Name : _____

Class : _____

TEMASEK JUNIOR COLLEGE

Unit 12: Temperature and Ideal Gases

Learning Outcomes

Candidates should be able to:

(a) show an understanding that a thermodynamic scale of temperature has an absolute zero and is independent of the property of any particular substance.

(b) convert temperatures measured in kelvin to degrees Celsius: $T / K = T / ℃ + 273.15$

(c) recall and use the equation of state for an ideal gas expressed as $pV = NkT$, where N is the number of particles.

(d) state that one mole of any substance contains 6.02×10^{23} particles, and use the Avogadro constant $N_A = 6.02 \times 10^{23}$ mol^{-1} as well as the relationship $Nk = nR$ between the Boltzmann constant and the molar gas constant, where n is the amount of substance in moles and $N = nN_A$.

(e) state the basic assumptions of the kinetic theory of gases.

(f) explain how the random motion of gas particles exerts mechanical pressure and hence derive, using the definition of pressure as force per unit area, the relationship $pV = \frac{1}{3}Nm\langle c^2 \rangle$. (A simple model considering one-dimensional collisions and then extending to three dimensions using $\langle c_x{}^2 \rangle = \frac{1}{3}\langle c^2 \rangle$ is sufficient.)

(g) recall and apply the relationship that the mean kinetic energy of a molecule of an ideal gas is proportional to the thermodynamic temperature (i.e. $\frac{1}{2}m\langle c^2 \rangle = \frac{3}{2}kT$) to new situations or to solve related problems.

1 Temperature

1.1 Temperature and Heat

From the *macroscopic* perspective between systems, **temperature** is the physical property that determines the direction of heat flow. **Heat** then refers to the energy transferred between two systems at different temperatures. *Microscopically* however, we can define temperature as a measure of the **average kinetic energy** of molecules in a body.

2 Temperature Scales *LO(a)*

2.1 Temperature and thermometers

Thermometers are devices used to measure temperature. There are many kinds of thermometers, but their operation always depends on some **thermometric property**.

- **Thermometric property**: a physical property that increases or decreases *continuously* with temperature, such as the ones below

Type of Thermometer	Thermometric Property
liquid-in-glass thermometer	length of mercury in a capillary tube
resistance thermometer	resistance of platinum wire
thermocouple thermometer	emf of a copper-constantan thermocouple
constant volume gas thermometer	pressure of a fixed mass of gas at constant volume

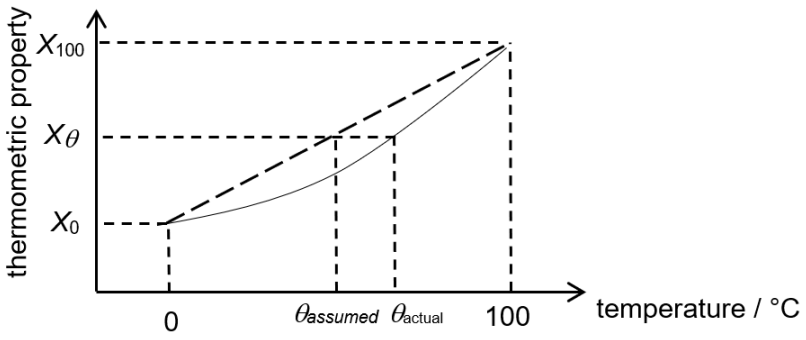
The fact that substances change state (from solid to liquid, or from liquid to gas) at fixed temperatures is used to define reference temperatures, which are called **fixed points**.

By taking the value of the thermometric property at two fixed points, and dividing the range of values into a number of equal units (or degrees) between the two points, we can set up what is known as an **empirical scale of temperature** for that thermometer.

2.2 Empirical Scales

'Empirical' means 'derived by experiment'. For example, if the fixed points are the melting and boiling points of water, and if we choose to have one hundred equal units between the temperatures corresponding to these fixed points, we can assign to these fixed points, values of 0 degrees and 100 degrees respectively. This is how the empirical centigrade scale of temperature for that thermometer is arrived at.

It is important to realise that the choice of a different thermometric substance and thermometric property would lead to a different centigrade scale. Agreement between scales occurs only at the two fixed points. This happens because the property may not vary linearly with temperature.



