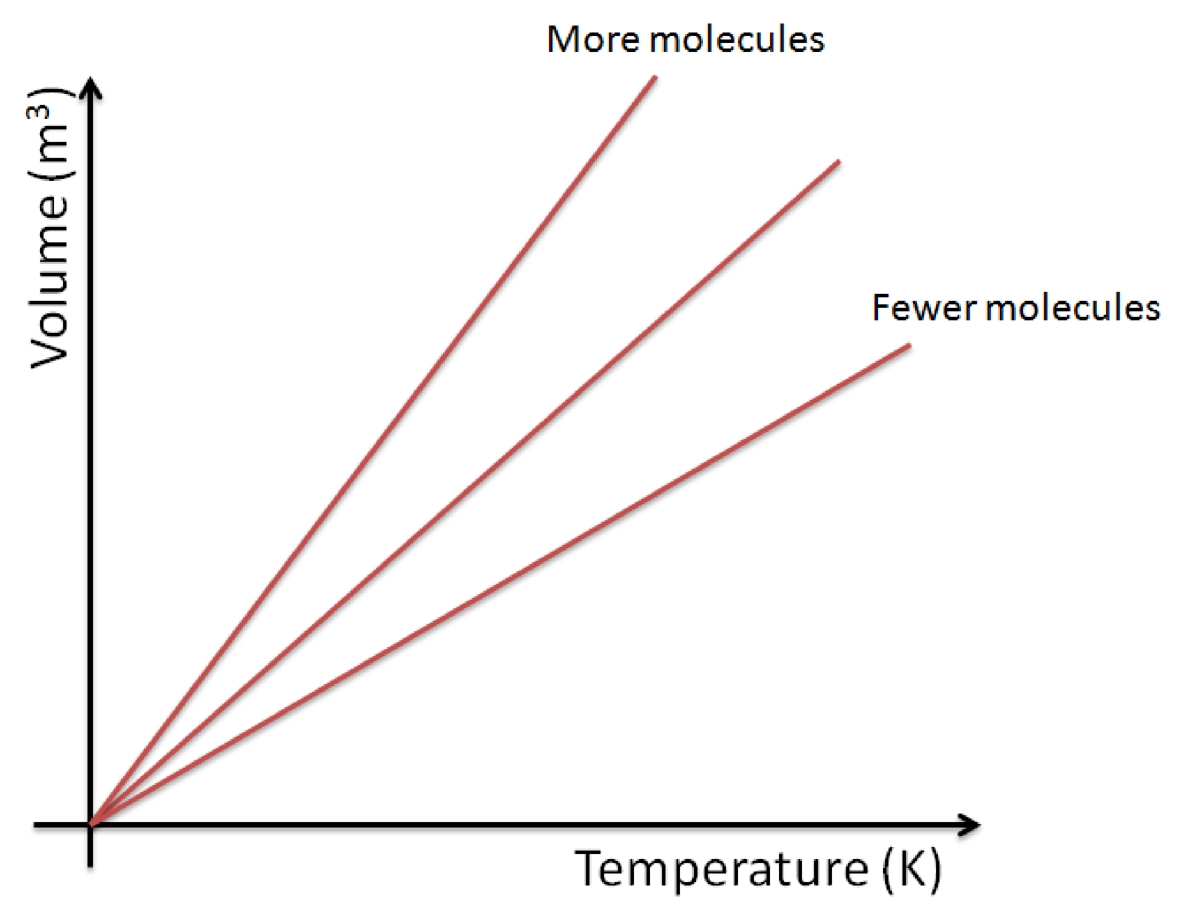
$$\frac{V}{T} = m$$

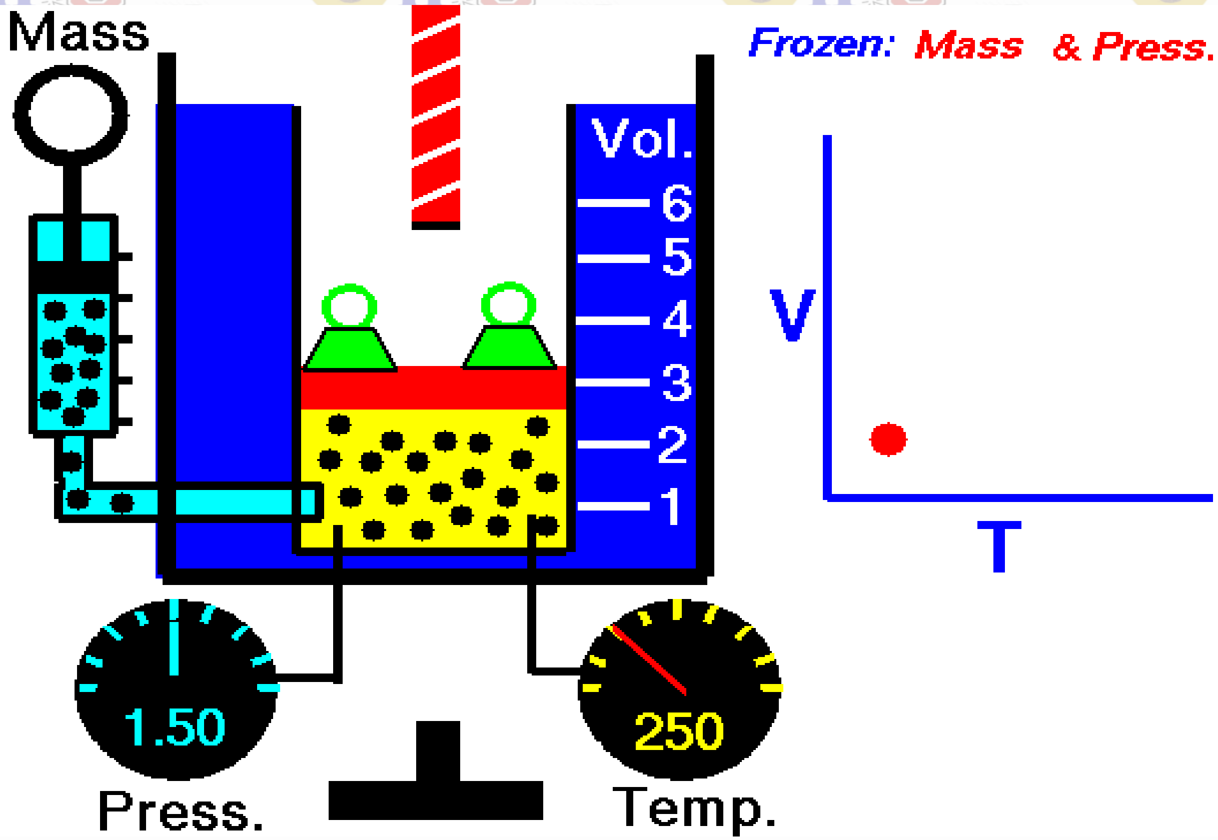
Now, consider a fixed mass of gas at one pressure at two different temperatures and volumes,

$$\frac{V_1}{T_1} = m \qquad \frac{V_2}{T_2} = m$$

elimenating the constant ***m***,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

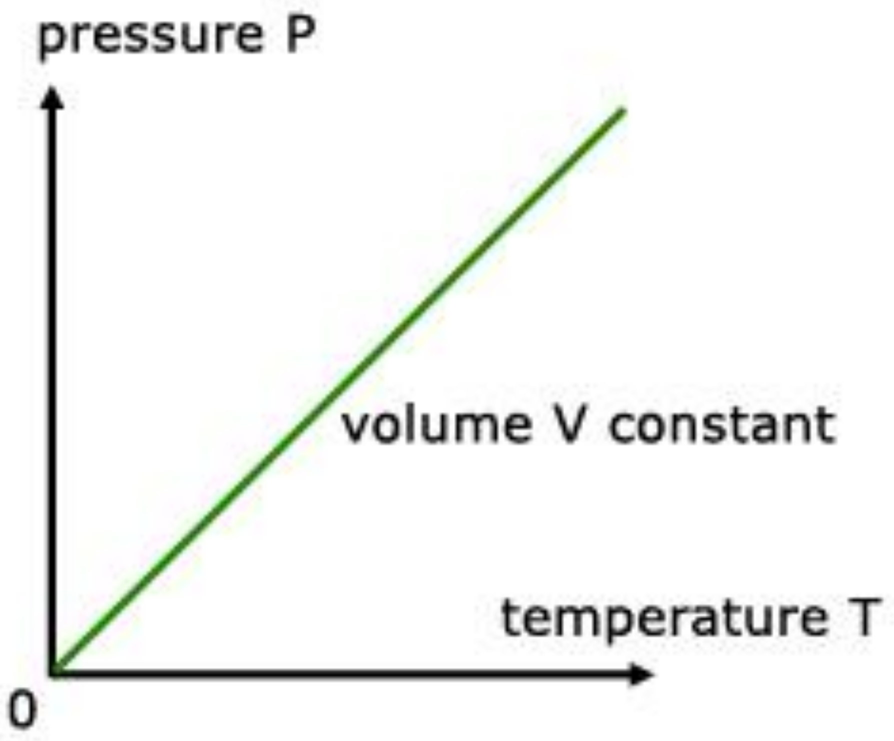




As the temperature increases the volume must increase, this is because (for constant pressure) if the particles are gaining kinetic energy with temperature, for them to have the same number of wall collisions per second (i.e. pressure) the walls of the container need to get further apart i.e. it expands.

Pressure Law

For a fixed mass of gas at constant temperature and pressure, the pressure is directly proportional to the temperature(K).



$$p \propto T$$

making the proportionality into an equality,

$$p = nT$$

where ***n*** is a constant

$$\frac{p}{T} = n$$

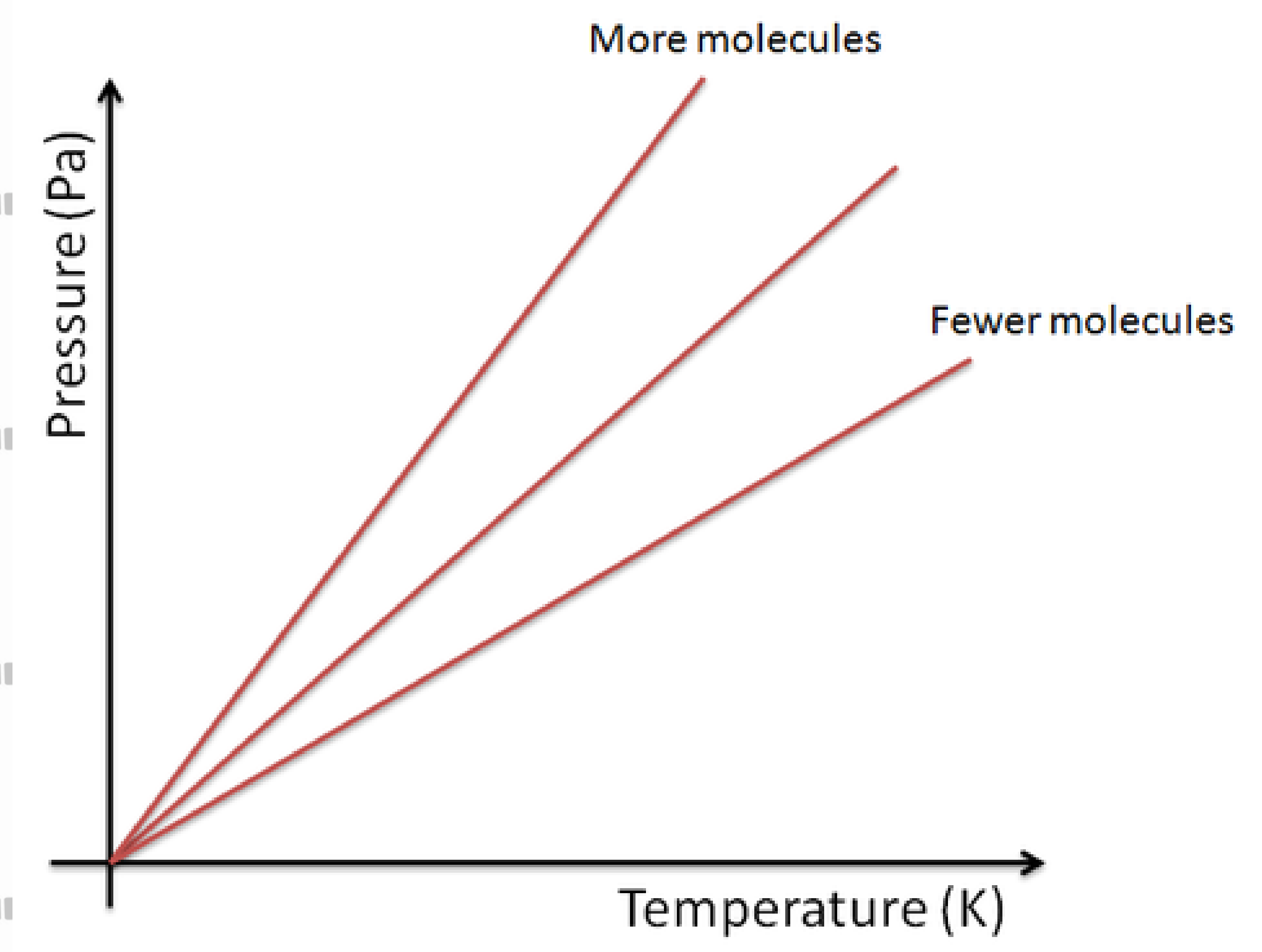
Now, consider a fixed mass of gas at one volume at two different temperatures and pressures,