This situation, with temperature values depending on the type of thermometer on which they are measured, is clearly unsatisfactory for scientific purposes.

2.3 The Thermodynamic Scale

It is found that the differences between empirical scales are small in the case of thermometers based on gases as thermometric substances. In the constant-volume gas thermometer (Fig. 1), the pressure of a fixed volume of gas (measured by the height difference *h*) is used as the thermometric property. The agreement among thermometers using various gases improves as the pressure is reduced. If the graphs shown in Fig. 2 are extended toward negative temperatures, we find in every case, the pressure is zero when the temperature is –273.15 °C. This significant temperature is used as the basis for the absolute temperature scale, which sets –273.15 °C as its zero point. This temperature is known as absolute zero on the thermodynamic scale of temperature.

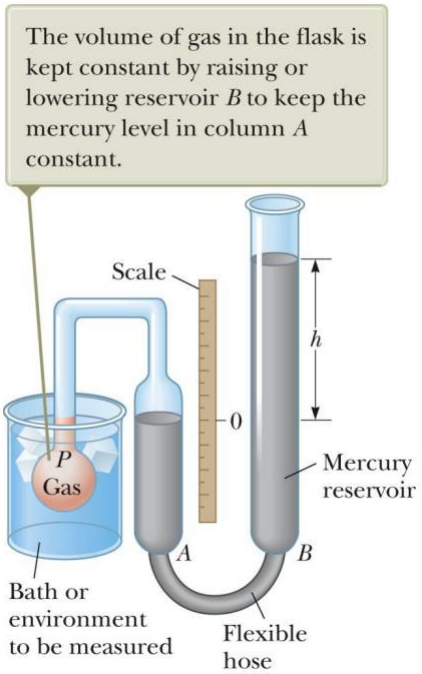


Fig. 1

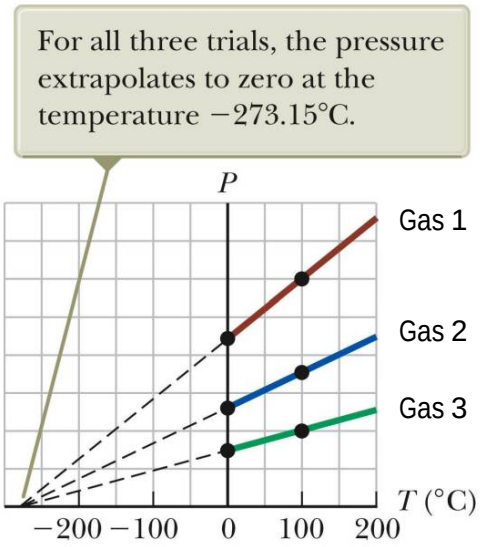


Fig. 2

The thermodynamic temperature scale is theoretical and is independent of the property of any real substance. The unit of thermodynamic temperature is the kelvin (symbol K).

The two **fixed points** in the Thermodynamic Temperature Scale are:

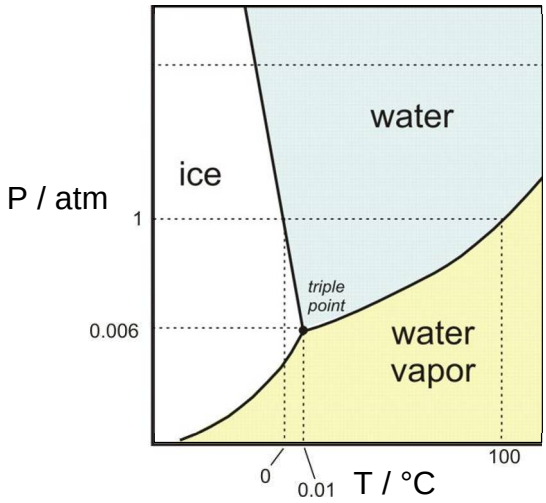
(a) **absolute zero (0 K)** – temperature at which the pressure of an ideal gas becomes zero. It is also the temperature at which all substances have a minimum internal energy.
(b) **triple point of water (273.16 K)** – temperature at which the three phases of water (i.e. ice, water and water vapour) coexist in dynamic equilibrium.