$$\frac{p_1}{T_1} = n \qquad \frac{p_2}{T_2} = n$$

elimenating the constant ***n***,

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

Once the volume is fixed if you increase the temperature you are giving more energy to the particles in the gas. By doing so their kinetic energies increase which will make them hit the walls of their container more frequently, causing the pressure to rise as well.



Combined Gas Equation

The three gas law equations, with constants ***k*** , ***m*** , ***n*** are :

$$pV = k \qquad \frac{V}{T} = m \qquad \frac{p}{T} = n$$

These can be combined into one equation:

$$\frac{pV}{T} = K$$

where ***K*** (upper case) is a new constant

Now, consider a fixed mass of gas at two different temperatures, volumes and pressures,

$$\frac{p_1V_1}{T_1} = K \qquad \frac{p_2V_2}{T_2} = K$$

elimenating the constant ***K***,

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

Ideal Gas Law

For sufficiently dilute gas,
pressure is:

- proportional to number of moles
- proportional to temperature
- inversely proportional to volume

$$PV = nRT$$

pressure

volume

number of moles

Ideal Gas Constant

One mole is NA =6.023x1023 molecules
(number of 12C atoms in 12 g of 12C)

R=8.31 N□m/mole□□K

The Ideal Gas Equation

The Ideal Gas Equation

How P, V and T are related:

P = pressure (Pa)
V = volume (m^3)
T = temperature (K)
n = number of moles
N = number of molecules
R = universal gas constant = 8.3145 Jmol^-1K^-1
kB = Boltzmann's constant = 1.38x10-23 JK^-1
NA = Avagadro's number = 6.023x1023 mol^-1

$$\boxed{PV = nRT = Nk_BT}$$

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

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

Ideal gas law

- Ideal gas law with Boltzmann's constant:

$$PV = Nk_BT \qquad k_B = 1.38 \times 10^{-23}\, JK^{-1}$$

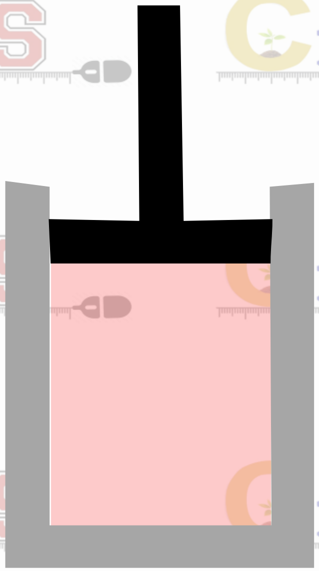
- The number of molecules N may be measured in moles n using **Avogadro's number** N_A

$$1\, mole = N_A = 6.022 \times 10^{23}\, molecules$$

- The ideal gas law may also be expressed in terms of number of moles n using the **universal gas constant** R

$$PV = nRT \qquad R = 8.314\, JK^{-1}mol^{-1}$$

I double the volume of the cylinder and reduce the absolute pressure from $1\,atm$ to $0.5\,atm$. How does the final temperature compare to the initial ?



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1. $T_f > T_i$
2. $T_f = T_i$
3. $T_f < T_i$
4. **Can't tell without *n***

If quantity of gas is fixed (n, m or N constant) then the equation of state relating initial and final properties reduces to

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

Example 10.2

Pure helium gas is admitted into a leak-proof cylinder containing a movable piston. The initial volume, pressure, and temperature of the gas are 15 L, 2.0 atm, and 300 K.

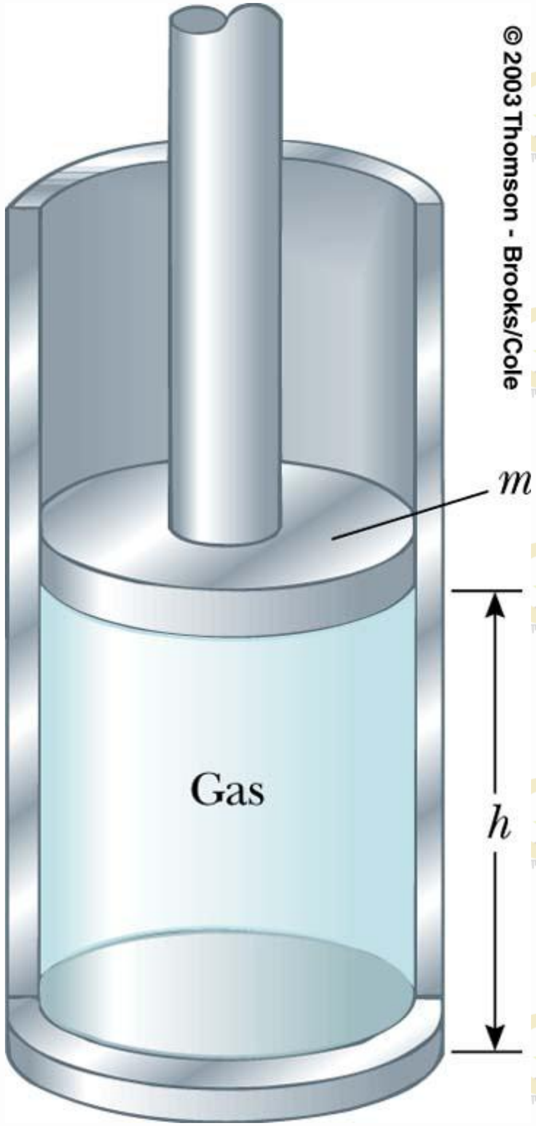
If the volume is decreased to 12 L and the pressure increased to 3.5 atm, find the final temperature of the gas. (Assume helium behaves as an ideal gas.)

420 °K

Example 10.3

A vertical cylinder of cross-sectional area 40 cm^2 is fitted with a tight-fitting, frictionless piston of mass 50.0 kg (see figure).

If there is 0.15 mol of an ideal gas in the cylinder at 500 K, determine the height h at which the piston will be in equilibrium under its own weight.



h=69.5 cm

The Kinetic Energy Of Gases

- Pressure
  - Directly proportional to number of gas molecules present
  - Directly proportional to the Kelvin temperature
  - Inversely proportional to volume

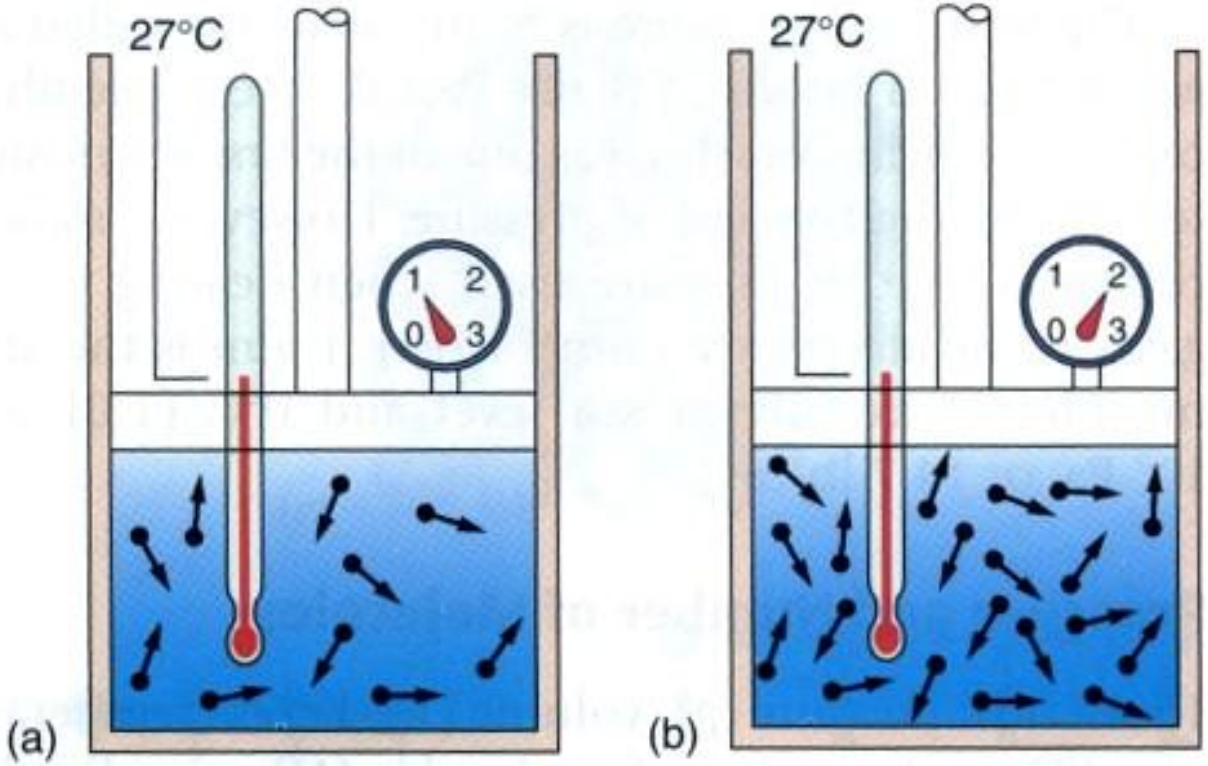
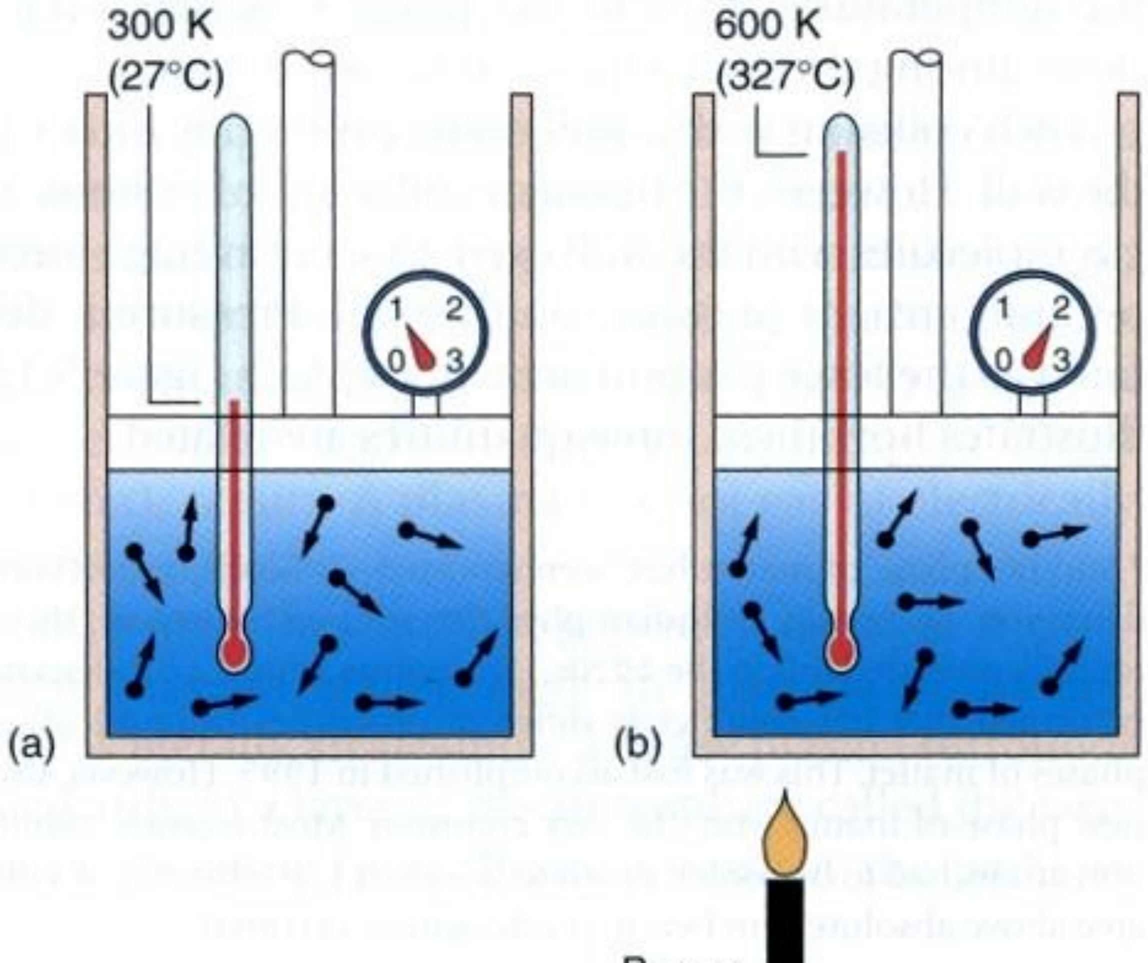


FIGURE 5.14 Pressure and Number of Molecules

In both containers, the temperature and volume are constant. However, in the container in (b) there are twice as many molecules as in the container in (a). This causes the pressure to be twice as great, as indicated on the gauge. (More molecules, more collisions, and greater pressure.)