Reasons for using triple point of water:

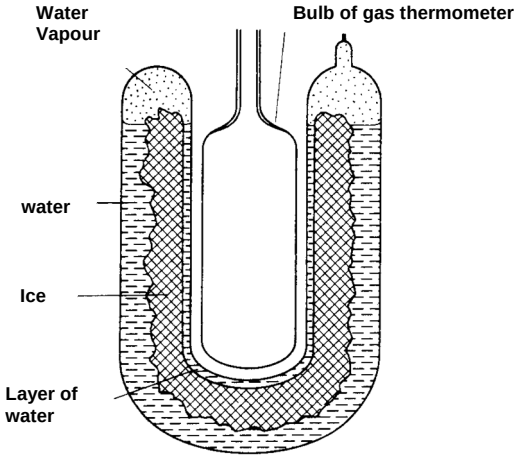
1. It is unique, invariant & occurs at only one temperature & pressure. On the pressure-temperature graph, the triple point occurs at a precise temperature and pressure, whereas other phase transitions may occur over a range of temperatures.

2. The conditions for triple point of water can be easily reproduced using a triple point cell.

One kelvin is defined to be 1/273.16 of the thermodynamic temperature of the triple point of water.



phase diagram of water



triple point cell

2.4 The Celsius Scale *LO(b)*

The Celsius scale is a *shifted* thermodynamic scale. The unit for this scale is degree Celsius, symbol ^{o}C (same symbol as for degree Centigrade).

The Celsius scale is related to the Thermodynamic scale by the exact equation:

$$\theta/°\text{C} = T/\text{K} - 273.15$$

Example 1

The temperature of a body at 100 °C is increased by $\Delta\theta$ as measured on the Celsius scale. How is this temperature change expressed on the Kelvin scale?

A $\Delta\theta$ **B** $\Delta\theta + 100$ **C** $\Delta\theta + 273$ **D** $\Delta\theta + 3\,73$

3 Ideal Gas

3.1 The Ideal Gas Equation *LO(c)*

$$pV = NkT$$

N = number of particles
k = Boltzmann constant = 1.38×10^{-23} J K^{-1}

The above equation is called the **equation of state of an ideal gas** or simply the **ideal gas equation**.

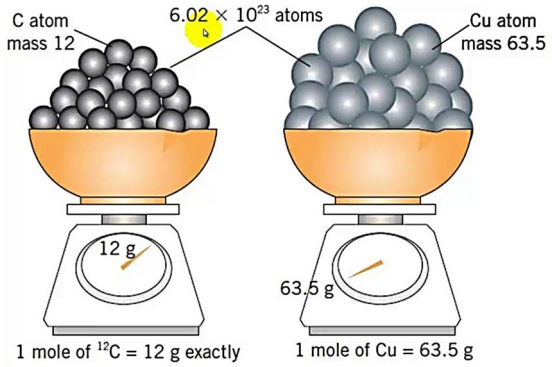
An *ideal gas* is one which obeys the equation $pV = NkT$ at all pressures p, volumes V and temperatures T, where N is the number of particles and k is the Boltzmann constant.

No **real gas** obeys the ideal gas equation exactly. For approximate calculations, the ideal gas equation can be used with real gases if the gas is well above the temperature at which it will liquefy (ie high temperature compared to boiling point) and the pressure is low. Under these conditions, the separation between the gas molecules is large so the intermolecular forces are negligible and hence their potential energies are close to zero. The internal energy is just kinetic energy – an approximation consistent with the characteristics of ideal gases.

3.2 Mole concept and Boltzmann constant *LO(d)*

1. One **mole** is the amount of substance which contains the same number of elementary entities as there are atoms in 12 g of carbon-12. This number is known as the **Avogadro constant**, denoted by $\boldsymbol{N_A}$.

$N_A = 6.02 \times 10^{23}$ mol^{-1}



2. Molar mass $\boldsymbol{M_m}$ is the mass of one mole of substance. Unit: kg mol^{-1}.

3. Molar volume $\boldsymbol{V_m}$ is the volume occupied by one mole of gas. Unit: m^3 mol^{-1}.

4. Useful relations:

$$n = \frac{N}{N_A} = \frac{M}{M_m} = \frac{V}{V_m}$$

where n = no. of moles; M = mass of gas (total mass of molecules)
N = no. of molecules; V_m = molar volume or volume of 1 mole
M_m = molar mass; V = volume of gas