FIGURE 5.15 Pressure and Kelvin Temperature

In both containers, the number of molecules and the volume are constant. However, the gas in (b) has been heated to twice the Kelvin temperature of that in (a), that is, 600 K (327°C) versus 300 K (27°C). This causes the pressure to be twice as great, as shown on the gauge. (Higher temperature, more kinetic energy, more collisions, and greater pressure.)



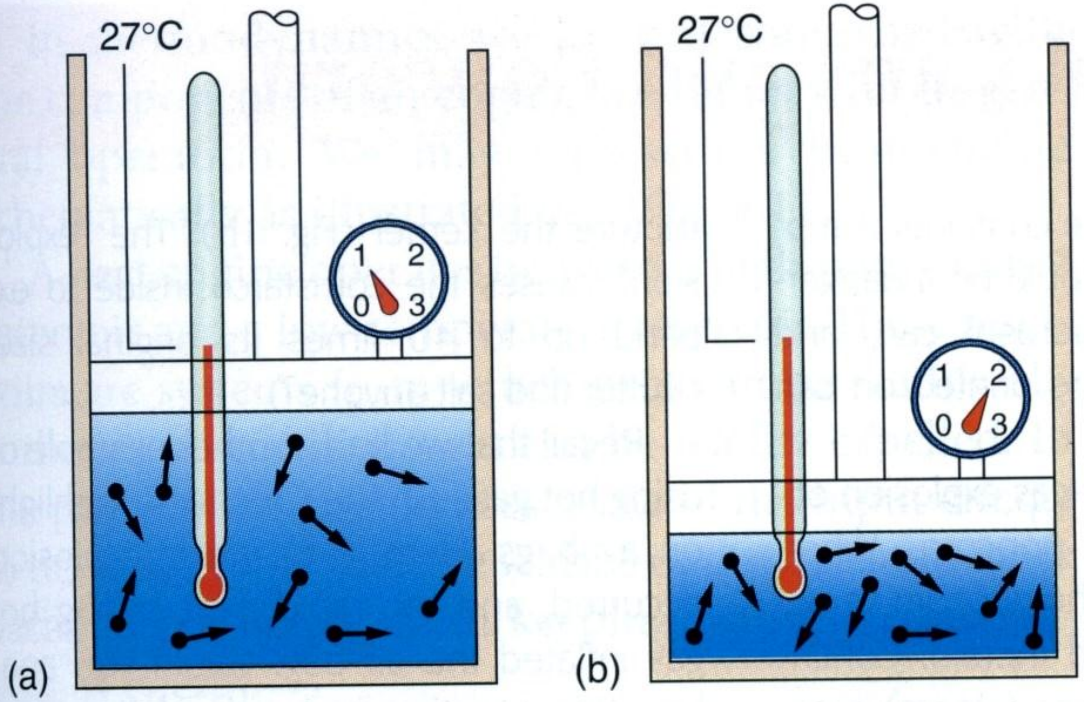
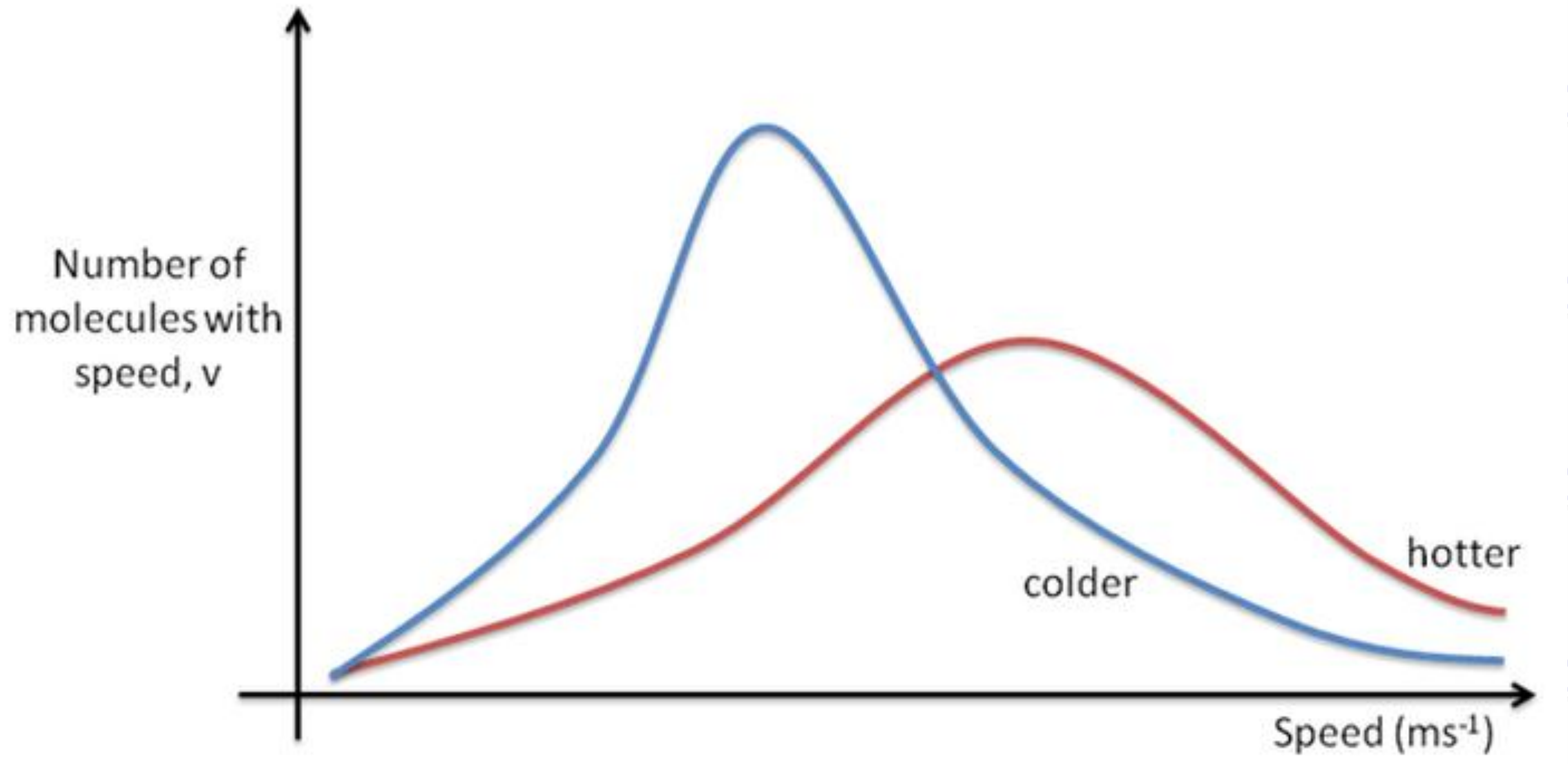