5. The **Boltzmann constant, $\boldsymbol{k}$** is related to the **molar gas constant, $\boldsymbol{R}$** by the relationship

$$Nk = nR$$

6. The ideal gas equation can also be expressed in terms of the number of moles of particles as follows, ie

$$pV = nRT$$

where n = no. of moles and $R = \frac{N}{n}k = N_A k$ = 8.31 J K^{-1} mol^{-1}

Example 2 [2012/1/Q19]

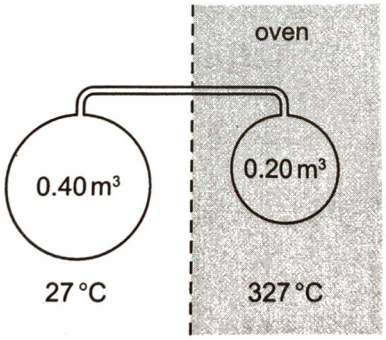
An ideal gas has a volume of 8.70 m^3 and contains 1.44 x 10^{26} molecules.
Its pressure is 9.80 x 10^4 Pa.

What is its temperature?

A 156 K **B** 429 K **C** 4290 K **D** 29 600 K

Example 3 [2014/1/Q19]

Two glass bulbs of constant volume 0.40 m^3 and 0.20 m^3 are connected by a fine tube of negligible volume. This sealed system contains a mass of ideal gas at atmospheric pressure 1.00 x 10^5 Pa at a temperature of 27°C. The smaller bulb is then placed in an oven and heated to 327°C**.**



What is the new pressure in the system?

A 1.20 x 10^5 Pa **B** 1.33 x 10^5 Pa **C** 1.44 x 10^5 Pa **D** 1.50 x 10^5 Pa

4 The Kinetic Model of Matter

The analysis of matter in terms of atoms in continuous random motion is called the **kinetic theory**. The kinetic theory of gases is an attempt to explain the *macroscopic* behaviour of an ideal gas (e.g. pressure, volume, temperature) by looking at the *microscopic* properties of its atoms (e.g. speed, mass). Certain assumptions are made about the properties of gas molecules.

4.1 Assumptions of Kinetic Theory for Ideal Gas *LO(e)*

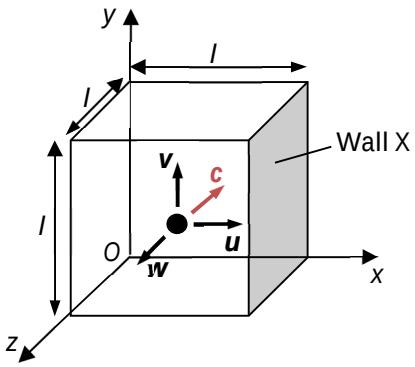
1. A gas consists of a very large number of molecules.
2. The gas molecules are in constant random motion.
3. The molecules of the gas make perfectly elastic collisions with one another and with the walls of the container.
4. The intermolecular forces are negligible except during the time of collision which is very brief compared to the time between collisions.
5. The total volume of the molecules is negligible compared to the volume of the gas.

The kinetic theory uses the idea that the pressure of a gas is due to the molecules bombarding the walls of its container. Whenever a molecule bounces off a wall, its momentum normal to the wall is reversed; the force which it exerts on the wall is equal to the rate of change of its momentum.

If the volume of the gas is reduced by half, the molecules are closer together and twice as many will be striking a given area of the wall per second. Hence we expect the pressure to be twice as great.

We can calculate quantitatively the pressure a gas exerts on its container based on the kinetic theory.

4.2 Derivation of the Equation $p = \frac{1}{3}\frac{Nm}{V} < c^2 >$ *LO(f)*



Step 1: Resolve the motion of molecule along *x*-*y*-*z* directions

Consider a cube of side l containing N molecules of gas each of mass m.
A typical molecule will have a velocity c at any instant and this will have components of u, v, w respectively in the direction of the three perpendicular axes O_x, O_y, O_z as shown.

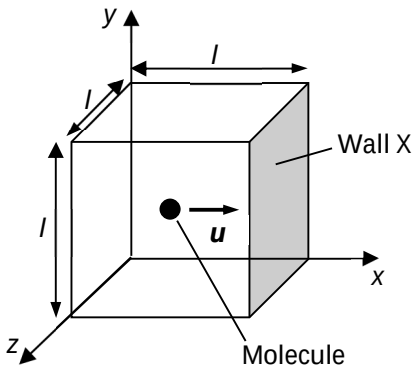
So $c^2 = u^2 + v^2 + w^2$.

Step 2: Find the change of momentum upon collision with a wall

- Consider the component of velocity, u, along the O_x axis, of one such molecule. Taking the direction to the right as positive,

  momentum of the molecule before collision with wall X, $p_i = mu$
- The molecule **collides elastically** with the wall and rebounds with a velocity of $-u$.
- momentum immediately after collision, $p_f = -mu$
- $\therefore$ change in momentum $\Delta p = p_f - p_i = -mu - mu = -2mu$

Step 3: Find the force on the wall due to the bombardments of molecules on the wall



- The molecule has to travel a distance of $2l$ (to the opposite face and back to X) before it next collides with wall X again.

  $\therefore$ time between collisions with wall X, $\Delta t = \dfrac{2l}{u}$
- number of collisions with wall X per unit time = $\dfrac{1}{\Delta t} = \dfrac{u}{2l}$
- Rate of change of momentum of molecule = $(-2mu)\ \dfrac{u}{2l} = -\dfrac{mu^2}{l}$
- By Newton's 2nd Law, rate of change of momentum of molecule = force exerted by the wall on the molecule

  $\therefore$ force exerted by wall X <u>on molecule</u> = $-\dfrac{mu^2}{l}$
- By Newton's 3rd Law,

  force exerted by the molecule <u>on wall X</u> = $\dfrac{mu^2}{l}$

  $\therefore$ Total force that N molecules exert on wall X = $\dfrac{m}{l}(u_1^2 + u_2^2 + u_3^2 + ... + u_N^2)$

  where u_1, u_2, u_3…u_N are the x-components of the velocities of the individual molecules.
- Consider $\langle u^2 \rangle$ = **mean square velocity** in the x-direction (i.e. the average value of all u^2)

$$\langle u^2 \rangle = \frac{u_1^2 + u_2^2 + u_3^2 + ... + u_N^2}{N}$$

giving $N\langle u^2 \rangle = u_1^2 + u_2^2 + u_3^2 + ... + u_N^2$

Hence, total force on wall $X = \frac{Nm < u^2 >}{l}$

Step 4: Find the pressure on the wall

- Pressure on wall X, $p = \frac{\text{force on wall}}{\text{area of wall}} = \frac{Nm < u^2 >}{l} \times \frac{1}{l^2} = \frac{Nm < u^2 >}{V}$

  where V = volume of the cube = l^3

Step 5: Express in terms of mean-square speed *c*

- Since $c^2 = u^2 + v^2 + w^2$,

  $<c^2> = <u^2> + <v^2> + <w^2>$

- Since the number of molecules is large and they are in random motion**,**
  $<u^2> = <v^2> = <w^2> = \frac{1}{3} <c^2>$

Finally we have $\boxed{p = \frac{1}{3}\frac{Nm}{V} < c^2 >}$ (1)

where V = volume of container = l^3
N = total no. of molecules
m = mass of 1 molecule

Since $Nm = M$ = mass of gas, and M/V = density ρ of gas, equation (1) can also be written as

$$\boxed{p = \frac{1}{3}\rho \left\langle c^2 \right\rangle} \quad (2)$$

4.3 Mean Translational Kinetic Energy of an Ideal Gas molecule *LO(g)*

Using $p = \frac{1}{3}\frac{Nm}{V} < c^2 >$ and Ideal Gas Equation $pV = NkT$

we have

$$pV = \frac{1}{3} Nm < c^2 > = NkT$$

$$\therefore \frac{1}{2} Nm < c^2 > = \frac{3}{2} NkT$$

$$\frac{1}{2} m < c^2 > = \frac{3}{2} kT$$

Total K.E. of N gas molecules =

$$\frac{3}{2} NkT = \frac{3}{2} nRT = \frac{3}{2} \rho V$$

Average K.E of a gas molecule = $\frac{3}{2} kT$

We can see that **average kinetic energy** of the particles of an ideal gas is **directly proportional** to the **thermodynamic temperature *T*** of the gas.