FIGURE 5.16 Pressure and Volume

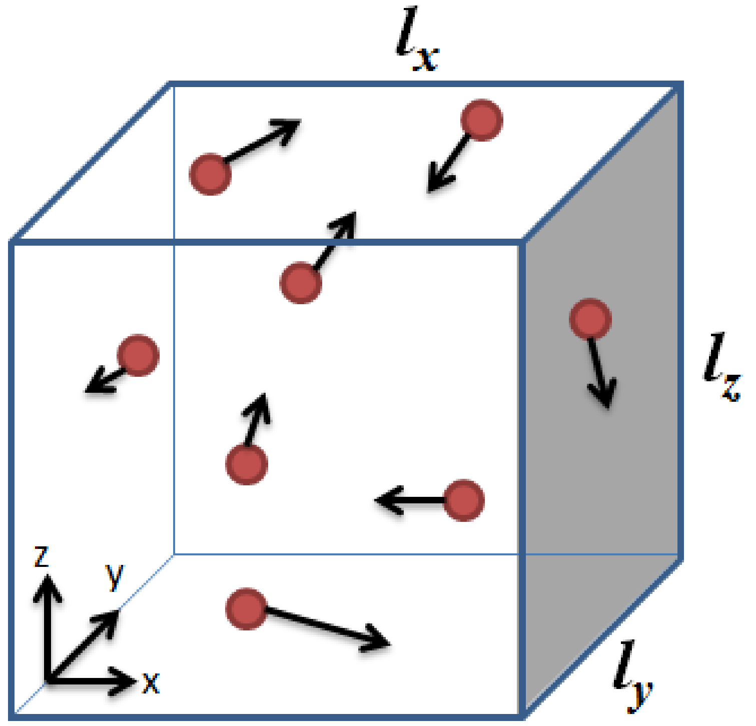
In both containers, the temperature and the number of molecules are constant. However, the container in (b) has only half the volume of the container in (a). This causes the pressure to be twice as great, as shown on the gauge. (Same average kinetic energy, but less distance to travel, on average, in a smaller volume, so more collisions.)

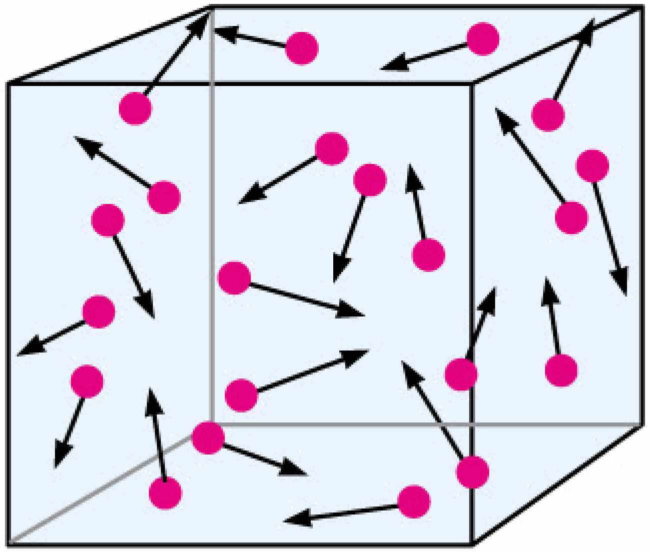
Kinetic Theory and Molecular Speeds

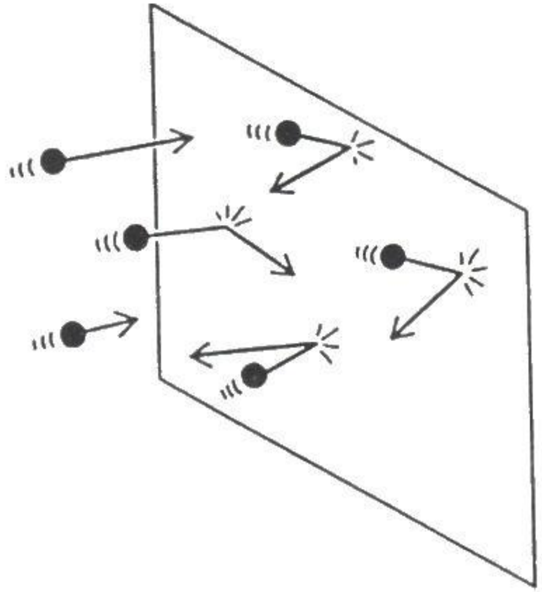
Molecules in an ideal gas have a continuous spread of speeds. The speed of a molecule can change when it collides with another. However, the distribution remains the same provided the temperature is constant.



Kinetic theory of gases







- On a microscopic level, a gas consists of *moving molecules*
- **Pressure** is generated by molecules *colliding with the walls*
- **Temperature** measures the **average kinetic energy** associated with random translational motion of an atom

The basic assumptions of the kinetic theory of gases.

1. Any gas consists of very large number of molecules.
2. The molecules of the gas are in straight, rapid, random motion.
3. Collisions between gas molecules are elastic.
4. Collisions between gas molecules and the walls of the container are elastic.
5. There are no intermolecular attractive forces.
6. Inter-molecular forces of repulsion act only during collisions between molecules.
7. The volume of the gas molecules themselves is negligible compared with the volume of the container, i.e., almost all the gas is empty space.
8. Newton's laws of motion apply.

- The kinetic theory of an ideal gas.
- The distributions of molecular speeds and root mean square speed.
- Presenting the equation $pV = \frac{1}{3} Nm\overline{c^2}$
- The pressure exerted by a gas $p = \frac{1}{3} \rho\overline{c^2}$

  and the mean square speed $\overline{c^2} = \frac{3RT}{M}$
- Mean kinetic energy of a gas molecule $E = \frac{3RT}{2N_A}$, $\frac{R}{N_A} = k$, Boltzmann constant

- Molecules are travelling in all directions (+ve and -ve). For the most meaningful mean of the speed of the molecules we must take the root mean square, rms. The rms speed of molecules in an ideal gas, this gives a mean of the magnitude of the speeds:
-

$$c_{rms} = \left[\frac{(c_1^2 + c_2^2 + \ldots + c_N^2)}{N} \right]^{1/2}$$

The rms speed of molecules can be used to link pressure and speed of molecules. This is sometimes referred to as the kinetic theory equation:

$$\boxed{PV = \frac{1}{3} Nmc_{rms}^2}$$

The mean kinetic energy of one molecule in a gas is given by the equation (NB this is independent of the mass of each molecule):

$$\boxed{E_{kin} = \frac{3}{2} k_B T}$$

$$\boxed{E_{kin_{Total}} = \frac{3}{2} N k_B T}$$

The total energy for n moles of an ideal gas is:

$$\boxed{E_{kin_{Total}} = \frac{3}{2} nRT}$$

Molecular KE and Temperature

$$p = \tfrac{1}{3}\rho\overline{c^2}$$

Multiplying the Kinetic Theory equation for pressure by ***V***, (the volume of the gas) we obtain:

$$pV = \tfrac{1}{3}\rho V\overline{c^2} \qquad \text{(i}$$

but density ***ρ*** (rho) is given by:

$$\rho = \frac{M}{V}$$

making the mass ***M*** the subject, (where ***M*** is the mass of gas)

$$M = \rho V$$

substituting for ***ρV*** into the Kinetic Theory equation (i ,

$$pV = \tfrac{1}{3}M\overline{c^2} \qquad \text{(ii}$$

With some simple arithmetic and a more detailed description of ***M***, this equation can be amended into a more useful form:

$$\frac{1}{3} = \frac{2}{3} \times \frac{1}{2}$$

If ***N*** is the total number of molecules and ***m*** is the mass of one molecule:

$$M = Nm$$

$$pV = \frac{2}{3}N\left(\frac{1}{2}m\overline{c^2}\right)$$

The **Ideal Gas Equation** is,

$$pV = nRT$$

where,

n is number moles of gas
R is the Universal Gas Constant
T is the temperature in kelvin

Elimenating **p*V*** between the last two equations,

$$\frac{2}{3}N\left(\frac{1}{2}m\overline{c^2}\right) = nRT$$

Making $\left(\frac{1}{2}m\overline{c^2}\right)$ the subject of the equation,

$$\frac{1}{2}m\overline{c^2} = \frac{3}{2}\frac{nR}{N}T$$

The Avagadro Number $\boldsymbol{N_A}$ is by definition the number of molecules per mole. It is obtained by dividing the total number of molecules by the number of moles of matter:

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

We can now modify equation (iii to include $\boldsymbol{N_A}$ by substituting for $\boldsymbol{n/N}$,

$$\tfrac{1}{2} m\overline{c^2} = \tfrac{3}{2} \frac{R}{N_A} T$$

By definition the **Boltzmann's constant** $\boldsymbol{k}$ is given by:

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

So the final form of the equation is:

$$\underline{\tfrac{1}{2} m\overline{c^2} = \tfrac{3}{2} kT}$$

$\tfrac{1}{2} m\overline{c^2}$ is called the **average translational KE of a molecule**

So the average kinetic energy of gas molecules is proportional to the temperature.

This can also be said in the converse:

temperature is a measure of the average kinetic energy of gas molecules

Speed of Molecules

The *root-mean-square* (rms) speed of molecules is:

$$\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3}{2} k_B T$$

$$v_{rms} = \sqrt{\frac{3\, k_B\, T}{m}} = \sqrt{\frac{3\, R\, T}{M}}$$

Lighter molecules move faster

Internal Energy

- In a monatomic gas, the translational K.E. is the only type of energy the molecules can have

$$U = \frac{3}{2} nRT$$

- U is the *internal energy* of the gas.

- **In a polyatomic gas, one also has rotational and vibrational energy & (3/2) --> bigger number**

Example 10.4

A cylinder contains a mixture of helium (^4He) and argon (^{40}Ar) gas in equilibrium at a temperature of 150°C. DATA: $m_{proton}=1.67\times10^{-27}$ kg

(a) What is the average kinetic energy of each type of molecule?

8.76×10^{-21} J

(b) What is the rms speed of each type of molecule?

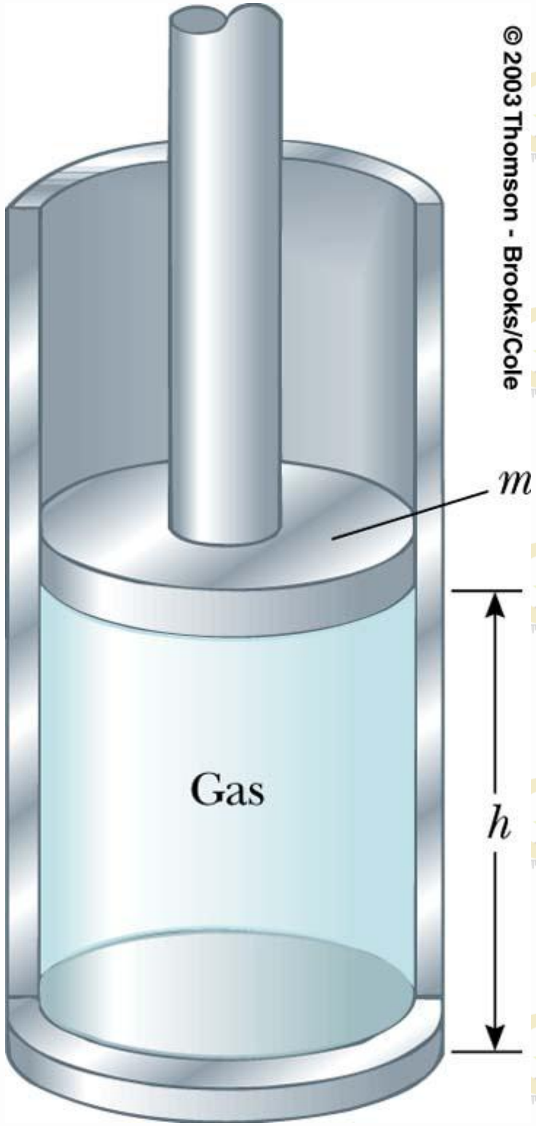
He: 1.62 km/s, Ar: 512 m/s

Example 10.5a

Consider the cylinder on the right which is filled with an ideal gas.