This relationship implies that at a given thermodynamic temperature, all ideal gas molecules, regardless of their mass, have the same average translational kinetic energy of $\frac{3}{2}kT$.

4.4 Root-mean-square speed

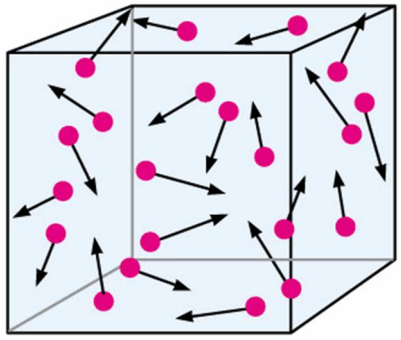
$\langle c^2 \rangle$ is known as the mean-square-speed.

$$\langle c^2 \rangle = \frac{c_1^2 + c_2^2 + c_3^2 + ... + c_N^2}{N}$$

Root-mean-square speed, c_{rms} = square root of the mean-square speed

$$c_{rms} = \sqrt{< c^2 >} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + ... + c_N^2}{N}} = \sqrt{\frac{3kT}{m}}$$

The root-mean-square speed denotes the representative speed of all the individual randomly moving gas molecules in the system.



Example 4

10 particles have the following speeds in m s^{-1}:

1.0	3.0	4.0	5.0	5.0	5.0	6.0	6.0	7.0	9.0

Determine
(a) the mean speed, and
(b) the root-mean-square speed of the particles.

Example 5

A container holds a mixture of hydrogen and oxygen in thermal equilibrium at a temperature of 227 °C. Find the mean translational kinetic energies of both types of molecules.

Example 6

The r.m.s. speed of the molecules in an ideal gas at 50.0 K is 800 m s^{-1}. What is their r.m.s. speed at 177°C?

TUTORIAL QUESTIONS
(Answers provided for Q1, Q4, Q5, Q7)

Temperature Scales

1. [J90/II/6 part]
Explain why the thermodynamic scale of temperature is called an absolute scale.

The temperature scale does not depend on the property of any thermometric substance

2. What is 273.00 K on the Celsius scale of temperature?

A –0.15 °C **B** 0.00 °C **C** 273.15 °C **D** 546.15 °C

3. What is the change in temperature in kelvin when the temperature falls from 540.85 °C to 502.02 °C?

A 38.83 K **B** 311.98 K **C** 273.15 K **D** 228.85 K

Ideal Gas

4. [N05/III/2 part]
(a) Explain what is meant by an *ideal gas.*

(b) The ideal gas equation is $pV = nRT$. Explain why non-SI units may be used for p and V but the temperature T cannot have the unit in ^{o}C.

Ans: (a) *An ideal gas is one that obeys the ideal gas equation, pV = nRT at all pressures, volumes and temperatures.*

(b) *In an ideal gas equation, if the molar gas constant R is used, the temperature must be in Kelvin.*
The product between p and V is always positive but T/^{o}C can be both positive and negative. Thus it cannot be used in the ideal gas equation.
T/^{o}C = T/K – 273.15 $\Rightarrow$ a multiplying factor will cancel out but a subtracting factor will not.

5. (i) "For the same mass, volume and temperature, the pressure exerted by a real gas is the same as the pressure exerted by an ideal gas".
Discuss whether this statement is true.
(ii) Under what conditions will a real gas behave like an ideal gas?

Ans (i) *False. Pressure of a real gas is less than that of an ideal gas for the same mass, volume and temperature because attractive force exists between the atoms/molecules in a real gas and not in an ideal gas.*

(ii) *A real gas at low pressure and high temperature compared to boiling point behaves like an ideal gas.*

6. An open flask contains 10^{-3} kg of air at 17 °C. What mass of air leaves the flask if its temperature is raised to 100 °C? [2.2×10^{-4} kg]

Kinetic Model of Matter

7. Use the kinetic model to explain the pressure exerted by a gas.

Molecules / atoms are in (constant) random motion. They experience a change in momentum when they collide with the walls. Thus a force is exerted on the molecules by the wall. By Newton's 3rd law, a force is exerted by the molecules on the walls. Pressure is the average from many molecules' collisions per unit area.

8. [N02/II/3 part]
(a) State three of the assumptions of the kinetic theory of gases.

(b) Consider a single molecule of mass *m* in a cubical container of internal side length *l*. The molecule is travelling with velocity *v* directly towards one of the walls W as shown in Fig. 1. Collisions between the molecule and the walls are elastic.

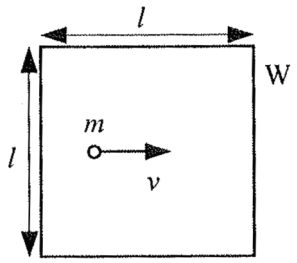


Fig. 1

Deduce
(i) the change in the molecule's momentum when it collides with wall W,
(ii) the time between collisions with wall W,
(iii) the momentum change per unit time for the molecule at wall W,
(iv) the average force on wall W as a result of impacts by the molecule,
(v) the average pressure on wall W.

(c) The pressure *p* of an ideal gas is given by the equation

$$p = \frac{1}{3}\frac{Nm}{V} < c^2 >$$

Explain briefly how this result can be deduced by modifying the equation derived in (b)(v).

9. (a) A balloon contains 0.400 mol of helium at 300 K. Calculate
(i) the number of helium atoms in the balloon,
(ii) the average kinetic energy of a helium atom in the balloon,
(iii) the total kinetic energy of the helium atoms in the balloon.

(b) The temperature of the helium in the balloon is increased.
State and explain, using the kinetic theory, the initial effect this has on the pressure of the helium gas.

[2.41×10^{23}, 6.21×10^{-21} J, 1500 J]

10. A vessel of volume 50 cm^3 contains hydrogen gas (molar mass = 2.0 g) at a pressure of 1.0 Pa and a temperature of 27°C. Estimate
    (a) the number of molecules in the vessel,
    (b) their distance apart, and
    (c) their r.m.s speed.

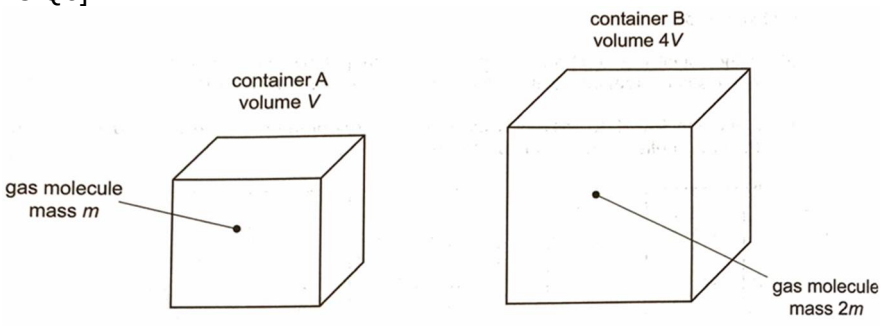
    [1.2×10^{16}, 1.60×10^{-7} m; 1930 m s^{-1}]

11. The temperature of an ideal gas in a cylinder is 273 K when its pressure is 1.01×10^5 Pa and its density is 1.24 kg m^{-3}. Calculate
    (a) the r.m.s speed of the gas molecules, and
    (b) the molar mass of the gas,

    The gas is now compressed slowly to half its initial volume, (i) keeping *T* constant, and (ii) keeping *P* constant. What is the new r.m.s speed?

    [494 m s^{-1}; 27.9 g, 494 m s^{-1}, 349 m s^{-1}]

12. [N2023 P3 Q6]



The volume of container A is *V*, and the volume of container B is *4V*.

The molecules of the gas is container A each have mass *m* and those in container B each have mass *2m*.

The gases in the containers are at the same temperature and pressure.

(a) Deduce a value for the ratio:

(i) $\dfrac{\text{mean kinetic energy of a gas molecule in container A}}{\text{mean kinetic energy of a gas molecule in container B}}$ [1m]

(ii) $\dfrac{\text{number of gas molecules in container A}}{\text{number of gas molecules in container B}}$ [1m]

(iii) $\dfrac{\text{root-mean-square (r.m.s.) speed of gas molecules in container A}}{\text{r.m.s. speed of gas molecules in container B}}$ [2m]

(b) There are 1.6 moles of gas in container A. The gas in container A has a molar mass of 4.0 g. The r.m.s. speed of the molecules in container B is 940 m s^{-1}.

Calculate the temperature of the gases. [4m]