If P is doubled while maintaining the same volume, T must change by a factor of ________ .

a) 1/2
b) $2^{1/2}$
c) 2
d) 4
e) Can not determine

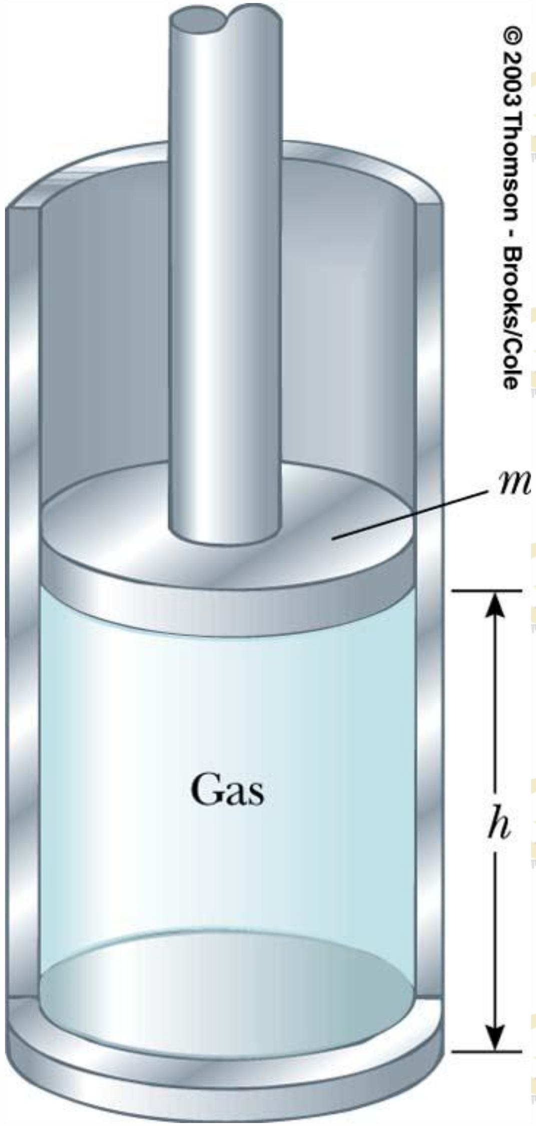


Example 10.5b

Consider the cylinder on the right which is filled with an ideal gas.

If P is doubled while maintaining the same volume, the r.m.s. speed of the molecules must change by a factor of ________.

a) 1/2
b) $2^{1/2}$
c) 2
d) 4
e) Can not determine

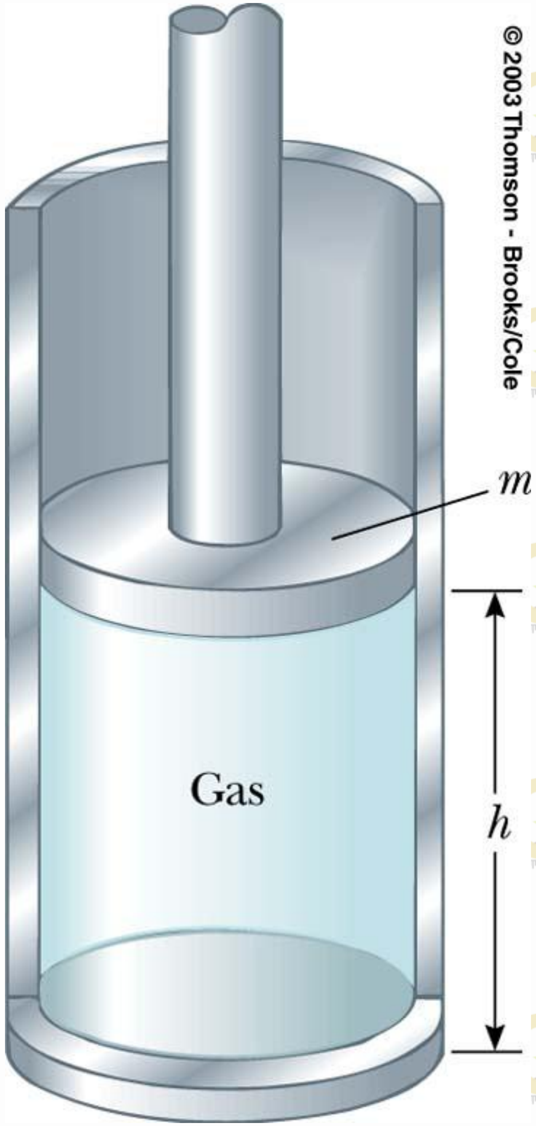


Example 10.5c

Consider the cylinder on the right which is filled with an ideal gas.

If T is doubled while letting the piston slide freely, the volume will change by a factor of ________.

a) 1/2
b) $2^{1/2}$
c) 2
d) 4
e) Can not determine



Two identical cylinders, one with H_2 and one with N_2, have **different** gauge pressures but the same temperature. Which cylinder has the fastest molecules.

1. **The high pressure vessel**
2. **The low pressure vessel**
3. **The one with Hydrogen**
4. **The one with Nitrogen**
5. **Insufficient information to tell**

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Two identical cylinders, one with H_2 and one with N_2, have **different** gauge pressures but the same temperature. Which cylinder has the fastest molecules.

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

Temperature and mass dictate velocity

Temperature is the same, but mass(H_2) < mass(N_2)

So speed(H_2) > speed(N_2)

Molecular Energy and Speed

Find the average kinetic energy of a molecule of air at room temperature ($T = 20℃$) and determine the speed of a nitrogen molecule (N_2) with this energy.

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

$$T = 293K \rightarrow \overline{KE} = \frac{3}{2} \times 1.38 \times 10^{-23} \times 293 = 6.07 \times 10^{-21}\ J$$

$$KE = \frac{1}{2}mv^2 \rightarrow v = \sqrt{2 \times KE/m}$$

$$m = 2 \times 14 \times 1.66 \times 10^{-27}\ kg = 4.65 \times 10^{-26}\ kg$$

$$\rightarrow v = \sqrt{2 \times 6.07 \times 10^{-21}/4.65 \times 10^{-26}} = 511\ m/s$$